MODELING OF GASEOUS PHOTOCHEMICAL POLLUTION AND PARTICULATE MATTER IN THE WESTERN MEDITERRANEAN BASIN (SPANISH LEVANTINE COAST) BY USING HIGH-RESOLUTION

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1. INTRODUCTION

The high levels of photochemical pollutants in the entire Western Mediterranean Basin (WMB), and, specially, in the Spanish Levantine coast, present a high impact on ecosystems and human health, exceeding thresholds established in European Directives (Millán *et al.*, 2000). This area is critically sensitive to photochemical pollution, due to its complex topography, which induces a complicated structure of the flow with important effects in the transport and transformation of air pollutants (Jiménez and Baldasano, 2004). The WMB is surrounded by high coastal mountains and in summer becomes isolated from the traveling lows and their frontal systems, which affect the weather at higher latitudes. The meteorology and the origin of the air masses arriving at the Iberian Peninsula are highly influenced by the Azores high-pressure system, which is located over the Atlantic Ocean and that intensifies during the warm season inducing very weak pressure gradient conditions all over the region (Lelieveld *et al.*, 2002). The canalization between the Pyrenees and the French Central Massif introduced northwestern flows into the Mediterranean. This canalization plays an important role, because it is the only pass bringing fresh air into the WMB (Gangoiti *et al.*, 2001). This work analyzes the levels of particulate matter in a domain of 216x314 km^2, located in the Spanish Eastern Levantine (WMB), during 13-16 August 2000.

2. METHODS

The MM5-EMIVAL2000-CMAQ model was applied with high spatial (2 km) and temporal (1h) resolution for different scenarios including a particulate matter speciation, which presents diverse emission profiles. A 48-hr spin-up was performed in order to minimize the influence of initial conditions. The generation of boundary conditions for MM5-EMIVAL2000-CMAQ was performed through simulations in the entire Iberian Peninsula, southern France and northern Africa, using a multiscale approach. The wider domain is coupled via one-way nesting to the domain of the Spanish Levantine coast. The emissions for the wider domain were derived from EMEP emission model (www.emep.int). Speciation of emissions follows the CBM-IV mechanism, as indicated in Jiménez *et al.* (2003), using the profiles of US EPA (2003) and Parra *et al.* (2005).

2.1 EMIVAL2000 Emission Model

The application and exploitation of Models-3/CMAQ in regions outside the US is conditioned by the applicability and potential adaptation of these emission tools; nevertheless, the flexibility of the model allows the use of specific emission models developed with additional tools and according to the proper characteristics of the zone under study, which can be used as a more accurate alternative. EMIVAL2000 is an emission model developed specifically for the Spanish Levantine Coast (Valencia Community), and implemented in a Geographical Information System (GIS) that includes emissions from biogenic sources, on-road traffic, industries, power generation, domestic sources and waste management. EMIVAL2000 provides emissions for NO_x, VOCs, SO_2, CO and particulate matter on vertical layers that correspond to 36, 73, 109 and 146 meters above ground level.

Results of EMIVAL2000 emission model (Fig. 1), developed specifically for the area of study with a resolution of up to 1 km, indicate that biogenic emissions are responsible for 42.1% of NMVOCs emissions. On-road traffic accounts for 62.3% of NO_x, 47.0% of particulate matter emissions and 33.2% of NMVOCs in the eastern Spanish coast. Industrial NO_x emissions (cement plants and co-generation plants) are distributed approximately uniformly within the territory. This industrial sector

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accounts for 52.7% of particulate matter emissions.

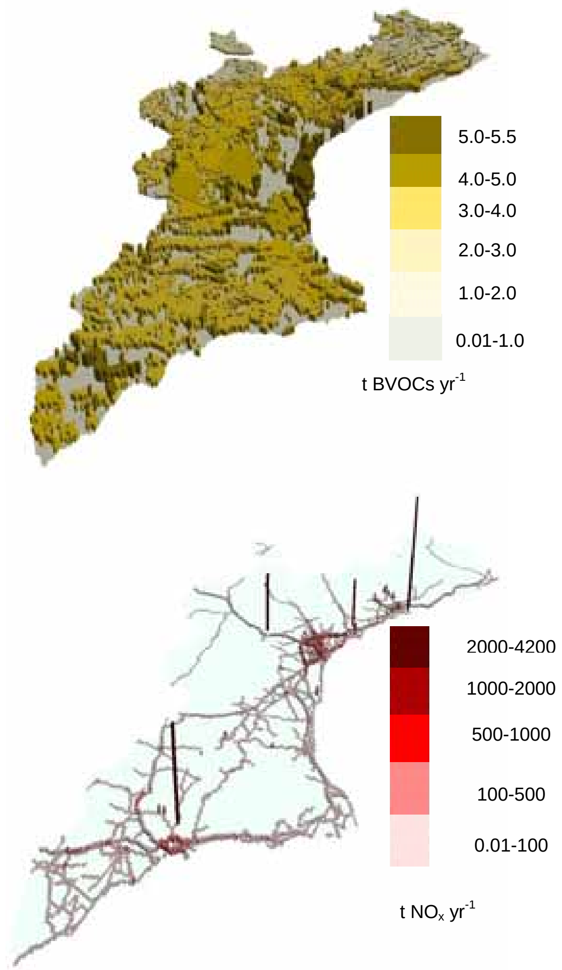

Fig. 1. (Up) Biogenic VOCs emissions and (down) NO_x emissions (both in t yr^{-1}) for the domain of study (Spanish Levantine Coast-Valencia Community) during year 2000.

2.2 Case Study: 13-16 August 2000

The episode selected for the analysis and simulation of photochemical pollution corresponds to a typical summertime low-pressure gradient with high levels of photochemical pollutants over the Iberian Peninsula. The sea-breeze regime, developed within the entire western Mediterranean coast, induced an anticyclonic circulation over all the WMB with general and compensatory subsidence over the region (Millán *et al.,* 1997). This situation is associated with weak winds in the lower troposphere and high temperatures.

A high sea level pressure and almost non-existent surface pressure gradients over the domain characterize this day, with slow northwesterlies aloft. Analysis at 500 hPa shows high pressures over the northwestern African continent; an Atlantic depression circulates in northern latitudes, and a weak zonal circulation turning northwest is observed over the Mediterranean coast of the Iberian Peninsula. This situation is representative of an episode of photochemical pollution in the WMB, since the occurrence of regional re-circulations at low levels represents 78% of the summertime flow transport patterns over the area of study (Jorba *et al.*, 2004) and these situations are associated with local-regional episodes of air pollution in the WMB that result in high levels of O_3 and an increase of PM within the boundary layer during summer.

3. RESULTS OF POLLUTION DYNAMICS

Maximum 1-hr O_3 levels (Fig. 2) are achieved downwind the city of Valencia (center of the domain at the coast) around 12.00UTC, when the sea breeze starts the transport of the polluted air masses from the metropolitan area inland. On-road traffic is the source controlling O_3 formation in the metropolitan area of Valencia, reinforced by industrial emissions of NMVOCs associated to furniture and plastic manufacture. At the same time, an O_3-enriched air mass from the reservoir layer of the Mediterranean increases the concentrations of this pollutant to over 170 $\mu g\ m^{-3}$. Respect to the Castellón area (northern part of the domain), the concurrence of industrial emissions of NMVOCs (refinery) and NO_x (ceramic industries) in the area yields important concentrations of O_3 and secondary aerosols. At noon, the transport of pollutants is conditioned by the front of the onshore winds. In the afternoon, the pollutants formed are transported by S-SE winds and therefore extracted from the domain of study during the afternoon. These phenomena are observed during each day of this episode and it is characteristic of the air dynamics of the Spanish Levantine coast during an episode of low-pressure gradient over the Western Mediterranean Basin. According to Millán *et al.* (1997), the high levels of pollutants measured in this area are also influenced by the transport of Mediterranean-aged O_3 as a consequence of the meso-high caused by the compensatory subsidence of the Iberian Thermal Low and the contribution of the Azores anticyclone that penetrates in the Mediterranean.

This transport is also the main contributor to photochemical pollution in Alicante (southern part of the domain), since the photochemical generation in this area is limited.

Respect to spatial distribution of $PM_{2.5}$ (Fig. 3) the highest concentrations are estimated in the industrial area of Castellón (over 30 $\mu g\ m^{-3}$ as maximum 1-hr concentrations), especially, crustal, sulfates and organic aerosols (OA), due to the high density of ceramic factories, as well as the presence of a power plant and refinery. The area downwind Valencia also presents an important contribution of OA (over 15 $\mu g\ m^{-3}$). The levels of nitrates during summertime in the Spanish Levantine Coast are negligible (because of the thermal instability of the nitrates and the high temperatures that are achieved in the area), and their levels are mainly influenced by the transport through the boundaries of the domain.

4. EVALUATION OF RESULTS WITH AMBIENT AIR QUALITY DATA

Air quality station hourly data, averaged over the domain of study, were used to evaluate the performance of MM5-EMIVAL2000-CMAQ for O_3, NO_x and PM over 13-16 August 2000. Hourly measurements of ambient pollutants were provided by air quality surface stations in the domain of study, which are part of the Environmental Department of Valencia Government (Spain). There are three urban stations: Renfe (city of Alicante), Pista la Silla (city of Valencia) and Paterna (downwind Valencia); an industrial station (Onda) and two background stations (Vilafranca and San Jorge).

The US Environmental Protection Agency has developed guidelines (US EPA, 1991) for a minimum set of statistical measures to be used for the evaluation of O_3 in regions where monitoring data are sufficiently dense. These statistical measures considered are the mean normalized bias error (MNBE); the mean normalized gross error for concentrations above a prescribed threshold (MNGE), and the unpaired peak prediction accuracy (UPA). In addition, the European Directive 2002/3/EC related with O_3 in ambient air assumes an uncertainty of 50% for the air quality objective for modeling assessment methods. This uncertainty is defined as the maximum error of the measured and calculated concentration levels during daytime.

The statistical results obtained for the O_3 when assessed against air quality data (Table 1) indicate that the model meets the standards set both by EU legislation and the US EPA guidelines, except in the urban station of Pista la Silla; the reason is an underestimation of traffic emissions and the particular location of the station. The aggregation of emissions to 2 km cells misses the local specificity of this station. The results also depict that the O_3 evaluation is satisfactory not only for urban stations (but Pista la Silla) but also for areas influenced by other emission sources such as the industrial station of Onda (with a negative bias of –3.6% and an underestimation of the O_3 1-hr peak of –20%, because of a not-sufficient reactivity of O_3 cause by an underestimation of VOCs) and the downwind station of Paterna (bias of –3.0% and UPA of 2.0%).

Table 1. Statistic figures of the evaluation of the O_3 simulations in different air quality stations of the domain for the episode of 13-16 August, 2000.

Station	MNBE (%)	MNGE (%)	UPA (%)
US EPA Standard	± 5-15%	+30-35%	± 15-20%
Pista la Silla	-37.0	37.0	-17.0
Renfe	-0.9	8.30	-9.3
Paterna	-3.0	11.8	2.0
Onda	-2.3	16.4	-20.0
Vilafranca	0.9	16.8	-4.2
San Jorge	-3.6	11.6	0.6

With respect to NO_x evaluation (Table 2), there is a clear tendency to the underprediction of NO_x ground-level concentrations. The results improve in background and downwind areas, showing the urban stations (Renfe, Paterna and Pista la Silla) the values further from the reference value of 50-60%.

Table 2. Statistic figures of the evaluation of the NO_x simulations in different air quality stations of the domain for the episode of 13-16 August, 2000.

Station	MNBE (%)	MNGE (%)	UPA (%)
Pista la Silla	-73.9	73.9	-65.9
Renfe	-42.0	85.6	-53.6
Paterna	-1.2	42.6	-67.2
Onda	-53.1	58.4	-20.0
Vilafranca	-19.5	32.1	-10.0
San Jorge	-48.2	50.7	-27.3

This underprediction in urban stations may be caused because the average volume defined by the model's horizontal grid spacing must be sufficiently small to allow the air quality to be reproduced accurately. The large averaging volumes used by regional models are feared to lead to unacceptable errors for many species that are formed via nonlinear chemical reactions, particularly in areas with significant chemical gradients, such as cities (Russell and Dennis, 2000). Therefore, it would become necessary to perform nested simulations with a higher resolution of at least 1 km to capture the ground values of NO_x. NO_x species is more sensitive than ozone to model grid structure since secondary species have more horizontal homogeneity than primary species (Jiménez *et al.*, 2005).

For the evaluation of the model respect to PM (Table 3), the air quality network of the Environmental Department of Valencia Government (Spain) measures PM2.5 only for the station of San Jorge. This is located over a non-paved roadway, which alters the measurements of this pollutant. The model shows a tendency for the underestimation of PM (bias of –2.45% and UPA of –22.3%, with a gross error of 36.1%), mainly because of the influence of natural outbreaks of Saharan dust, which was not considered in the photochemical simulations with MM5-EMIVAL2000-CMAQ. This natural dust may have a significant contribution on the Iberian Peninsula concentrations of PM (Pérez *et al.*, 2004). The hourly peaks of particulate matter are related with the on-road traffic daily timing of emissions, which achieves their maximum intensity at 06-08.00 UTC and 17-19.00 UTC in the evening.

Table 3. Statistic figures of the evaluation of the PM2.5 simulations in the station of San Jorge for the episode of 13-16 August, 2000.

Station	MNBE (%)	MNGE (%)	UPA (%)
San Jorge	-2.45	36.1%	-22.3%

5. REFERENCES

Gangoiti, G., Millán, M.M., Salvador, R., Mantilla, E., 2001. Long-range transport and re-circulation of pollutants in the western Mediterranean during the project regional cycles of air pollution in the west–central Mediterranean area. Atmospheric Environment, 35, 6267-6276.

Jiménez, P., Dabdub, D., Baldasano, J.M., 2003. Comparison of photochemical mechanisms for air quality modeling. Atmospheric Environment, 37, 4179-4194.

Jiménez, P., Baldasano, J.M., 2004. Ozone response to precursor controls: the use of photochemical indicators to assess O_3-NO_x-VOC sensitivity in the northeastern Iberian Peninsula. Journal of Geophysical Research, 109, D20309, doi: 10.1029/2004JD004985.

Jiménez, P., Jorba, O., Parra, R., Baldasano, J.M., 2005. Influence of high-model grid resolution on photochemical modeling in very complex terrains. International Journal of Environment and Pollution, 24, Nos. 1/2/3/4, 180-200.

Jorba O., Pérez, C., Rocadenbosch, F., Baldasano, J.M., 2004. Cluster Analysis of 4-Day Back Trajectories Arriving in the Barcelona Area (Spain) from 1997 to 2002. Journal of Applied Meteorology, 43, 6, 887-901.

Lelieveld, J., Berresheim H., Borrmann, S., Crutzen, P.J., Dentener, F.J., Fischer, H., Feichter, J., Flatau, P.J., Heland, J., Holzinger, R., Korrmann, R., Lawrence, M.G., Levin, Z., Markowicz, K.M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G.J., Scheeren, H.A., Sciare, J., Schlager, H., Schultz, M., Siegmund, P., Steil, B., Stepahanou, E.G., Stier, P., Traub, M., Warneke, C., Williams, J., Zieris, H., 2002. Global air pollution crossroads over the Mediterranean. Science, 298, 794-799.

Millán, M.M., Salvador, R., Mantilla, E., 1997. Photooxidant Dynamics in the Mediterranean Basin in Summer: Results from European Research Projects. Journal of Geophysical Research, 102(D7), 8811-8823.

Millán, M.M., Mantilla, E., Salvador, R., Carratala, A., Sanz, M.J., Alonso, L., Gangoiti, G., Navazo, M., 2000. Ozone cycles in the western Mediterranean basin: interpretation of monitoring data in complex coastal terrain. Journal of Applied Meteorology, 4, 487-507.

Parra, R., Jiménez, P., Baldasano, J.M., 2005. Development of the high spatial resolution EMICAT2000 emission model for air pollutants from the north-eastern Iberian Peninsula (Catalonia, Spain). Environmental Pollution (In Press).

Pérez, C., Sicard, M., Jorba, O., Comerón, A., Baldasano, J.M., 2004. Summertime re-circulations of air pollutants over the north-eastern Iberian coast observed from systematic EARLINET lidar measurements in Barcelona. Atmospheric Environment, 38, 3983-4000.

Russell, A., Dennis, R., 2000. NARSTO critical review of photochemical models and modeling. Atmospheric Environment, 34, 2283-2324.

US EPA, 1991. Guideline for Regulatory Application of the Urban Airshed Model. US EPA Report No. EPA-450/4-91-013. Office of Air and Radiation, Office of Air Quality Planning and Standards, Technical Support Division. Research Triangle Park, North Carolina, US.

US EPA, 2003. Air Chief 10, Emission Factor and Inventoy Group. US Environmental Protection Agency. Research Triangle Park, NC 27 711 (CD-ROM).

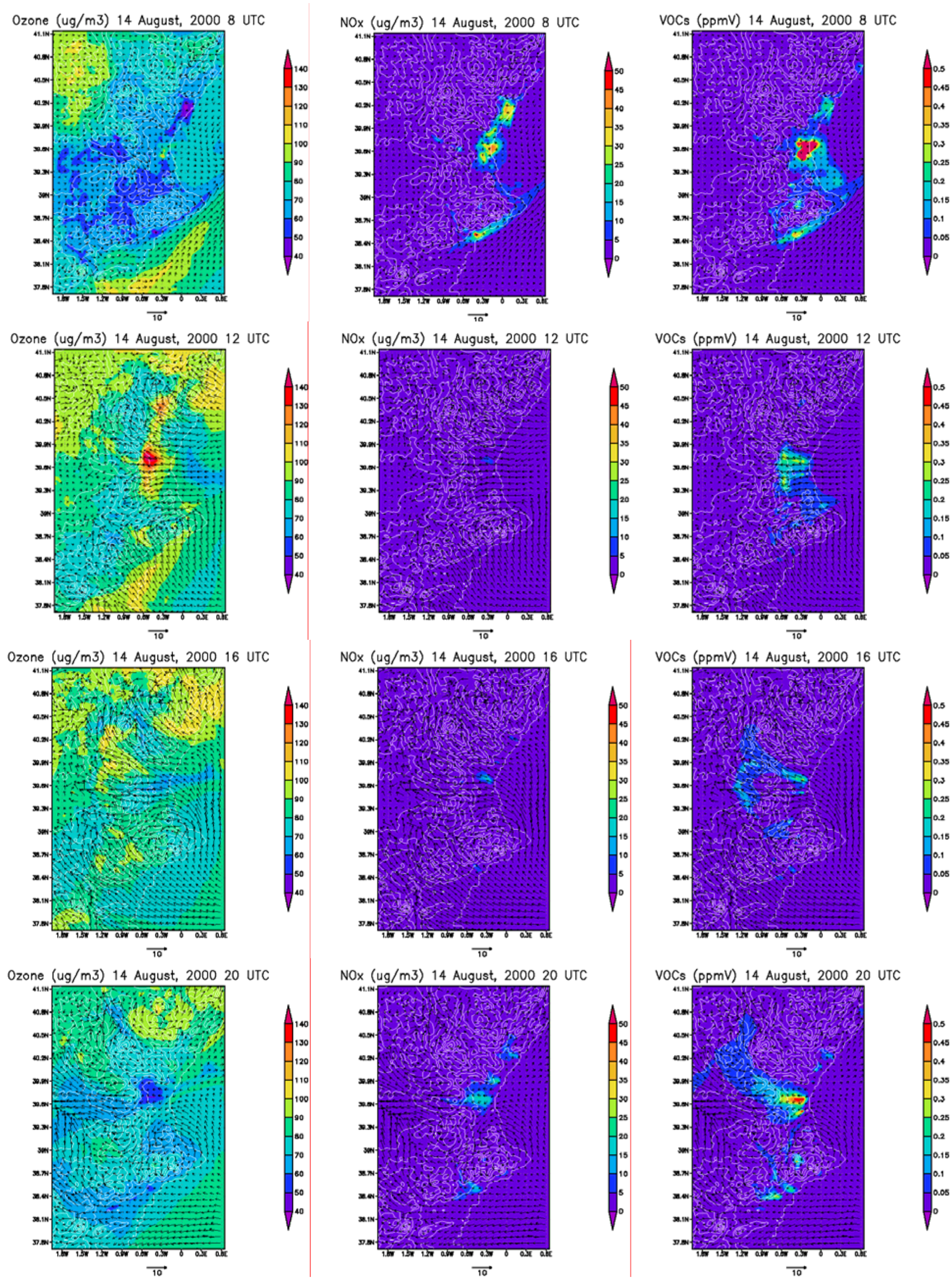

Fig. 2. Wind vectors (m s^{-1}) and O_3, NO and VOCs ground levels ($\mu g\ m^{-3}$), 14 August 2000

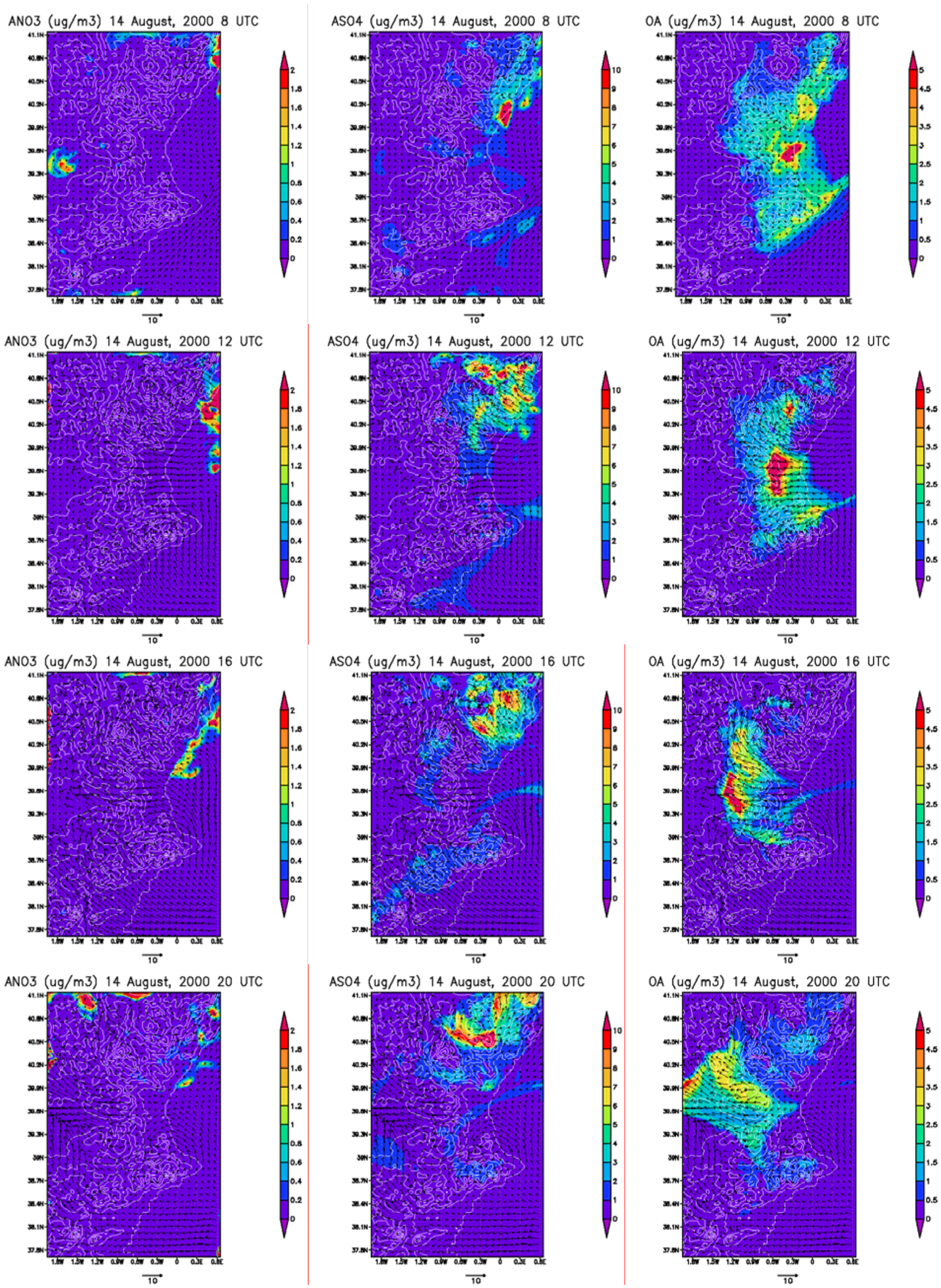

Fig. 3. Wind vectors (m s^{-1}) and ANO_3, ASO4 and OA ground levels ($\mu g\ m^{-3}$), 14 August 2000