Importance of handling organic atmospheric pollutants for assessing air quality

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Abstract

Volatile organic compounds (VOCs) are the main precursors of tropospheric ozone production, playing an important role in photochemical pollution of the atmosphere and, consequently, in the degradation of air quality. Air quality photochemical models require a specific VOC profile for each different main source, based on the most important group compounds. Chromatographic techniques have been used to identify and measure VOC in Portugal. These measured values were used to simulate photochemical pollution, and modelling results were compared with those from another simulation using VOC class distributions from the literature. Ozone concentration values estimated via both simulations indicate the importance of using VOC data from Portugal instead of those obtained in different conditions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photochemical pollution is one of the main current air quality problems. High levels of ozone (O_3) have been measured in several cities of the world, pointing to a clear problem with respect to urban and regional air quality [1]. Southern European countries, due to their specific characteristics, with a large number of solar radiation hours and large quantities of biogenic emissions, are frequently affected by episodes of photochemical smog [2–4].

In fact, ozone and other photochemical oxidants are almost exclusively secondary pollutants that are formed in the troposphere by chemical reactions between volatile organic compounds (VOCs) and nitrogen oxides (NO_x). Methane is only negligibly reactive in ambient air, and hence the VOCs are sometimes referred to as non-methane hydrocarbons (NMHCs) [1]. Mathematical modelling of photochemical smog requires the numerical simulation of all the chemical reactions that take place between NO_x and VOCs. An explicit treatment of all these reactions is practically impossible and, for most practical purposes, the numerical simulations use a condensed kinetic mechanism to avoid excessive simulation costs [5].

Air quality models, aiming to quantify the complex non-linear relationship between the emissions of primary precursors and the maximum ground level concentrations of O_3, require the input of a number of parameters which are currently either poorly defined and/or have large uncertainty. One of the main questions is related to the VOC speciation,

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meaning that hydrocarbon sources have to be treated species by species [6]. There are already some typical VOC class distributions regarding different conditions from those of Portugal (or Southern European countries) [7] where biogenic hydrocarbon sources should be taken into account. Nevertheless, local VOC speciation is needed in order to decrease the uncertainty of photochemical pollution simulations, which requires the measurement and characterisation of these compounds.

Different chromatographic processes have been applied as state-of-the-art techniques to accurately and precisely measure specific VOCs in the atmosphere [8–11]. The combination of enriching procedures for sample collection and the high sensitivity of the chromatographic detectors allows measurement of these compounds at sub-ppb (v/v) levels.

In order to determine the ozone precursors and the photochemical product concentrations in the atmosphere, specific measurement methods have been developed. While gas chromatography (GC) coupled with flame ionisation detection (FID) or mass-selective detection (MS) and electron-capture detection (ECD) is normally used to measure atmospheric non-methane hydrocarbons (C_2–C_{12}) [12,13] and peroxyacetyl nitrate (PAN) [14], respectively, high-performance liquid chromatography (HPLC) using ultraviolet (UV) detection is applied to quantify carbonyl compounds (aldehydes and ketones) [15].

The developments in analytical instrumentation which have been achieved in the last decade have allowed the instrument manufactures to build automated GC systems with integrated sampling and analysis, which can give VOC concentrations on an hourly basis in many cases [16–18].

The main purpose of this work was to measure specific VOC concentrations in the atmosphere and to compare photochemical simulation results using the estimated distribution of VOCs with those obtained from the literature, in order to contribute to our understanding of the role of VOCs for the photochemical potential of the atmospheric process. This approach should be seen as a step forward in the enormous need of combining different data to understand more about the numerical simulation of a complex phenomenon such as the photochemical production of ozone.

2. Experimental

The experimental work consisted of two different approaches: field measurements and numerical simulation experiments. Both measurement and simulation were performed in a coastal region in the central part of Portugal, covering 200×140 km^2. A topographic description of the study domain is presented in Fig. 1. The western part of the study region consist of relatively flat terrain dominated by the Aveiro lagoon, which is a large and branched lagoon extending in a north–south direction following the coastline (about 80 km^2). In contrast, the eastern part of the domain is characterised by rough terrain that follows four mountain ranges: Montemuro (reaching 1382 m), Arada (1119 m), Caramulo (1071 m) and Estrela (2000 m). The topography is also determined by the presence of the River valleys of Vouga and Douro.

The meteorological conditions in this region are strongly influenced by the nearby Atlantic Ocean, with the frequent occurrence of sea breeze winds in spring and summer.

The main anthropogenic emission sources in the region are located in the urban and industrialised areas of Oporto, in the north, with about two million inhabitants and the second largest refinery in Portugal (Matosinhos refinery), and Aveiro, in the south, with about 80 000 inhabitants and an important chemical complex (Estarreja). In the interior, anthropogenic pressure is replaced by the presence of large extensions of forest and agricultural fields.

The simulation domain agrees with the described study region. Concerning the fieldwork, hydrocarbon and carbonyl measurements were made at Giesta, a rural location 20 km SE of Aveiro (Fig. 1). The sampling site was in a large agricultural area, near a small village, surrounded for some kilometres by forest patches constituted mainly by pine and eucalyptus species. Sources of anthropogenic and biogenic emissions within a 20 km radius of the sampling site include Aveiro and other smaller towns, national roads such as the North Highway A1, eucalyptus and pine forests, agricultural crops, mainly maize, and the Pateira de Fermentelos lagoon. Measurement of ambient air concentrations was taken 3 m above ground level. Taking into account
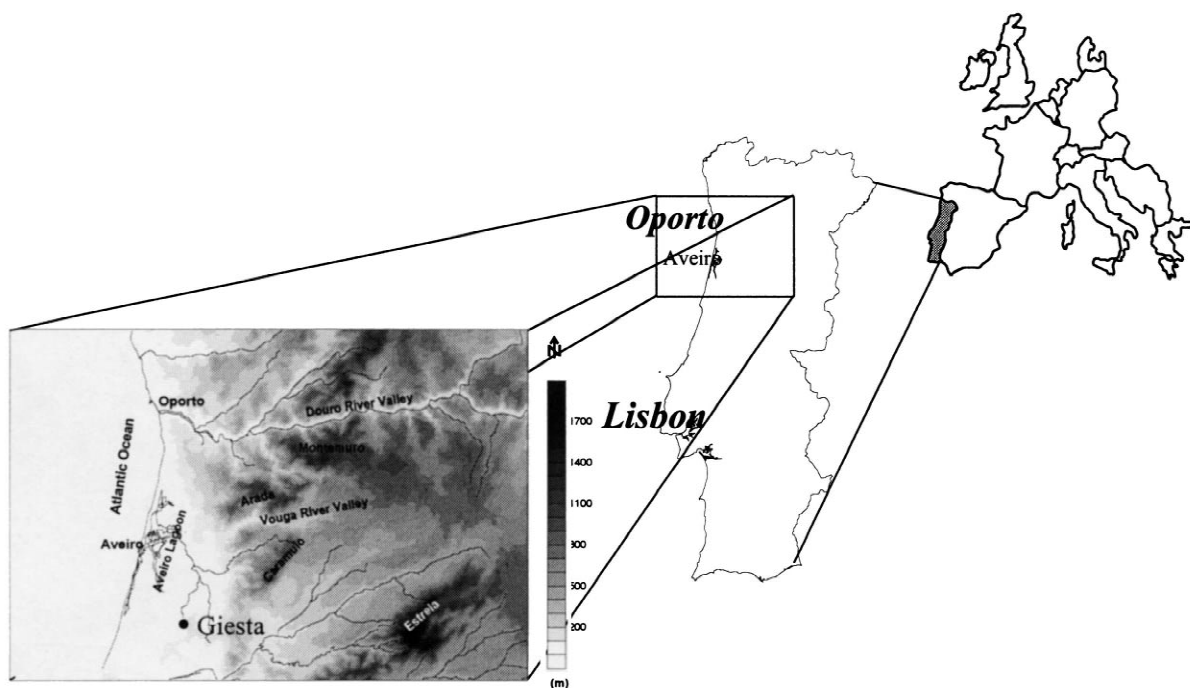
Fig. 1. Topographic description of the study domain.

the sampling site, it was assumed that this measurement height would be representative of air concentrations at the surface layer.

2.1. Sampling and analysis procedures

Several specific VOCs were measured, namely C_2–C_6 hydrocarbons, C_6–C_{11} hydrocarbons and carbonyl compounds.

2.1.1. C_2–C_6 hydrocarbon measurement
Air samples were collected in evacuated 6 l stainless steel electropolished canisters fitted with metal bellow Nupro valves. Opening of the valve allowed the canisters to fill to atmospheric pressure almost instantaneously. They were cleaned prior to sampling by simultaneous heating at 100°C and evacuating to $2 \cdot 10^{-3}$ mbar for 30 min.

The air samples were cryogenically preconcentrated and then analysed by GC, using a 50 m×0.32 mm I.D. Al_2O_3/KCl porous-layer open tubular (PLOT) capillary column (Chrompack) and FID,

according to a technique described previously [19,20].

Identification of NMHCs was made by comparison with reference gas mixtures and by GC–MS confirmation. Daily calibration was performed by injection of 1 ml samples of a commercial gas mixture containing 21 different hydrocarbon compounds in nitrogen in the ppm range.

The detection limit for a 1200 ml sample was 10 ppt for the majority of species measured, and <20 ppt for all quoted species. The precision of replicate canister determinations is <15% for concentrations >200 ppt (for four replicates and a level of confidence of 95%).

2.1.2. C_6–C_{11} hydrocarbon measurement
The hydrocarbon compounds in the C_6–C_{11} range were collected in stainless steel tubes at 2–4°C, filled with 100 mg Tenax TA and 120 mg Carbopack B (Supelco, Bellefonte, PA, USA), by sampling for 60 min at an approximate flow-rate of 50 ml min^{-1}. Pre-removal of water vapour from the air stream was
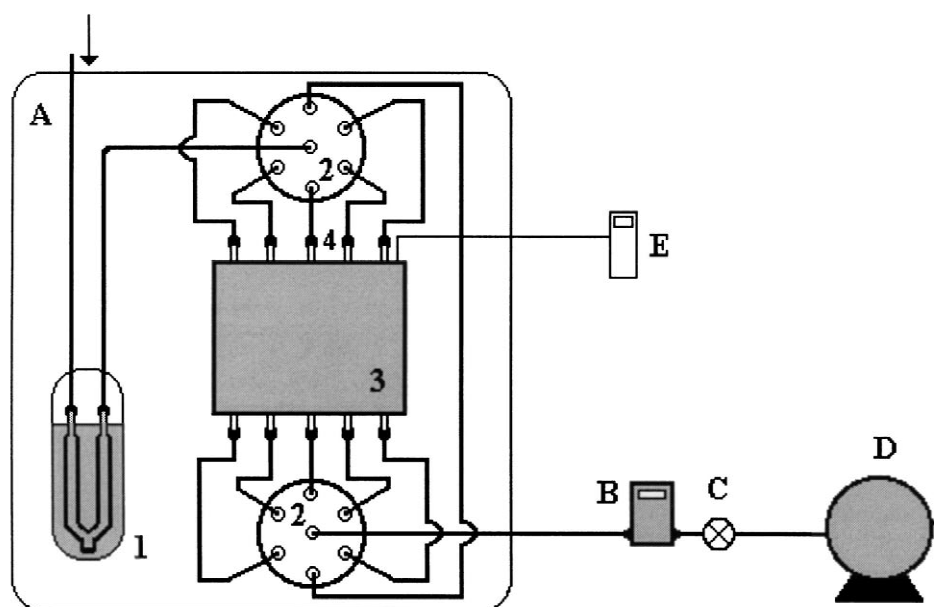
Fig. 2. Sampling system for collection of C_6–C_{11} hydrocarbons in ambient air by adsorption over Tenax TA and Carbopack B. A=Fridge (2–4°C); 1=glass U tube (water vapour condensation); 2=six-position PTFE rotary valve; 3=aluminium block; 4=adsorption tubes; B=mass flow meter; C=micro valve; D=pump; E=temperature probe.

carried out in a U glass tube filled with glass spheres, which was immersed in an ice bath. The field sampling setup is shown schematically in Fig. 2.

After sampling, each tube was transferred to a glass container and stored in a freezer until analysis. The tubes were analysed by a thermal desorption, cryogenic concentration method, using a Chrompack thermal desorption–cold trap injection (TCT) unit, followed by Chrompack CP 9000 gas chromatographic separation and FID. All separations were performed on a 60 m×0.32 mm I.D. 1 μm CP-Sil 5 CB capillary column (Chrompack, Middelburg, Netherlands). Identification of C_6–C_{11} hydrocarbons was made by comparison with reference gas mixtures and liquid standard mixtures in methanol, and by GC–MS confirmation. Daily calibration was performed by injection of 1 ml samples of a commercial gas mixture containing benzene and toluene in nitrogen in the ppm range and by the injection of a few microliters of liquid standard mixtures in methanol. The detection limit for a 3000 ml air volume sample was 25 ppt for the majority of species measured, and <60 ppt for all quoted species. The precision of replicate field determinations by this

procedure is <20% for concentrations >500 ppt (for five replicates and a level of confidence of 95%).

2.1.3. Carbonyl compound measurement

Carbonyl compounds were sampled by drawing air through a silica cartridge coated with 2,4-dinitrophenylhydrazine (Sep-Pak DNPH, Waters). A volume of between 500 and 1000 l of ambient air was sampled for periods of 6 h, during the day, and 12 h, during the night. An ozone trap, consisting of 1 m of 1/4 in. copper tube coated with KI, was connected to the upstream end of the cartridge. The derived products were extracted with 3 ml acetonitrile and analysed by HPLC with UV detection at 350 nm. Separation was performed on a 250 mm Supercosil LC-18, 5 μm column with gradient elution. A standard mixture of 15 DNPH derivatives of carbonyl compounds was used to identify the eluted peaks and for quantification of their concentrations in the eluent sample.

This method was used to identify and quantify two carbonyls in the ambient air samples: formaldehyde (HCHO) and acetaldehyde (CH_3CHO). Acetone was not quantified due to non-constant high blank values.

The precision of replicate field determinations by this procedure is <20% for concentrations >1 ppb (for four replicates and a level of confidence of 95%). The detection limit for a sample volume of 200 l is <0.040 ppb for formaldehyde and 0.530 ppb for acetaldehyde.

Some carbonyl samples were also analysed in a laboratory of the Ministry of the Environment (ME) by HPLC with a diode array detector. Fourteen carbonyl species were quantified with this analytical system.

2.2. Field measurements

Two sampling periods, each of 36 h duration, were established, 26–27 July and 1–2 August 1997. C_2–C_6 compound sampling was carried out every 2 h almost instantaneously by opening the canister in the middle of the C_6–C_{11} compound sampling period (1 h), in order to have the same average sampling time for the two different sampling techniques. In total, 32 samples were collected. Hydrocarbons from ethane to *n*-hexane were measured using the C_2–C_6 technique, while the C_6–C_{11} technique was used to measure hydrocarbons from methylcyclopentane to undecane.

Carbonyl samples were collected for 6 h during the day, and 12 h during the night. From these, only the samples corresponding to the first diurnal cycle were analysed in ME laboratories. Both cycles were analysed at the University of Aveiro for formaldehyde and acetaldehyde.

2.3. Numerical simulation

An air quality photochemical model was applied to the selected region (Fig. 1) with the aim of evaluating the main effects in air quality results derived from the use of different VOC class distributions, from the literature and from local measurement data. The numerical simulation was carried out by the application of the model system MAR IV [2]. This system results from the coupling of a mesoscale meteorological model, a version of the Colorado State University Mesoscale Model (CSU), with a photochemical grid model — the Urban Airshed Model (UAM). The mesoscale meteorological model is used to generate the gridded

meteorological input fields (wind, temperature and mixing height) for the photochemical ozone simulations. The CSU model used is a three-dimensional (3D) version of the hydrostatic, incompressible, primitive-equation model originally developed by Pielke [21]. The model includes a surface heat budget and parameterizations of the atmospheric surface and planetary boundary layers.

The UAM is a Eulerian transport model based on the resolution of the continuity equation, which expresses the conservation of mass of each pollutant in a turbulent fluid in which chemical reactions occur. Turbulent diffusion is parameterized using gradient transfer theory. Simulations are performed on a 3D grid selected by the user to cover the region of interest. UAM calculates the concentrations of both reactive and inert pollutants through the simulation of the numerous physical and non-linear chemical mechanisms that take place in the atmosphere. This medium-range transport model was specially developed for the calculation of ozone concentrations and the development of air quality control strategies.

Version IV of the Carbon Bond Mechanism (CB-IV) for solving chemical kinetics [22] is employed in MAR IV covering 85 reactions and 23 species. Table 1 presents the most important organic species utilised by this version of the MAR IV system.

Photochemical pollution was simulated for the described study area (200×140 km^2) with a horizontal resolution of 5×5 km^2. In the vertical direction the grid consisted of 28 non-equidistant layers until 8

Table 1
Most important organic species utilised by MAR IV (species with available experimental data are in bold type)

Species
Alkanes
Alkenes
Toluene
Xylene
Ethene
Formaldehyde
High-molecular-mass aldehydes (RCHO, R>H)
Peroxyacyl radical ($CH_3C(O)OO^·$)
Peroxyacyl nitrate ($CH_3C(O)OONO_2$)
Cresol and higher-molecular-mass phenols
High-molecular-mass aromatic oxidation ring fragment
Methylglyoxal
Isoprene

km for the mesometeorological model and seven layers up to 3 km for the photochemical transport model.

Simulations were performed for a typical summer synoptical circulation [23], which is related to the extension of the Azores anticyclone over the northern part of the Iberian Peninsula and to the location of a low pressure system to the west of the British Isles. A thermal low was created at the high and arid central plateau of the peninsula, producing a weak (3 m s^{-1}) N-NW wind over Portugal. Strong insolation promoted the formation of mesoscale circulation.

The MAR IV system was applied twice with different specifications for boundary and initial VOC concentrations: (i) based on bibliographic information [7] (Base Case, BC); (ii) based on data available from the field campaign (Experimental Case, EC). In the absence of experimental data, concentrations from the bibliography were also used in the EC simulation.

3. Results and discussion

3.1. Experimental results

The average and the concentration range for the 32 hydrocarbon samples and 10 carbonyl samples are shown in Table 2 for each of the 55 determined compounds.

Propane was the compound with the highest concentration during field measurements. Other compounds such as toluene, α-pinene, β-pinene, n-butane and ethene were also abundant in the Giesta atmosphere. α-Pinene and β-pinene were the most abundant monoterpene compounds found in Giesta air samples, while limonene and 1,8-cineol were also found but at lower levels. These compounds, which are associated with biogenic emissions from vegetation, showed a large diurnal variation with a maximum at night, normally immediately before sunrise. During the day, monoterpene concentrations showed minimum values, near the detection limit for limonene and 1,8-cineol.

The ambient isoprene concentrations showed a diurnal cycle that was the reverse of monoterpene compounds. Isoprene levels increased in the morning to a maximum of 3 ppb in the afternoon, occurring

Table 2
Concentration of hydrocarbons and carbonyl compounds in the Giesta area

Compound	Average (ppb)	Range (ppb)
Ethane	2.46	1.26–3.90
Ethene	3.92	0.79–13.32
Propane	12.22	1.89–45.69
Propene	1.29	0.17–3.88
Acetylene	3.04	0.85–7.07
Isobutane	4.30	1.16–14.13
Propadiene	0.06	<0.01–0.20
n-Butane	7.80	2.00–23.19
trans-2-Butene	0.07	<0.01–0.28
1-Butene	0.33	0.05–1.29
Isobutene	0.49	0.11–1.08
cis-2-Butene	0.05	<0.01–0.21
Cyclopentane	0.19	0.03–0.55
Isopentane	6.33	1.43–18.81
Propyne	0.18	0.04–0.57
n-Pentane	3.53	0.70–10.49
1,3-Butadiene	0.07	<0.01–0.26
trans-2-Pentene	0.09	<0.01–0.43
2-Methyl-2-butene	0.10	<0.01–0.54
1-Pentene	0.19	<0.01–0.56
2-Methyl-1-butene	0.12	<0.01–0.54
Cyclohexane	0.02	<0.01–0.12
2-Methylpentane	1.85	<0.01–6.69
3-Methylpentane	0.99	0.06–3.62
Isoprene	3.86	0.51–13.72
n-Hexane	1.23	<0.01–5.20
Methylcyclopentane	0.68	<0.01–1.80
Benzene	5.81	1.88–12.61
2-Methylhexane	1.06	0.16–3.19
3-Methylhexane	1.09	0.23–3.29
n-Heptane	0.92	0.35–2.42
Toluene	17.63	4.80–40.09
n-Octane	0.62	0.13–1.20
Ethylbenzene	2.65	0.81–6.00
p,m-Xylene	6.92	1.26–19.07
Styrene	0.79	0.18–2.57
o-Xylene	3.11	0.72–7.98
α-Pinene	11.62	0.30–67.38
β-Pinene	9.72	0.25–59.89
Limonene	1.30	<0.03–6.91
1,8-Cineol	0.45	<0.03–3.11
Undecane	0.82	0.32–1.68
Formaldehyde	6.14	1.16–11.70
Acetaldehyde	4.31	1.90–8.22
Acetone	1.04	0.39–1.83
Acrolein	2.75	1.67–4.50
Propanal	1.78	1.25–2.57
Methyl vinyl ketone	0.23	<0.10–0.40
Methacrolein	4.21	1.84–7.31
Butanal	1.17	<0.10–2.77
Benzaldehyde	2.33	1.41–4.43
Valeraldehyde	0.42	0.29–0.58
Hexanal	1.87	1.13–3.12
Glyoxal	1.54	0.52–2.42
Methylglyoxal	4.11	0.56–6.03

normally between 14:00 and 18:00 h. Concentrations decreased with nightfall to levels around 0.1 ppb. The remaining hydrocarbon compounds, which are usually associated with anthropogenic sources, showed similar behaviour, with maximum levels during the night and minimum values in the afternoon, during the period of higher atmospheric turbulence. Normally the highest concentrations were found between 00:00 and 02:00 h. A second, smaller peak maximum was observed for these VOCs in the morning period. Exceptions were observed for propane and ethane which, during the night, showed a constant increase in concentration, reaching a maximum only at dawn.

Formaldehyde and acetaldehyde were the carbonyl species with the highest concentrations. Other species such as methacrolein, butanal, pentanal, glyoxal and methylglyoxal were also observed but at lower levels. Maximum levels were reached during the daytime period for most of the identified carbonyl compounds. An exception was hexanal, which reached a clear maximum level during the night.

Table 3 presents the considered boundary and initial concentrations of the numerical simulations, obtained from the measurements. It can be seen that data from local measurements are higher than those from the literature. This may be related to the fact that these measurements reflect the proximity of the sampling site to urban and industrial areas, and also biogenic emission sources. Additionally, samplings were performed during the summer, when biogenic emissions are higher. Data from the literature only

consider isoprene as a biogenic VOC source which results from the average of several works.

3.2. Numerical results

In order to understand the importance of VOC speciation with regard to input data to photochemical models, namely concerning the study case, hourly ozone concentrations estimated using the two simulations were analysed carefully.

It should be pointed out that photochemical ozone production is not a linear process but dependent on the VOC/NO_x ratio. Ozone-forming potentials generally peak when VOC/$NO_x \approx 6$ [1]. In the case of a NO_x-limited atmosphere, like Portugals [2], even a large increase in the concentration of VOCs will only produce a relatively small increase in ozone production. In fact, the simulated averaged concentrations, temporal and spatial, are not very different for the two cases (<6%). However, the maximum concentration difference is higher, >10%, which shows the importance of VOC experimental data specification as initial and boundary air quality conditions.

With the aim of illustrating the perturbation caused to the study domain by the different VOC conditions, the ozone concentration field, utilised as a phenomena tracer, was plotted with the corresponding wind field for early morning and late afternoon (08:00 and 16:00 h) (Figs. 3 and 4) for BC and the EC. In the plots the wind velocity is scaled at 4 m s^{-1} (morning) and 7 m s^{-1} (afternoon) per grid

Table 3
Boundary and initial concentrations utilised for the Base Case and Experimental Case

|		
Alkene carbon bond	0.60	2.44
Alkane carbon bond	14.94	39.56
Toluene	1.26	15.77
Xylene	0.78	8.74
Ethene	1.02	3.41
Formaldehyde	2.10	6.14
High-molecular-mass aldehydes	1.11	6.73
Methylglyoxal	0.01	0.40
Isoprene	0.10	0.40
Methanol	0.1	0.1
Peroxyacyl nitrate ($CH_3C(O)OONO_2$)	0.01	0.01
Cresol and higher-molecular-mass phenols	0.01	0.01
High-molecular-mass aromatic ring oxidation fragment	0.01	0.01
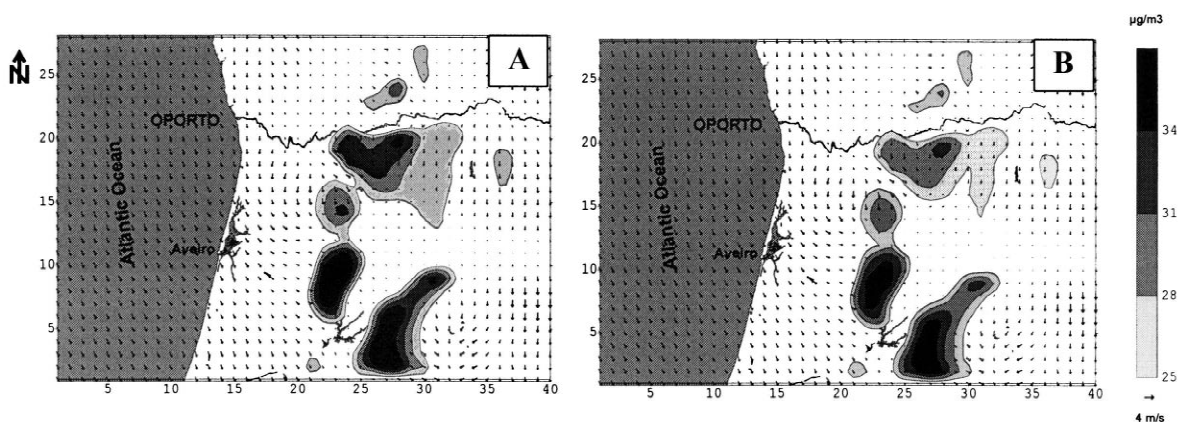
Fig. 3. Ozone concentration field (μg m^{-3}) for the study domain at 08:00 h. (A) Base Case; (B) Experimental Case.

spacing and the concentration of pollutants is represented as the hourly average in μg m^{-3}. In the morning, the photochemical process is still very weak because of the low availability of solar radiation (Fig. 3). In this case, ozone production is very low and the initial and boundary condition differences in air quality do not play an important role. In the afternoon (Fig. 4), ozone production is much more important and the initial and boundary conditions of VOCs play a significant role, inducing differences, either in extension of the area affected by elevated ozone values, or in the maximum ozone values achieved in the study domain.

The experimental results also point to a much more extended area with elevated O$_3$ levels associ-

ated with the Oporto urban and industrial plumes. In contrast, the Base Case indicates a smaller plume only associated with the Oporto urban area. Another difference is the localisation of the maximum values, near Oporto for the Base Case and much more distant from the urban areas in the Experimental Case, which reflect the perturbation of the VOC/NO$_x$ ratio introduced by the new VOC specification in initial and boundary conditions of the Experimental Case.

Thus, the results show that the patterns of photochemical pollutant production are strongly linked to the VOC boundary and initial conditions, in particular in the afternoon because of the photochemical production increase in the selected region.
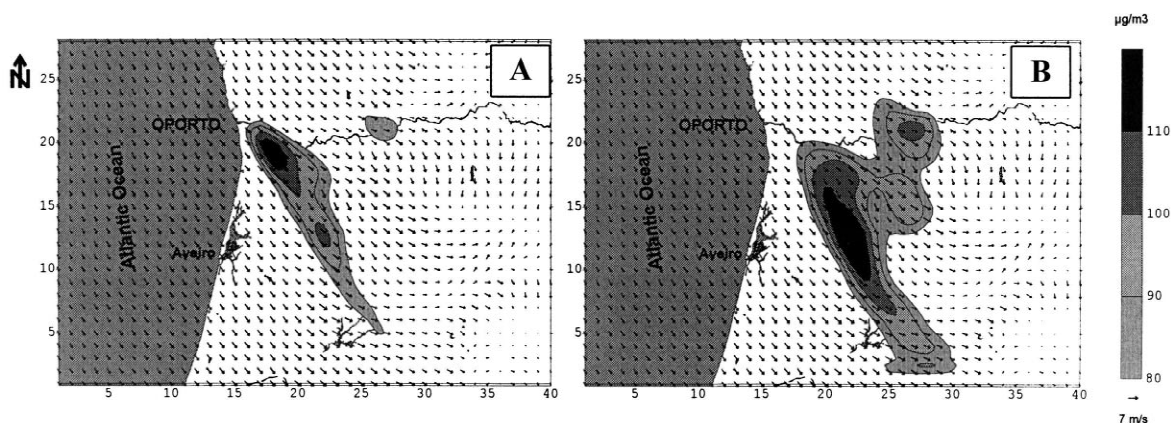

Fig. 4. Ozone concentration field (μg m^{-3}) for the study domain at 16:00 h. (A) Base Case; (B) Experimental Case.

4. Conclusion

Although an enormous amount of detailed atmospheric knowledge and data have been collected during recent years, such information cannot be used effectively to improve conditions on Earth due to the spatial and temporal variability, and lack of information on the different species. The only possible solution is to use that knowledge and data in a comprehensive manner: taken as a whole and in an integrated way. This realisation is causing a fundamental shift in scientific thinking in the air quality domain.

The results obtained with the MAR IV system show that the patterns of photochemical pollutant production are strongly linked to the VOC boundary and initial conditions, in particular in the afternoon because of the photochemical production increase. The results show the importance of an accurate specification of the initial and boundary air quality specifically for the VOCs.

As demonstrated, this need for complementary information and its great complexity may explain why only a few of the many air quality problems that have so far been identified have been solved. In fact, measurements and models should be understood as more than just two different approaches, both perhaps based on good and sound techniques (experimental and mathematical). They should instead be seen as a unique tool to overview complex systems and problems and to provide a solution for air quality management in an interdisciplinary and holistic approach.

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