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Detailed chemical analysis of regional-scale air pollution in western Portugal using an adapted version of MCM v3.1

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ARTICLE DATA

Article history:

Received 15 May 2008

Received in revised form

17 October 2008

Accepted 3 November 2008

Available online 21 December 2008

Keywords:

Chemical mechanism evaluation

Master Chemical Mechanism

Tropospheric chemistry

Field evaluation

Ozone modelling

ABSTRACT

A version of the Master Chemical Mechanism (MCM) v3.1, refined on the basis of recent chamber evaluations, has been incorporated into a Photochemical Trajectory Model (PTM) and applied to the simulation of boundary layer photochemistry in the Portuguese west coast region. Comparison of modelled concentrations of ozone and a number of other species (NO_x and selected hydrocarbons and organic oxygenates) was carried out, using data from three connected sites on two case study days when well-defined sea breeze conditions were established. The ozone concentrations obtained through the application of the PTM are a good approximation to the measured values, the average difference being ca. 15%, indicating that the model was acceptable for evaluation of the details of the chemical processing. The detailed chemistry is examined, allowing conclusions to be drawn concerning chemical interferences in the measurements of NO₂, and in relation to the sensitivity of ozone formation to changes in ambient temperature. Three important, and comparable, contributions to the temperature sensitivity are identified and quantified, namely (i) an effect of increasing biogenic emissions with temperature; (ii) an effect of increasing ambient water vapour concentration with temperature, and its influence on radical production; and (iii) an increase in VOC oxidation chain lengths resulting from the temperature-dependence of the kinetic parameters, particularly in relation to the stability of PAN and its higher analogues. The sensitivity of the simulations to the refinements implemented into MCM v3.1 are also presented and discussed.

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1. Introduction

The development and application of mathematical models describing chemistry, meteorology, and deposition (also designated air-shed models) is critical for the development and assessment of effective control strategies for ground level ozone (O₃) and related air pollution issues (e.g. Carter, 2000; Finlayson-Pitts and Pitts, 2000). A key component of an air-shed model is the description of atmospheric chemistry, which needs to describe the photochemical degradation of emitted volatile organic compounds (VOCs) and NO_x, generating O₃ and other oxidants (e.g. Carter, 2000; Dodge, 2000). If the applied chemical

mechanism is incorrect or incomplete in significant respects, then the air-shed model predictions of the formation of these secondary pollutants may also be incorrect, and its use might result in implementation of inappropriate air pollution control strategies (e.g. Carter, 2000).

Chemical mechanisms used in air-shed models vary considerably in size and complexity. Condensed mechanisms, usually using parameterizations (e.g. Carbon Bond Mechanism — Version IV (CB4) (Gery et al., 1988); Regional Acid Deposition Model (RADM) (Stockwell et al., 1990)), can be used to describe economically the general features of O₃ formation, and their sensitivity to emissions controls. Explicit

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mechanisms (e.g. Master Chemical Mechanism (MCM) (Jenkin et al., 1997); Statewide Air Pollution Research Center Mechanism (SAPRC) (Carter and Lurmann, 1991; Carter, 2000)), which are more fundamentally linked to elementary studies of atmospheric chemical reactions, allow a more detailed examination of the chemistry and the roles of played by individual VOCs in generating O₃ and related secondary pollutants. Because of their explicit nature, however, such mechanisms can contain several thousand species and reactions, such that their use is generally restricted to models containing simple representations of transport processes. Whether an applied mechanism is highly parameterized, highly explicit, or of intermediate complexity, its performance ideally needs to be evaluated by comparing its predictions with experimental data. Such evaluations should be made using both the results of environmental chamber experiments, and by comparing the predictions of an air-shed model, which includes the photochemical mechanism, against field measurements of appropriate species.

In the present study we describe the implementation and application of the most up-to-date version of a near-explicit photochemical mechanism, the Master Chemical Mechanism (MCM), into an air-shed model representing the Portuguese west coast region. As described in more detail below, the MCM describes the detailed degradation of a large series of emitted VOCs, and the associated formation of O₃ and speciated organic intermediates under conditions appropriate to the planetary boundary layer, (Jenkin et al., 1997). Various versions of the mechanism have previously been applied to the detailed study of ambient atmospheric photochemical processes on local and regional scales (Derwent et al., 1998; Derwent et al., 2005; Utembe et al., 2005; Johnson et al., 2006a,b; Evtyugina et al., 2007). However, only in recent years has the performance of the MCM been evaluated using the results of environmental chamber experiments (Saunders et al., 2003; Bloss et al., 2005a; Zádor et al., 2005; Hynes et al., 2005; Pinho et al., 2005, 2006, 2007).

The mechanism used in the present work is an adapted version of MCM v3.1 (denoted “MCM v3.1b”), which incorporates a number of refinements identified in our recent chamber evaluations (Pinho et al., 2005, 2006, 2007). MCM v3.1b is used in a trajectory model to simulate the chemical evolution of air parcels in the Portuguese west coast region, and the results are evaluated in relation to field observations of O₃, NO_x and selected hydrocarbons and oxygenates. The detailed chemistry is examined, allowing conclusions to be drawn concerning chemical interferences in the measurements of NO₂, and in relation to the sensitivity of the chemistry of ozone formation to changes in ambient temperature. The sensitivity of the simulations to the changes implemented in MCM v3.1b, relative to MCM v3.1, are also tested.

2. Photochemical Trajectory Model (PTM)

The air-shed model used in this study was a Photochemical Trajectory Model (PTM), which was integrated with the variable order Gear's method (Curtis and Sweetenham, 1987), using the software FACSIMILE.¹ The following paragraphs describe the treatment of transport, chemistry and emissions

in the model; the sources of meteorological data used to define the air parcel trajectories; and the observational air quality data used to evaluate model performance.

2.1. Transport model

The selected transport model was a simple trajectory one layer box model with a Lagrangian approach, thereby facilitating the use of a highly detailed description of chemical processing (see Section 2.2). Although this represents a compromise in the description of transport processes, a trajectory one layer box model provides an adequate description of air mass transport if several conditions are assured for the chosen application, namely good vertical dispersion and well-defined horizontal transport. The selected case study was a summer period in the coastal region of the north of Portugal (see Fig. 1), considering slow transport inland from the Portuguese coast during daytime. Good vertical dispersion and well-defined horizontal transport provide a reasonable approximation since, during the summer period, circulations from W/NW associated to the Azores anticyclone and with a thermal depression formed above the Iberian Peninsula result in local regional circulation in the form of strong sea breezes (Nadal, 1980; Coutinho, 1995). Also the starting time of the first daily wind trajectory takes place well after the breakdown of night time inversion guaranteeing a well mixed boundary layer. Another important feature of the selected domain is that the transport time between the coast at Aveiro (40°38'N, 8°39'W) and the inland measurement site at Covelo (40°18'N, 8°45'W) is ca. 4–5 h, and is therefore of the same order as that considered in our previous chamber evaluation studies (Pinho et al., 2005, 2006, 2007).

Air masses trajectories were calculated based on the back-trajectory principle. The trajectories were calculated, for 30 minute intervals, relative to the arrival of the air mass at Covelo. The trajectories were calculated using wind measurements taken at 10 m height, obtained in Aveiro and Sangalhos (40°25'N, 8°25'W) sites (see Fig. 1). The model therefore represents a well-mixed boundary layer box travelling along these trajectories. The box has horizontal dimensions of 2×2 km, has a height which varies with location and time, and which corresponds to the height of the mixed layer. This was defined on the basis of radio sounding results obtained in Sangalhos during the field campaign. The minimum and maximum heights for June 29 were 400 m and 630 m, and for June 30, 230 m and 500 m. The use of wind measurements taken at 10 m height implies some error since the wind speed and direction change with altitude.

The temperature and relative humidity used in PTM for each grid cell was calculated by interpolation of temperature measurements at Aveiro and Anadia meteorological stations and measurements in Covelo, during the CZCM field campaign 2001.

2.2. Chemical mechanism

The mechanism used in the present work is an adapted version of MCM v3.1, which incorporates a number of refinements identified in our recent chamber evaluations (Pinho et al., 2005, 2006, 2007), and which is hereafter referred to as MCM v3.1b. Version 3.1 of the MCM considers the oxidation of methane and 135 emitted non-methane VOC,

¹ FACSIMILE for Windows, version 3.5.5, ©UES Software 2000.

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