

# Photochemical pollution under sea breeze conditions, during summer, at the Portuguese West Coast

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Received 10 December 2005; received in revised form 15 May 2006; accepted 18 May 2006

## Abstract

Photochemical pollution was studied at three sampling places located on the Portuguese West Coast along the coast-to-continent breeze direction, during the summer period. A first basic campaign (June–July 2001) covered mainly the monitoring of trace gases, volatile organic compounds (VOCs) and the vertical profiles of O<sub>3</sub>. During a second auxiliary campaign (July 2002), the vertical profiles of pollutants (O<sub>3</sub> and VOCs) at the west coast point were further assessed. The important role of marine breezes on the formation and transport of photochemical pollutants has been confirmed.

Vertical profiles of O<sub>3</sub> revealed a depletion of ozone at altitudes lower than 100–300 m during the night and the early morning and a good vertical mixture during the day in the sea breeze boundary layer. The analysis of vertical profiles of VOCs revealed that lower concentrations tended to exist at the top of the sea breeze layer. However some compounds, such as *n*-hexane, showed a higher concentration at higher levels. The concentration of O<sub>3</sub> in the diurnal boundary layer, resulting from photochemical reactions of both the anthropogenic and biogenic precursors, gradually increased with the sea breeze inland, ranging from around 30 ppb at midday on the coast, to 70 ppb in the inland rural zone. However, in all sampling places, the photochemical pollution episodes at 80–100 ppb level took place under particular conditions of high photochemical activity and sea breeze circulation. As revealed from analyses of propylene equivalent concentrations, the photochemical formation of O<sub>3</sub> in the inland rural zone is strongly affected by biogenic VOCs (isoprene and monoterpenes), whereas a major contribution to the photochemical pollution with ozone in the coastal zone issued from anthropogenic VOCs (alkenes and aromatics).

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*Keywords:* Photochemical pollution; Air transport; Portuguese West Coast; Sea breeze

## 1. Introduction

Photochemical pollution is an important problem in many urban areas worldwide (Zhang and Oanh, 2002; Jenkin and Clemitshaw, 2000; Klemm et al.,

1998), related to a series of photochemical transformations of volatile organic compounds (VOCs) and nitrogen oxides in the atmosphere under solar irradiation, which result in the formation of secondary pollutants such as ozone and other photooxidation products (oxygenated and nitrogenated organics). Tropospheric ozone is considered the most important photo-pollutant affecting public health, agriculture and forests (Brauer and Brook,

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1997; Krupa, 1997, Hogsett et al., 1997; Ozen et al., 2002). The concentration profiles of photo-pollutants depend significantly on the atmospheric circulation and the vertical mixing rates (Cheng, 2002; Chen et al., 2002; Bonsang et al., 2001; Kambezidis et al., 1998; Hayden et al., 1997; Mckendry et al., 1997).

The photochemical pollution episodes occurring under high-temperature conditions in Europe (and in Portugal in particular) represent also a regional problem requiring the population to be alerted and public health protection measures to be taken. In Portugal, problems of air quality from primary and secondary pollutants, arise frequently in the littoral zone where most of the population and anthropogenic activities are concentrated, resulting in important emission rates of  $\text{NO}_x$  and VOC pollutants, principally from energy production and road transport. Simultaneously, the local climatic conditions (high temperatures and intensive solar irradiation), especially in the summer period, favour the formation of photochemically induced secondary pollutants. Several recent studies carried out in Portugal indicate that the coastal breezes play an important role in the air circulation during summer and, consequently, affect the regional air pollutants' distribution (Bonsang et al., 2001). Particularly, the sea breeze was suggested to be responsible for the inland transport of air pollutants emitted at the coastal urban and suburban zones (Bonsang et al., 2001). It might be highlighted that there is a lack of knowledge in Portugal on the ozone levels in rural areas, since the national monitoring network is localised essentially in coastal urban zones. At the same time, the only national station situated in the interior region (Lamas de Olo) registered in the last 3 years the highest ozone levels in the region. Also a wider study performed, using passive methods, clearly showed the existence of ozone levels in the interior areas of the country even higher than those registered on the coast (IA, 2003/2005).

Knowledge on the vertical/horizontal distribution of atmospheric pollutants and occurring meteorological parameters is essential for the evaluation of atmospheric transport conditions related to the air mass dilution and consequently for the quantification of pollutants emission (Baumbach and Vogt, 1995; Lawrimore et al., 1995). This information provides also input data for the modelling of the transport of pollutants thus allowing the prediction of air pollution occurrences. The levels of atmospheric pollutants on the western coastal part of

Portugal under sea breeze conditions have not yet been assessed. This lack of information limits the modelling of pollutants' transport and their photochemical transformations in mesoscale, which in turn is a very difficult task due to the complexity of former processes.

The main goal of this work is the experimental determination of air pollution levels in the coast-to-inland sea breeze direction aimed at evaluating the dominant processes and their parameters, affecting the production and the distribution of photochemical pollutants. Vertical profiles of atmospheric pollutants and their precursors have been determined for the better understanding of photochemical smog formation on the Portuguese West Coast.

## 2. Experimental

### 2.1. Experimental strategy

Two field campaigns were carried out aimed at investigating the impact of a sea breeze on the inland transport of air pollutants emitted on the west coast of Portugal and to assess the formation of photochemical pollutants during this transport. The basic campaign CZCM-2001 with simultaneous measurement of hydrocarbons, trace gases and meteorological data, was carried out during the period from 25 June to 2 July 2001 at three locations along the breeze direction (Fig. 1). In one of these locations in the middle of the studied air mass trajectory (Sangalhos), the vertical profiles of ozone concentration and the meteorological parameters were measured. The second auxiliary field campaign CZCM-2002 took place from 22 to 25 July 2002 on the western coast of Portugal with the objective of investigating the vertical profile pattern of pollutants concentration.

### 2.2. CZCM-2001 basic campaign

#### 2.2.1. Measurement sites

The coastal zone of the central and northern part of Portugal is a relatively populated region with a high industrial activity, and is associated with the most important urban centres (Aveiro, Coimbra and Oporto). Forestry, agriculture and cattle breeding are the predominant human activities in the plateau regions located in the interior of Portugal. These regions are characterised by a high-density forest coverage consisting mainly of *Eucalyptus globulus* and *Pinus pinaster*.

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