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Nocturnal surface ozone enhancement over Portugal during winter: Influence of different atmospheric conditions

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HIGHLIGHTS

- 4 distinct events of nocturnal surface ozone (NSO) enhancement were analyzed.
- WRF model was used to simulate the atmospheric conditions during NSO enhancement.
- Results show that different atmospheric mechanisms are responsible for each event.

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ABSTRACT

Four distinct nocturnal surface ozone (NSO) enhancement events were observed, with NSO concentration exceeding 80μg/m^3, at multiple ozone (O_3) monitoring stations (32 sites) in January, November and December between year 2000–2010, in Portugal. The reasonable explanation for the observed bimodal pattern of surface ozone with enhanced NSO concentration during nighttime has to be transport processes, as the surface ozone production ceases at nighttime. Simultaneous measurements of O_3 at multiple stations during the study period in Portugal suggest that horizontal advection alone cannot explain the observed NSO enhancement. Thus, detailed analysis of the atmospheric conditions, simulated with the Weather Research and Forecasting (WRF) model, were performed to evaluate the atmospheric mechanisms responsible for NSO enhancement in the region. Simulations revealed that each event occurred as a result of one or the combination of different atmospheric processes such as, passage of a cold front followed by a subsidence zone; passage of a moving surface trough, with associated strong horizontal wind speed and vertical shear; combination of vertical and horizontal transport at the synoptic scale; formation of a low level jet with associated vertical mixing below the jet stream. The study confirmed that large-scale flow pattern resulting in enhanced vertical mixing in the nocturnal boundary layer, plays a key role in the NSO enhancement events, which frequently occur over Portugal during winter months.

1. Introduction

Surface ozone (O_3) is a photo-chemically produced, highly reactive, secondary air pollutant and an important greenhouse gas (West and Fiore, 2005). Under clear sky conditions O_3 exhibits marked diurnal variability, particularly at urban and suburban areas and less prominent at rural areas. O_3 concentration starts increasing after sunrise, due to initialization of photochemical production involving nitrogen oxides (NO and NO_2) and volatile organic compounds (VOCs), and reaches the maximum concentration during early afternoon. O_3 concentration sharply decreases during late afternoon, while at night, due to surface deposition and

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chemical destruction, minimum values of O_3 concentration are measured (Zhang et al., 2004). In the presence of stable nocturnal boundary layer (NBL), O_3 generally has a positive gradient from the surface to the top of the NBL (Geyer and Stutz, 2004; Stutz et al., 2004) due to insufficient downward mixing because of the nocturnal capping (Kuang et al., 2011). The aforementioned pattern of O_3 diurnal variation is observed almost routinely, although occasional enhancement of nocturnal surface ozone (NSO) is reported at various sites by many researchers (Coulter, 1990; Corsmeier et al., 1997; Jain et al., 2005; Hu et al., 2012; Kulkarni et al., 2013, 2015; Klein et al., 2014). As photochemical production of O_3 ceases at nighttime and in the absence of any known sources of O_3 in the NBL, NSO enhancement can only be attributed to transport processes (Salmond and McKendry, 2002) influenced by favorable atmospheric conditions.

Various possible mechanisms for the NSO enhancement are proposed, such as mountain valley wind system and vertical mixing (Sanchez et al., 2005), land and sea breeze (Nair et al., 2002), horizontal transport (Sousa et al., 2011), role of low-level jet (LLJ) associated with vertical mixing (Corsmeier et al., 1997; Klein et al., 2014), titration of urban ozone in the late afternoon/early evening followed by vertical mixing (Chan et al., 1998; Leung and Zhang, 2001), and transport due to vertical wind (W) from residual layer (Sanchez et al., 2007). Depending on various conditions such as the geographical location, boundary layer dynamics, topography, type of environment (urban, suburban and rural) and local weather conditions, any one of the proposed mechanisms was considered responsible for the NSO enhancement. Some studies of NSO enhancement are reported all over the world but mostly on a single event, over a single site or small region (with few monitoring sites) with almost no repetition over the same study area, with some exceptions of Sousa et al. (2011) and Kulkarni et al. (2013, 2015). Due to aforementioned reasons, there is still no consensus among researchers on the mechanisms that lead to the NSO enhancement. Further, the study of NSO enhancements remains a challenge, since its occurrence cannot be predicted accurately and thus, it is difficult to plan an extensive field experiment due to financial constraints among others.

The adverse effects of high daytime O_3 concentration on flora and fauna and on human health are well established (Menezes and Shively, 2001; Anenberg et al., 2009). High NSO concentration, during NSO enhancement events (exceeding 80 $\mu g/m^3$, which is more than O_3 exposure index AOT40 (2008/50/CE Directive)), has harmful effects on vegetation and plants, particularly in C3 and C4 plant species (Segschneider et al., 1995; Musselman and Massman, 1999; Musselman and Minnick, 2000; Takahashi et al., 2005), causing water loss and reduced whole-plant production (Matyssek et al., 1995). However, the adverse effects of high NSO concentration, during NSO enhancement events, on the human health are still not studied, as on one hand NSO is well below 60 ppb (120 $\mu g/m^3$) threshold set by European Directives EU60 and, on the other hand, during nighttime, particularly in winter, the outdoor human activities are normally diminished eventually inexistent. The NSO enhancement is basically the spatial redistribution of ozone by vertical mixing from lower free troposphere or within the nocturnal boundary layer, which may be important since it may affect the photochemistry of the following day therefore the overall air quality (Ravishankara, 2009). Furthermore, enhanced NSO can result in increased absorption of the outgoing longwave radiation causing localized warming due to greenhouse effect (West and Fiore, 2005; Kulkarni et al., 2013).

The general opinion about NSO enhancement is that it is highly variable in time and space (Löffler-Mang et al., 1997) and considered as an isolated or a special event. However, Sousa et al. (2011) analyzed hourly O_3 data for the period 2005–2007 from 4 stations in Portugal and found it to be more frequent. They further concluded that there was a close relationship between wind direction and the observed NSO enhancement. Similarly, Kulkarni et al. (2013) analyzed long term (2000–2010) hourly O_3 data and reported that (i) NSO concentration exceeded 40 $\mu g/m^3$, 60 $\mu g/m^3$ and 80 $\mu g/m^3$ on more than 50%, 20% and 2% of the days respectively, during the study period, and (ii) observed an increasing trend in the NSO concentration over Portugal. The studies by Sousa et al. (2011) and Kulkarni et al. (2013) have performed statistical analysis, but lack to identify and perform in-depth analysis to determine the specific reasons for the NSO enhancement.

The aim of this study is to perform in-depth analysis of four NSO enhancement events and investigate the role of different atmospheric mechanisms responsible for repetitive occurrence of these events of varying periods and intensities with concentration exceeding 80 $\mu g/m^3$, over Portugal, using both observational data and modeled simulations. The Weather Research and Forecasting (WRF) regional climate model (V3.7.1) (Skamarock et al., 2008) was used to study the influence of atmospheric conditions, and inferred possible ozone transport mechanisms due to vertical mixing from residual layer or from the free troposphere to the surface (Jaffe, 2011) during NSO enhancement events over Portugal.

2. Study area, data and method

Portugal is located on the Iberian Peninsula and is surrounded by the Atlantic Ocean in the west and south coasts, and bordered by Spain in the north and east sides. It is located between 37° and 42°N latitudes, and 10° and 6° W longitudes. In order to take into account the spatial variation of the climatological and topographic conditions and to facilitate the data analysis and interpretation, Portugal is categorized into two regions, namely (I) North of Portugal (NoP) and (II) South of Portugal (SoP) (Fig. 1a) broadly following Koppen-Geiger Climate Classification. In general, NoP has Mediterranean climate with humid warm summers and mild rainy winters whereas, SoP has subtropical Mediterranean climate with mild winters and medium hot summers. The NoP is mountainous with several plateaus indented by river valleys, whereas the SoP is characterized by rolling plains.

2.1. Surface ozone observation

Hourly records of O_3 concentrations are obtained from 32 air quality monitoring stations, representing different type of environment (urban, suburban and rural) and type of influence (background, traffic and industrial), spatially distributed all over Portugal (Fig. 1a). All of these stations belong to the Portuguese Environmental Agency - APA network (http://www.qualar.org/). In this study, only sites with >90% data coverage for the whole period of our interest are used for analysis.

Table 1 gives detailed list of stations with information such as name of the stations, latitude-longitude-altitudes, type of environment, type of influence, operational status and data availability (%). 12 of the 32 monitoring stations are located in the NoP and the remaining 20 in the SoP. Monitoring stations are well scattered in the respective regions as shown in Fig. 1a, but are mainly clustered in and around Porto in the NoP and Lisbon in the SoP, the two biggest metropolitan areas in the respective regions.

2.2. Criteria to identify the NSO enhancement events

In this study, four distinct events of NSO enhancement (Table 2) were identified to investigate the repetitive occurrence of NSO events over the same geographical area (Portugal), based on the following criteria: