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Ambient levels and temporal trends of VOCs, including carbonyl compounds, and ozone at Cabañeros National Park border, Spain

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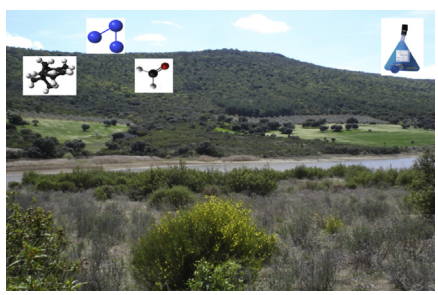
HIGHLIGHTS

- Atmospheric carbonyls, VOCs and ozone were monitored in gaseous atmospheric samples.
- Monthly variations of carbonyl compounds were apparent with maximum values observed in July and August.
- The levels of VOCs were very low ranged from not detected or below detection limit up to <0.54 μg m^{-3}.
- Ozone shows a clear seasonal variation with the maximum monthly value registered in March.
- Air mass back trajectories have been calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

Concentration levels of 15 carbonyls, 17 VOCs and ozone were studied at Cabañeros National Park border, Spain, in an area mainly constituted by holm oaks (*Quercus ilex*) and cork oaks (*Quercus suber*), along with scrubland formations such as rock-rose and heather. The compounds were collected by means of diffusive samplers from August–November 2010 and February–August 2011. Carbonyl compounds, VOCs and O_3 were analysed by HPLC with diode array UV–Vis detector, GC–FID and by UV–visible spectrophotometry, respectively. The most abundant carbonyls were hexanal, acetone–acrolein, formaldehyde and acetaldehyde. Seasonal variation was apparent with maximum values observed in summer months. Total carbonyl concentrations ranged from 2.8 to 19.7 μg m^{-3}. Most VOCs studied (using chemically desorbable cartridges) were either not detected or were below their detection limits, however, a parallel sampling using thermally desorbable cartridges, from May 22 to June 19, revealed the presence of much more VOCs, identified using GC–MS. O_3 concentration ranged from 27.2 to 90.5 μg m^{-3}, reaching the maximum monthly mean concentration in March (84.4 μg m^{-3}). The analysis of back trajectories indicates the transport of polluted air masses from remote areas, mainly from the Mediterranean basin that should contribute to the high levels of ozone observed.

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1. Introduction

The atmospheric reactivity of volatile organic compounds (VOCs) may influence the concentration of tropospheric photochemical ozone, both in pollution episodes and in the background troposphere (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). Recent years have seen a growing appreciation of the importance of naturally generated VOCs in the atmosphere. In some areas with warm climates such as the studied in this work, VOCs from vegetation can play an equal or greater role than anthropogenic sources in contributing to low-level ozone formation (Figueruelo and Dávila, 2004). This is particularly important in rural areas of great ecologic interest (e. g. Cabañeros National Park studied in this paper) because elevated concentrations of surface ozone have been shown to damage vegetation (Bergweiler et al., 2008; Fishman et al., 2010). In order to assess this ozone damage to vegetation, the European Directive established two limits using the AOT40 parameter. The critical daytime AOT40 value for trees over six months is 20 000 $\mu g\ m^{-3}$ h (10 000 ppb h), calculated from April to September, whereas the AOT40 to protect vegetation is 6000 $\mu g\ m^{-3}$ h, calculated from May to July.

Thus, emissions of VOCs in urban or rural areas and their impact on the environment are necessary to evaluate the exposure of the population and vegetation to gaseous pollutants better. Emission estimates of biogenic VOCs for regions in Europe are relatively uncertain and inventories are poor. Likewise, several measurements of VOCs in European rural and urban areas have been reported in the literature in recent years (Pilidis et al., 2005; Possanzini et al., 2007; Coll et al., 2010; Morknoy et al., 2011). However, only a few studies have been conducted in Spain (Parra et al., 2006; Gallego et al., 2008; Notario et al., 2013). In this sense, our group reported recently the first observations of VOCs concentrations, in the coastal, industrial area of Huelva near the Doñana National Park, South-west of the Iberian Peninsula (Villanueva et al., 2013). Acetone and formaldehyde were the most abundant carbonyls, followed by acetaldehyde and propanal. Maximum and minimum values for all these compounds in the period of measurement, and their relationship with meteorological parameters with influence of anthropogenic or/and biogenic emissions were also analysed.

This work presents the first measurements and analysis related to VOCs, including aldehydes and aromatic hydrocarbons for a whole year, in the important ecologic area of Cabañeros National Park in central-southern Iberian Peninsula, in order to cover the existing lack of VOCs emissions in the studied zone and their relation to ozone formation. With respect to that, we recently analysed the levels and surface ozone temporal variations in the study carried out by our group in this rural area (Notario et al., 2012, 2013). The obtained results showed a great background average ozone concentration. We also observed that the European Directive limits to protect the human health and vegetation were widely exceeded; these facts pointed out an ozone problem in this rural region, where VOCs emissions probably play an important role. Our study must contribute to the understanding of the photochemical air pollution in the Western Mediterranean Basin and in the central-southern of the Iberian Peninsula that could be affected by high concentrations of photochemical pollutants. Finally, we intended to extend the database and the inventories of VOCs emissions in these regions of Europe.

2. Experimental section

2.1. Site description

Field measurements were conducted on the southwestern border of the park at about 6 km east of the village of Horcajo de los Montes (39.2° N, 04.4° W, 617 m above sea level) in the region of Castilla La Mancha, in central-southern Spain (Fig. 1). The sampling point was located about 90 Km northwest of Ciudad Real, an urban area of around 72 000 inhabitants and about 116 km southwest of Toledo, an urban area of around 82 000 inhabitants.

The climate of this region of Toledo Mountains has been classified as temperate Mediterranean climate with oceanic tendency in its western side. While the entire park is included in the meso-Mediterranean floor. The most representative plant community, to the foothills of these mountains, is constituted by holm oak (*Quercus ilex*) and cork oak (*Quercus suber*), as the main species, along with other transition formations or scrubland formations such as rock-rose and heather that are accompanied by other aromatic plants such as Rosemary (*Rosmarinus officinalis*), the lavender (*Lavandula stoechas*) or Gorse (*Genista hirsuta*). The oaks, formation where dominates the holm oak, have a wide variety of associated plants and shrubs such as strawberry tree (*Arbutus unedo*), *labiérnago* (*Phillyrea angustifolia*), green olives (*Pistacea terebinthus*), honeysuckle (*Lonicera implexa*), common plants like peony (*Paeonia broteroi*) and thermophilic species as wild olive (*Olea europaea*) and mastic (*Pistacia lentiscus*).

In order to determine the origin and pathway of the air masses affecting the results involved in this study, back trajectories were computed using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model Version 4 developed by the NOAA's Air Resources Laboratory (ARL) (Draxler et al., 2009). The GDAS input meteorological files have a spatial resolution of 1° × 1° and 24 levels of vertical resolution. The three-dimensional kinematic back trajectories were calculated using the vertical wind component provided by the meteorological model. Back trajectory duration of 48 h was considered enough to represent the synoptic air flows in this area. Two back trajectories were calculated every day (00:00 and 12:00 UTC). In order to understand the behaviour of the air masses circulating in the planetary boundary layer (PBL), these trajectories were calculated at a 100-m height. A cluster methodology was applied to form air mass groups using the tool incorporated in the HYSPLIT model.

Air mass clusters for two periods 12–20 November 2010 and 20–27 March 2011 are shown in Fig. 2a and b, respectively. In November, air masses came clearly from the W–NW sector. Three have their origin in the Atlantic Ocean and the other two with higher occurrence frequency (30 and 32%) have their origin in the Iberian Peninsula. However, in March air masses came mainly from the Mediterranean basin. Another origin is found in air masses coming from the northern Iberian Peninsula. Therefore, the studied area may be affected by air masses loaded with air pollutants from Valencia metropolitan area (an eastern urban zone with a population greater than one million), Alicante and Cartagena (an industrial area) which may be injected into the Iberian Peninsula plateau thanks to the mesoscale processes developed in the coastal area (Millán et al., 2002). Although Madrid, in the North, is the largest urban area close to the measurement site, the air pollution generated in this area would reach the Cabañeros National Park with a lower frequency since the Toledo Mountains present an important orographic barrier.

2.2. Experimental design

Radiello® passive samplers (Fondazione Salvatore Maugeri, Padova, Italy) were used for monitoring VOCs, carbonyl compounds and ozone and were placed at about 1.8 m above the ground level. VOCs were sampled by two configurations of the Radiello® diffusive sampler: the chemically desorbable sampler and thermally desorbable one. Each cartridge was exposed for 1 week for