



Summertime high resolution variability of atmospheric formaldehyde and non-methane volatile organic compounds in a rural background area



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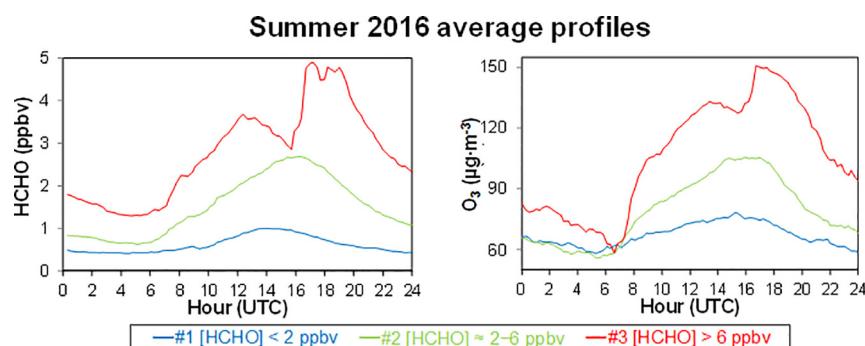
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HIGHLIGHTS

- Summertime HCHO mixing ratios were continuously measured in a rural forested area.
- A high-time resolution database was obtained: 15 min-averaged HCHO and hourly NMHCs.
- HCHO mixing ratios correlated with ozone and isoprene.
- Meteorological conditions determined HCHO peaks and daily profile.
- An extra amount of HCHO was observed in clear hot days.

GRAPHICAL ABSTRACT



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ABSTRACT

On rural background areas atmospheric formaldehyde (HCHO) is important for its abundance and chemical reactivity, directly linked to the tropospheric ozone formation processes. HCHO is also toxic and carcinogenic to humans. Atmospheric HCHO was continuously measured in summer 2016 during 81 days ($N = 6722$, average: 1.42 ppbv) in a rural background area in Northern Spain, Valderejo Natural Park (VNP) using a Hantzsch fluorimetric system. To better characterize the photochemical processes the database was completed with hourly measurements of 63 Non-Methane Hydrocarbons (NMHC) performed by gas chromatography and other common atmospheric pollutants and meteorological parameters.

HCHO mixing ratios were highly correlated with ozone and isoprene. Cloudy and rainy days, with low temperature and radiation, led to low HCHO mixing ratios, with maxima (<2 ppbv) registered around 14 UTC. On days with increased radiation and temperature HCHO maxima occurred slightly later (<6 ppbv, ≈16:00 UTC). During clear summer days with high temperature and radiation, two HCHO peaks were registered daily, one synchronized with the radiation maximum ($\approx 3–4$ ppbv, $\approx 13:00$ UTC) and an absolute maximum (<10 ppbv, $\approx 18:00$ UTC), associated with the addition of HCHO coming into VNP due to inbound transport of old polluted air masses. In the ozone episode studied, the processes of accumulation and recharge of ozone and of HCHO ran in parallel, leading to similar daily patterns of variation. Finally, HCHO mixing ratios measured in VNP were compared with other measurements at rural, forested, and remote sites all over the world, obtaining similar values.

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1. Introduction

Characterization of polluted air masses is a complex task, being affected by many factors such as emitted pollutants and sources, mixing and transportation processes, chemical transformations, local topographic effects, and so on. Hence, high time-resolution measurements of atmospheric pollutants and its main oxidation products are necessary, not only to characterize air pollution but to establish the appropriate strategies for its reduction and control, helping in the development and validation of the modelling of the transport and chemical transformation processes in the atmosphere.

Volatile Organic Compounds (VOCs) are ubiquitous in the troposphere and play a key role in the atmospheric chemistry as ozone and other oxidants' precursors (Crutzen et al., 1999; Monks et al., 2015; Wang et al., 2017). VOCs are present in significant amounts in urban areas, where the main emission sources are anthropogenic: fossil fuel and biomass combustion, industrial processes, and solvent evaporation (Barletta et al., 2005; de Blas et al., 2011; Durana et al., 2006; Valdenebro et al., 2011). In rural and forested areas biogenic VOCs (BVOCs) emitted by plants and natural processes, mainly isoprene and monoterpenes, may be more important than anthropogenic VOCs transported in polluted air masses from nearby industrial and urban areas (Chatani et al., 2018; Navazo et al., 2008; Tsagiris and Kanakidou, 2002; Zhu et al., 2017). Isoprene is emitted by vegetation, being about half of all BVOC emissions (Guenther et al., 2012). BVOCs are mainly emitted from spring to the end of summer, due to the increase in solar radiation, temperature, and foliar density. This fact combined with the high reactivity of BVOCs results in ozone episodes during summertime in rural areas (Possanzini et al., 2007; Ramón, 2014; Villanueva et al., 2014).

Formaldehyde (HCHO) is the simplest and the most abundant carbonyl in the urban and remote troposphere (Hak et al., 2005). Tropospheric HCHO mixing ratios range from 90 to 195 pptv in the Antarctic atmosphere (Preunkert et al., 2015), and higher values are measured worldwide in urban areas, ranging from 0.2 ppbv to almost 50 ppbv (Dasgupta et al., 2005; Guo et al., 2016; Jiang et al., 2016; Ling et al., 2017; Menchaca-Torre et al., 2015; Salthammer, 2013; Santana et al., 2017; Zheng et al., 2013). Rural areas show a wide range of average summertime HCHO mixing ratios from 0.1 ppbv to 7 ppbv (Dasgupta et al., 2005; Lin et al., 2012; Ling et al., 2017) with single peaks of 15–20 ppbv measured over a forest canopy (Choi et al., 2010).

HCHO is emitted by anthropogenic sources (combustion processes, industry, building materials, and consumer products) (Dutta et al., 2010; Yan Ma et al., 2016) and naturally produced by plants, animals, and humans (Wakefield, 2008) but its main source is the oxidation of VOCs, where CH₄ produces up to 60% of HCHO in remote areas (González et al., 2016; Kefauver et al., 2014) whereas other VOCs are the principal source in continental areas, mainly the ones with double bonds (Choi et al., 2010; Elshorbany et al., 2009; Fortems-Cheiney et al., 2012; Garcia et al., 2006; Li et al., 2014; Wert et al., 2003; Wolfe et al., 2016).

The following reactions (R1) to (R3) describe a simple scheme for the formation process of HCHO after oxidation of methane with hydroxyl radicals.



The hydroxyl radical oxidates methane to a methyl peroxy radical which, by oxidizing NO to NO₂, finally produces HCHO and an HO₂ (Atkinson and Arey, 2003; Finlayson-Pitts and Pitts Jr, 1999; Luecken et al., 2012; Seinfeld and Pandis, 2016).

The reaction (R4) summarizes a chain of reactions between isoprene (ISOP) and the OH radical, involved on about 95% or more of the total daytime isoprene sink.



The addition of OH and the reaction with O₂ generate different hydroxyl peroxy radicals able to finally produce HCHO being methyl vinyl ketone (MVK) and methacrolein (MACR) byproducts of the reactions. The HCHO yield of isoprene is variable (typically 0.5–0.6) but the dependence with respect to the concentration of NO_x has not been established for the majority of BVOCs (Choi et al., 2010; Wolfe et al., 2016). HCHO, MVK, and MACR are also products of the ozonolysis of isoprene (Atkinson and Arey, 2003; Holloway and Wayne, 2010) but that reaction is relatively slow. The nocturnal oxidation of isoprene by the NO₃ radical is probably a source, although smaller, of these carbonyls (Brown et al., 2009).

In typical summer conditions in Southern Europe the percentage of HCHO produced from isoprene is about 10%, whereas the photooxidation of anthropogenic precursors is five times higher (Borbon et al., 2004). Pang et al. (2009) studied this process between April and October in Beijing, and found that the reacted isoprene and its ozone formation potential (OFP) were in the range of 0.49–3.46 ppbv and 6.4–44.7 ppbv, respectively. The isoprene contribution to the formation of HCHO between April and October was found to be in the range of 0.35–2.45 ppbv, about 4.6–11.5% of surface HCHO. Other authors pointed also to isoprene as the main precursor of HCHO during summer in the East Coast of the USA, with a contribution of 20–60% of the total production, being these percentages highly variable from place to place (Luecken et al., 2012; Zhu et al., 2017). In July 2006 in several cities of China ambient HCHO was mainly coming from olefins as a secondary formation, being trans-2-butene the largest contributor (16%) followed by i-butene, cis-2-butene, and propene. In an urban site in the Pearl River Delta, Southern China, this secondary formation contributed approximately with 2.8 ppbv of O₃ and 1.1 · 10⁷ molecules·cm⁻³ of HO_x radicals (Ling et al., 2017). At a global scale isoprene is considered as the main precursor of HCHO in the low troposphere (Li et al., 2014; Marvin et al., 2017; Wolfe et al., 2016; Zhu et al., 2017), but the formation efficiency is directly related to the concentration of nitrogen oxides (NO_x = NO + NO₂). It has been estimated that in absence of NO_x the concentration of HCHO would be some 20–30% lower (Zhu et al., 2017).

Apart from dry and wet deposition, the main processes for removal of atmospheric HCHO during daytime are photolysis (R5) to (R7), and the reaction with OH radicals (R8) (Cooke et al., 2010; Dasgupta et al., 2005; Inomata et al., 2008; Seyfioglu et al., 2006; Stavrakou et al., 2015; Xiaoyan et al., 2010) with a HCHO characteristic lifetime of several hours at the radiation and temperature conditions at noon.



Two radicals (H and HCO), formed through (R5a), are subsequently converted in the presence of O₂ ((R6) and (R7)) into hydroperoxy radicals (HO₂), which are actively involved in other photochemical cycles responsible for ground-level ozone formation and degradation of most primary air pollutants (Finlayson-Pitts and Pitts Jr, 1999; Kaiser et al.,

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