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Seasonal, diurnal and nocturnal variations of carbonyl compounds in the semi-urban environment of Orléans, France

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ABSTRACT

Atmospheric carbonyls were measured at a semi-urban site in Orléans, France, from October 2010 to July 2011. Formaldehyde, acetaldehyde and acetone were found to be the most abundant carbonyls, with average concentrations of 3.1, 1.0, 2.0 ppb, respectively in summer, 2.3, 0.7, 2.2 ppb, respectively in autumn, 2.2, 1.0, 2.1 ppb, respectively in spring, and 1.5, 0.7, 1.1 ppb, respectively in winter. Photo-oxidation of volatile organic compounds (VOCs) was found to make a remarkable contribution to atmospheric carbonyls in the semi-urban site based on the distinct seasonal and diurnal variations of the carbonyls, as well as the significantly positive correlations between the carbonyls and ozone. The significantly negative correlations between NO_x and O_3 as well as the carbonyls and the positive correlations between wind speed and O_3 as well as the carbonyls implied that the carbonyls and O_3 at the semi-urban site were probably formed during air mass transport from neighboring cities.

Introduction

Carbonyl compounds are ubiquitous components of the atmosphere and play an important role in atmospheric chemistry. It is well documented that atmospheric carbonyls derive from both biogenic (vegetation) and anthropogenic sources (incomplete combustion of biomass and fossil fuels), including direct emission and secondary formation via photochemical conversion of volatile organic compounds (VOCs) emitted from both sources (Bakeas et al. 2003; Christensen et al. 2000; Ho et al. 2002; Nguyen et al. 2001; Possanzini et al. 2002). Some carbonyls are associated with adverse health impacts and most of them are precursors for radical and photooxidant formation in the atmosphere (Seinfeld and Pandis 1997; Possanzini et al. 2002).

To evaluate their influence on human health as well as atmospheric chemistry, field measurements of atmospheric carbonyls have been carried out in different areas, including urban (Cheng et al. 2014; Lü et al. 2010; Weng et al. 2009; Pang and Mu 2006; Pang and Lee 2010; Xu et al. 2010; Zhang et al. 2012; Feng et al. 2005; Ho et al. 2002; Nguyen et al. 2001; Possanzini et al. 2002), rural (Xie et al. 2008; Villanueva-Fierro et al., 2004; Wiedinmyer et al. 2001; Solberg et al. 2001; Shepson et al. 1991; Cheng et al. 2014) and remote areas (Singh et al. 2004; Zhou and Mopper 1993; Wagner et al. 2001; De Serves 1994). In comparison with urban areas, however, investigations on atmospheric carbonyls in rural or semi-urban areas are still sparse. Rural or semi-urban areas usually have less anthropogenic activities, and the atmospheric pollutants in these areas are often affected by air

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parcel transport from neighboring cities and as well as by vegetation, and hence measurements of atmospheric carbonyls in rural or semi-urban areas could provide scientific evidence about their various sources.

However, until now, research on carbonyl compounds in France has only been focused on large urban areas like Paris (Kalabokas et al. 1988). Very limited research work has been done on seasonal variations of carbonyls in the semi-urban atmosphere of France. In this study, atmospheric carbonyl compounds have been measured in a semi-urban site in Orléans, France, from October 2010 to July 2011. The major objectives were to determine their concentration levels and seasonal and diurnal variation characters, as well as possible sources, at this specific semi-urban site.

1. Experimental

1.1. Sampling sites

The map given in Fig. 1 shows the Orléans city site where the measurements were performed. Orléans city (47°59′12″N, 01°44′54″E) is located in the central part of France. In this study, a semi-urban site was selected as the sampling site, and it is positioned within the CNRS-campus (Centre National de la Recherche Scientifique) about 9.6 km away from Orléans city center. The site is close to a forest belt and farm. Air sampling was performed on a rooftop of the ICARE (Institut de Combustion, Aérothermique, Réactivité et Environnement) laboratory (about 10 m above ground) from October 2010 to July 2011. The detailed meteorological conditions and sampling dates are listed in Table 1.

1.2. Carbonyl sampling and analysis

The procedure used was based on EPA (Environmental Protection Agency) method TO-11 A (US EPA, 1999). The sampling medium was a silica cartridge. 2,4-dinitrophenylhydrazine (DNPH) had been purified by recrystallization in HPLC (high performance liquid chromatography) grade acetonitrile (ACN) three times. Each cartridge was rinsed with 10 mL of ACN and coated slowly with a solution containing 300 mg of dry DNPH crystals and 2 or 3 drops of phosphoric acid in 200 mL fresh ACN. The cartridges were then connected in series and dried with a gentle flow of pure nitrogen (99.9999%) for 15 min, and then wrapped in aluminum foil, sealed in Teflon bags, and stored in the refrigerator at 4°C until use. Three blank cartridges from each batch were analyzed, and carbonyl contamination was found to be below the EPA blank criteria (formaldehyde <0.05 μg/cartridge; acetaldehyde <0.06 μg/cartridge; acetone <0.08 μg/cartridge and other aldehydes or ketones <0.05 μg/cartridge). It is reported in the literature that the DNPH cartridges can be stored for at least 6 months when refrigerated below 4°C (Druzik et al. 1990). In our study, the storage time under the same conditions was less than 30 days before use.

An automatic and multi-channel sampler self-designed in the group was used for collecting air samples. The sampler contains 12 channels, and each channel is connected to a DNPH cartridge; two electromagnetic valves at each side of the cartridges are controlled by a computer program. Samples were collected at 2-hr intervals from 0:00 to 24:00 (Coordinated Universal Time, UTC), which meant 12 samples could be collected in a sunny sampling day. Ozone interference was eliminated by an upstream cartridge scrubber coated with potassium iodide (Supelco, Bellefonte, USA). DNPH cartridges trap aldehydes and ketones through reactions with DNPH to form stable hydrazine derivatives. The sampling flow rate (0.9–1.1 L/min) was measured with a digital flow meter (DryCal DC Lite, Bios Corp, USA)). After sampling, the cartridges were sealed with silicon caps immediately, transported back to the laboratory and stored in the refrigerator before analysis. Each sampling day included one laboratory blank and one field blank. The field blank was treated identically to the samples except

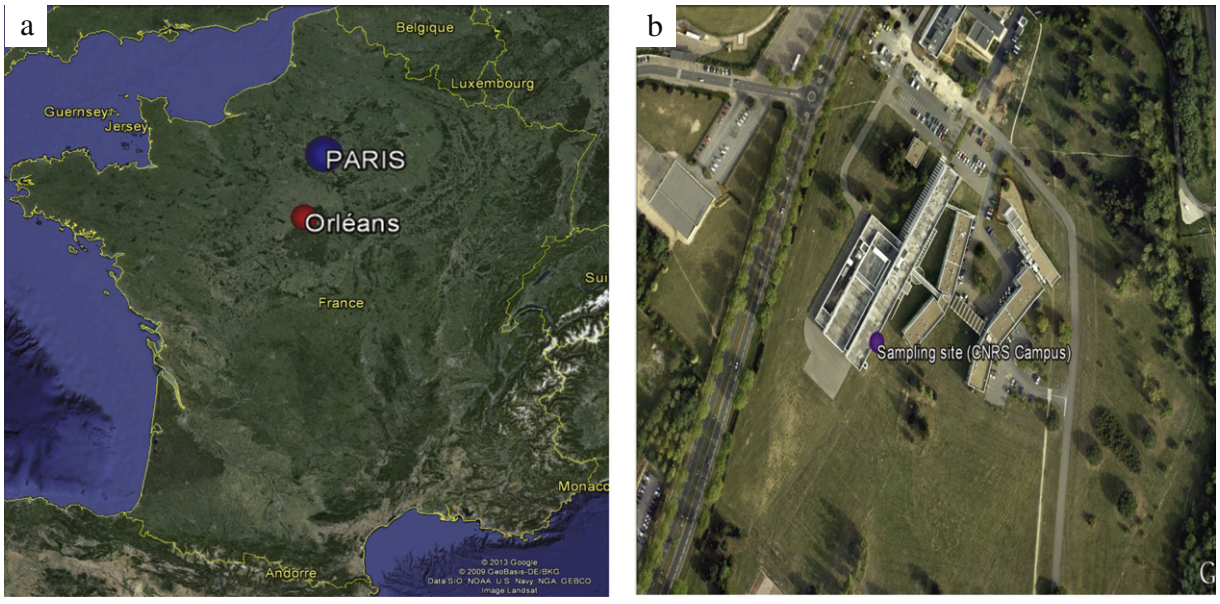

Fig. 1 – Sketch map of sampling sites in (a) Orléans in France and (b) CNRS (Centre National de la Recherche Scientifique)-campus.