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Temporal variations of atmospheric carbonyls in urban ambient air and street canyons of a Mountainous city in Southwest China

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ABSTRACT

Carbonyl compounds in urban ambient air and street canyons were measured from December 2008 to August 2009 in a mountainous city in southwest China (Guiyang). The formaldehyde yield from the photo-oxidation of isoprene emitted by vegetation was estimated to be in the range of 0.63–3.62 μg m^{-3} from May to August, which accounted for 28.8–33.4% of ambient formaldehyde. Based on the calculation of photolysis rates and rates of reaction with the OH radical, it was found that photolysis was the predominant sink for formaldehyde and acetone in both summer and winter. For acetaldehyde, photo-oxidation by OH radicals and photolysis were the major sinks in summer while photo-oxidation by OH radicals was the dominant sink in winter. Wet precipitation was found to be an important removal process for the atmospheric carbonyls. In the urban ambient air, the average concentrations of formaldehyde, acetaldehyde, acetone and all carbonyls were 4.8 ± 2.1, 5.7 ± 3.3, 5.1 ± 2.5, and 25.1 ± 9.2 μg m^{-3} ($n = 139$), respectively. The average concentrations of these species in street canyons were 18.8 ± 6.5, 9.4 ± 3.2, 10.9 ± 2.1, and 64.1 ± 16.3 μg m^{-3} ($n = 62$), respectively. The significantly higher carbonyl levels on weekdays (compared to weekends) highlight the contribution of vehicle emissions to carbonyls in the street canyons.

1. Introduction

Carbonyls are of critical importance in the tropospheric chemistry as a major source of free radicals, and are the precursors to ozone, peroxyacyl nitrates (PANs) and secondary organic aerosol (SOA) (Singh et al., 1995; Finlayson-Pitts and Pitts, 1997; Atkinson, 2000). Monitoring carbonyls in the ambient air is of fundamental importance in assessing the significance of photochemical activity and understanding the oxidation mechanisms of atmospheric VOCs. Furthermore, some carbonyls such as formaldehyde, acetaldehyde and acrolein are suspected to be carcinogenic and mutagenic to humans (WHO, 1987; Kim et al., 2008; Weng et al., 2009). Consequently, during the past two decades, considerable researches have been performed to investigate the atmospheric carbonyls in various environments including urban, rural, forest, coastal and industrial sites, as well as indoor microenvironments and background areas (Ho et al., 2002; Guo et al., 2004; Feng et al., 2005; Pang and Mu, 2006; Ceron et al., 2007; Mu et al., 2007; Wang et al., 2007; Huang et al., 2008; Khwaja and Narang, 2008; Kim et al., 2008; Santarsiero and Fuselli, 2008; Weng et al., 2009). In those studies, the ambient levels and the temporal and spatial variations of carbonyls were extensively reported. However, the contribution to the atmospheric carbonyls by individual sources was rarely discussed. The relative contributions of primary and secondary sources to ambient carbonyl levels was presumably estimated based on the correlations between carbonyls and other air pollutants such as CO, NO_2, O_3, propene, *n*-butane and benzene (Feng et al., 2005; Guo et al., 2004; Pang and Mu, 2006; Ceron et al., 2007; Khwaja and Narang, 2008). Additionally, although major loss processes for the atmospheric carbonyls are known (photolysis and reaction with OH radicals), the seasonal importance of each process is unknown (Possanzini et al., 2002; Guo et al., 2004; Pang and Mu, 2006). It is therefore necessary to estimate the contribution of various sources to the atmospheric carbonyls and to determine carbonyl loss rates if we want to control the pollution of carbonyl in urban ambient air.

Guiyang is a mountainous city in Southwest China. A great number of skyscrapers and narrow roads form many deep street canyons in the city. In street canyons, high levels of traffic-related air pollutants are usually observed, including CO, SO_2, NO_2, benzene, toluene, ozone and fine particulate matter (Kourtidis et al., 2002;

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Xie et al., 2003; Genikhovich et al., 2005; Li et al., 2007; Murena and Favale, 2007). These pollutants have significant negative impacts on human health. To the best of our knowledge, few studies had been conducted in investigating the carbonyls present in street canyons. Therefore, an investigation of carbonyls in street canyons is of utmost importance in assessing the health risk to humans exposed to the air in street canyons.

In the present paper, the photo-oxidation of biogenic VOC emissions (isoprene) to formaldehyde is quantified based on the measurement of methacrolein (MACR). The seasonal importance of the loss processes (sinks) for carbonyls is assessed according to calculations of their photolysis rates and rates of reaction with the OH radical. The temporal variations and vertical distribution profiles of carbonyls in street canyons and an urban ambient site are displayed and compared.

2. Experimental

2.1. Sampling sites

Guiyang city (26.8°N, 106.5°E) is located in a basin on the east edge of the Yunnan–Guizhou Plateau. The city has a continental monsoon climate with the highest air temperatures (22–25 °C) recorded in July and the lowest air temperatures (4–6 °C) recorded in January. The rainy season is usually from April to June.

In this study three types of air sample were collected: from an urban ambient site (S1), within street canyons (S2) and from a roadside building (S3). The position of the three areas in Guiyang is shown in Fig. 1. Detailed information about the sampling areas follows.

S1: This urban ambient site was the rooftop (about 20 m above ground) of an office building in the Institute of Geochemistry, CAS (GYIG). GYIG is located at the edge of the inner-ring-road of Guiyang and is surrounded by many residential buildings, office buildings and three main roads with moderate traffic. There are two laboratory buildings and two official buildings near S1. To our knowledge, acetonitrile, methanol, and ethanol were regularly used for experiments in the laboratories, which would have no significant effect on the atmospheric carbonyls in S1. However, the influence of acetone occasionally used in the laboratories is difficult to assess. The sampling campaign at site S1 was conducted from December 2008 to August 2009. Due to the Spring Festival, no sampling was conducted during February 2009. Samples in S1 were collected every 2 h from 08:30 to 20:00 (Beijing Time) throughout the campaign with the exception of July when samples were collected from 08:30 to 22:00. Six two-hour samples were collected per sampling day while seven samples were obtained during July. Samples were collected for two days during December and January, four days during March and three days during April, May, June, July and August, respectively.

S2: The street canyons were the four-lane streets surrounded by tall buildings within the inner-ring-road in Guiyang city. The width of the canyons was usually less than 20 m and the height greater than 20 m. The air sampling in S2 was conducted from the buses, which were driven through the street canyons. The sampling inlet was held out of the window of the buses to collect the ambient air. Air sampling in S2 was performed at 1 h intervals from 09:00 to 20:00 during five days in March having clear and stable weather. Eleven one-hour samples were collected per sampling day in S2. On 8 March (Sunday) and 10 March (Tuesday) we assessed the traffic volume in the street canyons between 10:00 and 14:00 to investigate the effect on carbonyl levels.

S3: A roadside building (S3) without residents was chosen to study vertical distribution of carbonyls in a street canyon. Air sampling was simultaneously conducted at four heights (1.5 m, 15 m, 45 m and 90 m) of this building on 10 August 2009. The sampling inlet was extended 1.5 m out of the windows to collect the ambient air. Five samples were collected at each height between 10:00 and 20:00. Each sample was collected over 2 h.

2.2. Carbonyl sampling and analysis

The sampling and the analysis procedures used for the atmospheric carbonyls are based on the EPA TO-11A method (EPA, 1999). The atmospheric carbonyls were collected by 2,4-dinitrophenylhenylhydrazine (DNPH)-coated Sep-Pak silica gel cartridges (Waters, USA) at a flow rate of 1.0 L min^{-1}. The collection efficiencies (CE) were calculated to be over 98.0% for most of the carbonyls for a 2 hour sampling period according to the following formula. $CE = 100\%(1 - A_b/A_f)$, where A_b and A_f are the carbonyl amounts collected on the back and front cartridges, respectively (Li et al., 2009). A KI scrubber was connected to the inlet of DNPH-coated cartridge to eliminate ozone interference. Carbonyls react rapidly with DNPH and transform into their corresponding hydrazones.

The hydrazones were eluted slowly from the cartridges with 5.0 mL acetonitrile and were analyzed by a HPLC system (HP 1100) with a UV/Vis detector at 360 nm. The analytical conditions were as follows: Supelcosil LC-18 column (250 × 5.0 mm, 5 μm); gradient

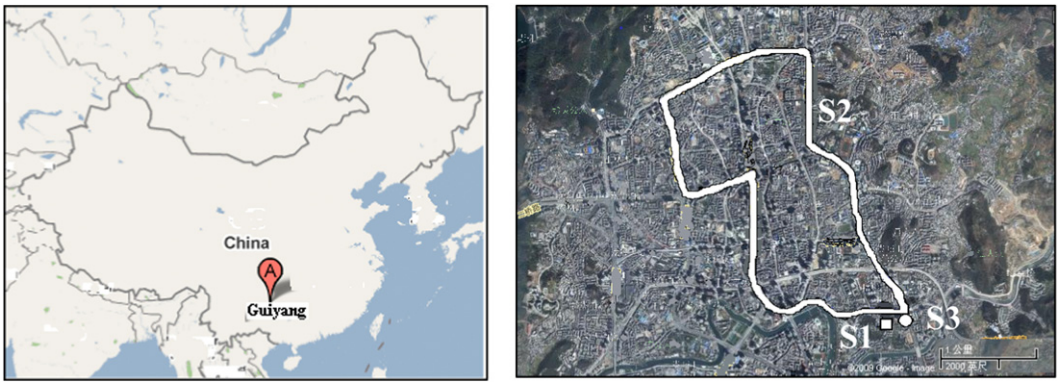

Fig. 1. Geographical location of Guiyang in China. Position of urban ambient site (S1) (white square), street canyons (S2) (white line) and the roadside building (S3) (white circle) within Guiyang are shown.