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The characteristics, seasonal variation and source apportionment of VOCs at Gongga Mountain, China

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HIGHLIGHTS

- This is the first time to study the VOCs in the remote station in southwest China.
- Aromatics and alkanes are the major components of VOC.
- The seasonal variation shows higher value in spring and lower value in autumn.
- Anthropogenic sources are the most important sources in the remote area.

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ABSTRACT

The mixing ratio, composition and variability of volatile organic compounds (VOCs) were measured from 2008 through 2011 at Gongga Mountain Forest Ecosystem Research Station (102°00′E, 29°33′N, elevation 1640 m), a remote station in southwest China. Weekly samples were collected in the Gongga Mountain area and were analyzed using a three-stage preconcentration method coupled with GC–MS. An advance receptor model positive matrix factorization (PMF) was applied to identify and apportion the sources of VOCs. The results show that the measured VOC mixing ratio at Gongga Mountain is dominated by aromatics (35.7%) and alkanes (30.8%), followed by halocarbons (21.6%) and alkenes (11.9%). The general trend of seasonal variation shows higher mixing ratios in spring and lower mixing ratios in autumn. The effect of alkanes and aromatics on the seasonal variation of total volatile organic compounds (TVOCs) is significant. Five sources were resolved by the PMF model: (1) gasoline-related emission (the combination of gasoline exhaust and gas vapor), which contributes 35.1% of the measured VOC mixing ratios; (2) solvent use, contributing 21.8%; (3) fuel combustion, contributing 29.1%; (4) biogenic emission, contributing 5.2%; and (5) industrial, commercial and domestic sources, contributing 8.7%. The effect on this area of the long-range transport of air pollutants from highly polluted areas is significant.

1. Introduction

There is no doubt of the importance of volatile organic compounds (VOCs) in the atmosphere, because they are the important precursors of secondary air pollutants and secondary organic aerosols in photochemical processes. Moreover, most of VOCs are also impact the environment and human health directly (Leuchner and Rappenglück, 2010; Pérez-Rial et al., 2010).

The study of VOCs is still very limited in China because most such studies have focused on mega-cities or city clusters, such as Beijing (Song et al., 2007; Yuan et al., 2009; Su et al., 2011), the Pearl River Delta (Chan et al., 2006; Guo et al., 2006, 2011; Ling et al., 2011) and the Yangtze River Delta (Cai et al., 2010; Geng et al., 2010; Huang et al., 2011). However, information about the source characteristics of VOCs in remote areas is insufficient because it is more difficult and more expensive to observe these areas than observe areas in cities. However, the study of VOC emissions from remote areas is crucial because these areas occupy more area than cities worldwide. Thus, the results of such studies are highly useful for studying the global temporal and spatial variation of VOCs. Unfortunately, this type of study is rare in China, especially in the remote area of the underdeveloped southwestern region of China.

Furthermore, it is not sufficient simply to measure the mixing ratios of VOCs to develop of an effective control strategy. We also need to obtain and understand accurate information about the sources of VOCs. One effective method for studying VOC sources

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involves the use of receptor models (Song et al., 2007; Lanz et al., 2009; Chan et al., 2011; Ling et al., 2011), such as positive matrix factorization (PMF). This receptor model has been successfully tested in comparison with other receptor models for VOCs (Song et al., 2007; Sauvage et al., 2009; Yuan et al., 2009) and particulate matter (PM) (Leuchner and Rappenglück, 2010; Chan et al., 2011). A very effective statistical method, it can apportion ambient concentration data to sources by identifying the intrinsic characteristics of the data while limiting all of the elements in the factor score (source profiles) and the factor loading (source contributions) matrix to positive values, making this method especially useful in environmental source analysis (Yuan et al., 2009).

In this paper, the mixing ratios, composition and seasonal variations of VOCs at Gongga Mountain, a station in a remote area of southwest China, are first presented. We then use the PMF receptor model to identify VOC source types and to apportion their contributions. To the best of our knowledge, this paper is the first to study VOCs at a remote station in southwest China.

2. Experiment and methods

2.1. VOC sampling and analysis

The measurements were performed at the standard meteorological field of the Gongga Mountain Forest Ecosystem Research Station (102°00′E, 29°33′N, elevation 1640 m) in Hailuogou Scenic Area, a remote site located in southeast Ganzi Tibetan Autonomous Prefecture in Sichuan province. This scenic area is famous for its large areas of glaciers and virgin forest and its large number of rare animal and plant resources. The forest area in Hailuogou is approximately 70 km^2 and the total resort area is approximately 200 km^2. The principal tourist seasons are spring and summer. There are approximately 30,000 inhabitants in the vicinity of the scenic area. During the tourist seasons, the population is several times more numerous than the local residents. This station is approximately 130 km to the northeast of Ya'an and 250 km from Chengdu, the capital of Sichuan province (Fig. 1). There are two major roads in the north and east, 500 m and 400 m from the station, respectively. A gas station is located 1000 m to the north of the station.

Air samples were collected twice a day every Tuesday from Jan. 2008 to Dec. 2011. A total of 380 samples were collected during the measurement period (approximately 40 samples were excluded for various reasons). The monitoring site is shown in Fig. 1. A pump was used to draw, ambient air samples from a gas inlet through a PFA-Teflon tube (OD: ¼ in). These samples were collected in pre-evacuated 1 L electropolished canisters. A 3 min integrated sample was taken for each canister sample at 8:00 and 14:00. Ambient air was collected at a flow rate of 1 L min^{-1}. After the canisters were pressurized to 60 psig, the valve was closed and the pump turned off. The samples were returned to Beijing for analysis within 7 days of collection.

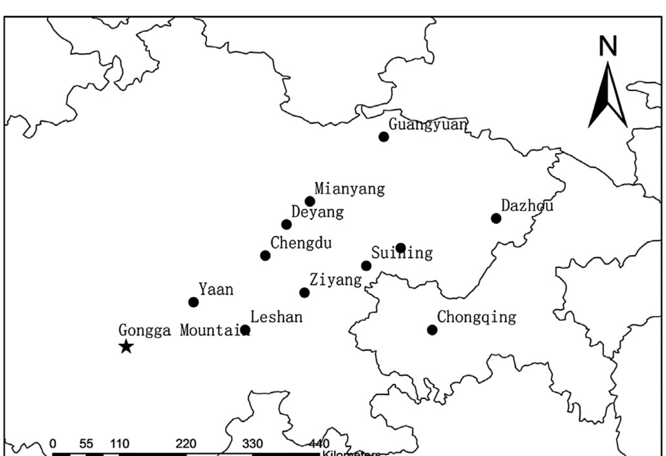

Fig. 1. Location of the sampling site and some important cities around it.

Measurements of VOCs were made using an Entech 7100A preconcentrator (Entech Inc., USA) followed by a GC–MS system (Finnigan Trace GC/Trace DSQ). The details of the VOC analysis procedures have been described previously by Mao et al. (2009) and will be described briefly here.

A 500 mL sample was concentrated in an Entech 7100A preconcentrator, a three-stage preconcentration was utilized to remove the water, carbon dioxide, nitrogen and oxygen in air samples. The VOCs were further focused with a capillary focusing trap for rapid injection prior to the analytical column. A DB-5 MS fused-silica capillary column (60 m × 0.25 mm × 0.25 μm, Agilent Technologies Inc.) coupled with a quadrupole mass spectrometer detector (Finnigan Trace 2000/DSQ. Thermofisher Inc. USA) was used for qualification and quantification.

Forty VOCs were identified and quantified. Each target species was identified by its retention time, mass spectrum and USEPA standard gases. The quantification of the target VOCs was performed with multi-point external standard curves and modified using Relative Responsible Factors (RRFs). The calibration curves were prepared using 100 ppbv external standard gases (Scott Specialty, TO14 standard; alkanes and alkenes) and 100 ppbv internal standard gases of dibromomethane at five different diluted concentrations plus nitrogen (0–100 ppbv). Internal standard gas was added to each sample to trace the analytical procedure (Mao et al., 2009). Five sets of replicate samples were collected to check the precision and reliability of the sampling and analysis methods. The RSD was within 10% for the target compounds in all five replicates. For most samples, the VOC species were above the detection limit of 5–10 pptv.

2.2. Positive matrix factorization (PMF)

2.2.1. Principles and application of PMF

The PMF method is comprehensively described by Paatero and Tapper (1994) and Paatero (1997) and has been used in many VOC source identification studies (Song et al., 2007; Sauvage et al., 2009; Yuan et al., 2009). In this paper, PMF 3.0 (USEPA, 2008) was used to apportion the contributions from emission sources. Several concepts that are relevant to the understanding of this work are briefly described here. For additional details about the method, the reader is referred to the publications cited above and to the PMF 3.0 user manual.

An ambient data set can be viewed as an i by j data matrix X in which i samples and j chemical species are represented. The goal of multivariate receptor modeling is to identify a number of sources p, the species profile f of each source and the amount of mass g contributed by each source to each individual sample as well as the residuals e_{ij}:

$$X_{ij} = \sum_{k=1}^{p} g_{jk} f_{kj} + e_{ij}$$

where e_{ij} is the residual for each sample/species.

The PMF solution minimizes the objective function Q based on these uncertainties (u):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2$$