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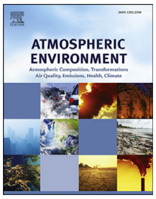

Atmospheric molecular hydrogen (H_2) at the Shangdianzi regional background station in China

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HIGHLIGHTS

- Observation of atmospheric H_2 in China.
- Nighttime depletion occurred in all seasons.
- H_2 concentration is the highest in July, and the lowest in October.
- Southerly air masses increased H_2 concentration, whereas northerly masses depleted.

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ABSTRACT

Atmospheric molecular hydrogen (H_2) mole fractions have been continuously measured at the Shangdianzi regional station in China. In this study, we present the atmospheric H_2 time series from January 2015 to April 2016, and investigate the diurnal and seasonal cycles, and the impact of meteorological factors on the observed values. Atmospheric H_2 mole fractions at Shangdianzi vary from a minimum of 381 ppb (parts per billion, 10^{-9} dry air mole fraction) to a maximum of 1535 ppb, with a median of 510 ppb and a mean (± standard deviation) of 555 ± 113 ppb during the observation period. The results indicate that H_2 mole fractions at Shangdianzi are frequently influenced by local sources and sinks. Regionally representative conditions account for 44.7% of the total records with a mean mole fraction of 488 ± 20 ppb. The highest regionally representative H_2 mole fraction is observed in July, while the lowest is observed in October. Peak-to-trough amplitude in the seasonal cycle is 63 ± 3 ppb. H_2 mole fractions show nighttime depletion in all seasons, with the lowest values in the morning (7:00–10:00 local time). The H_2 mole fractions are also influenced by local surface wind direction at Shangdianzi. Winds from NW-NNW-N-NNE-NE-ENE-E directions are always associated with negative contribution to atmospheric H_2 loading, whereas winds from SSW-SW-WSW-W directions generally enhance the H_2 values. The results of trajectory clustering analysis demonstrate that air masses from a southerly direction induce high H_2 mole fractions. Conversely, mean H_2 mole fractions are low when air masses are from the north, northwest, and east directions.

1. Introduction

Atmospheric molecular hydrogen (H_2) has received increasing attention recent years due to its potential as a sustainable energy carrier and fuel source for transportation, along with the possible environmental consequences that may accompany its large-scale adoption. The impact of hydrogen economy on the global climate has been investigated by a variety of studies (Derwent et al., 2006; Jacobson, 2008; Schultz et al., 2003; Tromp et al., 2003). Atmospheric H_2 affects global atmospheric chemistry in the same way as CO in the troposphere: H_2 photochemical loss reaction with the

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hydroxyl radical (OH) takes up one OH and releases one HO_2 radical. The net effect of adding H_2 to the atmosphere is to reduce the OH (the primary methane sink) and consequently increase methane abundance (Prather, 2003; Xu et al., 2011). Thus, atmospheric H_2 is commonly considered as a very important indirect greenhouse gas. In addition, the increase in the atmospheric H_2 burden could favor the production of tropospheric ozone (O_3) (Schultz et al., 2003; Warwick et al., 2004). In the stratosphere, H_2 reacts with OH to produce water vapor (H_2O), which may decrease ozone layer recovery (Tromp et al., 2003).

Major H_2 sources consist of photochemical oxidation of methane and other hydrocarbons (~50%), fossil fuel combustion in transport and industry (~25%) and biomass burning (~20%) (Price et al., 2007; Xiao et al., 2007). Small amounts of H_2 originate from the biological activity of nitrogen fixation in plants on continents and in oceans (Ehhalt and Rohrer, 2009; Rhee et al., 2006). H_2 is destroyed photochemically in the atmosphere through reaction with OH, and biologically at the land surface through consumption by soil microorganisms. Soil uptake accounts for ~75% of the global sink, and the remainder is ascribed to atmospheric chemical reactions (Ehhalt and Rohrer, 2009; Yonemura et al., 1999). The lifetime of H_2 in the atmosphere is around two years (Novelli et al., 1999).

The first reliable measurement of atmospheric H_2 were made by Paneth (1937) in Germany. Subsequently, a few surface observations were made in polluted air masses in Europe (Glueckauf and Kitt, 1957; Schmidt, 1974). The first long-term observation of H_2 was reported by Khalil and Rasmussen (1990) who undertook flask sampling at six clean air stations between 1985 and 1989. In the late 1980s, the National Oceanic and Atmospheric Administration/Earth System Research Laboratory (NOAA/ESRL) began to establish a global network of sampling stations for trace gas analysis. Novelli et al. (1999) presented the time series of the H_2 mole fractions measured at 50 background stations in the NOAA/ESRL network, and concluded that the globally averaged tropospheric H_2 mole fraction was ~531 ± 6 ppb from 1991 to 1996. Owing to the larger continental land area in the Northern Hemisphere, the H_2 mole fractions were generally lower than those in the Southern Hemisphere (Novelli et al., 1999). The longest known continuous H_2 record in the Northern Hemisphere was observed at Mace Head, which began in 1994 (Grant et al., 2010b; Simmonds et al., 2000). Since May 1991, China Meteorological Administration (CMA) has collected weekly air samples in glass flasks, which were shipped to the NOAA/ESRL and analyzed for a suite of greenhouse gases and related tracers including H_2 (ftp://aftp.cmdl.noaa.gov/data/trace_gases/). However, there was no in situ H_2 measurement in China until 2015.

In January 2015, a gas chromatograph equipped with a pulsed discharge helium ionization detector (HePDD) was installed at Shangdianzi station in China to continuously measure atmospheric H_2 mole fractions. In this study, the observed H_2 records from 2015 to 2016 are presented, along with preliminary analysis. To our knowledge, this is the first set of onsite in situ H_2 measurements in China.

2. Experimental

2.1. Sampling location

Shangdianzi station (40°39′ N, 117°07′ E, 293.3 m above sea level) is one of the World Meteorological Organization/Global Atmosphere Watch program (WMO/GAW) regional stations. It is located in a mountainous area approximately 55 km northeast of Miyun County, Beijing, 100 km northeast of Beijing, and 210 km northeast of Shijiazhuang city in the North China Plain (Fig. 1). The station is surrounded by arable land and occasional small villages. There is a small steel mill in the Shangdianzi village, which is the nearest one located in the south of the station. A railway running from the southwest to northeast is about 0.6 km away from the station. As shown in Fig. 2, the prevailing wind directions are NE/ENE/E and SW/WSW/W under the influence of two mesoscale circulations (sea-land and mountain-valley), with total frequencies of 39.9% and 26.8%, respectively. The prevailing wind is southerly from afternoon to midnight, and then changes to northerly until morning (Xu et al., 2011). Previous studies have also shown that the dominating winds are southwest and northeast (An et al., 2012; Liu et al., 2013; Yao et al., 2012).

2.2. Analytical method

A commercial gas chromatograph (7890A, Agilent Technologies, USA) equipped with a pulsed discharge helium ionization detector (HePDD, D-3-I-7890-220, Valco Instruments Co. Inc., USA) was used for measurements of atmospheric H_2. This system has been proved to be excellent for atmospheric measurements as it provides a wide linear range with high precision, stability and reproducibility compared with the widely used system involving reduction of mercuric oxide and detection of mercury vapor by UV absorption (Meredith et al., 2014; Novelli et al., 1999). The air samples, taken from a height of 80 m above ground level, were delivered to the laboratory by a vacuum pump (N022, KNF Neuberger, Germany) via a dedicated 1/2 inch OD sampling line (Synflex 1300 tubing, Eaton, USA). The inlet used was the same as in previous studies by Fang et al. (2014, 2016). Air samples were dried by passing them through a glass trap submerged in a −50 °C ethanol bath (MC480D1, SP Industries, USA) before injection. A 2-position, 10-port injection valve (UW type, 1/16 inch ports, purged housing, VICI, USA) was used to introduce 3 mL samples. After equilibration, the sample was injected into columns (Hay Sep Q, 1/8 inch OD stainless steel, 4.5 m, 80–100 mesh, Restek, USA) to separate H_2 from other components, which was then analyzed in the HePDD. An automated sampling module equipped with an eight port multi-position valve was designed to sample from standard gas cylinders and ambient air. The detail of the system was described in Luan et al. (2015). The temperature of the oven and HePDD were set at 45 and 100 °C, respectively. One injection analysis took around 10 min. Peak heights were used to calibrate the atmospheric H_2 mole fractions.

H_2 mole fractions were referenced to a working standard. A target gas was used to routinely check the precision of the system. The working standard and target gas were prepared by compressing ambient air into 35 L electropolished stainless steel canisters (Essex Cryogenics, USA) using a modified oil-free compressor (RA-3, RIX Industries, USA). The internal surfaces of the canisters were electropolished to remove active sites on the surface of the stainless steel. The H_2 mole fractions of the working standard and target were 881.7 ppb and 777.7 ppb respectively. These were referenced against higher rank standards and ultimately linked to NOAA/ESRL. The standard and target gas were analyzed by the system every 1.5 h and 30 h, respectively. The precision of H_2 mole fractions was within 2 ppb, which met the compatibility goal of WMO/GAW (GGMT, 2013).

3. Results and discussion

3.1. Molecular hydrogen records

The full record of atmospheric H_2 observed at Shangdianzi from January 22, 2015 to April 11, 2016 is shown in Fig. 3. Gaps in the record are mostly due to instrument failures. A total of 50 371 air samples were collected at 10 min sampling intervals, from which