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# Monsoon onset signal in the stable oxygen and hydrogen isotope ratios of monsoon vapor

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## HIGHLIGHTS

• Early detection of monsoon onset using stable isotopic composition of atmospheric vapour appears possible.

- The assumption of isotopic equilibrium between rain water and vapour during the monsoon is tested.
- Important data set for the validation of satellite observations of vapour isotopes in the atmosphere.

• Rare high resolution vapour isotopic data over Indian monsoon region.

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## ABSTRACT

Whereas data on deuterium (D) and oxygen (<sup>18</sup>O), effective tracers of hydrological processes, are available for global precipitation, such data on atmospheric water vapor are limited. With the advent of satellites capable of measuring D in atmospheric water vapor, mesoscale moisture transport processes (e.g. monsoons) could be detected early provided the signal is well above the noise. Our results of daily measurements of stable oxygen and hydrogen isotopic compositions of atmospheric water vapor ( $\delta^{18}O_{vapor}$ ,  $\delta D_{vapor}$ ) and rain ( $\delta^{18}O_{rain}$ ,  $\delta D_{rain}$ ) during 2007–2008 CE over Ahmedabad, India, show that this is indeed so: (i) the onset of monsoon is marked by a dramatic decrease of ~2.9% and ~60%, in  $\delta^{18}O_{vapor}$ ,  $\delta D_{vapor}$ ,  $\delta D$ 

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#### 1. Introduction

Water vapor plays an important role in global warming (Hartmann, 2002) and is a good tracer for atmospheric transport due to its long residence time (Webster and Heymsfield, 2003). The lower tropospheric water vapor reservoir, being very dynamic, quickly responds to ambient inputs. The amount of atmospheric water vapor (AWV) depends on evaporation from open water bodies, soil, plants; evaporation of rain drops too, is a significant

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source contributing to humidity, typically 20% in the lower troposphere and up to 50% near convective clouds (Worden et al., 2007). Increase of AWV in the lower troposphere is known to induce precipitation (rain) by saturating the under-saturated cloud systems, especially in convective zones.

Since long, deuterium (D) and oxygen (<sup>18</sup>O), have been important tracers of the natural hydrological processes (Friedman et al., 1964; Craig and Gordon, 1965; Clark and Fritz, 1997), because they fractionate during phase change, such fractionation being quite sensitive to changes in atmospheric parameters (e.g. temperature, humidity). Their usefulness in studying AWV transport (Jacob and Sonntag, 1991; Smith et al., 2006; Stichler et al., 2006), cloud physics (Jouzel and Merlivat, 1984; Jouzel, 1986; Scholl et al.,







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2007; Rao et al., 2008), paleoclimatology (Dansgaard et al., 1993; Duplessy, 1993; Ramesh, 2001; Tiwari et al., 2005; White et al., 1997) and oceanography (Delaygue et al., 2001; Srivastava et al., 2007) has been amply demonstrated. While several studies have reported the isotopic composition of rain water (Rindsberger et al., 1990; Rozanski et al., 1993; Gat, 1996; Araguas-Araguas et al., 1998; Celle-Jeanton et al., 2004: Vuille et al., 2005: Tian et al., 2007). isotopic measurements on AWV and clouds (He and Smith, 1999; Scholl et al., 2007; Angert et al., 2008; Froehlich et al., 2008; Wen et al., 2008; Frankenberg et al., 2009; Risi et al., 2010; Midhun et al., 2013; Steen-Larsen et al., 2013) are relatively recent, often limited to either a few cyclonic or rain events (Lee et al., 2006; Fudeyasu et al., 2008). Satellite observations of hydrogen isotopes of AWV have a large uncertainty, ~10‰ (Worden et al., 2007; Brown et al., 2008). If the isotopic change in AWV is demonstrably higher than this, it would help early monsoon detection and forecast. Ground-based observations of isotopic compositions of AWV can also validate satellite data and help improve their accuracy. Such data are also relevant for the study of plant-water isotopic relationship using models and thus in tree-ring based paleoclimatology (e.g., Sheshshayee et al., 2005).

This study reports the measurements of the  $\delta^{18}$ O and  $\delta$ D of both rain and water vapor for a year over the tropical monsoon region: (daily) rain water and AWV samples were collected during April 2007 to April 2008 (a normal monsoon year, with no extreme events such as cloud bursts) at Ahmedabad (23.03°N, 72.56°E, 55 m a.m.s.l.), India. Questions addressed include (i)Is there a significant change in the stable isotopic compositions of AWV during the onset of the monsoon? (ii) Is there an isotopic equilibrium between rain and water vapor? (iii) If yes, then on what time scales, and does it tally with theoretical prediction using the observed temperatures? (iv)What is the magnitude of annual/seasonal change in  $\delta^{18}$ O<sub>vapor</sub> and  $\delta$ D<sub>vapor</sub>?

#### 2. Sampling and methodology

Vapor samples were collected following the procedure of Fudeyasu et al. (Fudeyasu et al., 2008). A schematic diagram of vapor collection unit is shown in Fig. 1. AWV samples were collected at the Physical Research Laboratory (PRL), Ahmedabad at a height of ~8 m above the ground level. There are no open water bodies

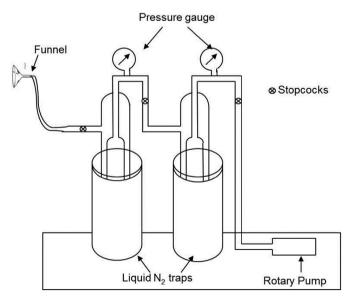


Fig. 1. Schematic diagram of vapor collection unit.

nearby for ~2 km. AWV samples were collected daily from 1000 Hrs–1200 Hrs Local Time (LT = 5:30 + Universal Time), except Sundays, when weekly cleaning and maintenance of the vapor sampling lines were carried out.

There were two major gaps in the vapor sampling during the pre and post monsoon dry seasons when the authors were away on an ocean cruise (9 May–14 June 2007, and 3 November–3 Jan 2008). These gaps are filled using ocean vapor data collected over Bay of Bengal (May–June cruise (SK234): over an area from 11.2°N to 13.3°N and 89.8°E to 91.6°E; Nov–Jan cruise (SK242): from 15.5°N to 20.2°N and 86.0°E to 89.0°E).  $\delta D_{vapor}$  could not be measured for SK242 samples due to limited sample amount.

Water vapor was collected cryogenically using liquid nitrogen (-196 °C) and an extraction line composed of U-shaped glass tubes. Three U-shaped vapor traps, with last trap filled with glass beads, were used to ensure efficient trapping of vapor, as partial trapping could cause fractionation. Ambient air was sampled using a rotary pump through a system consisting of a funnel, polyethylene tube, and an extraction line. The funnel was connected to the extraction line through the polyethylene tube. Proper arrangement was made to ensure that the rain water did not enter the extraction unit. The flow rate of air was about 2 l min<sup>-1</sup> for the water vapor collection (to obtain at least 1–2 ml of vapor sample). Generally, vapor samples were collected for a period of 2 h from 1000 Hrs-1200 Hrs LT (except in April 2007 when low humidity values necessitated the collection for 4 h, from 1100 Hrs-1500 Hrs to ensure sufficient amounts of sample). Trapped atmospheric CO<sub>2</sub> was removed by pumping out the extraction line at the end of the vapor collection by replacing the liquid nitrogen with ethanol slush (maintained at -90 °C). Thus, CO<sub>2</sub> free water vapor was collected and immediately transferred to double cap, good quality sample bottles for subsequent isotopic analysis.

To establish the analytical precision, three AWV samples were simultaneously collected by two independent persons at the same place (~30 m apart) and time. Their oxygen isotopic compositions were found to be in good agreement within  $3\sigma$  and are shown in Table 1.

Rain samples were collected with a rain collector, taking care to prevent any subsequent evaporation. As a further precaution, samples were kept at 25 °C to minimize evaporation within the sample bottle. Samples were transferred to the tight-fit narrow-mouth 20 ml capacity plastic bottles, filled up to the brim and taped to prevent evaporation. More experimental details were reported by Srivastava et al., 2007. Temperature and relative humidity were measured using a digital hygrometer (calibrated using a wet and dry bulb thermometer).

A mass spectrometer (Geo 20-20, PDZ Europa Ltd., Northwich, UK) was used for isotopic analysis, after equilibrating the samples with carbon dioxide/hydrogen gas (Epstein and Mayeda, 1953; Gonfiantini, 1981). For  $H_2$  – water isotopic equilibration, platinum coated beads (known as Hoko Beads) were used as catalyst. The isotopic compositions are expressed in the standard notation:

$$\begin{split} \delta^{18} O &= \left[ ({}^{18} O / {}^{16} O)_{sample} \Big/ ({}^{18} O / {}^{16} O)_{standard} \right. \\ &- 1 \right] * 1000 \quad per \ mil(\%) \end{split}$$

Table 1

Date of the AWV collection, oxygen isotopic compositions of AWV samples collected simultaneously at same place and time in PRL.

Date	This data $\delta^{18}O_{vapor}$ (‰)	Other data $\delta^{18}O_{vapor}$ (‰)
18/06/2007	-10.8	-10.2
19/06/2007	-10.7	-10.6
04/07/2007	-10.1	-10.2

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