Characteristics of Seasonal Variation of Near-Surface Water Vapor D/H Isotope Ratio Revealed by Continuous in situ Measurement in Sapporo, Japan

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Abstract

High-temporal measurements of the stable isotope ratio (δD) of near-surface atmospheric water vapor by an Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)-type water vapor isotope analyzer (WVIA) were performed in Sapporo from April 2009 to June 2011. The data obtained from the WVIA was corrected by comparing the δD values with those obtained from the cold trap method and subsequent cavity ring-down spectroscopy isotopic water analysis. The δD values showed a marked seasonal cycle but showed a different seasonal cycle from that of the surface air temperature. The δD values simulated by the isotopic-incorporated Global Spectral Model showed almost the same seasonal cycle as that of observed δD values, although simulated values showed about 10‰ difference from observed values in 10-month average. It is found that the monthly mean SSToff of the nearest sea was a better predictor for δDoff than the monthly mean air temperature. Based on the data measured by the WVIA deployed on the Oshoro-Maru of Hokkaido University, from the Sea of Okhotsk to the Pacific Ocean, we confirmed that δD of water vapor generally increased with increasing SST and the highest values of δD were almost the same as those of vapor in equilibrium with ocean liquid.

1. Introduction

Improved understanding of stable water isotope ratios (δD and δ18O) as tracers of the water cycle in the atmosphere and as indicators of climate change requires detailed knowledge of the isotope composition in all three phases of water. Many previous studies on δD and δ18O have concentrated on the condensed phases (e.g., International Atomic Energy Agency–World Meteorological Organization (IAEA–WMO) Global Precipitation Network; Schotterer et al. 1996). To date, the majority of water vapor isotope studies have relied on the cold trap/mass spectrometry method. Therefore, most studies on water vapor are limited to short-term campaigns and discrete sampling, except for that of Jacob and Sonntag (1991). They conducted continuous measurements of isotopic contents in water vapor for about eight years but with a rather coarse sampling period of 1–2 days.

In situ technological advances such as tunable diode laser (TDL) absorption spectroscopy (Lee et al. 2006; Wen et al. 2010) and off-axis integrated cavity output spectroscopy (OA-ICOS) (Bauer et al. 2004) have made it possible to measure δD and δ18O in water vapor at high-temporal resolution and on a continuous basis. Continuous measurement of the stable isotope ratios of water vapor (δ) has not only provided an excellent data base for verification of isotopic-incorporated atmospheric general circulation and regional-scale models (e.g., Schneider et al. 2010) but also opened a new window on the long-term and short-term water cycles (e.g., Gat 1996; He and Smith 1999; Yakir and Stenberg 2000; Lai et al. 2006; Lee et al. 2005 and 2006, Noone et al. 2011).

The objective of our study is to investigate meteorological processes that influence the amount of atmospheric water vapor as well as the stable isotopic ratios of water vapor. In this paper, we will show the seasonal variation in the stable isotope ratios of water vapor revealed by continuous in situ measurements. Section 2 gives a brief description of the instrument and the methods of calibration and correction of the data measured by the instrument. Section 3 presents the data used in this study and the observation results. Discussion and conclusions are given in Section 4.

2. WVIA and methods of calibration and correction

We used an OA-ICOS-type water vapor isotope analyzer (WVIA, DLT-100) from Los Gatos Research Inc. (LGR). The ambient air is sucked in through two tubes; one inlet for the WVIA and the other for the cold trap. δD and δ18O values were recorded at intervals between 0 and 20 s. Several researchers have presented calibration methods of the Los Gatos WVIA (Lis et al. 2008; Wang et al. 2009; Sturm and Knohl 2010; Johnson et al. 2011). Sturm and Knohl (2010) presented a detailed assessment of the WVIA and noted that it is essential to quantify the water concentration dependence when using such a water vapor isotope analyzer. Johnson et al. (2011) used a low-cost flask-based method (Strong et al. 2007) to accurately determine the δD value of water vapor, and corrected δD values of the isotopic laser spectroscopy instruments manufactured by Picarro and LGR based on a total of 12 flask samples at low atmospheric water vapor concentrations (from 1,500 to 11,000 ppm).

In the period between November 16th 2010 and February 14th 2011, we sampled ambient water vapor by the cold trap method once per day (sampling time was 24 h). The isotopic values of trapped vapor samples were analyzed at the laboratory of Research Institute for Global Change (RIGC) of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) using cavity ring-down spectroscopy isotopic water analysis (model LI1102; Picarro Inc., Sunnyvale, CA, USA) with a CTC Analytics’ auto sampler. The measurement precision including internal and external variation is better than ±0.2‰ for δ18O and ±2‰ for δD. The data obtained from the WVIA was corrected by comparing the δD values measured by the WVIA with those obtained from the cold trap method (a total of 72 samples). The difference between these δD values was plotted against the water vapor mixing ratio (w) measured by the WVIA (Fig. 1). A logarithmic-linear regression was found between these two variables as

\[ δD_{corr} (‰) = δD_{WVIA} (‰) - δD_{Cold Trap} (‰) = -21.89n w (g kg^{-1}) + 50.76 \]

with a coefficient of determination of approximately \( r^2 = 0.81 \). This expression is valid for a water vapor mixing ratio between 2000 ppm (1.32 g kg\(^{-1}\)) and 10,000 ppm (6.35 g kg\(^{-1}\)). Using this expression, we corrected all δD values. However, δD corresponding to a water vapor amount below 2000 ppm was not used in this study. δD retained the original value when the water vapor mixing ratio was greater or equal to 10,000 ppm. The difference between the mean δD measured by the WVIA and that measured by the cold trap method from November 16th 2010 to February 14th 2011 was smaller than 1‰.

The correction function of δ18O values is not simple as Eq. (1), but depends on ranges of the water vapor amount. We need careful and higher order calibration of WVIA-δ values if we discuss the deuterium excess, which reflects the kinetic fractionation process (e.g., Craig and Gordon 1965). One of the co-authors developed the same type of water vapor isotope standard source (WVISS) as Wen et al. (2008), Sturm and Knohl (2010), and Dong and Bauer (2010). We used the WVISS for real-time calibration of the WVIA from November 16th 2010 to February 14th 2011. We are preparing a paper that describes...
the novel WVISS, results of calibration of WVIAS$^{-18}$O values, and temporal change of the $d$-excess parameter.

Using a Los Gatos Research Liquid Water Analyzer, Lis et al. (2008) considered the long-term drift of the instrument. Based on more than 6 months of testing, they stated that the drift was random in the short term and the magnitude of drift for $d$ and $^{18}$O was about 0.6 and 0.4‰, respectively. We also did not see any monotonic drift for $d$ and $^{18}$O of the standard water vapor used in the WVISS from November 16th 2010 to February 14th 2011. Therefore, we did not consider the long-term drift of the instrument. We will discuss the effect of the long-term drift on the seasonal change of $d$ values in Section 4.

### 3. Observation results

#### 3.1 Observation sites and periods

Observations were carried out mainly at Institute of Low Temperature Science, Hokkaido University in Sapporo, Japan. Hokkaido is characterized by a warm but not humid summer and quite a cold and snowy winter, and its north coast experiences the lowest-latitude sea ice in the northern hemisphere. The observation in Sapporo was carried out in four phases: (I) April 28th 2009–June 25th 2009; (II) September 15th 2009–November 29th 2009; (III) April 1st 2010–May 21st 2010; and (IV) December 17th 2010–June 3rd 2011. We used auxiliary data such as air temperature, relative humidity, wind speed and direction, atmospheric pressure, and precipitation, all measured at the Sapporo District Meteorological Observatory, approximately 3 km south of the observation site.

#### 3.2 Seasonal variation of $d$O in Sapporo

Long-term measurement of the near-surface water vapor isotopic composition in Sapporo (43.08°N, 141.33°E) started in April 2009. The sampling level was 1.5 m from September 2009 to May 2010 and 9.6 m from December 2010 to June 2011. The measurement frequency for $d$O used in this report was between 6 and 20 s and was averaged to produce hourly mean values. Figures 2a–c show the time series of hourly averages of air temperature (T), water vapor mixing ratio (w), and $d$O values measured by the WVIAS. An isotopic-incorporated Global Spectral Model (IsoGSM; Yoshimura et al. 2010) data from a nudged run are available on a global scale since 1979 with a temporal resolution of 6 h and a horizontal resolution of 200 km. Figures 2d and 2e show time series of IsoGSM $d$O values (2 m above ground surface at (42.9°N, 140.6°E)) and the monthly mean sea surface temperature at the point (43.5°N, 141°E) in Ishikari Bay (we will explain the reason why this point was chosen later), respectively. Here we used high-resolution (0.05°-gridded) Sea Surface Temperature (SST) data (New-Generation Sea-Surface Temperature for Open Ocean (NGSST-O Ver.1.0)) (Sakaide et al. 2009). It is to be noted that the year of all data sets was changed in accordance with the four observation phases of the WVIA, that is, the year from January to March is 2011, that of April and December is 2010, and that from May to November is 2009.

The isotopic composition of the near-surface water vapor showed a marked seasonal cycle. In general, $d$O was higher during the warm season than during the cold season, consistent with the findings of Jacob and Sonntag (1991) in Germany, Lee et al. (2006) in the U.S.A., Wen et al. (2010) in China, and Schneider et al. (2010) in Sweden. It is to be noted that the seasonal cycle in surface temperature leads that of $d$O values by a few months.

Physically, the isotopic composition of the local water vapor is a variable independent of wind speed and air temperature. Nevertheless, it is often useful to establish a relationship between the variation of the isotopic composition and the local air temperature variation, especially when long-term climate variability is concerned. Taking advantage of the WVIA data, we investigated the correlation between $d$O and air temperature at time scales ranging from daily to seasonal. The coefficients of determination were relatively poor on the daily, weekly, and monthly time scales, as shown in Table 1, consistent with the result of Lee et al. (2006). However, the coefficient of determination improved significantly for the seasonal scale. Figure 3 shows the correlation of $d$O with air temperature (T). All the hourly averaged values of $d$O and air temperature are denoted by gray dots, while the monthly averages are denoted by black circles with their standard deviations (Fig. 3a). The empirical relationship between the monthly mean $d$O ($d$O$_{\text{mon}}$) and the monthly mean air temperature (T$_{\text{mon}}$) is

$$d$O$_{\text{mon}}$(‰) = 0.74 = 0.74.

The dependency of variation of isotopic composition, $d$O on temperature variation ($\Delta$T), that is $d$O/\Delta$T, was 2.72 in Sapporo. Jacob and Sonntag (1991) measured $\delta$O in Heidelberg, whose latitude (49.4°N) is close to Sapporo’s latitude (43.08°N), and reported nearly the same dependency (3.00 ± 0.18) as that in Sapporo. Figure 3b shows the correlation between $d$O$_{\text{mon}}$ and the monthly mean water vapor mixing ratio ($w_{\text{mon}}$). The empirical relationship between them is

$$d$O$_{\text{mon}}$(‰) = -8.6w_{\text{mon}}(g\cdotkg^{-1}) − 176.33

with a coefficient of determination of approximately $r^2 = 0.74$.

The correlation between $d$O$_{\text{mon}}$ in Sapporo and the monthly mean sea-surface temperature (SST$_{\text{mon}}$) surrounding Hokkaido was investigated. Although $d$O$_{\text{mon}}$ shows good correlation with T$_{\text{mon}}$ and $w_{\text{mon}}$, the values of $d$O showed a different seasonal cycle from that of the surface air temperature, that is, $d$O$_{\text{mon}}$ before summer (April–June) were lower than Eq. (3) and those after summer (September–November) were higher than Eq. (3) as shown in Fig. 3a. Angert et al. (2008) also reported that $\delta$O showed a different seasonal cycle from that of surface air temperature. They attributed this delay in the seasonal march of sea-surface temperature to the large heat capacity of the Mediterranean Sea.
Table 1. The coefficient of determination between near-surface δD and air temperature at time scales ranging from daily to seasonal.

<table>
<thead>
<tr>
<th>Time Scale</th>
<th>Coefficient of determination ($r^2$)</th>
<th>Averaged $r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day to Day</td>
<td>0.01−0.94</td>
<td>0.27</td>
</tr>
<tr>
<td>Week to Week</td>
<td>0.01−0.76</td>
<td>0.18</td>
</tr>
<tr>
<td>Month to Month</td>
<td>0.0−0.62</td>
<td>0.15</td>
</tr>
<tr>
<td>Seasonal to Seasonal</td>
<td>0.74</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. (a) The correlation of δD with surface air temperature in Sapporo. All the hourly averaged values of δD and air temperature are denoted by gray circles, while the monthly averages are denoted by black circles with their standard deviations (σ). (b) The correlation between δD<sub>max</sub> and the monthly mean water vapor mixing ratio (w<sub>mean</sub>), with the hourly averaged values of δD and mixing ratio denoted by gray triangles. Numbers on the figure indicate months of the year (e.g., 1 and 12 denote Jan. and Dec., respectively).

Unlike the air temperature, SST has a considerable effect on δD. Under equilibrium conditions, higher SST produces higher δD in the water vapor evaporating from the sea surface. As shown in Fig. 2, the SST at the point (43.5°N, 141°E) in Ishikari Bay before summer was colder than that at summer. Figure 4 shows the spatial distribution of the coefficients of determination between δD<sub>max</sub> at Sapporo and the SST<sub>max</sub> surrounding Hokkaido. Here we used NGSSST-O SST data (Sakaide et al. 2009). The values of SST<sub>max</sub> over the Sea of Okhotsk are unreliable in winter (from December to February) because of the development of sea ice. The coefficients of determination are very high (from 0.70 to 0.92). The highest coefficient of determination ($r^2 = 0.92$) was located in Ishikari Bay (43.5°N, 141°E), about 40 km from Sapporo. Figure 5 shows the correlation between δD<sub>max</sub> in Sapporo and SST<sub>max</sub> in Ishikari Bay (43.5°N, 141°E). The empirical relationship between them is given as

\[
\delta D_{\text{max}}(\%o) = 4.57 \times \text{SST}_{\text{max}}(°C) - 185.4. \tag{4}
\]

4. Discussion and conclusions

Using WVIA, we investigated the temporal change of near-surface δD in Sapporo from May 2009 to March 2011. Although the δD values showed an almost uniform day-to-day variability throughout the year, they were higher during the warm season than during the cold season, as reported by other researchers in different countries (Jacob and Sonntag 1991; Lee et al. 2006; Wen et al. 2010; Schneider et al. 2010). As shown in Fig. 2d, δD values simulated by the IsoGSM showed almost the same seasonal cycle as that of observed δD values. This fact indicates that our correction method shown in Section 2 successfully functioned, and that the long-term drift of the instrument might not affect the seasonal cycle of observed δD values. The difference between 10-month average of the observed and modeled δD is about 10‰ with the latter sometimes over-estimating δD, especially in the cold season. In order to improve the model, more detailed and continuous observation of δD, and subsequent comparison analysis would be most desirable.

The most important finding is that the SST<sub>max</sub> in Ishikari Bay (43.5°N, 141°E) is about 40 km from Sapporo, and it is reasonable that the coefficients of determination in the Pacific Ocean (close to Tomakomai), on the southern side of Hokkaido, are lower than those in Ishikari Bay, because northwesterly cold air outbreak in winter season strongly affects the seasonal march of SST over the Sea of Japan and air temperature in Sapporo. It should, however, be noted that water vapor evaporating in Ishikari Bay may not be the main moisture source of Sapporo. Rather, the observational result implies that the admixture of water vapor originating from Ishikari Bay plays an important role in biasing the temperature and water vapor dependences of δD in Sapporo. The amplitude of the bias would depend on the geographic feature of the observation site. To test the applicability and usability of Eqs. (2) and (4), continuous observation of δD in other places where geographic situation (e.g., the distance from the sea coast) is similar with that of Sapporo would be desirable.

There have been a few studies that directly correlate the stable isotope ratios of water vapor with SST. Craig and Gordon (1965) reported that the δD of water vapor was uniformly approximately 3‰ lighter than that of equilibrium water vapor. Uemura et al. (2008) also reported that the δD values did not reach isotopic equilibrium with sea water because of the kinetic isotope effects during evaporation, and showed that the deuterium excess correlated negatively with the relative humidity and correlated with SST. Lawrence et al. (2004), however, found that the highest δD values approached isotopic equilibrium with seawater during quiescent weather or downwind of different oceanic sources using δD. They reported that high δD results when moisture is advected from the Gulf of Mexico (warmer than the Pacific Ocean) and low δD results if moisture is advected from the Pacific Ocean. We found that the highest coefficient of determination between δD<sub>max</sub> at Sapporo and the SST<sub>max</sub> surrounding Hokkaido was located in Ishikari Bay, about 40 km from Sapporo. It is reasonable that the coefficients of determination in the Pacific Ocean (close to Tomakomai), on the southern side of Hokkaido, are lower than those in Ishikari Bay, because northwesterly cold air outbreak in winter season strongly affects the seasonal march of SST over the Sea of Japan and air temperature in Sapporo.
regions of organized convection. We deployed the WVIA on the T/S Oshoro Maru of the Faculty of Fisheries, Hokkaido University from the Sea of Okhotsk (45°N) to the Pacific Ocean (20°N) from June 8 to July 15th 2011. The grey line indicates calculated δD of water vapor in equilibrium with ocean liquid.

Figure 6 also shows that the δD values deviated from the equilibrium vapor and changed considerably over a short period of time and were mostly affected by such organized disturbances as cloud clusters, synoptic disturbances and tropical cyclones, as reported by other researchers (e.g., Gedzelman et al. 2003; Lawrence et al. 2004; Kurita et al. 2011). In Sapporo, short-term and large variations in δD were also observed frequently (see Fig. 2c) and the IsoGSM successfully simulated some of them (marked by A and B in Fig. 2d). Most of them were associated with low-pressure systems. Preliminary results using the isotopic-incorporated Regional Spectral Model (IsoRSM; Yoshimura et al. 2010) suggest that mesoscale upper air intrusion might possibly be the main process responsible for bringing light δD to the surface (vertical advection process). Our measurements in Sapporo also showed that development of sea ice over the Sea of Okhotsk caused a decrease in the δD values in Sapporo (horizontal advection effect). Although δD values simulated by the IsoGSM showed almost the same seasonal cycle as that of observed δD values, IsoGSM simulated lower δD values in autumn and higher δD values in winter than observed δD values. Further comparison studies will be needed to improve the IsoGSM and IsoRSM performances and quantitatively discuss the processes that cause the long-term and short-term variation in the stable isotope ratios of water vapor.

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References

Fig. 6. Relationship between δD values near the ocean surface and the SST during the cruise of the T/S Oshoro Maru of the Faculty of Fisheries, Hokkaido University from the Sea of Okhotsk (45°N) to the Pacific Ocean (20°N) from June 8th to July 15th 2011. The grey line indicates calculated δD of water vapor in equilibrium with ocean liquid.