Triple isotope variations of monthly tap water in China

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Tap water isotopic compositions could potentially record information on local climate and water management practices. A new water isotope tracer 17O-excess became available in recent years providing additional information of the various hydrological processes. Detailed data records of tap water 17O-excess have not been reported. In this report, monthly tap water samples (n = 652) were collected from December 2014 to November 2015 from 92 collection sites across China. The isotopic composition (δ2H, δ18O, and δ17O) of tap water was analyzed by a Triple Water Vapor Isotope Analyzer (T-WVIA) based on Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique and two second-order isotopic variables (d-excess and 17O-excess) were calculated. The geographic location information of the 92 collection sites including latitude, longitude, and elevation were also provided in this dataset. This report presents national-scale tap water isotope dataset at monthly time scale. Researchers and water resource managers who focus on the tap water issues could use them to probe the water source and water management strategies at large spatial scales.

Background & Summary

Stable isotopes of hydrogen and oxygen have been widely used to identify plant water uptake depths, partition evapotranspiration, and separate hydrographs5–7. Such applications rely on different isotopic compositions of different water pools and the isotope difference is fundamentally caused by isotope fractionation. There are two major isotope fractionation processes: equilibrium fractionation and kinetic fractionation when water vapor, liquid, or ice crystals are converted into each other. Equilibrium fractionation is mainly affected by different saturation vapor pressure (e.g., liquid condensation)8,9 and kinetic fractionation is mainly affected by diffusivities (e.g., evaporation and solid condensation at supersaturation)9,10. 17O is the least abundant (0.038%) oxygen isotope and can be used as a new tracer in meteorological and hydrological studies. Due to the advances of high-precision analytical methods11–13, 17O-excess (17O-excess = ln (δ17O + 1) − 0.528 x ln (δ18O + 1)), another important second-order isotope like d-excess (d-excess = δ2H − 8 x δ18O), becomes available to probe hydrological processes14,15. Taking precipitation formation as an example, the δ2H, δ18O, δ17O, and d-excess are all sensitive to both temperature and relative humidity10,15,16. However, 17O-excess is theoretically not affected by temperature and only affected by relative humidity between 10 °C to 45 °C because of the similar temperature sensitivity between δ18O and δ17O17,18. Therefore, combining 17O-excess and 18O measurements could separate the temperature (not affecting 17O-excess) and relative humidity (affecting both 17O-excess and 18O) effect on oxygen isotopes. 17O-excess can also be used to identify spectral contamination and improve direct vapor equilibration in plant and soil analysis19. According to the relationship between δ18O and δ17O (i.e., the slope of 1000 x ln (δ18O + 1) and 1000 x ln (δ17O + 1)), synoptic drought related to El Nino and local drought is distinguishable20. Fog and dew are also differentiated using the δ18O and δ17O relationship at the Namib Desert21. Moreover, based on the conceptual evaporation model, the relationship between δ18O and δ17O, and the relationships between 17O-excess and δ18O (or d-excess) are used to estimate whether water (e.g., precipitation, river waters, and lake waters) is affected by equilibrium fractionation or kinetic fractionation associated with evaporation14,17,22–28. Up to now, the studies of water 17O-excess variations at large spatiotemporal distribution have mainly focused on snow and ice cores in high-latitude regions29–36, where 17O-excess of snow is sensitive to temperature because of kinetic fractionation associated with supersaturation conditions under extremely cold condition (−80 to −15 °C)30,31,32. There are only few studies focused on the mid-latitude regions24,25,27,38.

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The Intergovernmental Panel on Climate Change reported extending durations of severe droughts, increasing surface temperatures, and decreasing rainfall. Thus, tap water, as an essential part of the domestic water use, should be paid more attention due to the trend of water scarcity and severe water pollution. The isotope variations of tap water could reveal the regional water supply sources, and reflect water-resource management strategies that integrate human geography, climate and socio-economic development. The tap water in some regions can be used as a precipitation proxy to study the local precipitation, while other regions may be supplied from inter-basin water transfers, deep groundwater or montane snowmelt. The water resources in the north of China are less than those in the south due to special geographical location, climate change, extensive water-intensive economic activities, and population growth. Therefore, the spatiotemporal distribution of tap water isotopes in China are needed to better understand water sources, thus informing water resource management.
To our best knowledge, there is no monthly tap water isotope dataset including $^{17}$O-excess publicly available. Here, we provide monthly isotope dataset ($\delta^{2}H$, $\delta^{18}O$, $\delta^{17}O$, $d$-excess, and $^{17}$O-excess) of tap water in China collected between December 2014 to November 2015. The instrument operation ($\delta^{2}H$, $\delta^{18}O$, and $\delta^{17}O$) using Triple Water Vapor Isotope Analyzer (T-WVIA-45-EP; Los Gatos Research Inc. (LGR), Mountain View, CA, USA) based on Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique has been described in details in our previous studies\textsuperscript{24,37}, as well as the detailed description of $^{17}$O-excess quality control method. We have published the tap water isotopic variations in Tian et al.\textsuperscript{47}. In this new dataset, we present the first publicly available monthly tap water isotope dataset to fill the gap in global tap water isotope datasets, especially for $^{17}$O-excess, which would be used to study water resource issues in the sustainable development of human societies.

Fig. 2 The relationships between monthly tap water $\delta^{18}O$ and $\delta^{2}H$ (a) as well as $\delta^{16}O$ and $\delta^{17}O$ (b) for all the samples.
Methods

Sample collections. The monthly tap water samples across China were collected in 2015 (from December 2014 to November 2015) by Zhao et al.47, and conventional isotopes (δ2H and δ18O) were measured in Hydrology Laboratory of Tsinghua University. To obtain 17O-excess values, the samples were delivered to the IUPEI (Indiana University-Purdue University Indianapolis) Ecohydrology Lab to measure δ17O and δ18O (δ2H was also measured simultaneously). 652 samples from 92 sites in China were measured (Online-only Table 1), which have been reported by Tian et al.47. In here, we reported the detailed geographical location and monthly isotopic variations especially for 17O-excess values.

Isotope measurements and 17O-excess data processing. The details of the measurement process have been described by Tian et al.47,49. In brief, each sample was run at 1 Hz for 2 min under 13000 ppm to attain 120 data points using a Triple Water Vapor Isotope Analyzer (T-WVIA-45-EP, Los Gatos Research Inc. (LGR), Mountain View, CA, USA; preheated to 80 °C)49. To avoid memory effects between samples, the WVSS nebulizer was first purged for at least two minutes, and then the “stabilize” option of the device was turned on for two minutes to expel residual air inside the vaporizing chamber. The operation is different from the liquid water analyzer as described in other studies50,51. LGR#1 to LGR#5, as working standards with known and wide range of isotopic composition, were analyzed after every five tap water samples to ensure the accuracy of the T-WVIA performance. Furthermore, normalizing all of the isotope ratios using Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) to reduce differences between laboratories once a day42,52.

Accurate 17O-excess value of each sample (120 data points) require two steps for quality control. Firstly, calculated λ value (λ = ln (δ17O + 1)/ln (δ18O + 1)) of each data point, the same as theoretical kinetic and equilibrium fractionation coefficient (θ) between liquid and vapor, should be between 0.506 and 0.5302,53. Secondly, the calculated 17O-excess value of each data point should be between −100 per meg and +100 per meg (1 per meg = 0.001%), which is the range for almost all of the 17O-excess values of global precipitation2,17,23,25,54. The data points that meet the above two conditions were averaged to obtain the 17O-excess value for that sample.

Data Records

Monthly tap water isotope samples are archived in PANGAEA in a single table including 652 rows and 10 columns55. Each row presents a monthly tap water event at one site. Each column corresponds to the geographic location information (including latitude, longitude, and elevation) and isotope variables including three measured individual stable isotopes (δ2H, δ18O, and δ17O) and two calculated second-order isotopic variables (d-excess and δ17O-excess). A summary of the tap water in 2015 for 92 sites in China is presented in Table 1. The database spanned over 30.21° in latitude (from 20.03°N to 50.24°N) and 51.50° in longitude (from 75.99°E to 127.49°E). The elevation varied from 5 m to 3657 m with a mean value of 708 m. Fig. 1 depicts the distribution of monthly stable isotopes. The δ18O values varied from −132.40‰ to −22.36‰ with a mean value of −60.52 ± 19.54‰ (Table 1). The δ17O values varied from −17.74‰ to −3.88‰ with a mean value of −8.72 ± 2.49‰. The δ2H values varied from −8.38‰ to −1.97‰ with a mean value of −4.58 ± 1.32‰. The d-excess values varied from −5.99‰ to 20.8‰ with a mean value of 9.2 ± 4.5‰. The 17O-excess values varied from 19 to 66 per meg with a mean value of 39 ± 8 per meg. The tap water line (TWL) in China between δ18O and δ2H based on the 652 tap water samples within one year was δ2H = 7.65 (±0.07) x δ18O + 6.15 (±0.63) (R2 = 0.95, p < 0.001), which is close to the Global Meteoric Water Line (GMWL, δ2H = 8 x δ18O + 10) (Fig. 2a). The tap water line (TWL) between δ18O and δ17O was ln (δ17O + 1) = 0.5290 (±0.0001) x ln (δ18O + 1) + 0.000048 (±0.000001) (R2 = 1, p < 0.001), similar to the GMWL for oxygen (ln (δ18O + 1) = 0.528 x ln (δ18O + 1) + 0.000035, normalized to the VSMOW-SLAP scale25,54 (Fig. 2b).

Technical Validation

The precision of our measurement (δ2H, δ18O, δ17O, and 17O-excess) have been described in our previous studies using two international standards (SLAP and Greenland Ice Sheet Precipitation) and the five working standards from LGR, as well as comparing the reported precision in other studies21,26,57. They demonstrated that the precision of our OA-ICOS technique is comparable with other methods including IRMS technique25,31,32,34,52,54, CRDS method26,58, and other type of OA-ICOS water analyzer41.

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**Author contributions**
C.T. analyzed the samples and wrote the manuscript. L.W. conceived the idea and edited the manuscript. W.J. and F.L. commented on the manuscript. F.T. and S.Z. collected the samples.

**Competing interests**
The authors declare no competing interests.

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