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## Periodicity analysis of $\delta^{18}O$ in precipitation over Central Europe: Time–frequency considerations of the isotopic 'temperature' effect



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#### SUMMARY

In this paper the periodic patterns of the isotopic composition of precipitation ( $\delta^{18}$ O) for 22 stations located around Central Europe are investigated through sinusoidal models and wavelet analysis over a 23 years period (1980/01–2002/12). The seasonal distribution of  $\delta^{18}$ O follows the temporal variability of air temperature providing seasonal amplitudes ranging from 0.94% to 4.47%; the monthly isotopic maximum is observed in July. The isotopic amplitude reflects the geographical dependencies of the isotopic composition of precipitation providing higher values when moving inland. In order to describe the dominant oscillation modes included in  $\delta^{18}$ O time series, the Morlet Continuous Wavelet Transform is evaluated. The main periodicity is represented at 12-months (annual periodicity) where the wavelet power is mainly concentrated. Stations (i.e. Cuxhaven, Trier, etc.) with limited seasonal isotopic effect provide sparse wavelet power areas at the annual periodicity mode explaining the fact that precipitation has a complex isotopic fingerprint that cannot be examined solely by the seasonality effect. Since temperature is the main contributor of the isotopic variability in mid-latitudes, the isotope-temperature effect is also investigated. The isotope-temperature slope ranges from 0.11%/°C to 0.47%/°C with steeper values observed at the southernmost stations of the study area. Bivariate wavelet analysis is applied in order to determine the correlation and the slope of the  $\delta^{18}O$  – temperature relationship over the time– frequency plane. High coherencies are detected at the annual periodicity mode. The time-frequency slope is calculated at the annual periodicity mode ranging from 0.45%/°C to 0.83%/°C with higher values at stations that show a more distinguishable seasonal isotopic behavior. Generally the slope fluctuates around a mean value but in certain cases (sites with low seasonal effect) abrupt slope changes are derived and the slope becomes strongly unstable.

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#### 1. Introduction

Stable water isotopologues have been used as natural indicators in several eco-hydrological, geological, climatological, meteorological, etc. applications (Rozanski et al., 1993; Gat, 1996; Henderson-Sellers et al., 2002; McDermott, 2004; Yoshimura et al., 2010). The stable isotopic values of water (<sup>18</sup>O and <sup>2</sup>H) provide an integrated product of the various phase changes occurred within the global hydrological cycle reflecting the different fractionation phenomena associated to water evaporation and vapor condensation.

The overall spatial isotopic pattern is mainly reproduced by the Rayleigh distillation process where the temperature and precipitation effects are mainly responsible for the isotopic variability. The Rayleigh model explains in a certain extent the latitudinal, continental and altitudinal isotopic responses but is unable to describe adequately the isotopic composition at local scale where the sub-cloud phenomena (partial evaporation of falling raindrops, isotopic-exchange and moisture recycling) (Stewart, 1975; Froehlich et al., 2008) lead to extremely different isotopic signatures on the observed precipitation in comparison to the expected values from the Rayleigh model.

Air temperature is the most prominent contributor in the observed isotopic variation of precipitation in mid and high latitudes while precipitation amount is better correlated with the stable isotope content in the equatorial (tropical) regions. The interest for exploring the isotopic–temperature relationship was stimulated due to the application of the stable isotopic species for paleo-climatic reconstruction (Dansgaard, 1964; Rozanski et al., 1993). Dansgaard (1964) investigated the apparent link between the isotopic composition of precipitation and local surface temperature using three years of isotopic information from mid

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and high latitude coastal stations reporting slopes  $(\Delta \delta^i / \Delta T)$  equal to 0.69%/°C and 5.6%/°C for <sup>18</sup>O and <sup>2</sup>H respectively. Those slopes have been extensively applied as an isotope-thermometer for the reconstruction of past temperatures using isotopic measurements from global archives (speleothems, ice cores, tree rings, etc.). Rozanski et al. (1993) using long term mean annual  $\delta^{18}$ O and temperature data from stations included in the IAEA/WMO network found a  $\delta^{18}$ O-temperature slope equal to 0.58%/°C for long term mean annual temperatures ranging between 0 and 20 °C. The isotopic composition of precipitation is not correlated to temperature for T > 20 °C. For stations with T > 20 °C (i.e. in the tropics), the isotopic content is affected mainly by the rainfall amount explaining the non-significant relation to temperature. A similar  $\Delta \delta^{18} O/\Delta T$ was found for the European stations (0.59%/°C) (Rozanski et al., 1992). In case of coastal locations  $\Delta \delta^{18} O/\Delta T$  is substantially lower ranging from 0.2%/°C to 0.4%/°C (Rozanski et al., 1993). The 'continental effect' is imprinted in the isotope-temperature slopes with higher isotope-temperature slopes at more inland locations. Vachon et al. (2010) reported  $\Delta \delta^{18} O/\Delta T$  between 0.1%/°C and 0.3%/°C for coastal stations around the United States where  $\Delta \delta^{18}$ O/ $\Delta T$  increases when moving inland (0.4–0.7%/°C).

Even if the general pattern and the main parameters that affect the isotopic composition of precipitation have been widely investigated, a limited number of studies have dealt with the temporal variation of stable isotopes and its connection to climate variability. Time series analysis provides a powerful tool for the identification of temporal trends, periodic oscillations and long-range persistence within climatic data series but requires long term datasets. The limited data availability of isotopic information emerges as the strongest disadvantage in the usage of time series analysis in precipitation isotope studies since isotopic measurements are mainly available at a monthly time scale spanning over few years of observations. The sparseness of the isotopic monitoring sites worldwide indicates that the investigation of the temporal distribution of stable isotopes can be investigated mainly in specific regions with sufficient station coverage and adequate temporal isotopic information. On the other hand, the application of isotopic tracers in the study of the global hydrological cycle highlights the necessity of the better knowledge of the isotopic variability at multi-temporal scales. Lykoudis and Argiriou (2011) applied nonparametric statistical approaches (Mann-Kendall non parametric test) for the detection of possible trends in the isotopic composition of precipitation for various stations located in Central Europe and Eastern Mediterranean. They found some significant positive trends loosely related to trends in meteorological variables (temperature and precipitation amount). Also they showed that the trend differences between and within the two regions are associated to different factors that determine the isotopic composition of precipitation. More recently, Klaus et al. (2014) applied Mann-Kendall trend tests on the isotopic time series over Germany using also seasonal autoregressive integrate moving average (ARIMA) models which account for first and higher order serial correlations. Their results are in agreement with the findings of Lykoudis and Argiriou (2011); they also suggested that the existence of higher autoregressive orders in the isotopic time series requires more attention since they appeared significant on the presence and the strength of the detected trends.

Those efforts constitute one step forward on the study of long term trends in isotopic time series. Little knowledge has been acquired for the possible oscillatory patterns included in the isotopic data series, how those periodicities evolve in the time-frequency domain and how they can be linked to the local climatic variability. Spectral methods may provide some responses to this question. Fourier analysis is the most commonly used spectral method for the determination of the periodicity components included in a signal under the assumption of stationarity, but is

unable to explain the frequency changes over time. For the identification of the variability modes in the time–frequency domain, wavelet analysis could be an alternate. Wavelets perform a local time–frequency decomposition of a time series (Daubechies, 1990) offering interesting insights into the dominant oscillatory patterns and on how these patterns develop in time (Torrence and Compo, 1998). Wavelet analysis can also be extended to two or more signals in order to quantify the possible co-oscillations between a target and explanatory time series.

The general purpose of this paper is to present a discussion for the temporal isotopic composition of precipitation over Central Europe and how this is related to air temperature ("isotope temperature effect") under a spectral point of view. This analysis is separated in two parts,

- The temporal variability of δ<sup>18</sup>O in precipitation (δ<sup>18</sup>O) over Central Europe is examined through periodic models and wavelet methods.
- $\bullet$  The possible spectral co-variation of  $\delta^{18}O$  with air temperature ('isotope–temperature effect') is examined using bivariate wavelet analysis.

#### 2. Data

The area of interest extends between 5-17°E longitude and 45-55°N latitude (Fig. 1b). The selection of Central Europe as the study area is not arbitrary since the spatial distribution of the monitoring locations is quite satisfactory representing one of the densest isotopic networks worldwide. Monthly isotopic measurements of precipitation were obtained through the Global Network of Isotopes in Precipitation (GNIP) database (IAEA/WMO, 2014) for the period of 1980/01-2002/12. Generally climatological studies are based on 30 years of data; however for stable isotope studies shorter time periods can be considered as adequate - due to the limited availability of data. Here a 23-year period is used for trend detection and the interpretation of the possible oscillatory patterns involved in time series at intra-annual and inter-annual time scales. The isotope sampling sites were selected according to the data availability across the selected time span (Fig. 1b). The quality of the isotopic time series is relatively high whereas the data gaps correspond only to 1.5% of the total number of the isotopic measurements  $(N_{\text{total}} = 6072)$ .

Globally the stable isotopes ( $\delta^2 H$  and  $\delta^{18}O$ ) in meteoric waters are clustered along a straight line, the so called Global Meteoric Water Line (GMWL),  $\delta^2 H = 8 * \delta^{18}O + 10\%$  (Craig, 1961). At local scale the isotopic composition changes due to a variety of factors and the water samples lie along the Local Meteoric Water Line ( $\delta^2 H = s * \delta^{18}O + d$ ) where the slope and intercept values generally differ from those of the GMWL. The LMWL over Central Europe (LMWL<sub>CE</sub>) for the selected observation period is,  $\delta^2 H = (7.75 \pm 0.02) * \delta^{18}O + (5.3\% \pm 0.2\%)$  (Fig. 1a). Apart from the LMWL<sub>CE</sub>, the LMWL is calculated separately for each sampling site (Table 1). The individual slopes range between 7.52 and 8.35 while the intercept values range between 3% and 17% implying the different geographical and climatic characteristics within the study area. For further information about the MWLs especially for the German isotopic stations refer to Stumpp et al. (2014).

Apart from the isotopic composition ( $\delta^{18}O$  and  $\delta^{2}H$ ), simple meteorological information (temperature, precipitation amount and vapor pressure) is generally included in the GNIP. Since many temperature gaps are represented, possible missing values were filled using the ECA&D database (Klein Tank et al., 2002). ECA&D does not include measurements for Klagenfurt and Villacher Alpe and therefore those stations are excluded from the isotopic-temperature analysis.

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