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Technical note

Isotopic composition of river water across a continent

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HIGHLIGHTS

- The plot of slopes versus intercept from the plot of $\delta^{18}O$ and $\delta^{2}H$ of various locations are done giving new pattern.
- This new pattern is analyzed to arrive at a isotopic composition of precipitation to be on GMWL.
- The continent is divided on the basis of original isotopic composition to be taken as injected tracer ($\delta^{18}O$ and $\delta^{2}H$).

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ABSTRACT

Isotopic composition of water across United States is available and also baseline data prepared for more than 4800 samples (with depth and width-integrated stream samples) from 391 selected sites within USGS National Stream Quality Accounting Network (NASQAN). Data had been analyzed with respect to arrival at National Meteoric Water Line (NMWL). Large number of NMWL water samples has much lower slopes than 8 and intercepts ranging from +10 to −39. These lower slopes and intercepts need a re-look to ascertain coherent $\delta^{2}H$ and $\delta^{18}O$ across USA in precipitation. A method is worked out by plotting slopes versus intercepts on $\delta^{2}H$ axis to arrive at the isotopic composition of water on GMWL and also to look the regional pattern that reflects the origin of vapour mass.

1. Introduction

Stable isotopes of water molecules are powerful tracers in hydrosphere and water cycle especially ^{2}H and ^{18}O. Stable isotopes ratio $^{2}H/^{1}H$ and $^{18}O/^{16}O$ are expressed as $\delta^{2}H$ and $\delta^{18}O$, where δ sample$=(R_{sample}/R_{SMOW}-1)1000$ where $R={}^{2}H/^{1}H$ or $^{18}O/^{16}O$ as taking standard of sea mean ocean water (SMOW). Lot of measurements are available for $\delta^{2}H$ and $\delta^{18}O$ on global basis. One of the important investigations was made by Craig (1961) as co-relation of $\delta^{18}O$ and $\delta^{2}H$ in the fresh precipitation on global scale known as Craig's Global Meteoric Water Line (GMWL) in ‰ to be $\delta^{2}H=8\delta^{18}O+10$‰. Plot between $\delta^{2}H$ and $\delta^{18}O$ and the slopes and intercepts are being studied globally through a network known as Global Network for Isotope in Precipitation (GNIP) established by collaboration between International Atomic Energy Agency (IAEA) and World Metrological Organization (WMO).

Isotopic composition of water in different environmental conditions had been studied and has established the natural spatial distribution of $\delta^{18}O$ and $\delta^{2}H$ over continental area. These were primilarily a function of fraction of water remaining in the air mass as it moves inland over topographic features. Sub-continent studies had been carried out by Kendall and Coplen (2001) for distribution of ^{18}O and ^{2}H (deuterium) in river water in the United States of America. The experimental results of plot of $\delta^{2}H$ and $\delta^{18}O$ had been both theoretically and experimentally discussed by various investigators (Friedman, 1953; Craig, 1961; Dansgaard, 1964; Singh and Kumar, 2005; Yurtsever, 1975). All these studies reflect the variation of slope and intercept on $\delta^{2}H$ axis on plot of $\delta^{2}H$ and $\delta^{18}O$ water in various stages of hydrological cycle. One would like to know the original isotopic composition of meteoric water source prior to evaporation (temperature and humidity) and other hydrological process at a place or in a region as suggested by Singh (2013) now to extend to continent studies so as to take $\delta^{2}H$ and $\delta^{18}O$ as injected tracer. This is the important aspect for the present interpretation of the data and to further find the pattern of isotopic composition of precipitation/river water across USA.

2. Experimental data

More than 4800 samples from 391 selected sites were collected with depth and width-integrated stream using USGS National Stream Quality Accounting Network (NASQAN). The data thus obtained was analyzed for $\delta^{18}O$ and $\delta^{2}H$ (http://water.usgs.gov/pubs/ofr/ofr00-160/pdf/ofr00-160.pdf). Each site was sampled bi-monthly or quarterly for 2.5 to 3 years. This data set for the water composition of modern precipitation is supported by excellent agreement between the river data set and the isotopic

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composition of adjacent precipitation of monitoring sites. Kendall and Coplen (2001) were able to generate a National Meteoric Water Line (NMWL) for 48 contiguous States and compared with the Global Network Isotopic precipitation of International Atomic Agency and World Meteorological Organization (WMO). It is found that a water sample gives a diverse local condition where the local meteoric water lines usually have much lower slopes and the slopes of the regional MWL, do reflect the environmental condition i.e. humidity and temperature.

The sample collection over the years has the potential for significant seasonal bias. The size of the drainage area ranges from 6 to almost 3×10^6 km^2. The medium drainage area is approximately 8000 km^2 which corresponds to drainage basin 90 km on the site and about 90% of the sites has the basin area, which is less than 133,000 km^2. Entire data set has been reported by Coplen and Kendall (2000). The analysis has been given between the plot of δ^2H and δ^{18}O and all the data set is around GMWL in the form of a flatter ellipse around it.

Table 1
(a) Slope and intercept on δ^2H at different states.

Group	State	Slope	Intercept	Intercept
1	Washington	8.50	15.50	
	Oregon	8.70	17.50	
	Nevada	5.00	−37.70	
	California	7.80	5.40	
	Idaho	7.90	6.60	
	Utah	6.70	−12.60	
	Arizona	7.00	−5.10	
	Colorado	6.30	−18.00	
	New Mexico	6.70	−5.50	
2	Montana	5.00	−46.50	
	Wyoming	5.30	−39.20	
	North Dakota	6.80	−15.40	
	South Dakota	7.10	−10.50	
	Minnesota	5.70		−16.90
3	Kansas	8.40	10.90	
	Oklahoma	6.20	0.20	
	Texas	7.50	2.30	
	Wisconsin	7.40	4.70	
	Illinois	7.80	6.60	
	Missouri	8.80	14.00	
	Arkansas	6.30	1.10	
	Iowa	9.30	18.80	
	Nebraska	9.20	18.20	
4	Albama	5.30	−0.80	
	Missisipi	7.30	7.80	
	Verginia	6.30	4.30	
	Tansese	7.00	6.20	
	North Carolina	6.30	2.90	
	South Carolina	7.10	7.50	
	Georgia	5.50	0.50	
	Florida	5.40	1.30	
	Lousiana	4.10	−3.60	
	Maryland	7.30	7.00	
	New Jersey	6.90	6.60	
5	Ohio	5.20	−8.20	
	Kentucky	6.40	1.20	
	Pennsylvania	6.70	2.00	
	West Virginia	6.40	0.40	
	Michigan	7.10	1.60	
	Indiana	5.90	−1.60	
	New Hampshire	7.30	5.30	
	Maine	7.10	3.60	
	Massachusetts	5.50	−5.60	
	Connecticut	6.50	0.70	
	Rhode Island	5.50	−3.60	
	New York	6.50		−3.00
	Vermont	6.50		−5.00

d-Excess (deuterium excess) is defined by Dansgaard (1964) as $d=\delta^2H-8\delta^{18}O$ for 391 sites ranges from −8 to +17‰. About 8% of 4800 river samples have d-excess value less than 0. The special distributions of d-excess values for 317 sites within 48 states are also plotted. It was suggested that in d-excess the slopes are more dependent on small scale local processes or conditions. In most of the states, the slopes range from 6 to 8 even lesser than 6 except for the four states having slopes greater than 8 found in isolated patches. The slopes and intercepts of the LMWL are listed for all the 48 states. This list is given in Table 1 and slopes and intercepts are plotted as shown in Fig. 1(a). This is a very interesting plot showing some sort of pattern between slopes and intercepts.

3. Analysis of the pattern as given in Fig. 1(a)

In order to analyze certain pattern of the plot as given in Fig. 1(a), the data has been grouped together in such a manner that states are adjacent to each other so as to get the best fit line between slopes and intercepts and this has been given in Fig. 1(b)–(f). The data have been fitted in five groups of states as given in Fig. 2 in different colour codes. Care has been taken to find the best fit line with better R^2. The correlation between slopes and intercepts are given in figures along with the best fit line with R^2. These are given below

$$\text{Fig. 1}\ (b)\quad y=14.82x-110.1 \quad \text{or} \quad -110.1=-14.82x+y \qquad (1)$$

Therefore, $\delta^{18}O=-14.82$; $\delta^2H=-110.1$ to be on GMWL

$$\text{Fig. 1}\ (c)\quad y=16.71x-129.01 \quad \text{or} \quad -129.01=-16.71x+y \qquad (2)$$

Therefore, $\delta^{18}O=-16.71$; $\delta^2H=-129.01$ to be on GMWL

$$\text{Fig. 1}\ (d)\quad y=6.02x-38.92 \quad \text{or} \quad -38.92=-6.02x+y \qquad (3)$$

Therefore, $\delta^{18}O=-6.02$; $\delta^2H=-38.92$ to be on GMWL

$$\text{Fig. 1}\ (e)\quad y=3.65x-19.12 \quad \text{or} \quad -19.12=-3.65x+y \qquad (4)$$

Therefore, $\delta^{18}O=-3.65$; $\delta^2H=-19.12$ to be on GMWL

$$\text{Fig. 1}\ (f)\quad y=5.37x-34.46 \quad \text{or} \quad -34.46=-5.37x+y \qquad (5)$$

Therefore, $\delta^{18}O=-5.37$; $\delta^2H=-34.46$ to be on GMWL

x and y are experimental slopes and intercepts as given in data set in Table 1. It is interesting to note that slope versus intercept are straight line for all the five groups of states.

4. How to interpret these straight lines between slopes and intercepts

In search of a method to interpret these data we may consider the GWML for meteoric water as suggested by Craig (1961) and finally adopted international as given by Rozanski et al. (1993) to be $\delta^2H=8.13\delta^{18}O+10.8$.

Now if we take water having $\delta^{18}O=-5$‰, −7‰, −10‰, −15‰ and −20‰ on GMWL, as given by Rozanski et al. (1993), then corresponding values for δ^2H shall be $\delta^2H=-29.85$‰, −46.1‰, −70.5‰, −111.16‰, −146.34‰ and −151.8‰ respectively.

Let us take the water of these composition and take different slopes similar to those of LMWL for example 7.4–8.1 and calculate the intercept by the equation

$$\delta^2H=\text{slope}\ \delta^{18}O\ (x-\text{axis})+\text{intercept}\ (y-\text{axis}).$$

These slopes thus calculated with intercept for different isotopic compositions of water, are plotted as shown in Fig. 3. All the 6 lines plots are straight lines similar to the experimental plots i.e. slopes and intercepts are on x and y axes respectively. Therefore δ^{18}O and δ^2H are isotopic composition on GMWL as suggested by Singh (2013).