Stable oxygen and hydrogen isotopes measurement by CF-IRMS with applications in hydrology studies

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Abstract. The major changes in isotopic composition of natural waters occur in the atmospheric part of the water cycle and in surface waters which are exposed to the atmosphere. This study demonstrated the utility of the Continuous Flow – Isotope Ratio Mass Spectrometry method for measuring natural variation of the occurring isotopes of hydrogen (^2H) and oxygen (^18O) in meteoric waters. The variation of δ^18O and δ^2D values from precipitation fallen in Raureni-Valcea area between May-December 2007 and September 2008-March 2009 were measured together with the δ^18O and δ^2D values from the Bistrita River. The Local Meteoric Water Line was reported for this area. Also, the variation of δ^18O and δ^2D values was correlated with the temperature and humidity in the same period.

1. Introduction
Stable and radioactive isotopes can be used as tracers, marking a water body or a certain quantity of water. A good example is the phenomenon that the rain water during a heavy storm is often depleted in the heavy isotope (deuterium or oxygen 18) with respect to the most abundant isotope (^1H and ^16O, respectively). This offers the possibility to follow the rain water in the surface runoff and even quantitatively analysing the runoff hydrograph. Craig’s global meteoric water line defines the relationship between ^18O and ^2H in worldwide fresh surface waters:

δ^2H=8δ^18O+10 (‰) [vs SMOW]

The meteoric relationship of ^18O and ^2H arises from fractionation during condensation from the vapour mass. The Rayleigh distillation during rainout is responsible for the partitioning of ^18O and ^2H between warm and cold regions. Craig’s line is only global in application, and is actually an average of many local or regional meteoric water lines, which differ from the global line due to varying climatic and geographic parameters. This partitioning was soon recognized as a tool for characterizing groundwater provenance studies.
2. Sampling and sample preparation
The samples were collected monthly from precipitation fallen in Raureni-Valcea area (latitude 45.6°N, longitude 24.22°E) between May-December 2007 and September 2008-March 2009 and from Bistrita River in the same period. The Bistrita River is the source water from population who lives in Raureni-Valcea. The main concern during sampling, transport and storage was to avoid isotope fractionation through evaporation or diffusive loss of water vapour, and/or isotope exchange with the surroundings as well as with the bottle material. Only for transportation, we used food-quality PET bottles, available pre-sterilised and pre-treated with sodium thiosulphate for the neutralisation of chlorine in samples. Each bottle was clearly identified with batch code, daily date, hour, and temperature.

3. Materials and methods
The conversion of any type of organic or inorganic compound into simple gases is the basic principle for IRMS. We analysed the water samples using the Gas Bench II device together with Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) Delta V Plus. The Gas Bench II is a flexible continuous flow preparation device and inlet system with Repetitive loop injection of gases. It is controlled by a robotic using septum-sealed sample vials.

The most common sample preparation method for $^{18}$O/$^{16}$O in water is the CO$_2$-H$_2$O equilibration, in which about a mill mole amount of CO$_2$ (10 to 20 ml) is brought into isotopic equilibrium with a few micro litres of sample water and reference material (generally at 25.0 ± 0.2°C):

$$H_2^{18}O + C^{16}O_2 \rightleftharpoons H_2^{16}O + C^{18}O^{16}O$$

Similar to the equilibration method for $^{18}$O/$^{16}$O analysis, the $^2$H/$^1$H ratio of a water sample can be transferred to H$_2$ by isotopic exchange (Coplen et al 1991):

$$^2H^1HO + ^1H_2 \rightleftharpoons ^1H_2O + ^2H^1H$$

The results are reported as deviations versus international standards in the $\delta$, notation in ‰:

$$\delta * X/X(\%e) = \left( \frac{(X/X)_{sample}}{(X/X)_{standard}} - 1 \right) \times 1000$$

The $^2$H/$^1$H and $^{18}$O/$^{16}$O ratios are measured and reported as $\delta^2$H and $\delta^{18}$O relative to Standard Mean Ocean Water (SMOW) with 1SD of ± 0.1 $^{13}$C/$^{12}$C ratios is measured and reported as $\delta^{13}$C relative to Pee Dee Belemnite (PDB) from South Carolina, USA.

The experimental conditions for analysing the D and $^{18}$O using Gas Bench II were:

|                         | a) Deuterium analysis | b) $^{18}$O Analysis |
|-------------------------|-----------------------|----------------------|
| Sample size             | 200 µl of water extract from sample | 500 µl of water extract from sample |
| H$_2$/He                | 2%                    | CO$_2$/He 0.36%      |
| Equilibration           | 60 min at 25°C        | Equilibration 20h at 25°C |
| Sampling loop           | 10 µl                 | Sampling loop 10 µl |
| Replicates (loop switches) | 10                    | Replicates 10          |
| GC column               | Pora Plot Q 25 m      | GC column            |
| Primary standard        | VSMOW, GISP, SLAP     | Primary standard VSMOW, GISP, SLAP |

4. Results and discussion
The experimental results obtained for precipitation together with mean temperature and humidity are shown in table 1.

The isotopic composition of oxygen and hydrogen in rainwater varies with time of the year. According with Craig’s relation, we obtained the Local Meteoric Water Line, as is shown in figure 1.
Table 1. The results of measurements the D/H and $^{18}O/^{16}O$ isotope ratios from precipitation in period September 2008-March 2009 in Raureni-Valcea area, the values for local mean temperature and humidity (latitude 45.6°N, longitude 24.22°E), the extend incertitude for $^{18}O$ measurements $\nu_c = 1\%$ ($k = 2$) and for deuterium measurements $\nu_c = 0.65\%$ ($k = 2$).

| Samples    | $\delta^{18}O/^{16}O$ (%$\epsilon_{SMOW}$) | $\delta^2H/^{1}H$ (%$\epsilon_{SMOW}$) | Mean Temp. (°C) | Humidity (%) |
|------------|--------------------------------------------|----------------------------------------|-----------------|--------------|
| 15.09.08   | -8.47                                      | -57.62                                 | 12.3            | 91.5         |
| 16.09.08   | -8.96                                      | -61.55                                 | 18.4            | 80.5         |
| 17.09.08   | -9.63                                      | -66.97                                 | 13.7            | 90.0         |
| 05.10.08   | -10.07                                     | -70.56                                 | 12.6            | 87.5         |
| 26.11.08   | -6.91                                      | -45.07                                 | 5.3             | 92.5         |
| 03.12.08   | -4.46                                      | -25.25                                 | 7.9             | 96.5         |
| 14.12.08   | -8.05                                      | -51.51                                 | 3.9             | 92.0         |
| 15.12.08   | -7.22                                      | -50.64                                 | 4.8             | 90.0         |
| 22.01.09   | -5.58                                      | -37.85                                 | 11.5            | 85.0         |
| 28.01.09   | -5.15                                      | -35.26                                 | 8.8             | 88.0         |
| 29.01.09   | -9.05                                      | -59.41                                 | 5.9             | 86.5         |
| 02.02.09   | -16.99                                     | -125.92                                | 1.5             | 84.0         |
| 03.02.09   | -11.85                                     | -87.86                                 | 3.0             | 89.5         |
| 04.02.09   | -5.03                                      | -18.43                                 | 8.6             | 85.0         |
| 18.02.09   | -16.19                                     | -117.82                                | 3.0             | 82.5         |
| 19.02.09   | -15.12                                     | -110.99                                | 2.7             | 84.5         |
| 20.02.09   | -14.61                                     | -106.85                                | 5.3             | 64.0         |
| 06.03.09   | -9.14                                      | -62.61                                 | 13.3            | 75.0         |
| 07.03.09   | -11.31                                     | -80.21                                 | 12.0            | 78.0         |
| 09.03.09   | -11.26                                     | -79.77                                 | 13.1            | 69.5         |
| 10.03.09   | -14.69                                     | -107.49                                | 5.1             | 84.0         |
| 11.03.09   | -14.23                                     | -103.78                                | 9.0             | 90.0         |
| VSMOW      | 0.00 ± 0.03                                 | 0.0 ± 0.3                              | -               | -            |
| GISP       | -24.76 ± 0.09                               | -189.5 ± 1.2                           | -               | -            |
| SLAP       | -55.50 ± 0.03                               | -428.0 ± 0.3                           | -               | -            |
| IA-R052    | -19.64 ± 0.11                               | -                              | -               | -            |
| IA-R053    | -10.18 ± 0.20                               | -                              | -               | -            |
| IA-R054    | +0.56 ± 0.23                                | -                              | -               | -            |

Figure 1. The results of measurements the D/H and $^{18}O/^{16}O$ isotope ratios from precipitation in period May-December 2007 (left) in Raureni-Valcea area (latitude 45.6°N, longitude 24.22°E), compared with the results of measurements the D/H and $^{18}O/^{16}O$ isotope ratios from precipitation in period September 2008-March 2009 in the same area (right).

This equation for "meteoric water line" which traced the isotopic compositions of natural waters originating from atmospheric precipitation in Raureni-Valcea area in period September 2008-March 2009 (latitude 45.6°N, longitude 24.22°E) is:

$$\delta^2H = 8.079 \times \delta^{18}O + 11.9 \quad (R^2 = 0.984)$$
But, the dependencies of isotope compositions on temperature and amount of precipitation are now considered to be more complex (Aggarwal et al 2004, Alley and Cuffey 2001, Hendricks et al 2000) than were suggested in earlier reviews of GNIP data. These complexities arise from the much greater influence of moisture source and transport patterns on isotope composition compared to the influences of temperature and/or humidity alone. We have such of dependence, as are shown in figure 2.

Figure 2. Correlation between $\delta^{18}O$ in precipitation, local air temperature (left) and humidity percent (right) in period September 2008-March 2009 in Raureni-Valcea area (latitude 45.6°N, longitude 24.22°E).

Figure 3. The results of measurements the D/H and $^{18}O/^{16}O$ isotope ratios from Bistrita River (Valcea-Romania) in period May-December 2007 and September-December 2008.

In Figure 3 we can see a little seasonal variation in isotopic composition from water content in Bistrita River. The average for these values represents the isotope fingerprint for water content in Bistrita River: $\delta^2H/^{1}H$ (%o) vs SMOW = -80.02 ± 0.52 (k = 2) and $\delta^{18}O/^{16}O$ (%o) vs SMOW = -10.93 ± 0.11 (k = 2).

5. Conclusions
The Isotope Ratio Mass Spectrometer (Delta V Plus, Thermo-Bremen), coupled with the continuous flow GasBench II unit, was used for the measurements of the D/H and $^{18}O/^{16}O$ isotope ratios in water collected from precipitation and Bistrita River during 2 years, 2007-2009. The Local Meteoric Water Line was reported for this area. Also, the variation of $\delta^{18}O$ and $\delta^2D$ values was correlated with the temperature and humidity in the same period.

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