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Abstract of PhD. Thesis

The study of drinking water sources using environmental isotopes

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Content

INTRODUCTION

Availability of water, and especially drinking water, is one of the biggest problems facing mankind due to population growth and, consequently, due to water demand for drinking, agricultural and industrial processes. As a consequence, water sources require constant management in terms of their quality and quantity required, leading to the development of research in hydrology.

On the Earth's surface the water is subject to phase transformations, interacts with minerals and the atmosphere, participating in complex metabolic processes essential to life. During these processes, isotope effects involving the hydrogen and oxygen isotopes in the water molecule occur, making them tracers of the complex phenomena that take place.

"Isotope hydrology" uses isotopic and nuclear techniques to study the water cycle. In 1960 a program was initiated for the global monitoring of isotopes in water, originally tritium, extended afterwards to oxygen-18 and to the other heavy isotope of hydrogen - deuterium. This program involved measurements of different isotopes in rivers, lakes, groundwater and precipitation in different climate zones, which gave a great deal of information on the dynamics of the water cycle. This information could not be obtained using classical methods and regarded the residence time of water in various hydrological reservoirs, identifying different sections in water currents, velocity and exchange mechanisms between the stratosphere and the troposphere, between the northern and southern hemispheres etc. Using these information regarding the dynamics of the water cycle, more specific issues were addressed, such as the connection between surface water and groundwater, the geographical origin and time of groundwater recharging, the water balance of a hydrological system etc.

Similarly, information on stable isotopes in precipitation were vital to analyze atmospheric vapor routes and for determining the link between isotopic composition and major climate characteristics. Because the heavy isotope content of precipitation is dependent on climatic parameters and atmospheric routes, it became obvious that it can help monitor climate change.

Increasing human activity has resulted in loading the hydrological network with a large amount of pollutants (e.g. nitrogen and phosphorus compounds, heavy metals, agrochemicals, etc.), which produced a rapid deterioration of the water quality. As a result, water sources require constant monitoring in terms of their quality and identifying sources of contamination, in order to establish pollution reduction measures. Environmental isotopes have proved useful in identifying sources of pollution, as the isotopic composition of the contaminants together with the spatial and

temporal variations of their concentration provide information about the source and that processes that take place.

This thesis is a study of isotope hydrology of drinking water sources and contains data on surface water, groundwater and precipitation. In **the first chapter** are presented the theoretical principles describing the isotopic separation and the thermodynamic and kinetic isotopic effects of H, O and N in natural processes, since isotope separation processes and environmental isotopes distribution are important in interpreting the data from the studies carried out. **The second chapter** is a bibliographic study on the use of environmental isotopes in water source characterization. **The third chapter** presents the experimental data, including the methodology for sampling, sample preparation and analysis, along with information about quality assurance results. In the first part of this chapter the drinking water sources in Vâlcea County, Romania, are characterized within the county's hydrographic network using the ^{2}H and ^{18}O stable isotopes. A study to identify the sources of inorganic nitrogen pollution in the industrial area of the county using ^{15}N is also presented. The second part of chapter three presents the study of the main mineral water resources of Romania using the ^{18}O and ^{2}H environmental isotopes. All hydrological studies include isotopic characterization of precipitation. The thesis ends with the main **conclusions** and **bibliography**.

The most important original contribution of the thesis is the characterization of the hydrological network of Vâlcea County using the ^{2}H, ^{18}O and ^{15}N stable isotopes. Pollution source determination in the hydrological basin of the Rm. Vâlcea chemical platform using ^{15}N variations in inorganic nitrogen compounds (nitrates, nitrites and ammonium) is the first study of this type in Romania.

1. NATURAL ABUNDANCE AND FRACTIONATION OF ENVIRONMENTAL ISOTOPES

1.1 Natural abundance of hydrogen, oxygen and nitrogen isotopes. Isotopic composition

The isotopes of an element are atom species with the same atomic number (Z), electron (e) and proton (n) numbers, but with different mass number (A) due to the difference in neutron number (n).

The isotopic abundance is given in percents and is the relative number of atoms of an isotope from a mixture of isotopes of an element, in more detail, the ratio between the number of atoms of the isotope and the total number of atoms in that element. In Table 1 the natural mean abundances of the hydrogen, oxygen and nitrogen stable isotopes are presented.

Table 1. The natural mean abundances of the hydrogen, oxygen and nitrogen stable isotopes [1-3]

	Hydrogen		Oxygen			Nitrogen	
Isotope	^1H	^2H	^{16}O	^{17}O	^{18}O	^{14}N	^{15}N
Abundance (at %)	99,985	0,015	99,757	0,038	0,205	99,630	0,370

The stable isotopes of hydrogen and oxygen form 9 molecular isotopic species of water. Due to the low abundance of heavy isotopes, the natural occurrence of molecular species containing more than one heavy isotope is negligible, the molecules of interest in isotope hydrology being only three: $^1H_2^{16}O$, $^1H^2H^{16}O$ and $^1H_2^{18}O$.

The isotope ratio (R) of an isotopic molecule is:

$$R = \frac{abundance\ of\ the\ rare\ isotopic\ molecule}{abundance\ of\ the\ predominant\ isotopic\ molecule} \qquad (1).$$

For example, for the ^{18}O and ^{16}O isotopes in the water molecule, the following isotope ratio can be described:

$$R_{^{18}O / ^{16}O(H_2O)} = \left(\frac{[H_2{}^{18}O]}{[H_2{}^{16}O]} \right)_{H_2O} \qquad (2),$$

where $[H_2{}^{18}O]$ and $[H_2{}^{16}O]$ are the concentrations of the isotopic molecules.

Because natural variations in isotope abundances are small and the absolute value of the isotope abundances is difficult to measure, the difference between the isotope ratio of the sample (*X*) and the isotope ratio of a reference compound (*Std*), as δ value, is introduced:

$$\delta_x = \left(\frac{R_X - R_{Std}}{R_{Std}} \right) \cdot 1000 = \left(\frac{R_X}{R_{Std}} - 1 \right) \cdot 1000 \qquad (3),$$

where R are the $^2H/^1H$, $^{18}O/^{16}O$, $^{15}N/^{14}N$, etc., isotope ratios. The 1000 coefficient transforms the δ value in parts per thousand (permil) - ‰. Negative δ values indicate lower abundances of the heavy isotope in the sample than in the reference material, while positive ones will show that the heavy isotope is more abundant than in the reference [4-6]. The reference materials with assigned value of 0‰, to which all isotope ratio measurements are reported, are "*V-SMOW*" (Vienna Standard Mean Ocean Water) for oxygen and hydrogen and atmospheric air for nitrogen.

Molecules containing different isotopes of the same element have different physico-chemical properties, mainly due to differences in the mass of the isotope. The isotopic effects lead to different distribution of the isotopes of an element in the molecules of the same compound found in different states, or between non-equivalent positions of the same compound, processes called isotope fractionations [7,8].

The isotope fractionation factor (α) describes the distribution of the isotope between two phases of the same compound or between two compounds (A and B), being the ratio between the isotope ratios of the two phases or of the two compounds:

$$\alpha_{A-B} = \frac{R_A}{R_B} \qquad (4).$$

If $\alpha > 1$, A is enriched in the heavy isotope and if $\alpha < 1$, A is depleted in the heavy isotope. In order to determine the direction and magnitude of the change in isotopic composition, the isotopic enrichment factor was introduced:

$$\varepsilon_{A-B} = \alpha_{A-B} - 1 = \frac{R_A}{R_B} - 1 \qquad (5).$$

If $\varepsilon > 0$, A is enriching in the heavy isotope compared to B, while if $\varepsilon < 0$, A depletes in the heavy isotope compared to B, its value indicating the size of the isotopic effect.

2. STABLE ISOTOPES IN ENVIRONMENTAL STUDIES

2.1 Hydrogen and oxygen

The main water reservoir are the oceans and, due to the stability of their isotopic composition - ^{2}H and ^{18}O, the ocean water represents the standard with an assigned value of 0‰ (Standard Mean Ocean water or "SMOW), against which all measurements of oxygen and hydrogen isotope ratios are made. δ^{18}O and δ^2H for precipitation, surface water and groundwater are mostly negative compared to the ocean water, except for sources of water that underwent strong evaporation (e.g. short term precipitation during summer, rivers and lakes in semi-arid and tropical regions, etc.).

The ^{18}O and ^{2}H isotope fractionations are influenced by:

- *latitude*: depletion in heavy isotopes with the increment of latitude [4,9];

- *temperature*: the isotope fractionation is bigger at low temperatures [10].

- *distance from the coast*: as the water moves towards inland, a progressive depletion in heavy isotopes takes place;

- *altitude*: lower δ^{18}O and δ^2H with increasing altitude [10,11];

- *amount of precipitation*: precipitation is more depleted in heavy isotopes during bigger events [4];

- *year*: δ^2H and δ^{18}O mean annual values for precipitation varies depending on weather conditions [4];

- *humidity*: precipitation in wet regions is more depleted in heavy isotopes compared with those formed at lower humidity [10].

The Global Meteoric Water Line defined by Craig [12] showes the correlation between δ^2H and δ^{18}O:

$$\delta^2H = 8x\delta^{18}O + 10 \text{ (‰)} \qquad (6).$$

Data on the global distribution of heavy isotopes in precipitation are obtained within GNIP (Global Network of Isotopes in Precipitation), which was established by the IAEA (International Atomic Energy Agency) together with WMO (World Meteorological Organization) in the early 1960's. Under this program, monthly samples (weighted means) of precipitation are collected worldwide and are analyzed to determine the content of ^{18}O, ^{2}H and ^{3}H.

After the fall of precipitation, additional processes take place that alter the isotopic composition of surface water, such as evaporation that causes enrichment in heavy isotope. The

heavy isotopes of water (^{18}O and ^{2}H) usually enrich in waters with high residence time (lakes), in areas with strong winds, in hot and arid areas and deplete with increasing altitude and latitude, the lowest values being found in Antarctica [4]. Lakes, rivers and other water sources show a lower isotopic variation range than meteoric water. As a result, the waters develop unique isotopic compositions that can give indications about their source and transitions.

In temperate and wet climates the isotopic composition of groundwater is similar to that of precipitation in the recharge area, a reservoir keeping its isotopic fingerprint in time. Seasonal variations in precipitation are leveled during their transport and storage in the ground. The degree of attenuation varies with depth, surface and geological characteristics of the rocks, but in general, deep groundwater does not show seasonal variations of δ^{2}H and δ^{18}O and has an isotopic composition close to that of mean annual precipitation. For a goundwater reservoir, isotopic studies can determine the source of recharge, can differentiate the diffuse or precise source recharging [4], can determine the contribution of various sources (surface water, rain, snowmelt, groundwater) using mathematical models [13], can identify the direction of movement in the reservoir [14], etc.

2.2 Nitrogen

Water nitrogen can be of atmospheric origin (N_2) or from pollution from fertilizers or organic matter (animal waste or sewage). Increment in the concentration of nitrogen in surface and groundwaters has been attributed to urbanization, land cultivation, livestock and disposal of waste. The main sources of excess nitrogen in surface and groundwaters are:

- increased mineralization of organic nitrogen compounds from the soil used for cultivation [15]. Nitrate produced by the mineralization of soil organic compounds tends to have similar δ^{15}N values (+4 to +9 ‰) [15];

- agricultural run-off during heavy precipitation;

- use of nitrogen fertilizers. Most nitrogen from fertilizer keeps the δ^{15}N of atmospheric nitrogen (0‰), without exhibiting significant isotopic fractionation [16];

- discharge of waste from livestock and industrial effluents [17];

- increment in atmospheric depositions [18].

The processes that can affect the concentration of nitrogen compounds in stream water are mineralization (conversion of organic nitrogen into ammonia), immobilization (conversion of ammonium or nitrate in organic nitrogen), nitrification (the oxidation of ammonia to nitrate), denitrification (reduction of nitrate to N_2 or N_2O) and ammonia volatilization. Mixing with water from other sources (e.g. precipitation, tributaries, and groundwater) can also affect the nitrogen cycle in stream water [19]. Spatial and temporal variations in the concentrations of nitrogen compounds, together with their isotopic variations give information about the processes occurring in the water source [20].

3. EXPERIMENTAL RESULTS

3.1 Measurement of δ^2H, δ^{18}O and δ^{15}N using mass spectrometry

δ^2H, δ^{18}O and δ^{15}N were measured by Isotope Ratio Mass Spectrometry (IRMS), using isotopic equilibration with gas (δ^2H and δ^{18}O) and elemental analysis (δ^{15}N). Measurement uncertainty was ± 1‰ for δ^2H, ± 0.1‰ for δ^{18}O and ± 0.3‰ for δ^{15}N.

3.2 The study of drinking water sources in Vâlcea County using environmental isotopes

The study of drinking water sources in Vâlcea County using environmental isotopes presented in this chapter of the thesis, focuses on Brădişor reservoir, part of the Lotru catchment, component of the middle Olt River basin; and Bistriţa River, a tributary of the Olt River. Brădişor reservoir covers for about 85% of the drinking water needs of Vâlcea County, while the Bistriţa River provides the remaining 15% and is used as process water source for the Rm. Vâlcea industrial platform.

The first step in this study was the isotopic fingerprinting of the middle Olt River basin, which included the drinking water sources. The multi-annual Local Meteoric Water Line was obtained for the study area [21-25]. Using this data, the changes and processes that took place in water sources were determined and explained [26-31].

Increasing human activity has resulted in loading the hydrological network with a large amount of pollutants (e.g. nitrogen and phosphorus compounds, heavy metals, agrochemicals, etc.), which produced a rapid deterioration of the water quality. As a result, water sources require constant monitoring in terms of their quality and identifying sources of contamination, to establish pollution reduction measures. Environmental isotopes have proved useful in identifying sources of pollution, as the isotopic composition of the contaminants together with the spatial and temporal variations of their concentration provide information about the source and that processes that take place. Thus, the sources of nitrogen pollution in the industrial area of Rm. Vâlcea were identified, the data being included in the last part of this section of the thesis.

3.2.1 Middle Olt River basin

This study covers the middle portion of the Olt River, located in Vâlcea County, crossing from north to south a distance of 135 km. In the northern part of the investigated area there is mountainous terrain, Olt River crossing the Carpathians through a gorge that separates peaks of 1800 - 2000 m, region called the Olt Valley. After exiting the gorge, the river crosses the Subcarpathic Meridional Plateau, gradually widening its riverbed. Water samples collected between November 2007 and October 2013 from 21 points from Olt River and its main tributaries were analyzed [26-31].

In addition, between September 2008 and October 2013 individual and weighted mean precipitation samples were collected at Rm. Vâlcea [21-25], which were used to calculate the multi-annual mean ($\delta^{18}O$ = -8.44‰, δ^2H = -58.3‰) and to obtain the multi-annual Local Meteoric Water Line (LMWL), having the equation $\delta^2H = 8.04x\delta^{18}O + 9.79$ [26].

The oxygen isotopic composition ($\delta^{18}O$) for all water samples ranged from -12.30‰ to -7.73‰, with a mean value of -9.83‰ and a standard deviation of ± 0.67‰. Hydrogen isotopic composition (δ^2H) of the water samples ranged between a minimum of -90.3‰ and a maximum of -54.6‰, with a mean of -70.2‰ and a standard deviation of ± 6.5‰ [26]. Isotopic values for the middle Olt River basin (Olt River and its tributaries) were distributed along the LMWL and had a linear correlation of $\delta^2H = 7.11x\delta^{18}O - 0.21$ (Fig. 1).
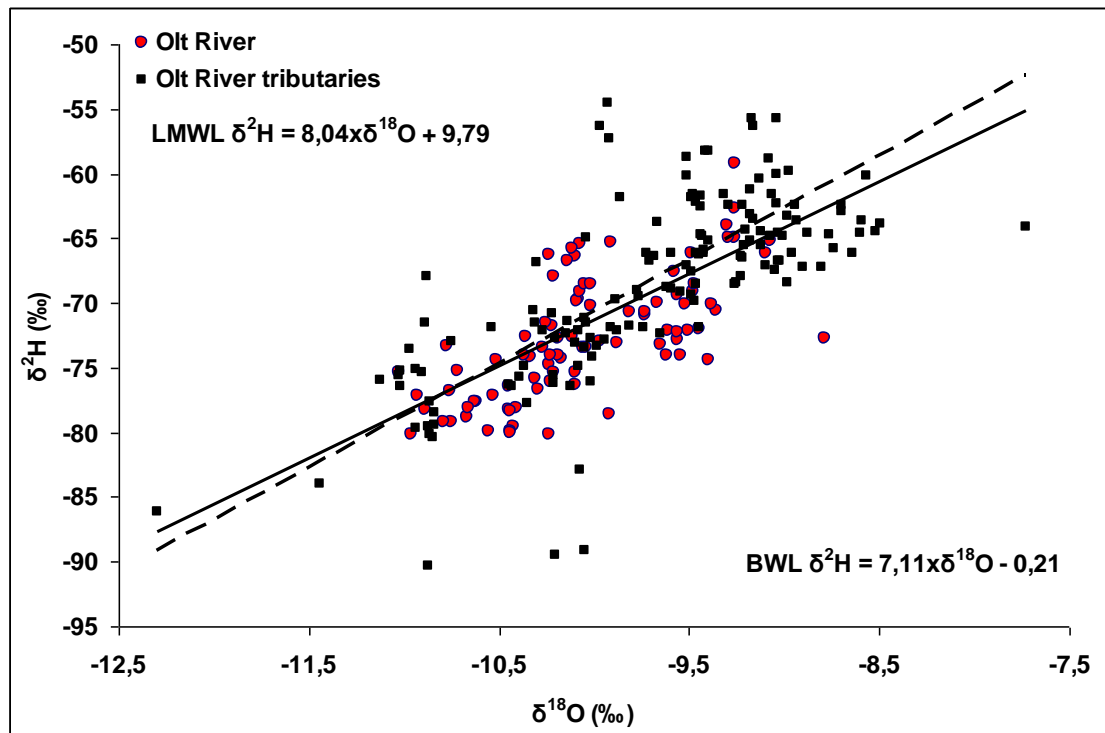
Fig. 1 δ-plot for the middle Olt River basin, November 2007 - October 2013 (LMWL - Local Meteoric Water Line, interrupted line; BWL – Basin Water Line, full line)

Olt River presented low values and smaller variations for both isotopes. For Olt River the $\delta^{18}O$ values were between -8.79‰ and -11.03‰ (range of 2.24 ‰), with a mean of -10.10 ± 0.50‰; while the tributaries had greater variations (4.57‰), between -7.73‰ and -12.30‰, with a mean of -9.70 ± 0.73‰. δ^2H values of Olt River ranged from -80.2‰ to -59.2‰, in a range of 21.0‰, with a mean of -72.7 ± 4.7‰. The tributaries had a variation of 35.7‰ for δ^2H, between -90.3‰ and -54.6‰, with a mean of -68.6 ± 7.0‰. The small isotopic variations in Olt River can be explained by the presence of dams (which control the flow, thereby reducing seasonal isotopic variations [32]) and the addition of groundwater with depleted and constant isotopic composition. Enrichment in ^{18}O of Olt River is due to evaporation or precipitation addition, while the isotope depletion is due to the addition of groundwater and/or snowmelt, which have a low content of ^{18}O.

Mixing calculations

Fig. 2 [26] presents the $\delta^{18}O$ variation along the middle course of Olt River between November 2010 and August 2011 in order to identify the effects of evaporation, addition of groundwater and tributaries that gather water from alpine and hill areas. Mixing calculations made at the entry point of the tributaries show that only Lotru River in February had a significant influence (0.11‰) on the ^{18}O content of the Olt River, enriching it from -10.17‰ to -10.07‰. The other tributaries had smaller influences (from 0.01 to 0.06‰), that were not reflected in the isotopic composition of the Olt River.
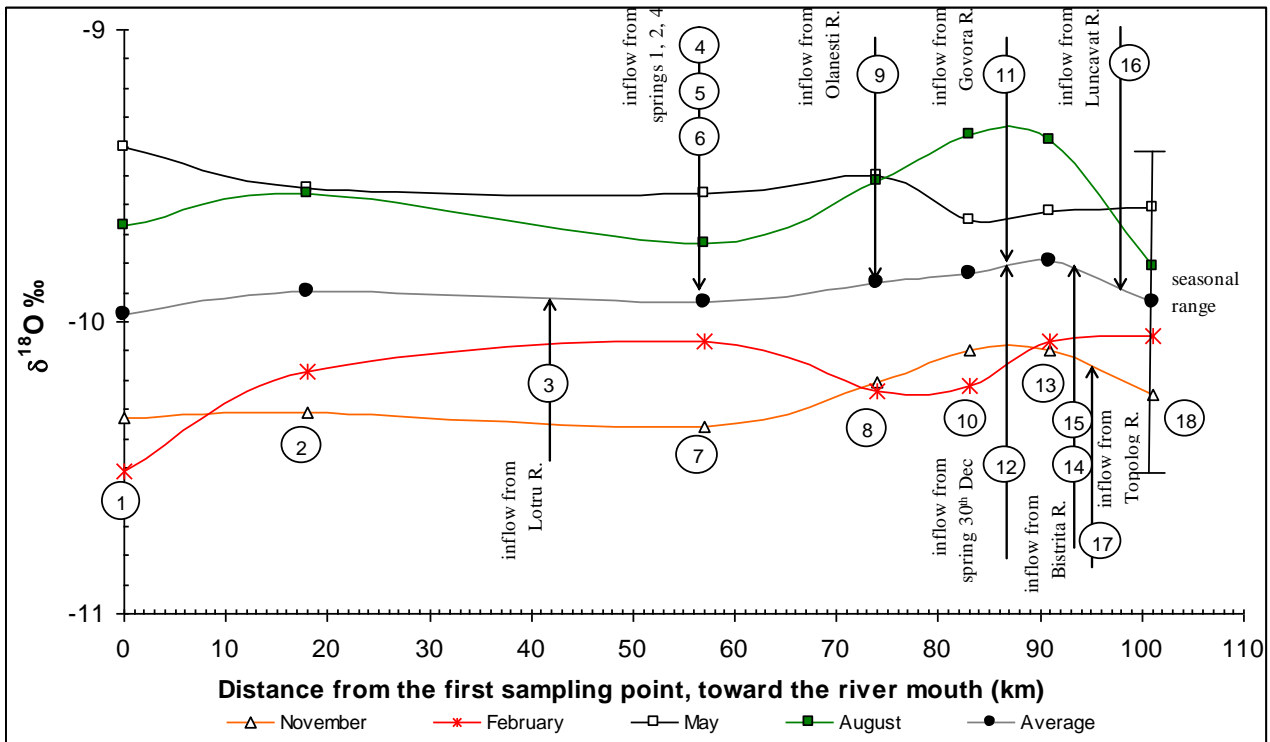
Fig. 2 δ^{18}**O variation along the middle course of Olt River (the entry points of the tributaries represent their confluence from north to south) (modified after [26])**

Seasonal variations of ^{18}**O and** ^{2}**H** - Figure 3 shows the variations of ^{18}O and ^{2}H in Olt River and its tributaries (including the reservoir and springs) as mean values (with their range of variation) for each month of the year, compared with the mean amount of precipitation for that month.

Regarding the variation of δ^{18}O, low values were observed in the colder months (October to April) and higher ones in the warm period (May to September). Also, the Olt River is more depleted in ^{18}O than its tributaries, except for January, September and December, when the composition is similar to or slightly enriched in ^{18}O. δ^{2}H shows seasonal variations similar to those of δ^{18}O, with the difference that May does not present the highest values, July - September corresponding to the largest isotopic enrichment. Similarly, the Olt River is more depleted in ^{2}H than its tributaries.
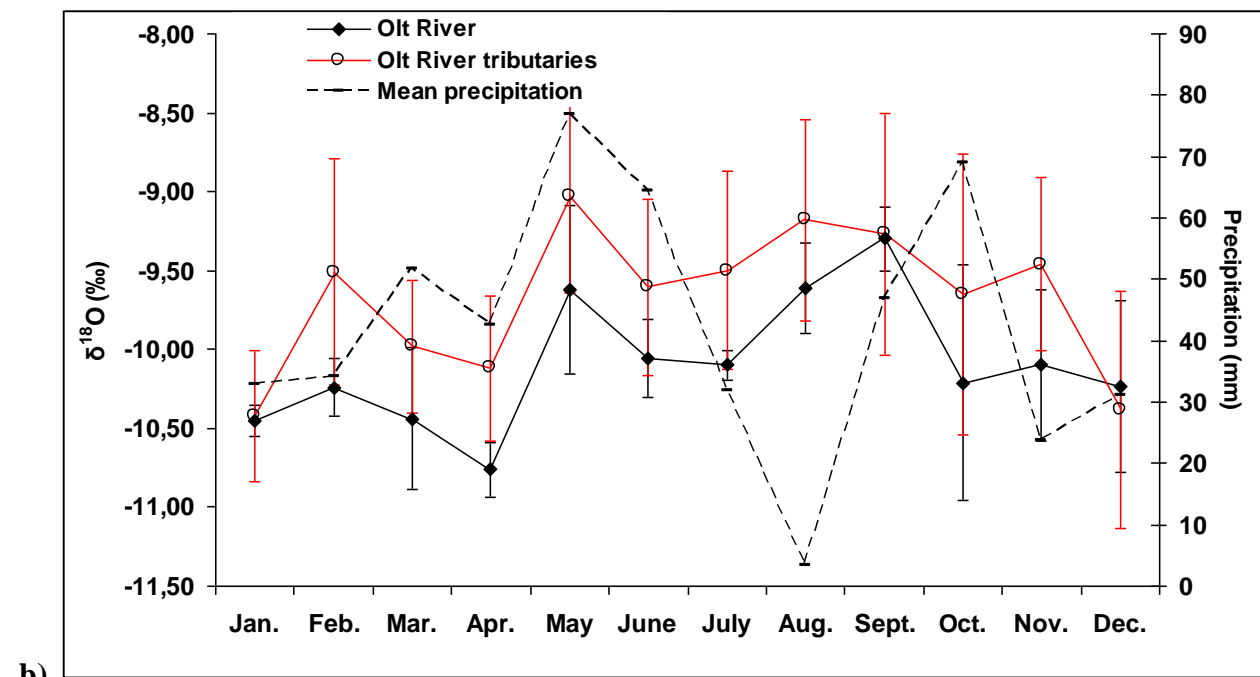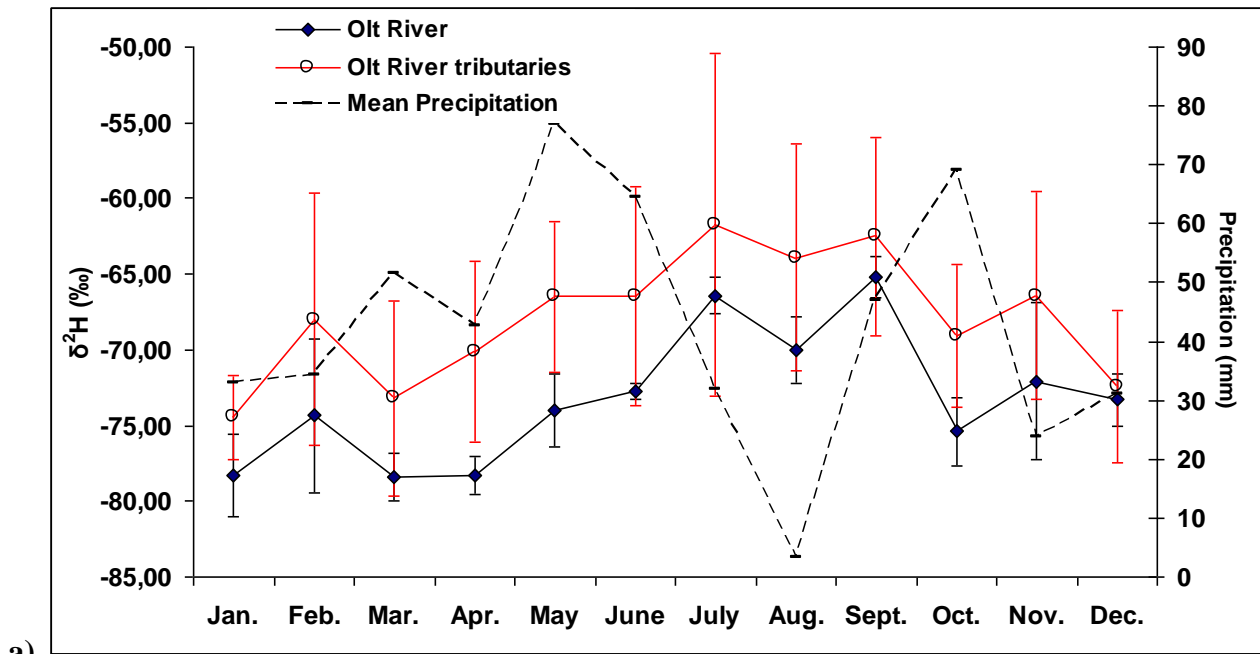
Fig. 3 Seasonal variations of $\delta^{18}O$ (a) and $\delta^{2}H$ (b) for Olt River and its tributaries, compared with the mean precipitation.

3.2.2 Brădişor reservoir and Bistriţa River

Brădişor reservoir, the drinking water source of Rm.Vâlcea and the neighboring towns, which supplies a population of about 300,000 people, has a volume of 39 million m^3 and its own hydro-electric power plant and is the last step of the Lotru River basin, before flowing into the Olt River.

Bistriţa River is situated south of the Brădişor reservoir, in the hilly region of the Subcarpathic Meridional Plateau. It has a length of 42 km, with a mean flow of 2.9 m^3/s, supplying drinking water to a population of 65,000 people and is the source of process water for the industrial platform of Rm. Vâlcea city.

Samples were taken monthly from the Brădişor reservoir (before entering the hydro-electrical station, where the water was homogenous and representative of the entire reservoir) and Bistriţa River during November 2007 - October 2008, November 2010 - August 2011 and November 2012 - October 2013.

The δ^{18}O and δ^2H results are summarized in Table 2, as mean values, between minimum and maximum ones [26,33-35].

Table 2. Isotopic composition of the Vâlcea County drinking water sources [26,33-35]

Water source	Location	δ^{18}O (‰)	δ^2H (‰)
Brădişor reservoir	Malaia	-10,24 ± 0,35 (-10,89 ÷ -9,92)*	-71,9 ± 11,8 (-89,5 ÷ -54,6)
Bistriţa River	Bărbăteşti	-9,30 ± 0,21 (-9,47 ÷ -9,03)	-66,5 ± 2,1 (-69,9 ÷ -64,6)
Bistriţa River	Băbeni	-10,07 ± 0,80 (-11,12 ÷ -8,60)	-71,3 ± 7,4 (-90,3 ÷ -60,2)

mean ± standard deviation (minimum ÷ maximum)

In Figures 4 and 5 are showed the variations of δ^{18}O and δ^2H in the drinking water sources of Vâlcea County (Fig. 4 and 5). These were interpreted using the monthly mean precipitation.

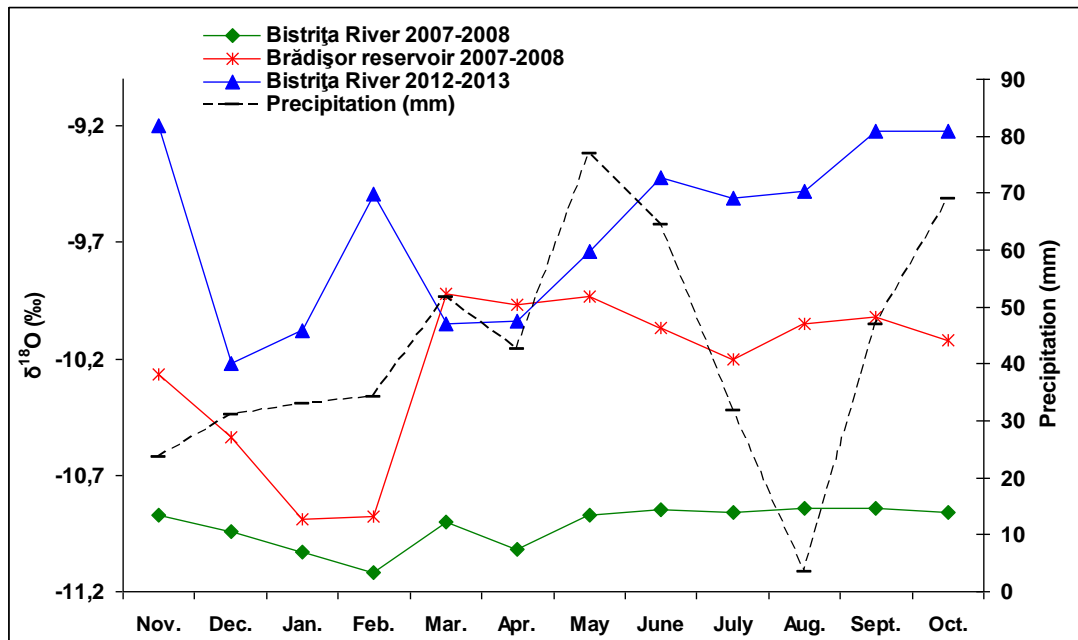**Fig. 4** *δ*[18]O (‰) variations (November 2007 - October 2008 and November 2012 - October 2013), compared with the monthly mean precipitation
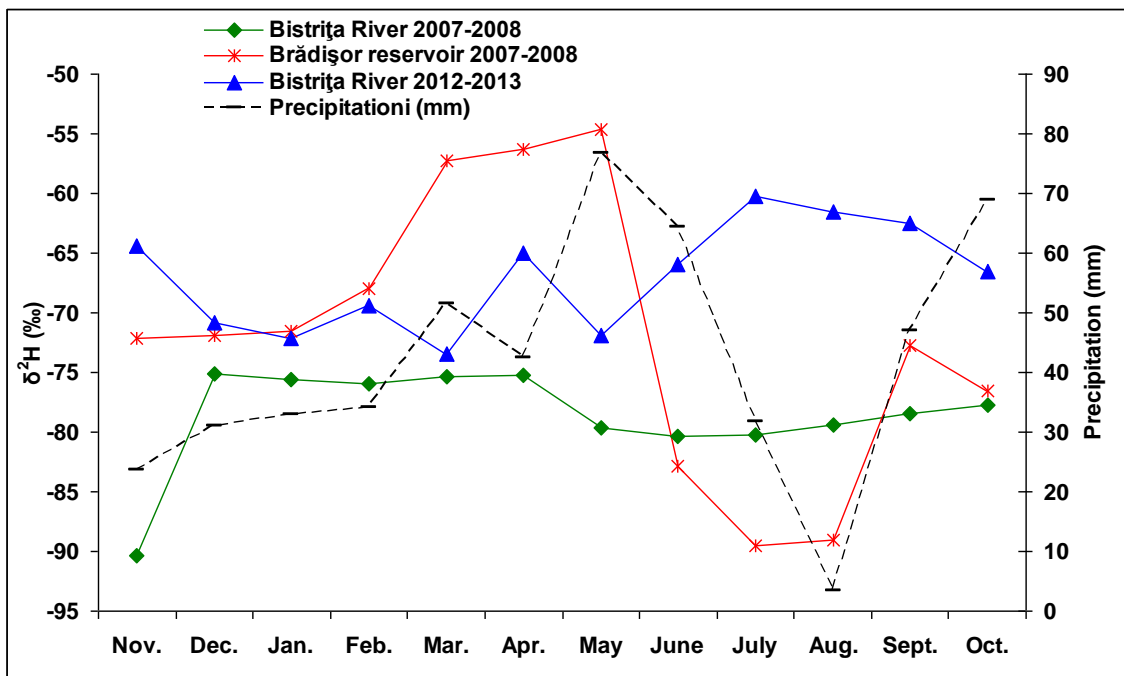
Fig. 5 *δ*[2]H (‰) variations (November 2007 - October 2008 and November 2012 - October 2013), compared with the monthly mean precipitation

By correlating the two sets of isotopic values (δ^{18}O and δ^2H), the following water lines were obtained (Figure 6):

$$\text{Bistrița River:} \qquad \delta^2\text{H} = 7.63\text{x}\delta^{18}\text{O} + 5.38‰ \qquad (7)$$

$$\text{Brădișor reservoir:} \qquad \delta^2\text{H} = 3.72\text{x}\delta^{18}\text{O} - 33.77‰ \qquad (8),$$

which have lower slopes than the Local Meteoric Water Line (LMWL with the equation δ^2H = 8.04xδ^{18}O + 9.79‰), indicating an isotopic enrichment due to evaporation. Of the two drinking water sources, the Bistrița River better resembles the Local Meteoric Water Line, indicating precipitation as the main source of recharge.

Fig. 6 δ^{18}O (‰) and δ^2H (‰) correlation (δ-plot) for the Brădișor reservoir (November 2007 - October 2008 - full black line) and Bistrița River (November 2007 - October 2008, November 2010 - October 2011, November 2012 - October 2013 – green line), LMWL - Local Meteoric Water Line (interrupted line)

3.2.3 Pollution source identification using ^{15}N

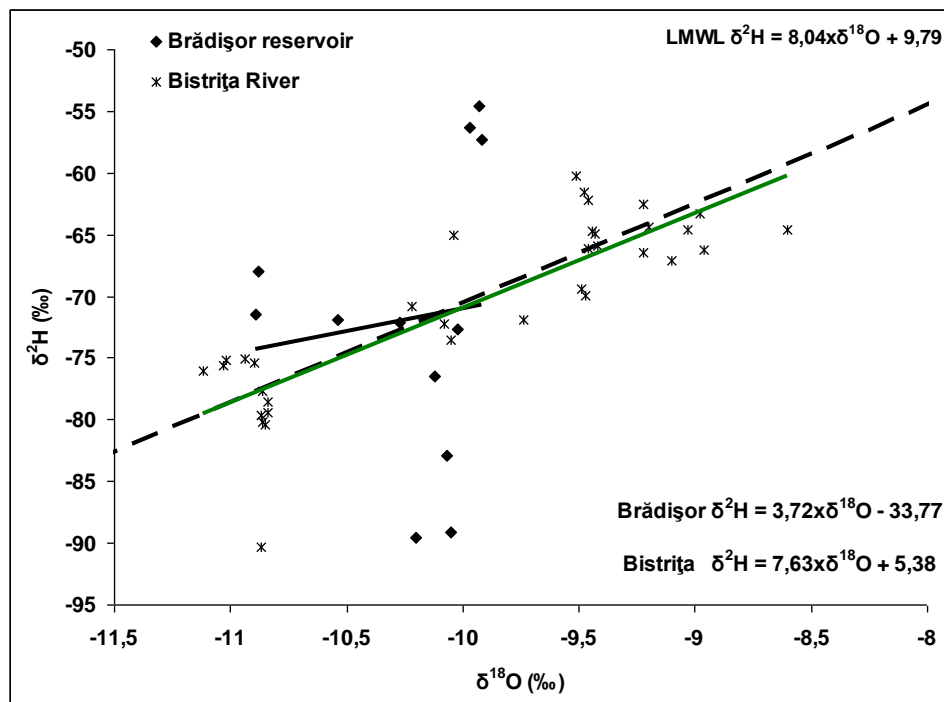In this study the basin of a major chemical platform in Romania, the industrial area of Rm. Vâlcea, was chemically (inorganic nitrogen compounds concentrations) and isotopically (δ^{15}N of inorganic nitrogen compounds) characterized [35,36]. For a period of one year (November 2012 - October 2013) water samples were taken monthly from the Olt River and its tributaries in the industrial area, in order to determine the spatial and seasonal variations of the studied physico-chemical parameters and the pollution source.

The Olt River basin was studied in the residential and industrial areas of Rm. Vâlcea city, namely Olt River on a length of 50 km and six tributaries, with a catchment of about 2,500 km^2. The waters of the basin have residential, industrial and farming use, and are used for drinking, sewage disposal, electricity production and as process water. This area has a population of about 170,000 in Rm. Valcea city and ten other smaller towns. The chemical platform of Rm. Vâlcea consists mainly of Oltchim and Govora Soda Ash - Ciech Chemical Group companies and Govora thermo-electrical plant. The platform produces hundreds of thousands of tons of soda ash, sodium silicate, derivatives of salt (sodium hydroxide, hydrochloric acid, hypochlorite, chlorinated polymers, and other organochlorine compounds), polyols, polyurethanes, carbonyl derivatives, etc. per year.

Analyses were conducted on surface water samples taken from 11 locations in the residential and industrial areas of Rm. Vâlcea city. Another set of samples were the monthly mean precipitation samples from the study area.

For all nitrogen compounds high levels of concentration and bigger ranges were measured in the colder months (November 2012 - April 2013). In the warmer months (May - October 2013) concentrations were lower and the variations were smaller (Fig. 7 - [35]). This behavior is explained by a lower microbial activity in the colder months, compared to the biological active conditions during the warmer months, leading to faster processing of nitrogen compounds in the water supply [37].
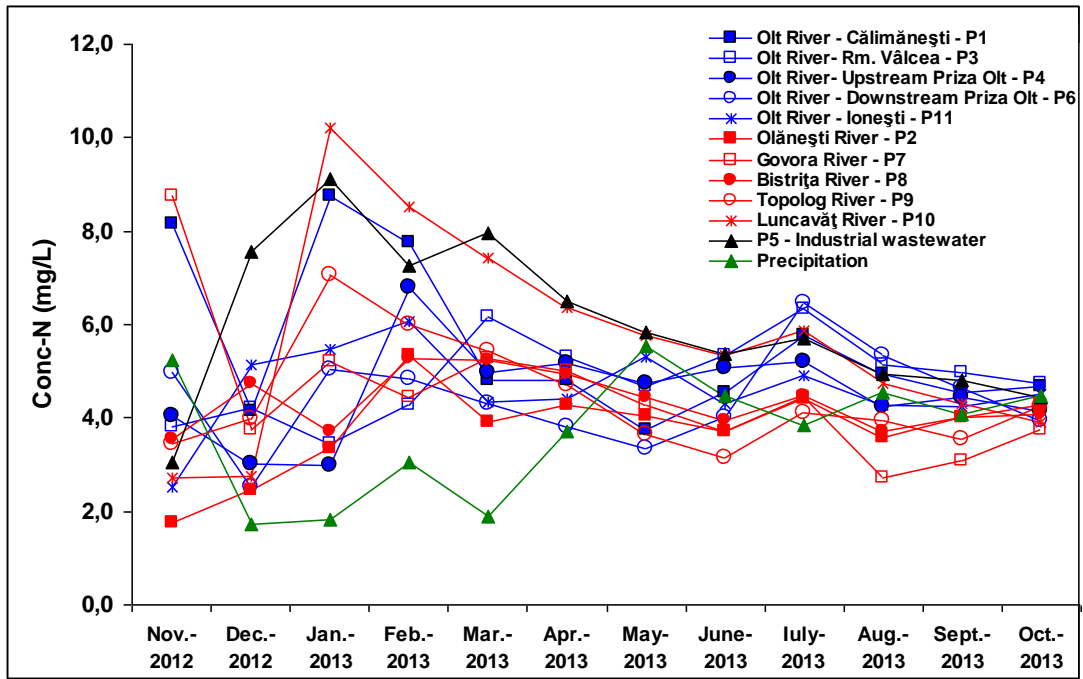
Fig. 7 Variations in total inorganic nitrogen concentration for each sampling point during the study period (November 2012 - October 2013) (modified after [35])
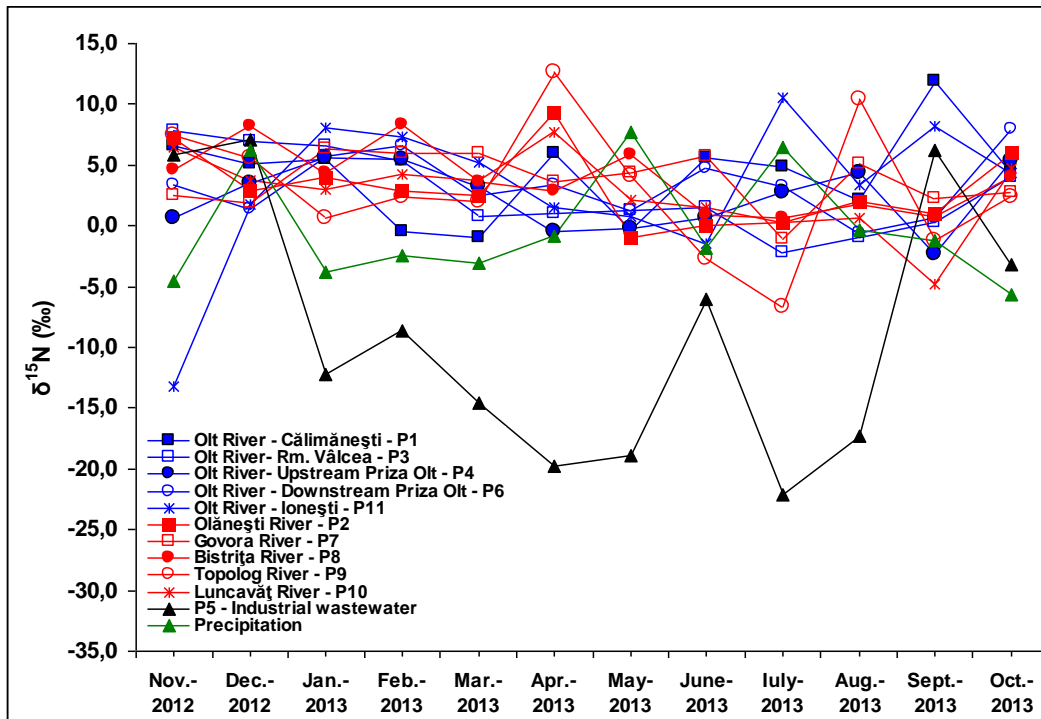

Fig. 8 δ^{15}N variation for each sampling point during the study period (November 2012 - October 2013) (modified after [35])

The δ^{15}N ranged between -22.1‰ and +12.6 ‰, with a mean of +1.9‰. Different from the total nitrogen concentration higher variations were observed in the warmer months (April - October 2013) than in the colder period (Fig. 8 - [35]). The waste water from the chemical platform (P5) had a specific δ^{15}N fingerprint, the depleted values (-8.6‰ mean) indicating an industrial source for the inorganic nitrogen compounds. Mean precipitation samples had values lower than that of surface waters, between -5.7‰ (October 2013) and +7.7‰ (May 2013), with a mean of -0.3‰. δ^{15}N for the surface water samples had mean values between +2.4‰ and +4.2‰. The Olt River water sample at Ioneşti in November 2012 (-13.2 ‰), indicates an inorganic nitrogen discharge of industrial origin [35].

Mixing calculations - By correlating the total inorganic nitrogen concentrations and their δ^{15}N values and taking into account the surface water flows and mean precipitation, calculations were made for each month of the study period, to determine the processes occurring along the Olt River.

Most nitrogen compounds transformations took place from April to October 2013. For another number of transitions (~ 15%), the total nitrogen concentration did not change, but δ^{15}N varied, indicating a mixture of nitrogen transformations (forming coupled with decomposition of inorganic nitrogen compounds). Inorganic nitrogen additions from other sources, mainly anthropogenic sources [37], were observed during December 2012 - May 2013. These diffuse sources of nitrogen were agricultural and sewage discharges [35].

3.3 The study of mineral water resources in Romania using environmental isotopes

In the Romanian Carpathians, there are many mineral springs, which are used as drinking water or for therapeutic purposes. The majority of the mineral springs are found in the Eastern Carpathians and less in the Meridional and Western Carpathians, due to the influence of exogenous (rainfall, temperature, and terrain morphology) and endogenous (geological and tectonic characteristics [38]) factors.

In the Eastern Carpathians there are many mineral springs, especially cold and rich in CO_2 springs, chemically complex due to the diverse geological structure and the presence of the volcanic Oaş-Gutâi-Călimani-Harghita chain [34]. Compared to the Eastern Carpathians, the Western and Meridional Carpathians contain fewer sources of mineral water, such as those from Cerna Valley (Herculane), Arad (Lipova) and Stâna de Vale. For these mineral springs, no isotopic data are published.

The study presents the chemical and isotopic composition of mineral waters (sparkling and still) in six areas in the Carpathians recognized for the quality of the water (Vatra Dornei, Borsec, Sf. Gheorghe/Bodoc from the Eastern Carpathians; Băile Herculane/Domogled from the Meridional Carpathians; Lipova and Stâna de Vale from the Western Carpathians), to determine their genesis and recharge mechanisms [39]. For each study area, the isotopic composition (δ^2H and δ^{18}O) of monthly mean precipitation samples (obtaining the Local Meteoric Water line for each study area) and mineral springs (groundwater) was analyzed in order to determine the relationship between the two. Over a period of one year, groundwater samples were collected from 17 wells and springs from the six regions in the Carpathians [39].

Precipitation - Table 3 presents the Local Meteoric Water Lines (LMWLs) [39].

Table 3. Local Meteoric Water Lines of the studies regions [39]

Region	LMWL
Borsec	δ^2H = 7,68 δ^{18}O + 6,49
Vatra Dornei	δ^2H = 7,78 δ^{18}O + 6,80
Bodoc	δ^2H = 8,02 δ^{18}O + 4,98
Domogled	δ^2H = 8,72 δ^{18}O + 15,00
Lipova	δ^2H = 9,10 δ^{18}O + 16,41
Stâna de Vale	δ^2H = 8,31 δ^{18}O + 5,72

Groundwater isotopic composition - δ values of the groundwater samples were from -89‰ to -67‰ for δ^2H (mean = -77‰) and from -11.7‰ to -8.1‰ for δ^{18}O (mean = -10.1‰), the majority of samples having values in the -80 to -70‰ range for δ^2H, and, respectively, from -9 to -11‰ for δ^{18}O (Fig. 9) [39].
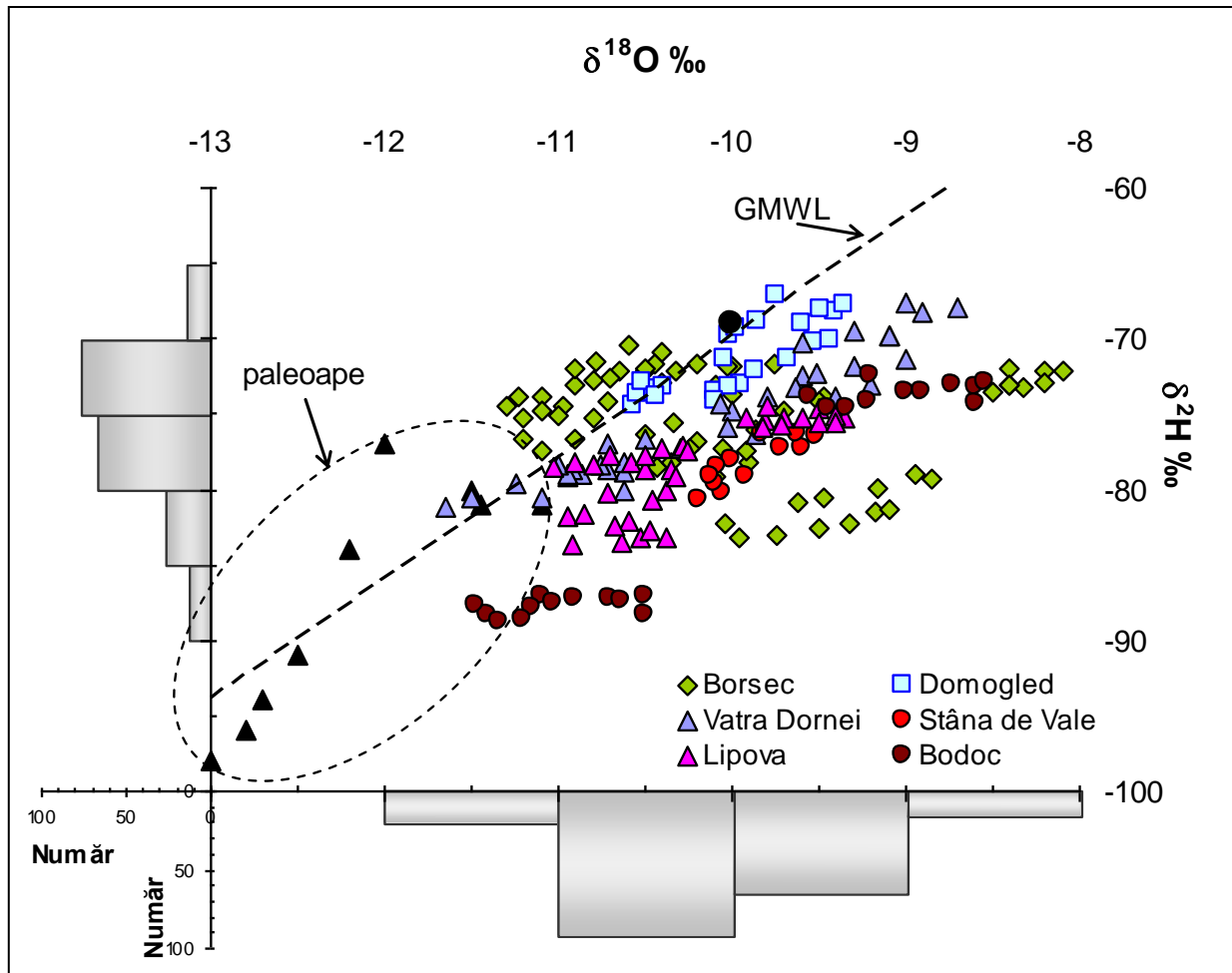
Fig. 9 δ^{18}O and δ^2H values for all groundwater samples compared with modern precipitation data from [14] (black dot) and Pleistocene groundwater in Romania (black triangles) (modified after [39])

Most water sources that reflect the mean isotopic composition of precipitation are found in the west of Romania, at Stâna de Vale and Domogled. Sources interacting more with the geological structures and deep groundwater sources are found in the Eastern Carpathians, at Vatra Dornei, Bodoc and Borsec (Table 4 - [39]).

Table 4. Isotopic composition ($\delta^{18}O$ and δ^2H) of the groundwater sources [39]

Region/Source		$\delta^{18}O$ (‰)	δ^2H (‰)
Vatra Dornei	well PN	-10,2 ± 0,5* (-11,0 ÷ -9,5)	-76 ± 2,3 (-80 ÷ -72)
	well MD1	-9,2 ± 0,3 (-9,6 ÷ -8,7)	-71 ± 2,1 (-74 ÷ -68)
	MD2	-11,0 ± 0,3 (-11,7 ÷ -10,6)	-79 ± 1,1 (-81 ÷ -77)
Borsec	BS1	-11,0 ± 0,3 (-11,3 ÷ -10,4)	-74 ± 2,1 (-78 ÷ -70)
	BS2	-10,5 ± 0,3 (-10,9 ÷ -10,0)	-72 ± 0,5 (-73 ÷ -72)
	BS3	-10,4 ± 0,4 (-11,1 ÷ -9,8)	-75 ± 2,4 (-79 ÷ -72)
	BS4	-9,4 ± 0,4 (-10,0 ÷ -8,9)	-81 ± 1,4 (-83 ÷ -79)
	well BF1	-10,0 ± 0,3 (-10,4 ÷ -9,5)	-76 ± 1,8 (-79 ÷ -74)
	well BF2	-8,3 ± 0,1 (-8,5 ÷ -8,1)	-73 ± 0,6 (-74 ÷ -72)
Sf.Gheorghe/ Bodoc	B1	-11,0 ± 0,3 (-11,5 ÷ -10,5)	-88 ± 0,6 (-89 ÷ -87)
	B2	-9,0 ± 0,4 (-9,6 ÷ -8,5)	-74 ± 0,7 (-75 ÷ -72)
B.Herculane/ Domogled	D1	-10,3 ± 0,3 (-10,6 ÷ -9,7)	-72 ± 2,4 (-74 ÷ -67)
	D2	-9,7 ± 0,3 (-10,1 ÷ -9,4)	-71 ± 2,3 (-74 ÷ -68)
Lipova	well L1	-10,6 ± 0,2 (-11,0 ÷ -10,4)	-82 ± 1,2 (-84 ÷ -80)
	well L2	-9,6 ± 0,2 (-9,9 ÷ -9,4)	-75 ± 0,4 (-76 ÷ -75)
	well L3	-10,6 ± 0,3 (-11,0 ÷ -10,3)	-78 ± 0,6 (-79 ÷ -77)
Stâna de Vale	well IM	-9,9 ± 0,2 (-10,2 ÷ -9,5)	-78 ± 1,5 (-81 ÷ -76)

mean ± standard deviation (minimum ÷ maximum)

CONCLUSIONS AND FINAL OBSERVATIONS

The results of the hydrological studies carried out in this thesis emphasize that environmental isotopes (^{2}H, ^{18}O, ^{15}N, etc.) are the most useful tracers in determining the origin of water, the relationship between precipitation, surface and groundwater, the water migration and identification of pollution sources, providing information that can not be obtained using traditional investigation techniques.

The study of drinking water sources in Vâlcea County.

• The isotopic values for the basin were distributed along the Local Meteoric Water Line, Olt River having a composition more depleted in heavy isotopes (^{18}O and ^{2}H) and smaller variations than its tributaries. This behavior, which is observed in high flow rivers, is due to the presence of dams (which reduce seasonal variations) and groundwater addition.

• The larger variations and isotopic compositions observed for the tributaries are due to lower flow and different recharging sources compared with the Olt River, mainly precipitation.

• The isotopic composition of the middle Olt River basin is distributed on a lower slope than the Local Meteoric Water Line, indicating for these water sources an enrichment in heavy isotopes, which occurs during the warm season (spring - autumn).

• The study of the drinking water sources in Vâlcea County, Brădişor reservoir and Bistriţa River, using environmental isotopes showed that in the seasons with heavy precipitation (winter, spring and autumn) they recharge with water from precipitation and during summer the recharge takes place mainly from groundwater. In the warm season (spring and summer), the two drinking water sources are enriched in heavy isotopes due to evaporation.

^{15}N study conducted in the industrial area of Rm. Valcea.

• Higher concentrations of inorganic nitrogen were measured from November 2012 to April 2013, which were designated by the mixtures calculations, as additions from agriculture/residential sources.

• The inorganic nitrogen from the industrial wastewater presented a specific δ^{15}N fingerprint. Also, one industrial nitrogen discharge in Olt River at Ioneşti in November 2012 was identified.

• The concentrations of inorganic nitrogen compounds and their isotopic fingerprint indicated that the main source of nitrogen pollution were agriculture and residential wastewater, the industrial sources contributing only to a small extend, due to their small volume and the presence of treatment stations before the discharge in the natural environment.

- The mean precipitation samples had the lowest concentrations of nitrogen and a specific $\delta^{15}N$ fingerprint in comparison with the surface water and industrial wastewater.

The study of the mineral springs from the Carpathian Mountains in Romania.

- The chemical composition of the rocks encountered along the underground path, the transit time and mixing with other sources of groundwater, are all factors that influence the physico-chemical properties of a mineral spring.

- Most water sources that reflect the mean isotopic composition of precipitation are found in the west of Romania, at Stâna de Vale and Domogled.

- Sources interacting more with the geological structures and deep groundwater sources are found in the Eastern Carpathians, at Vatra Dornei, Bodoc and Borsec.

- The different ways of recharging gives the great diversity of mineral waters in Romania.

ORIGINAL CONTRIBUTIONS

The most important original contribution of the thesis is the characterization of Vâlcea County's hydrological basin using the ^{2}H, ^{18}O and ^{15}N stable isotopes. In this study, the multi-annual Local Meteoric Water line and the isotopic fingerprint (δ^2H and δ^{18}O) of Olt River and its tributaries, including the county's drinking water sources (Brădişor reservoir and Bistriţa River), were obtained and the main processes of water recharge within the basin were determined. It should be noted that this is the first study to characterize the hydrologic basin of Vâlcea County using the ^{2}H and ^{18}O environmental isotopes.

Another original contribution of this thesis was to develop a method for determining the δ^{15}N of the inorganic nitrogen compounds (nitrates, nitrites and ammonium), in order to characterize and identify different sources of pollution. It was established that the main pollution sources of the hydrological basin of the Rm. Vâlcea industrial area are the agricultural activities and residential waste discharge. The δ^{15}N isotopic fingerprint of the inorganic nitrogen compounds with industrial origin was also obtained, which was used to identify an industrial discharge into the environment. It should be noted that the determination of the pollution source using δ^{15}N of inorganic nitrogen compounds represents the first study of its kind in Romania.

The third study in the thesis was of the main mineral springs in Romania, from the Eastern, Meridional and Western Carpathians, using ^{2}H and ^{18}O environmental isotopes. The Local Meteoric Water Lines and the main processes of recharge for the mineral springs were determined. It was observed that the mineral springs in western Romania reflect the mean isotopic composition of precipitation, while the Eastern Carpathians springs come from deep groundwater sources and interact more with the geological structures.

The results of the thesis were presented to the scientific community by:

- publishing 4 original papers in journals with impact factor (IF = 0.266 - 4.099);
- publishing 5 original papers in journals indexed in national and international data bases;
- participating at 4 international conferences;
- participating at 10 national conferences.

List of the published papers in the doctoral thesis field

Journals with impact factor (IF):

1. **Vremeră R.**, Costinel D. and Ionete R.E., Isotopic characterization of the major water source of Rm. Vâlcea area, Romania, Asian Journal of Chemistry, **2011**, vol. 23(12), pp. 5202-5204, (**IF: 0.266/2011**);

2. **Popescu R.**, Costinel D., Ionete R.E. and Damian Axente, *Isotopic fingerprint of the middle Olt River basin, Romania,* Isotopes in Environmental and Health Studies**, 2014**, vol. 50(4), DOI:10.1080/10256016.2014.959443, (**IF: 1.294/2014**);

3. Ionete R.E., **Popescu R.*** and Costinel D., An isotopic survey of some mineral water resources in the Carpathian chain (Romania), Environmental Engineering and Management Journal, accepted for publishing: **2014**, (**IF: 1.258/2014**), *corresponding author*;

4. **Popescu R.**, Mimmo T., Dincă O., Capici C., Costinel D., Şandru C., Ştefănescu I., Ionete R. and Axente D., Industrial area investigation using stable isotopes, In Press: Science of the Total Environment (**IF: 4.099/2014**).

Journals indexed in national and international data bases:

1. Costinel D., **Vremeră R.** and Grecu V.V., Stable isotope signature (D/H, $^{18}O/^{16}O$) in a hydrologic study, Progress of Cryogenics and Isotopes Separation, **2008**, vol.21+22, pp. 18 – 23;

2. Costinel D., Voicu V.V., **Vremeră R**. and Cună S., Stable oxygen and hydrogen isotopes measurement by CF-IRMS with applications in hydrology studies, Journal of Physics: Conference Series, **2009a**, vol. 182(012038), IOP Publishing, DOI: 10.1088/1742-6596/182/1/012038**;**

3. Costinel D., Grecu V.V., Cună S., **Vremeră R.** and Făurescu I., The stable isotopes in the hydrology studies at Râureni – Vâlcea area, Progress of Cryogenics and Isotopes Separation, **2009b**, vol. 23+24, pp. 19-24;

4. Costinel D., Ionete R.E. and **Popescu R.**, Environmental Isotopes in Hydrological Investigation at Râureni-Vâlcea Area, Progress of Cryogenics and Isotopes Separation, **2011**, vol. 14(1), pp. 121-126;

5. Şandru C., David E., **Popescu R.** and Ionete R.E., Determining Ammonium and Nitrate Pollution of the Olt River Basin in Rm. Vâlcea Industrial Area, Progress of Cryogenics and Isotopes Separation, **2013**, vol.16(1), pp. 81-88.

List of national and international conferences participation in the doctoral thesis field

International conferences:

1. "Isotopes 2009" International Conference, 25-29.05.**2009**, Cluj-Napoca - **Vremeră R.**, Axente D., Costinel D. and Ionete R.E., "Hydrogen isotopic variations in the major water source of Rm.Vâlcea, Romania", **oral presentation**;

2. The 37th International Conference of the Slovak Chemical Engineering Society, SSCHE 2010, 24-28.05.**2010**, Taranske Matliare, Slovakia - **Vremeră R.**, Costinel D. and Ionete R.E., "Isotopic characterization of the major water source of Rm.Vâlcea area, Romania";

3. "Isotopes 2013" International Conference, 16-21.06.**2013**, Sopot, Poland **- Popescu R.,** Costinel D. and Ionete R.E., " Isotopic fingerprinting of the Middle Olt River Basin, Romania";

4. IAEA "Isotope Hydrology" International Symposium, 11-15.05.**2015**, Vienna, Austria - **Popescu R.**, Ionete R.E., Costinel D., Dincă O.R., Ioniţă G. and Axente D., "Industrial area investigation using stable isotopes".

National conferences:

1. The Second „The European Polar Research Icebreaker AURORA BOREALIS – FP7 project", 16-17.11.**2007**, Bucharest - Costinel D., Iordache A. and **Vremeră R.**, „Stable isotope signature (D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$): important element in paleoclimate reconstruction";

2. "Nuclear 2008" International Conference - Sustainable Development through Nuclear Research and Education, 28-30.05.**2008**, Piteşti - Costinel D., Iordache A. and **Vremeră R.**, "Stable isotope signature (D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$): Important element in Paleoclimate Reconstruction";

3. Physics National Conference (CNF), 10-13.09.**2008**, Bucharest - Costinel D., **Vremeră R.** and Grecu V.V., "Stable isotope signature (D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$): important element in paleoclimate reconstruction", **Second prize in posters**;

4. The 14th Conference "Progress of Cryogenics and Isotopes Separation", 29-31.10.**2008**, Călimăneşti-Căciulata:
   a) Costinel D., **Vremeră R.** and Grecu V.V., "Stable isotope signature (D/H, $^{18}O/^{16}O$) in a hydrologic study";
   b) Ferdeş O.S., Mladin C., Petre R.M., Mitu F., Costinel D., **Vremeră R.** and Şandru C., "The characterization of physical and chemical properties of Qlarivia line of deuterium depleted water";

5. The 15th Conference "Progress of Cryogenics and Isotopes Separation", 28-30.10.**2009**, Călimăneşti-Căciulata - Costinel D., Grecu V.V., Cună S., **Vremeră R.** and Făurescu I., "The stable isotopes in the hydrology studies at Râureni-Vâlcea area";

6. "Water Quality" International Workshop, **2010**, Bucharest:

    a) Costinel D., Ionete R.E., **Vremeră R.** and Ştefănescu I., "The Climatic Information Contained in Water Isotopes – a review";

    b) Costinel D., Ionete R.E., **Vremeră R.**, Ştefănescu I. and Tiţescu G., "CF-IRMS Applications for Isotopic Fingerprinting of Different Water Sources";

7. "Nuclear 2010" International Conference on Sustainable Development through Nuclear Research and Education, 26-28.05.**2010,** Piteşti - **Vremeră R.**, Costinel D., Ionete R.E. and Soo C.J., "Isotopic Fingerprinting of Brădişor Reservoir from Rm. Vâlcea, Romania";

8. The 16th Conference "Progress of Cryogenics and Isotopes Separation", 13-15.10.**2010**, Călimăneşti-Căciulata - Costinel D., Ionete R.E., **Vremeră R** and C. Soo C.J., "The Potential of Deuterium and Oxygen Isotopes in Evaluating Different Water Sources";

9. TIM 10 Physics Conference – Timişoara West University, 25-27.11.**2010**, Timişoara - **Popescu R.**, Costinel D. and Ionete R.E., "Stable Isotopes Distribution in the Olt Valley Rivers";

10. Tritium Management Workshop, 21.06.**2013**, Rm. Vâlcea - **Popescu R.**, Costinel D., Dincă O.R. and Ionete R.E., "Stable isotopes characterization of the Middle Olt River Basin".

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