„BABEŞ-BOLYAI” UNIVERSITY CLUJ-NAPOCA
FACULTY OF PHYSICS

DOCTORAL THESIS SUMMARY

STUDY OF ENVIRONMENTAL PROCESSES USING THE NATURAL TRACER ISOTOPE DEUTERIUM

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Content

INTRODUCTION

Any water distribution in space and time that alters the hydrological balance of surface waters, ground moisture and the loads of underground waters leads to socio-economical adjustments with implications on human activity. That's why the knowledge of parameters that can modify the space-time distribution of the hydrological balance has scientific and practical importance.

The water circulation in nature is studied in meteorology, hydrology and hydrogeology. The link of waters natural cycle with the biosphere is accomplished by meteorology, the soil science, biology, agriculture. The development of nuclear technologies has made available for scientists a set of tools for specific analysis – isotopic analysis – with which information can be validated from the water cycle in nature domain obtained with non-nuclear technologies and new information can be obtained which can't be found with classic methods of the sciences mentioned above.

The ratios of stable isotopes of hydrogen and oxygen from natural waters are not constant. Understanding the way the isotopic composition of water in its natural cycle is affected by isotopic fractioning phenomena (evaporation, condensation, diffusion, isotopic exchange) would not be possible without the progresses made in the analytics of isotopes which allowed the high precision measurement of small changed in the hydrogen and oxygen isotope concentration in water molecules. The environment isotopes technique uses the isotopic variations established in water by the natural processes, which determines an isotopic marking of water at a global scale. This natural isotopic marking can't be controlled by man, only measured and used for understanding and interpreting certain problems in the natural sciences domain.

The studying method used is that of natural stable isotopic tracers of water. The method has the advantage of tracer techniques and brings the advantages of natural tracers: they're cheap, being available in nature, they are non-polluting, non-invasive, they do not disturb the environment and are not limited in space and time as usage, being ideal for the study of ecosystems.

The isotopic techniques applied in the nature sciences domain have developed in the last 40 years in different versions in advanced laboratories in Europe and America. The International Atomic Energy Agency in Vienna has an isotopic hydrology department which promotes international programs [1].

First group from Romania which used deuterium as a natural tracer was the team headed by dr. Blaga Liviu, Natural Isotopic Abundances, from ITIM Cluj-Napoca. In 1965 dr. Blaga Liviu addressed the problem of isotopic distribution of hydrogen in hydrocarbon deposits [2, 3, 4]. Further, the studies were oriented towards problems concerning the hydrology and hydrogeology of mineral water deposits [5] and geothermal ones [6], of lakes with balneoclimatic importance [7, 8], of water infiltration in soil [9].

From 1992 until 2008 the isotopic hydrology studies were oriented towards ecosystems [10, 11, 12] because the natural marking method is best suitable for these systems.

The interpretation of the isotopic analysis is effective and offers valuable information concerning the processes that take place in nature only if the results obtained from collected samples in the experimental field are of quality. In order to obtain quality it is necessary to respect all the sampling and storing procedures for the samples, the preparing for the isotopic analysis and making measurements of isotopic ratios on modern equipment. The classic method for analysis of isotopic reports is the mass spectrometry (IRMS), which has continuously improved as an analysis technique. Lately the accordable laser-diode absorption spectroscopy method has begun to develop (TDLAS), for measuring isotopic ratios in water.

The thesis is structured on 5 chapters, as follows:

The **first chapter** presents the theoretical principles underlying the natural isotopic marking phenomenon of waters. The stationary and non-stationary processes of isotopic fractionation are analyzed which determine the existence of the natural isotopic marking process of water as well as the isotopic effects induced by these phenomena in waters natural cycle. Under this aspect the isotopic fractionation processes and the space-time distribution of hydrogen and oxygen-18 isotopes is important for understanding and interpreting the results concerning the water input in different basins of the system tied to the natural cycle of water.

Chapter 2 presents the experimental methodology, as well as two options for determining the isotopic ratio.

Chapter 3 is destined to the interpreting way of the results from the isotopic analysis from rainfall and the correlations with different physical parameters.

Chapter 4 presents in detail the study of the isotopic content of deuterium and oxygen-18 in rainfall in Cluj-Napoca during the 2009-2012 period, correlations with different physical parameters as well as a comparative analysis of data for isotopic content in the 1975-2008 period with the data from the 1975-2012 time period in order to see how the isotopic content data from local rainfall is influenced by global warming in the last years.

The conclusions are presented in **Chapter 5** and the bibliographic part studied is presented in the end followed by the list of published works and participation in conferences.

Keywords: precipitations, water isotopes, deuterium, Rayleigh model, evapotranspiration.

TERMINOLOGY

The stable isotopes of hydrogen (^{1}H - protium and ^{2}H – deuterium, D) and of oxygen (^{16}O, ^{17}O and ^{18}O) give birth to 9 isotopologues of water, with molecular masses between 18 (the lightest isotopologue - $H_2{}^{16}O$) and 22 (the heaviest isotopologue - $^2H_2{}^{18}O$).

In nature the abundency of the istotopologues which contain more than one of the heavy isotopes (^{2}H, ^{17}O or ^{18}O) is neglectable, which reduces the number of important components to four: $^1H_2{}^{16}O$, $^1H^2H^{16}O$, $^1H_2{}^{17}O$ and $^2H_2{}^{18}O$, and if we consider the values of the average isotopic abundances for hydrogen and oxygen (**Table 1**), the isotopic species of interest are reduced to three: $^1H_2{}^{16}O$, $^1H^2H^{16}O$ and $^2H_2{}^{18}O$.

Table 1. The average abundancy of the stable isotopes of hydrogen and oxygen.

	The Isotope	**Abundance (%)**
Hydrogen	^{1}H	99,985
	^{2}H	0,0155
Oxygen	^{16}O	99,759
	^{17}O	0,037
	^{18}O	0,204

The abundancy of an isotopic species (the isotopic concentration) is defined as the number of atoms of the considered isotope reported to the total number of atoms of the considered element. An example for the hydrogen isotopes:

$$\mathrm{c}_{^2\mathrm{H}}(\%) = \frac{[^2\mathrm{H}]}{[^1\mathrm{H}+^2\mathrm{H}]}*100 \quad \text{and} \quad c_H(\%) = \frac{[^1\mathrm{H}]}{[^1\mathrm{H}+^2\mathrm{H}]}*100$$

$$c_{^2H}(ppm) = \frac{[^2\mathrm{H}]}{[^1\mathrm{H}+^2\mathrm{H}]}*10^6 \quad \text{and} \quad c_H(ppm) = \frac{[^1\mathrm{H}]}{[^1\mathrm{H}+^2\mathrm{H}]}*10^6$$

and for water:

$$c_{^2H}(\%) = [^2\mathrm{H_2O}](\%) = \frac{[^2\mathrm{H}^1\mathrm{HO}]}{[^2\mathrm{H}^1\mathrm{HO}]+[^1\mathrm{H_2O}]}*100$$

The isotopic ratio (the isotopic fraction) in a molecular species is defined as the ratio between the rare (heavy) isotope abundancy to the abundant (light) isotope abundancy from that species, for example hydrogen in water: $^2R_{H_2O} = \frac{[^1\mathrm{H}^2\mathrm{HO}]}{[^1\mathrm{H_2O}]} = \frac{c_{^2H}}{1-c_{^2H}}$

because of the very small natural abundances of deuterium.

The isotopic abundancy can be expressed in δ units (‰ - promill) as the ratio between the variation of the sample isotopic fraction – the standard and the isotopic fraction of the standard:

$$\delta(‰) = \frac{R_{proba} - R_{s\tan dard}}{R_{s\tan dard}}*1000 = \left(\frac{R_{proba}}{R_{s\tan dard}} - 1\right)*1000$$

For the isotopic content in a molecular species the δ notations must be followed by the symbol of the followed isotope and the used standard. Ex: $\delta^2H_{V\text{-}SMOW}$, $\delta^{18}O_{V\text{-}SMOW}$, $\delta^{18}O_{PDB}$.

For the isotopic content of water the following standards distributed by IAEA (International Atomic Energy Agency) Viena are used:

- V-SMOW (**V**ienna **S**tandard **M**ean **O**cean **W**ater) prepared from distilled ocean water which has the following values of the isotopic ratios:
  - $\delta^{18}O_{SMOW} = 0$ ‰ $\delta^{2}H_{SMOW} = 0$ ‰
- For water that is very depleted isotopically the SLAP standard (**S**tandard **L**ight **A**ntarctic **P**recipitation) is used
  - $\delta^{18}O_{SLAP} = -55.50$ ‰ V-SMOW $\delta^{2}H_{SLAP} = -428.0$ ‰ V-SMOW
- At intermediary values the GISP standard (**G**reenland **I**ce **S**heet **P**recipitation) is used
  - $\delta^{18}O_{GISP} = -24.78$ ‰ V-SMOW $\delta^{2}H_{GISP} = -189.5$ ‰ V-SMOW

The isotopic fractioning process between two molecular species is cuantified with the help of the isotopic fractioning factor which is defined as the ratio of the isotopic fractions of the two molecular species

$$\alpha_{1-2} = \frac{R_1}{R_2} = \frac{(heavy/light)_{species\,1}}{(heavy/light)_{species\,2}} = \frac{\dfrac{[^2\mathrm{H}]}{[^1\mathrm{H}]_1}}{\dfrac{[^2\mathrm{H}]}{[^1\mathrm{H}]_2}}$$

In the evaporation process of water the isotopic fractioning factor is defined as the ratio between the relative abundancy of deuterium in a phase (*l*) and the relative abundancy of deuterium in the other phase (*v*):

$$\alpha_{l-v} = \frac{R_l}{R_v} = \frac{\dfrac{[^1\mathrm{H}^2\mathrm{HO}]_l}{[^1\mathrm{H}_2\mathrm{O}]_l}}{\dfrac{[^1\mathrm{H}^2\mathrm{HO}]_v}{[^1\mathrm{H}_2\mathrm{O}]_v}} \quad \text{or} \quad \alpha_{v-l} = \frac{R_v}{R_l} = \frac{\dfrac{[^1\mathrm{H}^2\mathrm{HO}]_v}{[^1\mathrm{H}_2\mathrm{O}]_v}}{\dfrac{[^1\mathrm{H}^2\mathrm{HO}]_l}{[^1\mathrm{H}_2\mathrm{O}]_l}} \Rightarrow \alpha_{l-v} = \frac{1}{\alpha_{v-l}}$$

When $\alpha > 1$ the *l* (liquid) phase is enriched in the heavy isotope, and if $\alpha < 1$ the *l* is depleted in the heavy istope. Generally the isotopic effect is small $\alpha \approx 1$, and because of this the ε (enrichment) measure is used, this being the deviation from 1 of the fractioning factor. The concentration ($\varepsilon > 0$) or impoverishment ($\varepsilon < 0$) of the heavy isotope in phase 1 (liquid) relative to the phase 2 (vapours).

$$\varepsilon_{1-2} = \alpha_{1-2} - 1 = \frac{R_1}{R_2} - 1 \quad \text{şi} \quad \varepsilon_{1-2} = \frac{-\varepsilon_{2-1}}{1+\varepsilon_{2-1}} \approx -\varepsilon_{2-1}$$

Because ε is a small number, it is generally expressed in ‰. For example $\varepsilon = 0.005$ is defined as 5‰.

For the phase transformation using the *l* symbol for liquid, *v* for vapours and *st* for standard we have the following relations:

$$\varepsilon_{l-v} = \alpha_{l-v} - 1 = \frac{R_l}{R_v} - 1 \quad \text{and} \quad \varepsilon_{l-v} = \frac{-\varepsilon_{v-l}}{1+\varepsilon_{v-l}} \approx -\varepsilon_{v-l} \Rightarrow \alpha_{l-v} = \frac{R_l}{R_v} = \frac{\delta_l + 1000}{\delta_v + 1000}$$

$$\varepsilon_{l-v} = \alpha_{l-v} - 1 = \frac{R_l/R_{st} - R_v/R_{st}}{R_v/R_{st}} = \frac{(\delta_l + 1) - (\delta_v + 1)}{\delta_v + 1} = \frac{\delta_l - \delta_v}{\delta_v + 1} \approx \delta_l - \delta_v \Rightarrow \delta_v = \delta_l - \varepsilon_{l-v}$$

1. THEORETICAL ASPECTS

1.1. ISOTOPIC FRACTIONATION OF WATER IN NATURE.

The phenomenon which induces differences in the content of isotopes of molecules elements, having as consequence changes in the physical properties and chemical behavior of molecules, is defined as isotopic fractionation. During the isotopic fractionation, the heavy and light isotopes partition differently between two compounds or phases.

The isotopic fractionation takes place because the bonding energy of each isotope is slightly different, heavier isotopes having stronger bonds and smaller reaction speeds. The difference between the bonding energies and the reaction speeds are proportional with the difference of mass between isotopes.

This paper presents the study of isotopic effects if water in nature, with special reference to the stable isotopes of hydrogen and the species $^{1}H_2{}^{16}O$ şi $^{1}H^{2}H^{16}O$.

1.1.1. The evaporation process

The isotopic fractionation takes place in any thermodynamic reaction because of the differences in the reaction speeds for different molecular species. The result is a disproportionate concentration of an isotope to another in one part of the reaction. Isotopic fractionation is quantified using the measure α . For balance fractionation the measure α is a thermodynamic quantity which does not depend on the conduct course or mechanism of the reactions, only on the differences between the energies of the reactants.

The fractionation factor defined as the ratio between the heavy isotope content from the two phases depends on the temperature. A general approximation of the ex pression for the fractionation factor depending on temperature can be written as:

$$\alpha = Ae^{B/T}$$

where the coefficients A and B do not depend on temperature but contain independent quantities of temperature (mass and vibration frequency). At high temperatures the contributions of the translation and rotation energies become important and balance the contribution of the vibration energy at the isotopic fractionation, so that at high temperatures $\alpha \cong 1$ and the isotopic effects tend to zero at high tempreatures.

1.1.1.1. Evaporation in stationary conditions

1.1.1.1.1. The isotopic fractionation factor α

The fractionation factor at the evaporation and condensation of water is defined as the ratio between the values of concentraction of an isotope before and after fractionation, depends on temperature and the reaction speed which determines the fractionation. The firest determinations of the values α were done in 1933 [13] an 1935 [14] obtaining the following formulas:

$$\alpha_{^2H} = 0{,}86\times\exp(130/RT) \qquad \alpha_{^{18}O} = 0{,}987\times\exp(13/RT)$$

The most known values $\alpha_{^2H}$ are due to Merlivat (1963) [15].

1.1.1.1.2. Rayleigh's law

The change of concentration of the heavy isotope component in a two phase system will be considered in a relation with the isothermal evaporation from the initial quantity of water. The vapors are continuously transported from the system and the process takes place so slowly that virtually there is balance at the surface of the two phases. The relations of the Rayleigh evaporation with the δ notations become:

$$R_l = R_{l_0} F^{\left(\frac{1}{\alpha_{l-v}} - 1\right)} \qquad R_v = R_{l_0} \cdot \frac{1 - F^{\frac{1}{\alpha_{l-v}} - 1}}{1 - F}$$

$$\delta_v = \left(\delta_{l_0} + 1000\right)\frac{1 - F^{\frac{1}{\alpha_{l-v}} - 1}}{1 - F} - 1000 \qquad \delta_l = (\delta_{l_0} + 1000) F_l^{\frac{1}{\alpha} - 1} - 1000$$

1.1.1.2. Evaporation in non-stationary conditions

All the results obtained based on the assumption of the balance conditions represents an approximation more or less good of the real natural processes. They are strictly true only in infinitely slow processes, which take place under very clearly defined conditions (controlled). As a process of isotopic fractionation, evaporation has been also studied in non-stationary terms because the natural processes do not take place in balance plus intervening kinetic factors which alter a lot the value of α from the Rayleigh [16-24] evaporation process.

1.1.2. The condensation process

1.1.2.1 Isothermic condensation from a limited quantity of vapors

Precipitations form through condensation of humidity in the atmosphere after a Rayleigh process and removing them right after the formation of the distilled. The precipitations are isotopically enriched in comparison with the vapors from which they came, but their isotopic composition becomes progressively depleted in the heavy isotopes of water as the condensation process evolves, tending to the value of the initial isotopic concentrations of the vapors from which they came. The first fractions of the discharge of a cloud are more enriched in heavy isotopes of water comparative to the last fractions of the condensate.

1.1.2.2. Condensation in non-stationary conditions

Isothermic condensation never takes place in atmosphere. Any forming of precipitations is caused by different types of cooling processes. The isotopic composition of the amount of rainfall cannot be used as an indicator of the condensation temperature because the isotopic composition of precipitations depends on more parameters which act all at once, they overlap and influence one another, so in the end the isotopic composition represents the physico-chemical processes which take place with isotopic fractionation in globality.

In the absence of adequate data over the behavior of deuterium in conditions so complicated it is necessary to use an image overly simplified of the metrological events to examine the acceptability of the physics theory of isotopic fractioning.

1.2. ISOTOPIC EFFECTS ASSOCIATED TO WATER IN ITS NATURAL CYCLE

As a study instrument in hydrology and climatology environment isotopes have captured the interest of the science world for their practicability. The world of science has gathered in work groups for scientific contributions to knowing the global changes in climate. International organizations patronage by IAEA-Viena are collecting data from the GNIP (**G**lobal **N**etwork for **I**sotopes in **P**recipitation) stations relative to the isotopic composition of rainfall [25]. As the isotopic composition of precipitations depends on the location and the forming conditions of these and their travel history, precipitations have an isotopic distribution in space and time according to the isotopic effects caused by the processes discussed before. The effects caused by the evaporation – condensation processes can be grouped by the scale on which they exercise their action:

1. Global
    a. The latitude effect
    b. The continental effect
2. Local
    a. The altitude effect
    b. The seasonal effect
    c. The amount effect

2. EXPERIMENTAL METHODOLOGY

The interpretation of the isotopic analysis is better and offers information of great scientific value over the processes which take place in nature only if the results obtained from the collected samples in the experimental field are of good quality. In order to obtain accurate results it is necessary to respect all the collecting and depositing procedures for samples, the preparation steps for the isotopic analysis. Beside this, the measurement equipment used for the determination of isotopic ratios is necessary to have high analytical performances. The classic method of analysis of isotopic ratios is mass spectrometry (IRMS), which has improved continuously as an analysis technique. Recently, the absorption spectroscopy with connected laser-diode (TDLAS) has begun to develop for measuring isotopic ratios in water.

2.1. DETERMINING THE ISOTOPIC RATIO

2.1.1. The mass spectrometer (IRMS)

The ***deuterium concentration*** methods were performed with a Thomson THN 202 mass spectrometer (type CEA Saclay, France) type Nier (**Fig. 1**), which it is specialized for determining the concentration of deuterium at normal values [26]. Mainly the spectrometer is based on the diversion and separation of electrically charged particles moving perpendicular on the force lines of a magnetic induction field and has the same functional blocks as any other mass spectrometer.

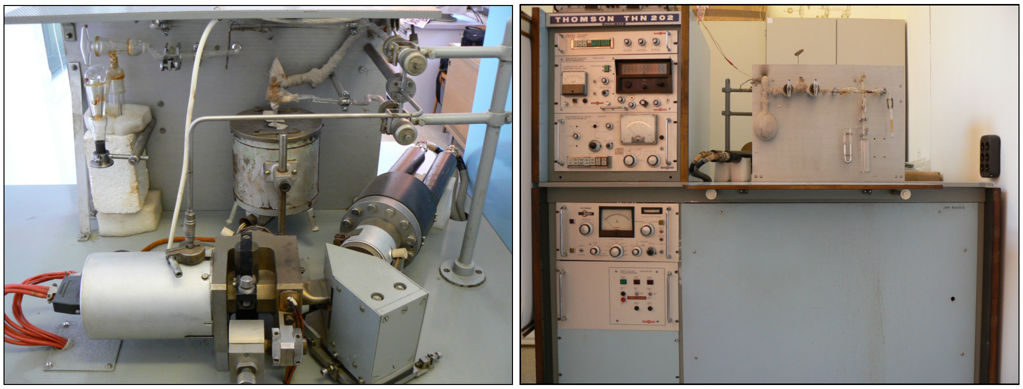

Fig. 1. The Thomson THN 202 mass spectrometer.

2.1.2. The liquid water isotope analyzer (LWIA)

The samples measured with the Thomson THN 202 mass spectrometer were measured comparatively with the Liquid Water Isotope Analyzer (LWIA) made by Los Gatos Research (LGR) type DLT-100.

This analyzer uses laser absorption spectroscopy using as a functioning principle Beer's Law (**Fig. 2**), which can be expressed as:

$$\frac{I_0}{I_\nu} = e^{-SL\chi P\phi_\nu}$$

where I_ν represents the intensity transmitted through the sample at the ν frequency, I_0 is the laser intensity (reference) prior to the penetration of the cell, P is the pressure of the gas, S is the absorption intensity of the transited sample, L is the length of the optic path, χ is the mixture proportion and ϕ_ν is the linear form function of the transition at the ν frequency.

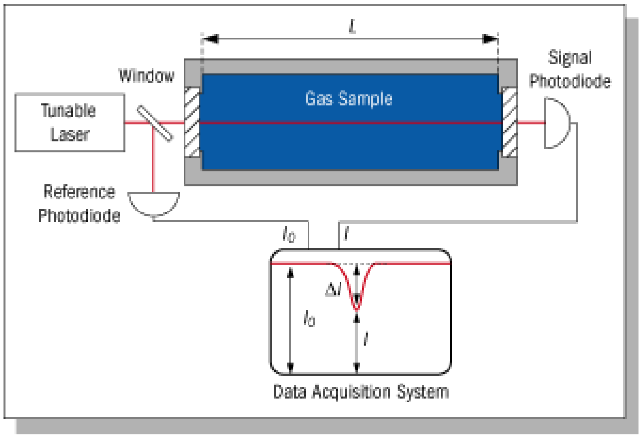

Fig. 2. Typical setting of the laser absorption spectroscopy [27].

The water isotope analyzer provides measurements for $^{18}O/^{16}O$ and D/H from water samples, with a high accuracy. By equipping the analyzer with an autoinjector measurements can be conducted over a long term without the intervention of the user. (**Fig. 3**). The accuracy of the measurements on the DLT-100 liquid water isotope analyzer is of 0,6‰ (0,15 ppm) for $^{18}O/^{16}O$.

Fig. 3. DLT-100 Liquid water isotope analyzer.

3. INTERPRETATION OF THE RESULTS

The measurements of the stable isotopes of hydrogen and oxygen in water samples (natural water or water extracted from different materials – plants, juices, rocks, organic materials) make up the database which helps obtain new scientific information or validate old information obtained through classic methods. Concerning the isotopic content in water, the questions that the scientists are faced with are:

1. How and why do the values of the isotopic content in water vary in water's natural cycle: periodically, randomly, by what laws?
2. What is the time and space distribution of the isotopic content in water on Earth?
3. What is the magnitude and the variation model of the changes in isotopic composition of water in a natural system from the hydrosphere, biosphere, lithosphere?
4. What are, and how big, are the interactions between the components of a natural system which contributes to the changing of the isotopic composition of water?
5. What is the response time between interactions?

The theoretical considerations answer the first question: why and how does the isotopic composition vary in a physical process in which water participates (evaporation, condensation, sublimation, diffusion, percolation and infiltration, transpiration, isotopic exchange, thermical convection, blending). The following questions find their answer in the information obtained in researches based on measurements of isotopic composition in water samples collected in correlated sites with other parameters which characterize the process or the location.

Basically, the following aspects must be analyzed:

1. the variation in time of the measured δ^2H and δ^{18}O values;
2. the variation in space of the measured δ^2H and δ^{18}O values;
3. the variation domain of the measured δ^2H and δ^{18}O values;
4. correlations of the δ^2H and δ^{18}O values and correlations of δ^2H and δ^{18}O with other parameters.

In the natural cycle of water, rainfall constitutes the input for many natural systems, and water in its natural cycle constitutes the main array carring pollutants in nature. That's why, in the isotopic study of water in its natural cycle, the isotopic study of rainfall is the first step in researches, and the theoretical approach is made only for the processes that essentially modify the isotopic content of rainfall. With the data of isotopic content in rainfall, information about the link between rainfall, as input, water stocked in different reservoirs of a natural system and output water in the considered system can be obtained (ex. from the atmosphere – soil – plants system).

The methodology of interpretation of the δ^2H and δ^{18}O values measured in water samples depends on the basic requirements which must be fulfilled for the environment studies.

3.1. THE TIME SCALE

The time distribution of the measured values is given by the chosen time scale. The time scale is chosen accordingly to the frequency of the measurements that need to be appropriate to the purpose followed in research, and the time period must cover the development of the entire process that controls the water flux.

For the study of the processes and components in the natural cycle of water through isotopic methods, the minimum study length for preliminary data is a year and a half, the period that covers a complete meteoric cycle, and for a complete study that includes preliminary results, checking and validating the results and the elaborated models, the ideal period of the measurements is 4 years.

3.2. THE SPACE SCALE

The chosen space scale gives us the space distribution of the measured δ^2H and δ^{18}O values from natural water samples which have a continuous spread (one-dimensional – vertically or horizontally -, two dimensional in 2D representation and/or three dimensional in 3D representation). For choosing the best space scale it is necessary for the measurements to be made on samples collected in a representative selection of ecosystem sampling points (the sampling points need to depend one on another, but the values can have spatial heterogeneity) and to identify the maximum space scale where the homogeneity conditions are constant (the representative elementary volume concept) which will be the sampling area. The space scale must be chosed according to the extent of the studied process, the space extent of the effects of certain disturbances (extreme events), the precision of the measurements (eg: the effect caused by altitude cannot be highlighted in the isotopic composition of oxygen 18 from rainfall if measurements are taken with a precision of ±0,1‰ from rainfall sampled at 100m intervals and the altitude effect is 0,15‰/100m).

3.3. THE VARIATION DOMAIN OF THE ISOTOPIC CONTENT IN RAINFALL

As main water input in soil, rainfall has different isotopic composition according to the source area of the moist air mass, to the phenomena which take place along the movement trajectory of the moist air masses and the condensation temperature. Due to the isotopic fractioning processes, the δ^2H and δ^{18}O values in rainfall vary in time, but also in space at la global, regional and local scale. The isotopic signature of the rainfall is at the base of the isotopic studies of the cycle of water in nature. From the data concerning the isotopic content of rainfall recorded on long-term at the stations connected to the GNIP-IAEA Viena network, the variation domain of the rainfall events for deuterium is -450‰ <

$\delta^2H < +100‰$, respectively $50‰ < \delta^{18}O < +50‰$, for oxygen-18, and for the multi-anual average values the variation domain of deuterium is $-271,7‰ < \delta^2H < 32,6‰$ respectively $-35,5‰ < \delta^{18}O < 2,8‰$ for oxygen-18 [28].

3.4 CORRELATIONS OF THE δ^2H ŞI δ^{18}O VALUES

3.4.1.The covariation of the δ^2H şi δ^{18}O values

The isotopic content of rainfall is dictated firstly by the isotopic fractionation at evaporation and condensation. The isotopic content of rainfall and the covariation of the δ^2H and $\delta^{18}O$ values reflect of origin of the water masses in clouds, the altitude, the latitude, the proximity to the coastal shores, the rainfall conditions, the air mass dynamics, in one word the history of the rainfall. The temperature variation with latitude, altitude, season and geographical factors (the remotness or the proximity to the marine areas) leads to variability's of the isotopic content in rainfall. Further the pluviometric conditions, the air masses dynamics and the orography contributes additionally to the isotopic fractionations.

Craig [29] and Dansgaard [30] have found a linear relation between the $\delta^{18}O$ and δ^2H values in monitored rainfall in stations across the globe and which were subordinated to AIEA Viena. The regression line of the δ^2H-$\delta^{18}O$ correlation is called Craig's line or Global Meteoric Water Line (GMWL) and has the slope of 8 and interception of 10.

$$\delta^2H = 8\ \delta^{18}O + 10$$

The correlation line of the δ^2H and $\delta^{18}O$ values for a single location is called the Local Meteoric Water Line (LMWL) and can be significantly different from GMWL. Thus, for rainfall that has suffered strong evaporations or mixes with strongly evaporated fronts, the LMWL has values between 2 and 5 and intersects the global meteoric line at the value of the unevaporated isotopic composition.

3.4.2. The temperature relation

Dansgaard [30] in his classic analysis presented the empirical relation between the annual averages of $\delta^{18}O$ from rainfall and the local surface air temperature, derived from the data collected during the first 3 years of operation of the IAEA/WMO network. The relation was developed for costal networks with average and high northern latitudes. The slope of this relation is $0.69‰ / {}^oC$ for $\delta^{18}O$ and $5.6‰ / {}^oC$ for δD.

Mainly, three different types of isotope-temperature relations can be derived from the database of the IAEA/WMO network: (1) the special relation between the long term averages (annual) of $\delta^{18}O$ (δD) from rainfall and the surface air temperature for different stations; (2) the time relation between the short term changes (seasonal) of $\delta^{18}O$ (δD) and the temperature for a single station or a group of stations, and (3) the time relation between the long term changes (multianual) of $\delta^{18}O$ (δD) and the temperature for a certain location.

4. THE STABLE ISOTOPES OF WATER IN THE STUDY OF ENVIRONMENT PROCESSES. RESULTS AND DISCUSSION

The determinations of the concentration of the stable isotopes of water provide a basis for many applications in the research of processes and phenomena which occur in the natural cycle of water. The transport studies of water in its natural cycle using as natural tracers the stable isotopes of hydrogen and oxygen are based on determinations of the isotopic concentrations from samples from rainfall, the precipitations being one of the main inputs of water in different reservoirs of water from the components of water's natural cycle. As integral constituents in water molecules, the environment isotopes ^{2}H, T, ^{18}O, are ideal tracers of water movement, because they are very sensitive to ambient stress and to the reactions that occur in nature, and the time/space isotopic response of the natural systems to any changes is very prompt. In terms of the water cycle, ^{2}H and ^{18}O, are ideal tracers fulfilling all the features imposed to a tracer.

4.1. THE ISOTOPIC STUDY OF LOCAL RAINFALL

In terms of geography, the city of Cluj-Napoca is located within the corridor of the Somesul Mic river, which is at the contact of three major geographical units: The Transilvanian Plain, The Somes Plateau and The Apuseni Mountains, at and average altitude of 360 m, being intersected by the 46°46' northern latitude parallel and the 23°36' eastern longitude meridian.

The geographical position is also felt in the climatic features of the city. The climate of Cluj-Napoca is moderate continental, specific to the hill regions in the north-west of the country, with local differences resulted from the position of the city, being sheltered by the Apuseni Mountains, and the particularities of the landscape, which determine substantial changes in the processes which define the general flow of the atmosphere.

The starting of the measurements of isotopic concentration of hydrogen in local rainfall (in Cluj-Napoca) begins in 1974 by dr. Liviu Blaga. Until 1975 the research connected to the local rainfall was done without a proper rain gauge, following from 1975 The Department of Natural Isotopic Abundances within the Institute of Stable Isotopes Cluj-Napoca, to own a proper rain gauge for the studies. After 1990 the isotopic research of local rainfall are continued by dr. Feurdean Victor [31, 32, 33] following the author of the thesis to take over the isotopic database of rainfall starting from 2009 and so the studies can be continued and completed with data connected to oxygen 18.

The measurements of isotopic content and the amount of rainfall are made from each sample collected in the rainfall event. With the recorded values for each rainfall event of these two units the monthly, annually, multiannual average values are calculated.

The weighted averages of the isotopic content in rainfall are specific for a certain season and for a certain area where the same meteorological influences are felt (average temperature, movement direction of the air masses, atmospheric moisture).

It needs to be considered that Cluj-Napoca must be looked at not as a point in which rainfall forms, but a point in which it unloads.

4.1.1. The study of the isotopic content of δ^2H and $\delta^{18}O$ in rainfall from Cluj-Napoca in 2009-2012

The 2009-2012 period includes the δ^2H and $\delta^{18}O$ values recorded in local rainfall, the δ^2H values continuing the activity began in 1975, and the $\delta^{18}O$ values being new in Romania.

The purpose of the study is to present, analyze and discuss the data about the isotopic composition of local rainfall.

The importance of this study is that the information obtained from the isotopic content in rainfall provides the first step in the complete understanding of the water input in different reservoirs of the system connected to the natural cycle of water.

The utility of this study is:

1. Creating an isotopic database, for fundamental and applied research using the natural isotopes of water as tracers connected to:

a. the circulation of water in nature(atmosphere – climatology, lithosphere-hydrology, hydrogeology, karstology, extractive industry, biosphere-dendrology, agriculture, forestry), for verifying and improving the existing models;
b. the traceability of certain food products (vegetables, fruits, wines, fruit juices, oils);
c. paleoarchives.

2. The integration of the isotopic data in the GNIP database of the International Agency of Atomic Energy in Vienna, to increase the confidence rank of isotopic maps for the Transylvania, the maps being made using interpolation.

Basically, for a single station, with the isotopic content data from rainfall three correlations can be obtained:

1. temporal relation between the short term changes of the δ^2H and $\delta^{18}O$ values and meteorological parameters (mainly temperature and amount of rainfall), from the analysis of the data recorded for each rainfall event;

2. temporal relation between the average and long term changes of the δ^2H and $\delta^{18}O$ values and temperature and the amount of rainfall, from the analysis of the data averages recorded over several years of monitoring;

3. the spatial correlation of the recorded data, from the comparison of data recorded for the studied station and data from literature.

In this context, the isotopic study of rainfall in Cluj-Napoca follows to determine the variability of the isotopic composition of rainfall events and of monthly averages, to correlate these variations with general meteorological parameters, to determine the factors that influence the isotopic signature of rainfall, to calculate the ^2H – T, $\delta^{18}O$ – T relations, to compare the values with data from literature.

4.1.1.1. The time series of the δ^2H – $\delta^{18}O$ values for 2009-2012

The discussions for the time series 2009-2012 (**Fig. 4**) are focused on the characterization in terms of the isotopic composition of the δ^2H – $\delta^{18}O$ values, on highlighting the abnormal values, the extreme events and validating the results obtained with data from the weather stations.

During the monitoring period (2009-2012) the values of the deuterium content (δ^2H) and oxygen 18 ($\delta^{18}O$) from all the successive rainfall events (**Fig. 4**) are between:

$-213,70‰ < \delta^2H < +15,11‰$ respectively $-28,25‰ < \delta^{18}O < +5,76‰$

The domain of the recorded values is in the domain of values obtained globally for a continental area, located at great distances from oceans or seas.

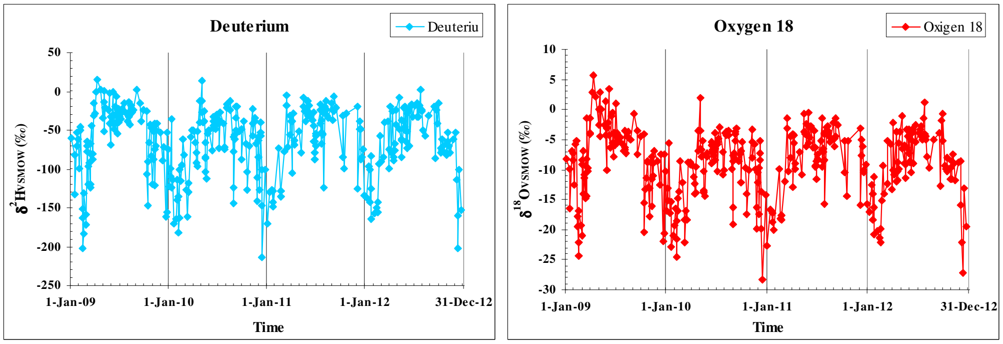

Fig. 4. The time series 2009-2012 of the δ^2H and $\delta^{18}O$ values from all the succesive rainfall events in Cluj-Napoca.

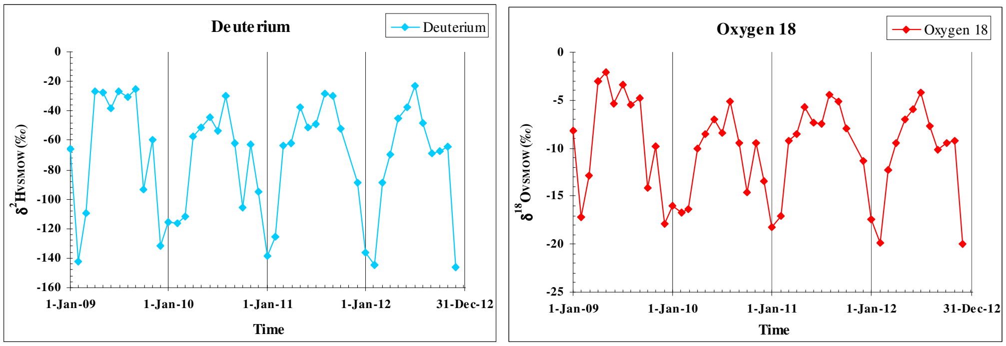

Fig. 5. The time series 2009-2012 of the monthly average values (weighted average) of δ^2H and $\delta^{18}O$ from rainfall in Cluj-Napoca.

The monthly weighted average values for δ^2H and $\delta^{18}O$ (**Fig. 5**) are between:

$-146,6‰ < \delta^2H < -23,24‰$ respectively $-19,98‰ < \delta^{18}O < -2,16‰$

The time series 2009-2012 of the δ^2H and $\delta^{18}O$ values (**Fig 4, 5**) highlight:

1. the seasonal character of the recorded values: during summer high values, in winter low values in correlation with the average temperature of the season. The amplitude of the isotopic signal of the seasonal variation is large, reflecting the continental character of the local climate.

2. similarity between the δ^2H-time and $\delta^{18}O$-time profiles;

3. large variability's of the δ^2H and $\delta^{18}O$ values from one rainfall event to another, highlighting some cases when the characteristic variations of a season were exceeded, these cases highlighting abnormal values: δ^2H and $\delta^{18}O$ values corresponding to the cold season recorded in summer rainfall and δ^2H and $\delta^{18}O$ values corresponding to the warm season recorded in winter rainfall.

4. the extreme events: maximum and minimum values recorded.

4.1.1.2. The correlation of the δ^2H – $\delta^{18}O$ pair of values for the 2009-2012 period

With the δ^2H and $\delta^{18}O$ pair of values from the rainfall events the graph of the regression line is built, a line called by Craig the Meteoric Water Line. This has for each area different parameters, and that's why it is called the Local Meteoric Water Line. The different values of the parameters highlight the influence of the local environmental factors over the isotope of rainfall.

The equations of the regression lines for the δ^2H – $\delta^{18}O$ values recorded for all the rainfall events (**Fig. 6**) are the following:

2009	$\delta^2H=7,27*\delta^{18}O-3,0$	$R^2 = 0,9241$;
2010	$\delta^2H=7,71*\delta^{18}O+9,0$	$R^2 = 0,9785$;
2011	$\delta^2H=7,76*\delta^{18}O+4,5$	$R^2 = 0,9798$;
2012	$\delta^2H=7,58*\delta^{18}O+3,6$	$R^2 = 0,9767$;
2009 - 2012	$\delta^2H=7,45*\delta^{18}O+2,4$	$R^2 = 0,9571$;

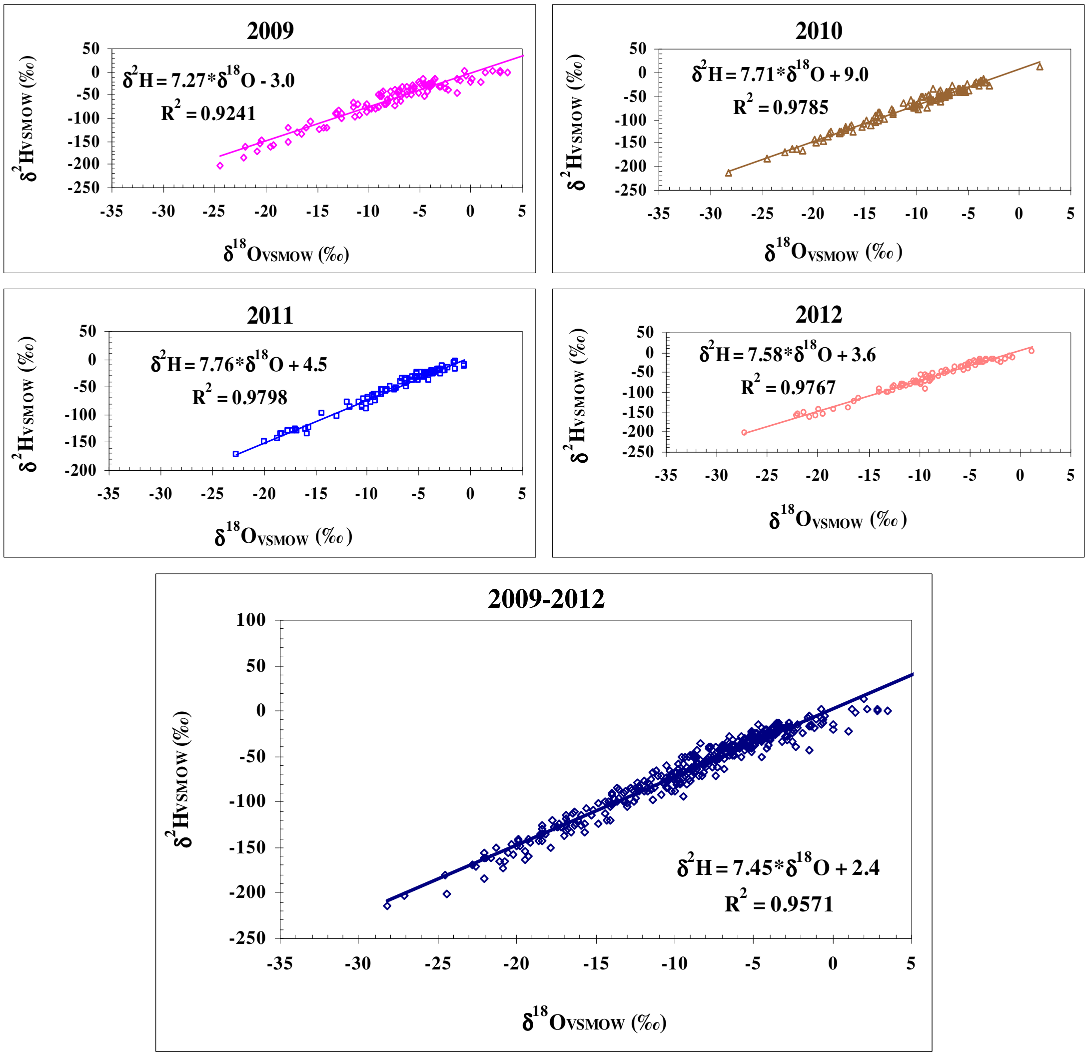

Fig. 6. The correlation of the δ^2H – δ^{18}O pairs based on rainfall events in the 2009-2012 period.

The equations of the regression lines for the average monthly values (weighted averages) of δ^2H – δ^{18}O (**Fig. 7**) are the following:

2009	$\delta^2H=7{,}62*\delta^{18}O+1{,}4$	$R^2 = 0{,}9491$;
2010	$\delta^2H=7{,}83*\delta^{18}O+12{,}4$	$R^2 = 0{,}9860$;
2011	$\delta^2H=8{,}06*\delta^{18}O+9{,}1$	$R^2 = 0{,}9937$;
2012	$\delta^2H=7{,}98*\delta^{18}O+9{,}8$	$R^2 = 0{,}9947$;
2009 - 2012	$\delta^2H=7{,}71*\delta^{18}O+6{,}5$	$R^2 = 0{,}9706$;

It can be seen that the slope of the regression lines for the δ^2H – δ^{18}O pairs of values, differ a little from one year to another, and the correlation factor between the δ^2H – δ^{18}O values is very good, for each year individually but also for the time period 2009-2012.

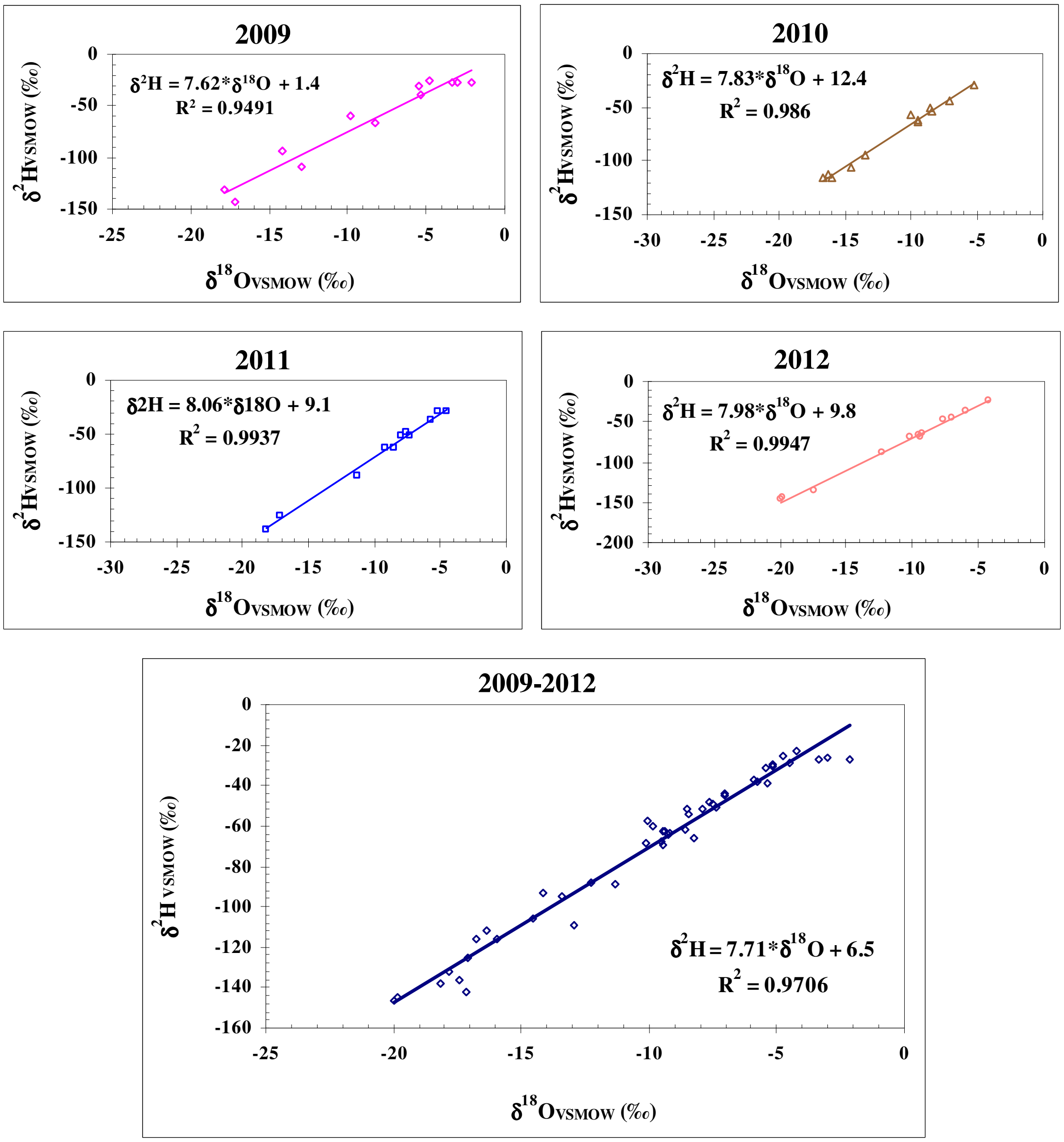

Fig. 7. The correlation of the pairs of monthly average values of $\delta^2H - \delta^{18}O$ for the time period 2009-2012.

The parameters of the local meteoric lines are very close to the parameters of the global meteoric line - GMWL [30, 34]

$$\delta^2H=8 *\delta^{18}O+10$$

Generally, the parameters of the regression lines for the weighted average values of δ^2H - $\delta^{18}O$ are lower than those of the regression lines calculated for the δ^2H and $\delta^{18}O$ values from individual samples (without considering the amount of rainfall). For Cluj-Napoca the local meteoric lines for the weighted average values of δ^2H - $\delta^{18}O$ for the 4 years monitored have the values of the slopes and interceptions slightly higher than the values of the slopes and interceptions for the δ^2H and $\delta^{18}O$ correlations in all the individual events of rainfall, that being because there were many rainfall events with extreme values of isotopic composition in small amounts of rainfall (< 2mm). The isotopic composition of samples from small amounts of rainfall is influenced by the secondary evaporation of water drops joined by the isotopic fractioning during the fall of the rain drops from clouds to the earth surface.

The parameters of the correlation lines (the local meteoric lines or LMWL) are different even if the correlation is done on seasons: warm from April until September and cold from October until March. The variation of the parameters is due to the amount of rainfall in these periods, the evapotranspiration and the temperature of the air, different for the two mentioned periods. The equations for the monitored period have the slopes and the interceptions smaller for the warm season than for the cold season (**Fig. 8, 9**).

warm $\delta^2H=6{,}53*\delta^{18}O - 1{,}66$ (events) $\delta^2H=6{,}07*\delta^{18}O - 3{,}28$ (average values)

cold $\delta^2H=7{,}62*\delta^{18}O + 3{,}14$ (events) $\delta^2H=7{,}78*\delta^{18}O + 6{,}56$ (average values)

The smaller slope and the low value of the interception for the LMWL calculated for the warm season are due to the dry climate, the poor rainfall and in small amounts subjected to the secondary evaporation phenomenon, the isotopic composition of summer rainfall being modified by the evaporation of the rain drops from under the cloud layer during their fall on the ground, which was recorded especially in warm regions with dry conditions. In the warm period, with rainfall in small amounts and subjected to extra evaporation, the correlation coefficients of the regression lines are smaller than for the linear regression lines for the cold season (**Fig. 8, 9**), when rainfall is abundant and rarely presents abnormal influences.

Similar values were recorded for the correlations of the weighted average values of $\delta^2H - \delta^{18}O$ from monitored rainfall in all the european stations of the GNIP network in the 1960-1980 period [35].

April. - Sept. $\delta^2H=(6{,}0\pm0{,}4)*\delta^{18}O+(-6{,}3\pm2{,}8)$ $R^2 = 0{,}85$

Oct. - Mart. $\delta^2H=(7{,}6\pm0{,}2)*\delta^{18}O+(6{,}5\pm2{,}1)$ $R^2 = 0{,}98$

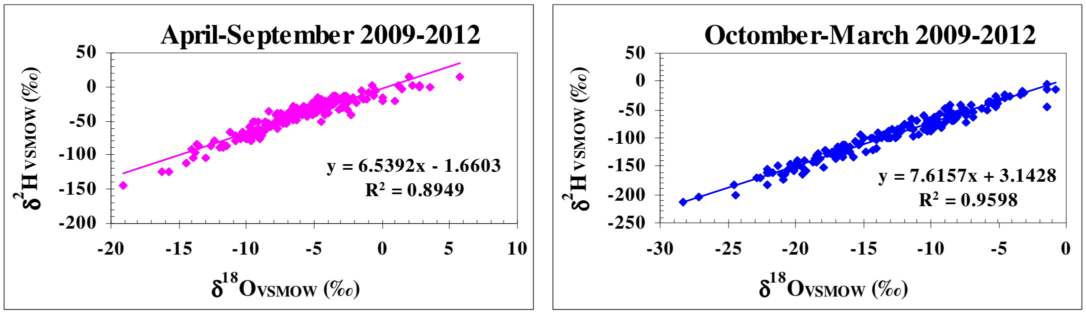

Fig. 8. The correlation of the $\delta^2H - \delta^{18}O$ values based on events for the 2009-2012 time periods in the warm season (left) and the cold season (right).

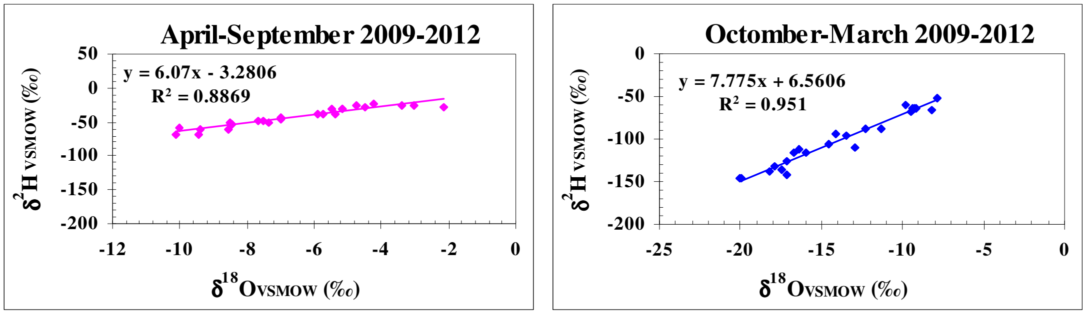

Fig. 9. The correlation of the average monthly values of $\delta^2H - \delta^{18}O$ for the 2009-2012 time periods in the warm season (left) and the cold season (right).

4.1.1.3. The correlation of the δ^2H and $\delta^{18}O$ values with temperature for the 2009-2012 time period

Changes in the air temperature from the surface of the ground reflect changes of the air masses, so there is a significant correlation between the isotopic composition from rainfall and the air temperature from the surface of the ground [36, 37] known as the temperature effect. Representing the weighted average values of δ^2H and $\delta^{18}O$ with temperature the slope of the fitting line gives a good correlation between these values.

The correlation of the δ^2H and $\delta^{18}O$ values with the air temperature at the surface of the ground for the 2009-2012 time period represented in **figures 10** and **11** for single events of rainfall and in figures 12 and 13 for the weighted average values. The correlation factor is satisfying for the values on events and for the monthly averages is good, because the used temperature in correlations is the average temperature of a month and the rainfall events take place randomly and the number of events differs from month to month, and from year to year. This unevenness of the number of rainfall events leads to some months with a large number of events and others with a small number of events (for example, a single event) for a single value of temperature. The fact that the used temperature in correlations is the monthly average temperature and does not correspond totally to the air temperature and the surface of the ground at the moment the condensation of the water vapours took place from the air masses, the correlation with the two isotopes is just satisfying for the values on events and for the monthly average values the correlation factor is good for the recorded values in Cluj-Napoca. The data used for the local temperature in Cluj-Napoca are taken from the following source [38, 39].

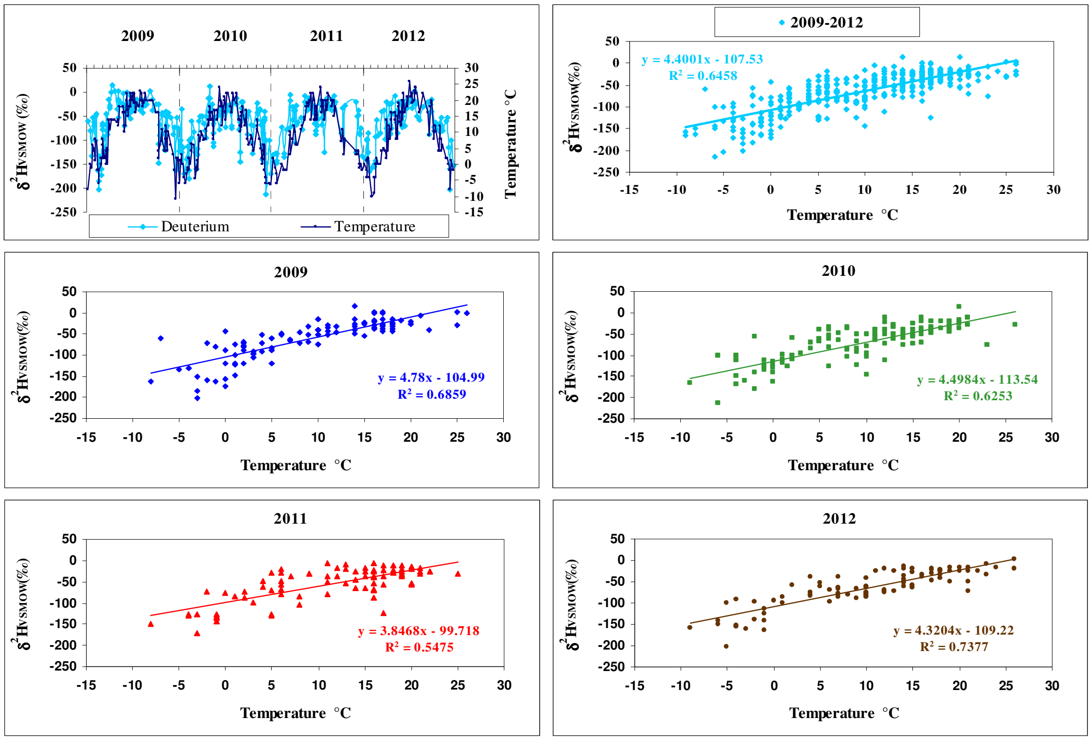

Fig. 10. The δ^{2}H – temperature correlation for rainfall events in the 2009-2012 time period.

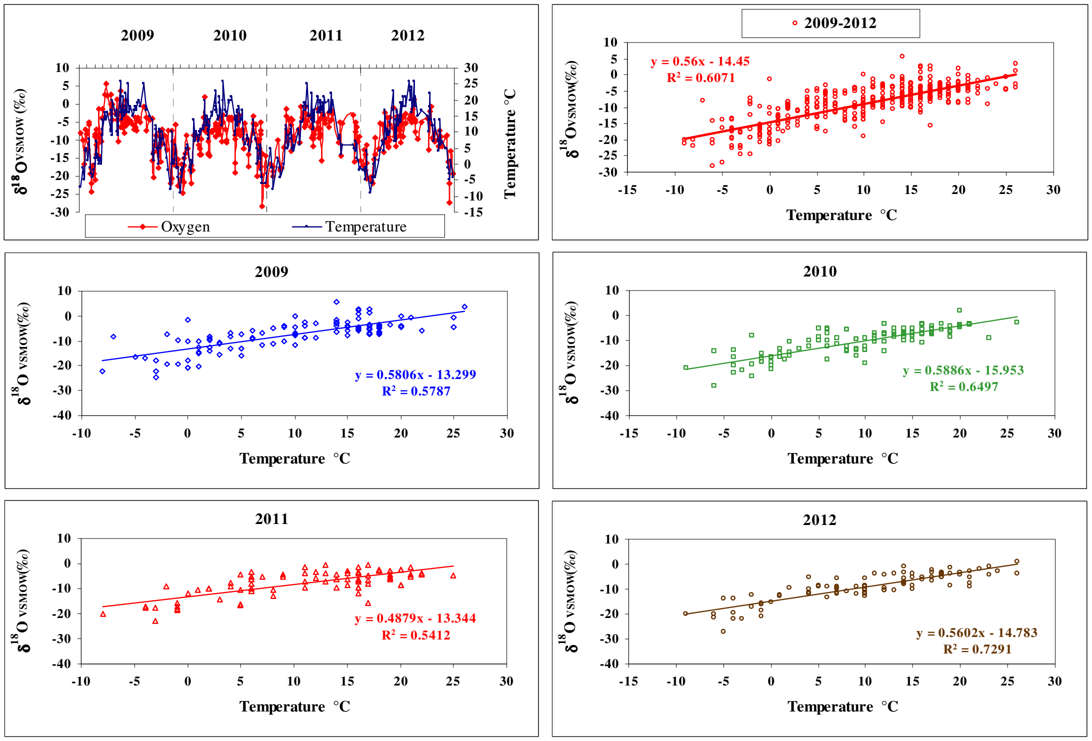

Fig. 11. The δ^{18}O – temperature correlation for rainfall events in the 2009-2012 time period.

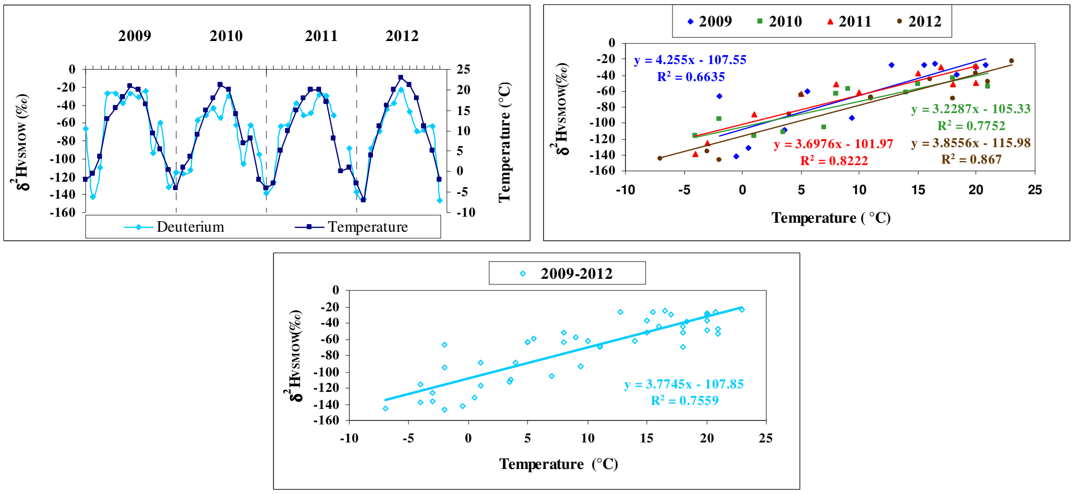

Fig. 12. The correlation of the monthly average values of δ^2H with the monthly average temperature for the 2009-2012 time period.

The equations of the regression lines for the monthly average values of δ^2H – temperature (**Fig. 12**):

2009	δ^2H=4,26*T-107,55	R^2 = 0,6635;
2010	δ^2H=3,23*T-105,33	R^2 = 0,7752;
2011	δ^2H=3,70*T-101,97	R^2 = 0,8222;
2012	δ^2H=3,86*T-115,98	R^2 = 0,8670;
2009 - 2012	δ^2H=3,77*T-107,85	R^2 = 0,7559;

The equations show that at a variation of 1°C of temperature the isotopic composition of deuterium from rainfall in Cluj-Napoca differs with 3,75‰.

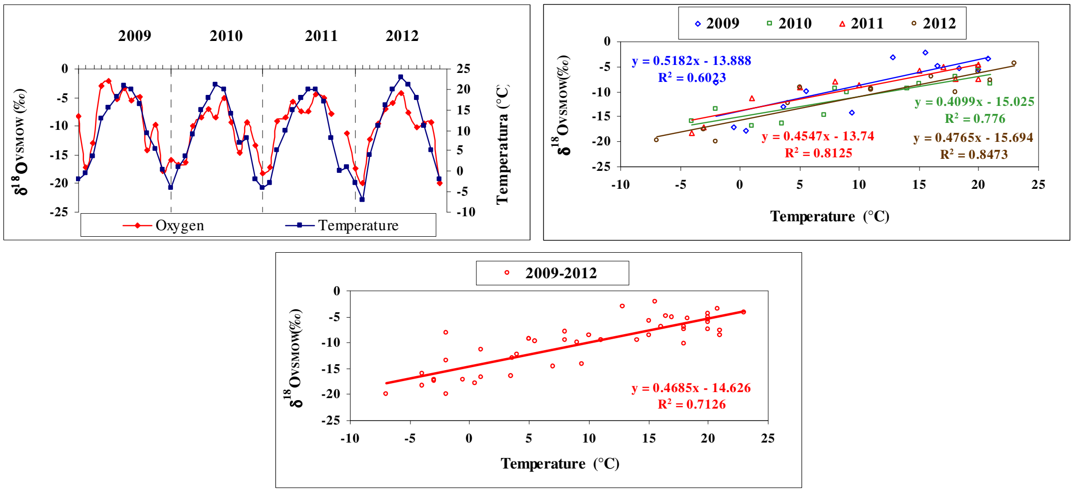

Fig. 13. The correlation of the monthly average values for δ^{18}O with the monthly average temperature for the 2009-2012 time period.

The equations of the regression lines for the monthly average values of δ^{18}O-temperature (**Fig. 13**):

2009 $\delta^{18}O = 0,52*T - 13,888$ $R^2 = 0,6023$; monthly averages
2010 $\delta^{18}O = 0,41*T - 15,025$ $R^2 = 0,7760$; monthly averages
2011 $\delta^{18}O = 0,45*T - 13,740$ $R^2 = 0,8125$; monthly averages
2012 $\delta^{18}O = 0,48*T - 15,694$ $R^2 = 0,8473$; monthly averages
2009 - 2012 $\delta^{18}O = 0,47*T - 14,626$ $R^2 = 0,7126$; monthly averages

It can be concluded that at a temperature variation of 1°C the isotopic composition of oxygen-18 from rainfall in Cluj-Napoca differs by 0,46‰ [40].

4.1.1.4. The correlation of the δ^2H and δ^{18}O values with the amount of rainfall for the 2009-2012 time period

Generally for rainfall in Cluj-Napoca between the δ^2H and δ^{18}O values and the amount of rainfall there is no correlation (**Fig 14, 15, 16**).

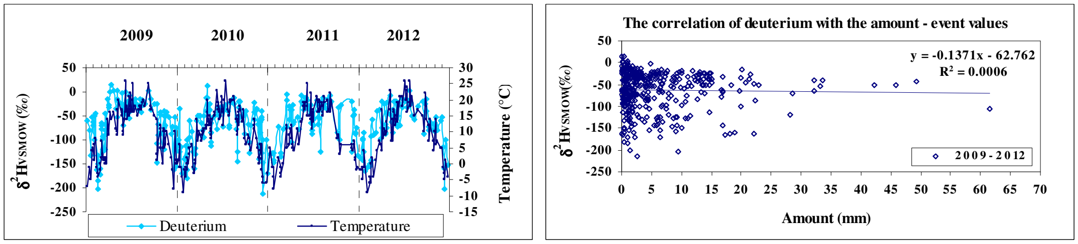

Fig. 14. The correlation of the δ^2H – amount of rainfall values based on rainfall events in the 2009-2012 time period.

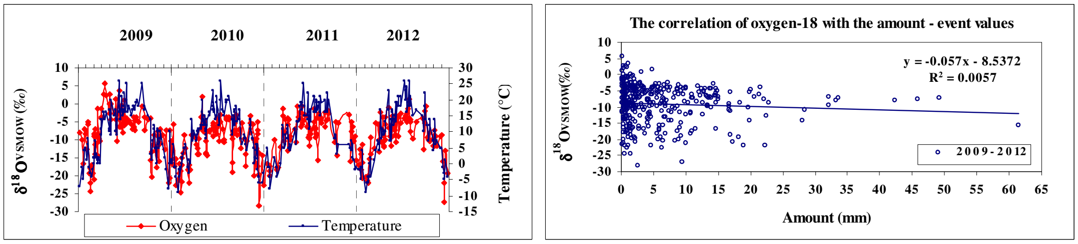

Fig. 15. The correlation of the δ^{18}O – amount of rainfall values based on rainfall events for the 2009-2012 time period.

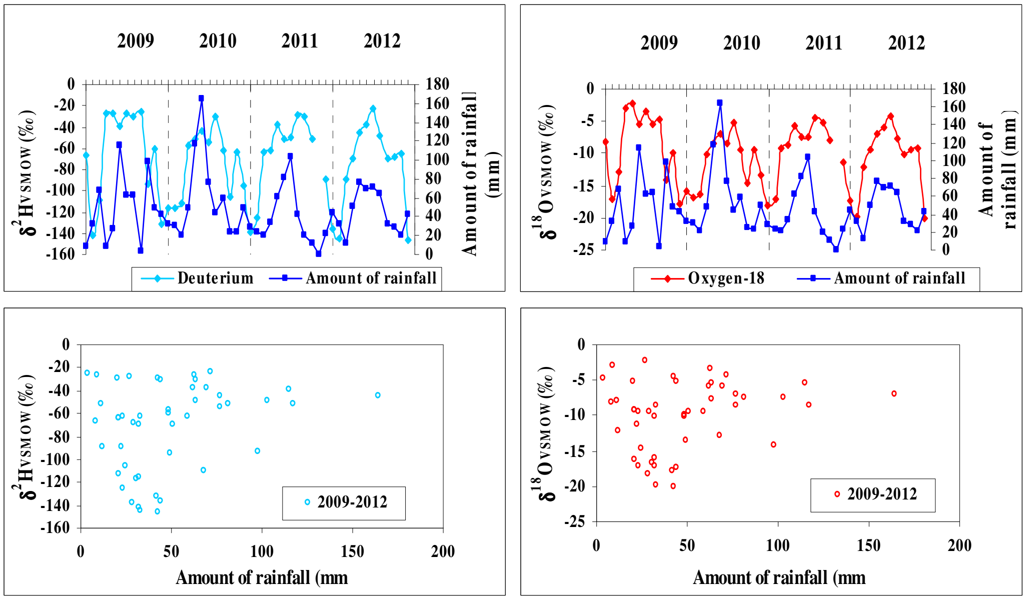

Fig. 16. The correlation of the monthly average values of δ^2H and δ^{18}O with the amount of rainfall for the 2009-2012 time period.

The absence of the correlation between the isotopic composition (δ^{18}O and δ^2H) and the amount of rainfall is frequently reported in literature [41].

Table 2. Values of the variation domain of the δ^2H values.

	The events		Monthly average		Monthly average multiannual		Annual averages	
	Min	**Max**	**Min**	**Max**	**Min**	**Max**	**Min**	**Max**
2009-2012	-213,70	15,11	-146,60	-23,24	-132,36	-34,44	-69,40	-58,45
Estimate maps [42]			-102	-30	-102	-30	-78	-54

Table 3. Values of the variation domain of the multiannual monthly average values for δ^2H (‰).

	Data recorded 2009-2012		Estimates of [42]	
	minim	**maxim**	**minim**	**maxim**
January	-138,26	-66,16	-102	-78
February	-145,03	-116,40	-102	-78
March	-112,03	-63,33	-78	-54
April	-69,48	-26,57	-78	-54
May	-51,25	-27,23	-78	-54
June	-51,19	-37,48	-54	-30
Julie	-53,86	-23,24	-54	-30
August	-48,13	-28,59	-54	-30
September	-68,91	-25,04	-78	-54
October	-105,86	-51,99	-78	-54
November	-64,30	-59,84	-102	-78
December	-146,60	-88,49	-102	-78

Table 4. The multiannual monthly average values of δ^2H (‰) for the 2009-2012 period.

	Data recorded 2009-2012	**Estimates of** [42] **(median interval)**	**Estimates of** [43]
January	-114,15	-90	-80
February	-132,26	-90	-79
March	-93,27	-66	-63
April	-53,91	-66	-56
May	-40,29	-66	-46
June	-42,83	-42	-44
Julie	-38,28	-42	-36
August	-34,44	-42	-38
September	-46,49	-66	-46
October	-79,78	-66	-53
November	-62,38	-90	-70
December	-115,46	-90	-78

Table 5. The δ^2H values in rainfall at 46° latitude, 23° longitude, 360 m altitude: (CLUJ-NAPOCA) the annual average on long term.

	δ^2H (‰, V-SMOW)
2009-2012	-71,32
Estimates of [42]	-66,00
Estimates of [43]	-54,00

Table 6. The values of the variation domain of the δ^{18}O values.

	The events		**Monthly average**		**Monthly average multiannual**		**Annual averages**	
	Min	**Max**	**Min**	**Max**	**Min**	**Max**	**Min**	**Max**
2009-2012	-28,25	5,76	-24,26	-3,38	-19,48	-5,69	-10,90	-8,38
Estimate maps [42]			-17	-5	-17	-5	-11	-8

Table 7. The values of the variation domain of the multiannual monthly average values for δ^{18}O (‰).

	Data recorded 2009-2012		**Estimates of** [42]	
	minim	maxim	minim	maxim
January	-18,18	-14,16	-14	-11
February	-24,26	-16,73	-17	-14
March	-19,64	-9,19	-11	-8
April	-10,04	-8,55	-11	-8
May	-8,53	-5,75	-8	-5
June	-7,34	-5,37	-8	-5
Julie	-8,45	-3,38	-8	-5
August	-7,66	-4,47	-8	-5
September	-10,11	-4,77	-11	-8
October	-14,56	-7,91	-11	-8
November	-9,83	-9,22	-14	-11
December	-19,98	-11,32	-14	-11

Table 8. The multiannual monthly average values for $\delta^{18}O$ (‰) for the 2009-2012 period.

	Data recorded 2009-2012	**Estimates of [42] (median interval)**	**Estimates of [43]**
January	-16,44	-12,5	-11,3
February	-19,48	-15,5	-11,4
March	-14,35	-9,5	-9,2
April	-9,22	-9,5	-8,3
May	-7,06	-6,5	-6,9
June	-6,41	-6,5	-6,5
Julie	-5,89	-6,5	-5,9
August	-5,69	-6,5	-6,0
September	-7,36	-9,5	-7,1
October	-11,53	-9,5	-8,0
November	-9,49	-12,5	-10,4
December	15,65	-12,5	-11,0

Table 9. The δ^2H values in rainfall at 46° latitude, 23° longitude, 360 m altitude: (CLUJ-NAPOCA) the annual average on long term.

	$\delta^{18}O$ (‰, V-SMOW)
2009-2012	-10,74
Estimates of [42]	-9,5
Estimates of [43]	-8,0

Comparing the data from **tables 2, 3, 4** and **5** for the isotopic values of δ^2H from rainfall in Cluj-Napoca in the 2009-2012 period it can be observed that compared to the values obtained from estimates, the δ^2H values recorded in Cluj-Napoca present a larger variation domain and shifted towards more negative values in the winter months (the minimum is smaller, meaning rainfall more depleted isotopically - , and the maximum is generally higher – rainfall enriched isotopically), and for the summer months the variation domain is more narrow and closer to the estimated values. For the transition months from warm to cold and vice versa, the variation domains of the δ^2H values are different from the estimates from the isotopic maps. The average δ^2H values recorded in Cluj-Napoca are much lower isotopically in the winter months, close to the estimate values in the summer months and with variations towards larger or smaller values in the transition months. The large differences compared to the long term estimates from maps and the calculation programs [42, 43] from the transition months are due to the instability of the meteorological factors in the last years: small amounts of rainfall or heavy showers with δ^2H values not specific for the respective month, meaning in a month the origin of the atmospheric fronts changes fast, due to the movement of the air masses in atmosphere [44].

Comparing the data from **tables 6, 7, 8** and **9** for the isotopic values of $\delta^{18}O$ from rainfall in Cluj-Napoca during the 2009-2012 period it can be observed that compared to the values obtained from estimates, generally the variation domains of the monthly values are shifted towards negative values, the minimum and maximum values are much smaller (isotopically depleted) in the cold season months and slightly lower in the warm season months. For $\delta^{18}O$ monthly average values from rainfall in the cold season the values are lower and for rainfall in the warm season the values do not differ significantly from the values obtained from estimates.

The difference between the trend of the $\delta^{2}H$ and $\delta^{18}O$ values is due to, most likely, an accumulation of phenomena: the reevaporation of rain drops, the isotopic exchange between the local atmospheric moisture and the rain drops that fall from the wet air masses from heights, the evapotranspiration of the vegetation, phenomena that is felt much better for deuterium rather than oxygen 18.

4.2. THE STUDY OF THE DEUTERIUM CONCENTRATION FROM RAINFALL IN CLUJ-NAPOCA DURING THE 1975-2012 PERIOD

The primary database for the deuterium concentration from all the rainfall events in Cluj-Napoca from 1975 until 2012 which we own at the National Institute for Research and Development of Isotopic and Molecular Technologies Cluj-Napoca is, worldwide, the only isotopic database of rainfall with such a long continuity for the same location. Until 2009 only data concerning the deuterium content in rainfall was collected, from 2009 due to the acquired equipment measurement of the O-18 content in rainfall were done. In what will follow a comparative analysis will be done between data of isotopic content from the 1975-2008 period [45] (2704 samples analyzed) with the data from the 1975-2012 [46] period (3092 samples analyzed) in order to see how the isotopic content data from local rainfall is influenced by global warming in the last years.

4.2.1. The deuterium $\delta^{2}H$ content from rainfall events

The chart of the $\delta^{2}H$ values of all the rainfall events, as well as the amount of rainfall from 1975 until 2009 can be seen in the **figures 17, 18** and the domain of variation of the values is: $-221{,}88‰ < \delta^{2}H < +65{,}74‰$

For the 1975-20012 period the $\delta^{2}H$ values chart from all the rainfall events, as well as the amount of rainfall is in **figures 19, 20**, and the variation domain is the same, <u>in the last 4 years</u> no extreme values were recorded outside the variation domain above.

The lowest values for the deuterium concentration in all the rainfall events ($\delta^{2}H < -210‰$) (**Fig. 21**) were recorded in march 1987 ($\delta^{2}H= -221{,}88$ ‰), November 1993 ($\delta^{2}H= -210{,}00$ ‰), February 1999 ($\delta^{2}H= -211{,}29$ ‰) and December 2010 ($\delta^{2}H= -213{,}70$ ‰).

The highest values for the deuterium concentration in all the rainfall events ($\delta^{2}H > 50‰$) were recorded in October 1976 ($\delta^{2}H= 65{,}74‰$), August 1985 ($\delta^{2}H= 50{,}33‰$), July 1993 ($\delta^{2}H= 53{,}86‰$), May 2006 ($\delta^{2}H= 54{,}70‰$).

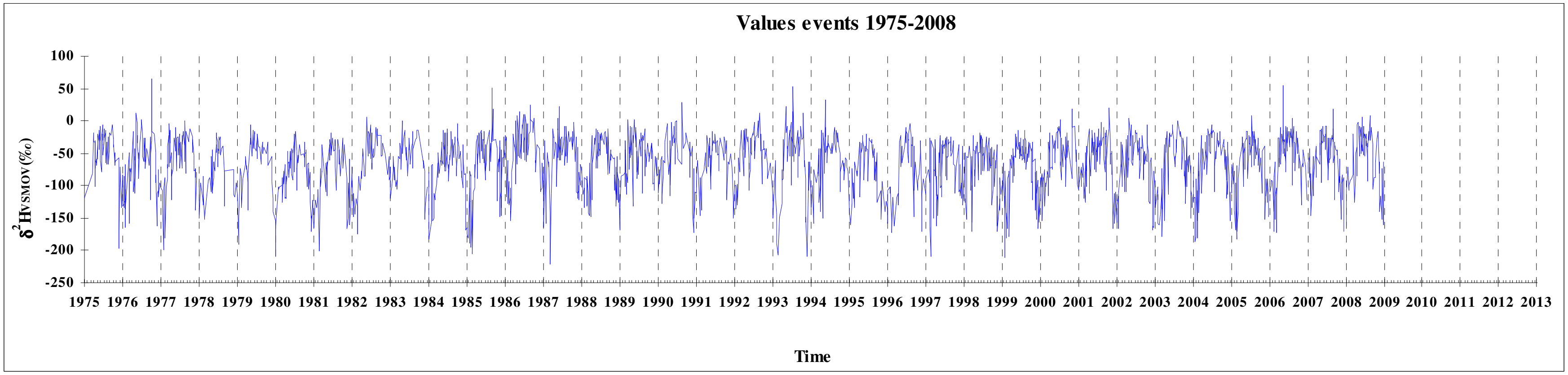

Fig. 17. The time series of the δ^2H values in all the rainfall events in Cluj-Napoca during the 1975-2008 time period.

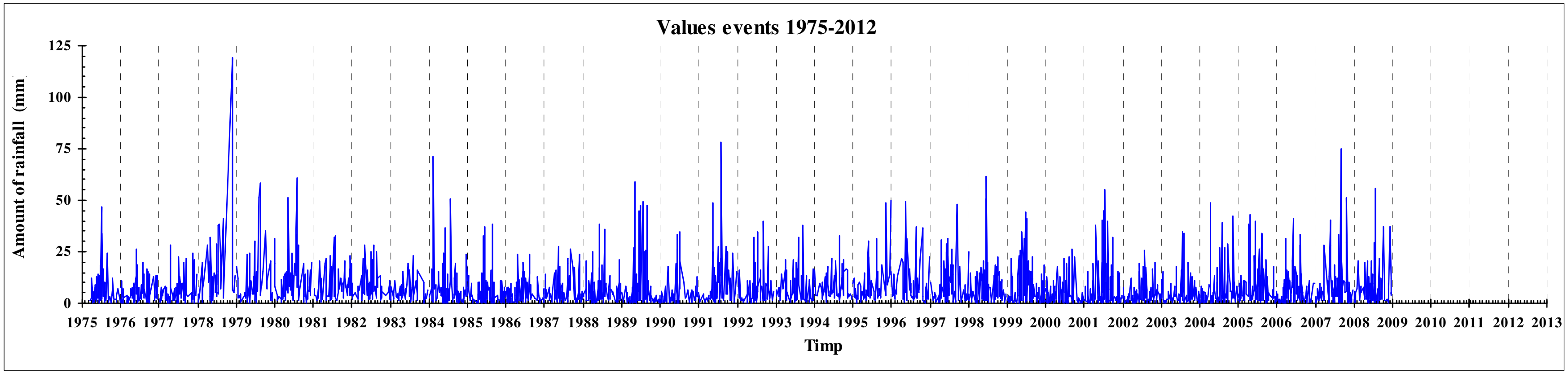

Fig. 18. The time series of the amount of rainfall for all the rainfall events in Cluj-Napoca during the 1975-2008 time period.

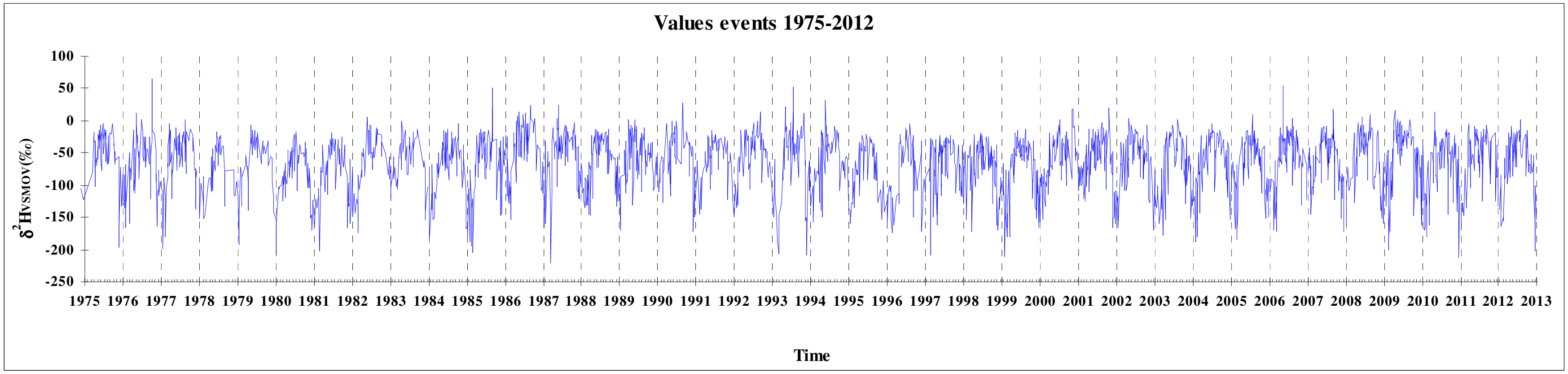

Fig. 19. The time series of the δ^2H values in all rainfall events in Cluj-Napoca during the 1975-2012 time period.

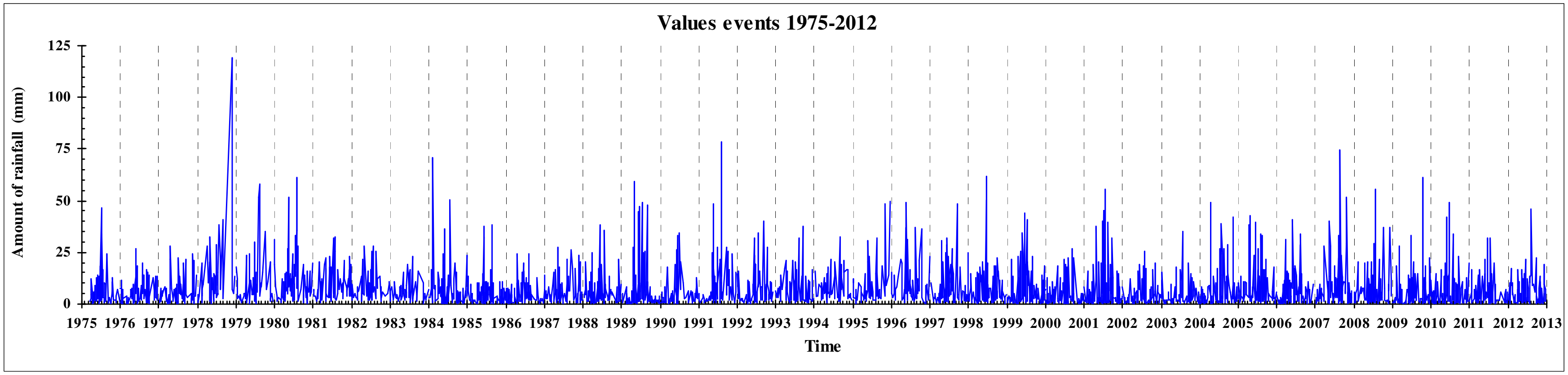

Fig. 20. The time series of the amount of rainfall for all rainfall events in Cluj-Napoca during the 1975-2012 time period.

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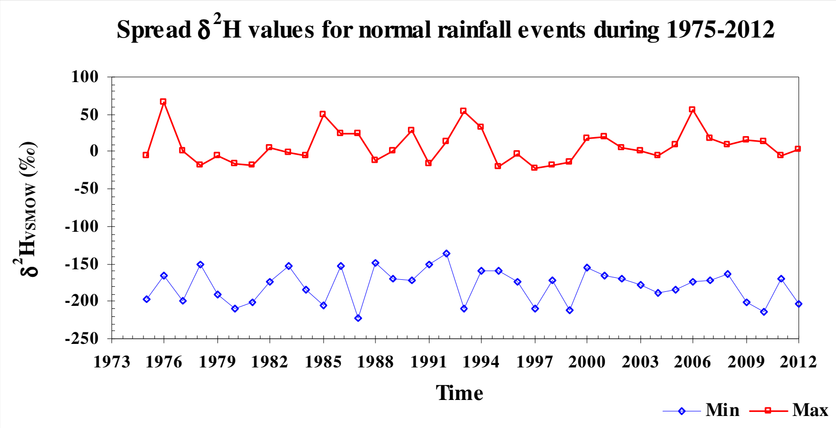


Fig. 21. The minimum and maximum δ^2H values recorded in annual rainfall events in the 1975-2012 time period.

The years for which the difference between the maximum δ^2H value and the minimum δ^2H value was bigger than were: 1976 (231,12‰), 1985 (255,52‰), 1987 (245,57‰), 1990 (200,31‰), 1993 (263,87‰), 2006 (227,80‰), 2009 (217,01‰), 2010 (227,37‰), 2012 (205‰). It is noticeable that, in the 1975-2012 time series, in 3 of the last 4 years big differences were recorded between extreme values, highlighting the growth of the frequency of appearance of extreme meteorological events. The 1975-2012 time series of the δ^2H values from all the rainfall events highlights the years with smaller differences between the extreme values (1978, 1983, 1988, 1991, 1992, 1995, 1998), when $\Delta(\delta^2H) <$ 150 ‰.

After 1990 the apparition frequency of the extreme rainfall events has grown, and thus recording more δ^2H values abnormal to the collecting period of the rainfall. After 1990 the global climate changes (**Fig. 22**) were highlighted in temperature variations of the global and local temperature and these were reflected very well in the values of the deuterium content in rainfall for the years 1991-1885 (**Fig. 23**).

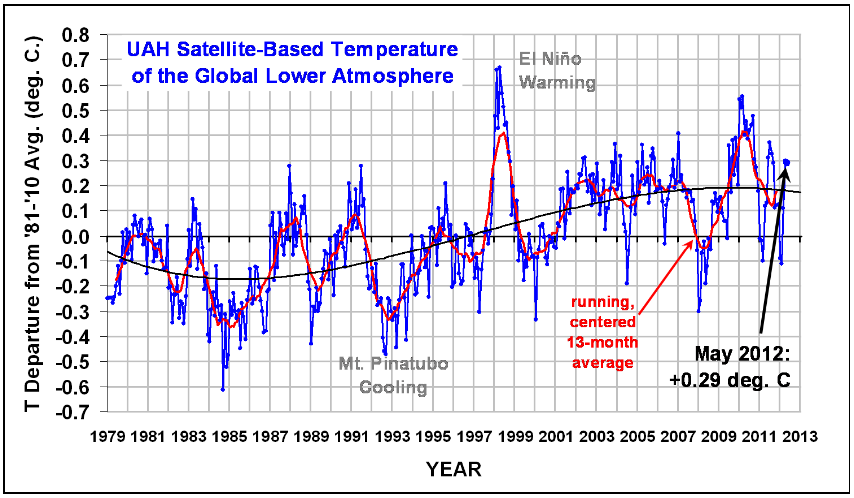


Fig. 22. The variation of the average global temperature in the atmosphere. [47].

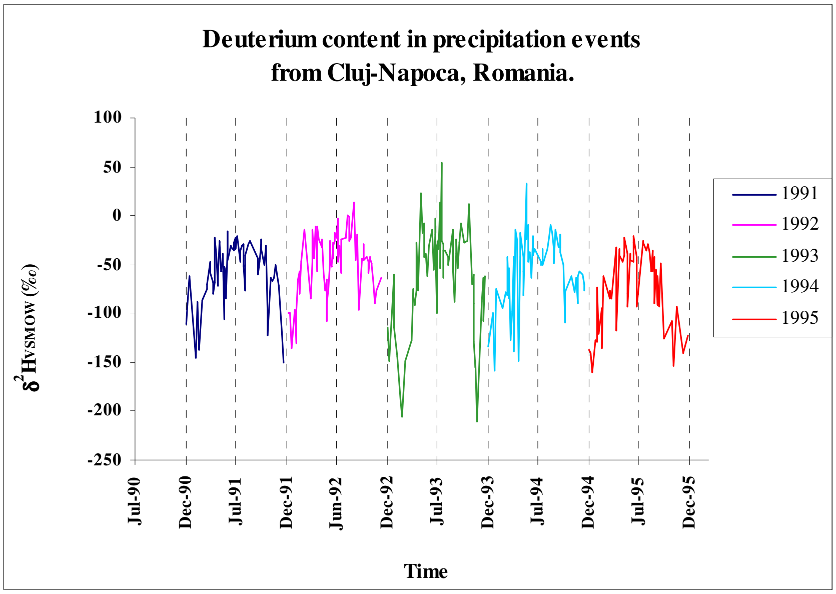


Fig. 23. The δ^2H values from rainfall events in Cluj-Napoca in the 1991-1995 time period.

Rainfall with δ^2H values typical to the cold season fell in the warm season, but alse rainfall with high δ^2H values, typical for the warm season were recorded in the cold season.

The correlation between the deuterium content in rainfall and the amount of rainfall for all the events in the 1975-2012 time's period is given in **Fig. 24**. The diagram shows that for local rainfall there is no correlation, the amount effect is not highlighted.

The δ^2H-temperature correlation for all the events in the 1975-2012 time period could not be established due to reasons concerning the accurate determination of the air temperature in the rainfall event.

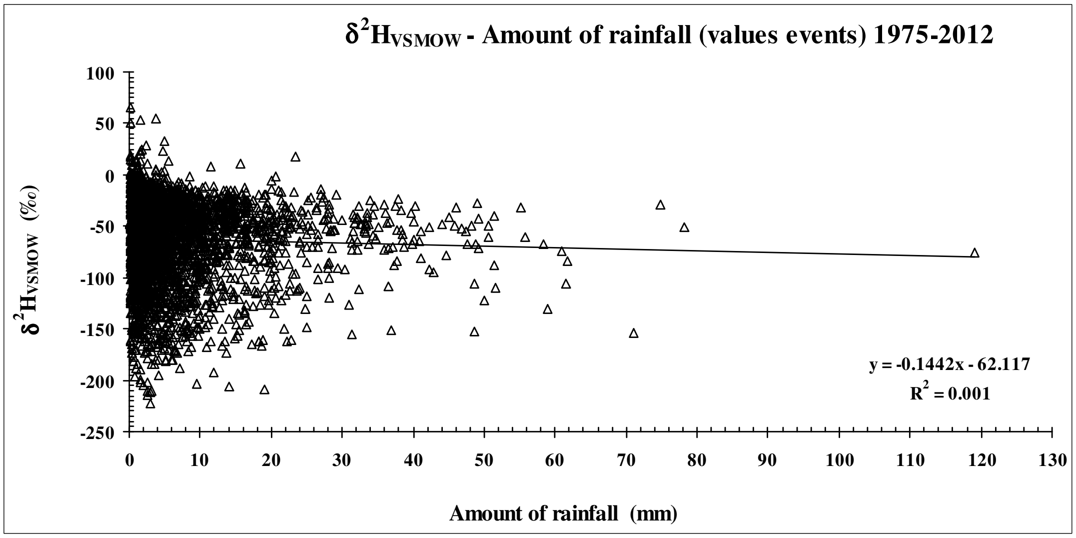


Fig. 24. δ^2H-amount of rainfall for the 1075-2012 time period.

4.2.2. The time serious of the weighted average δ^2H values in rainfall

4.2.2.1. Monthly averages

The variation domain of the weighted monthly average δ^2H values for the 1975-2012 period is between : -183,89 ‰ $< \delta^2$H $<$ -3,90‰.

For the 1975-2012 time periods the domain of the weighted monthly averages is the same, the last 4 years have not influenced the variation domain of the weighted monthly average δ^2H (**Fig. 25**)

The variation domain of the monthly average δ^2H values has a different magnitude for each month of the year: the amplitude of the spread of the average δ^2H is small in the summer months and large in the cold season months and the transitional period between seasons. (**Table 10**)

Table 10. The extreme monthly average values and the variability of the recorded values for the deuterium concentration in local rainfall in the 1975-2012 time period.

Month	Minimum δ^2H value(‰)	Maximum δ^2H value (‰)	Difference δ^2H value (‰)	The σ variability
January	-169,02	-61,61	107,41	26,66
February	-183,89	-55,50	128,39	27,36
March	-161,85	-35,86	125,99	27,02
April	-117,95	-26,58	91,37	21,16
May	-84,95	-24,50	60,45	17,84
June	-64,95	-12,89	52,06	13,08
July	-91,07	-25,94	65,13	13,56
August	-60,89	-18,28	42,61	10,86
September	-95,25	-3,90	91,35	20,57
October	-126,22	-12,58	113,64	26,42
November	-141,51	-7,61	133,90	23,87
December	-141,91	-54,93	86,98	22,58

From **table 10** and the chart in **Fig. 25** a small variability and variation of the deuterium concentration for the months June, July and August can be observed, which indicates a constant of the source of the rainfall front. The transition months between the seasons with extreme values April, May and September have a moderate variability of the deuterium concentration in rainfall, and the months belonging to the cold season (Jan., Feb., Mar., Oct., Nov. and Dec.) have a large variability of the deuterium concentration. The large variability of the deuterium concentration in the months belonging to the cold season (**Fig. 25**) indicates the fact that in the adjacent area to the collecting point of rainfall there are rainfall fronts from different directions, different influences, the N-W one (the north area of the Atlantic Ocean) with low values of deuterium and the S-W one (the mediterranean area) with high values of deuterium concentration.

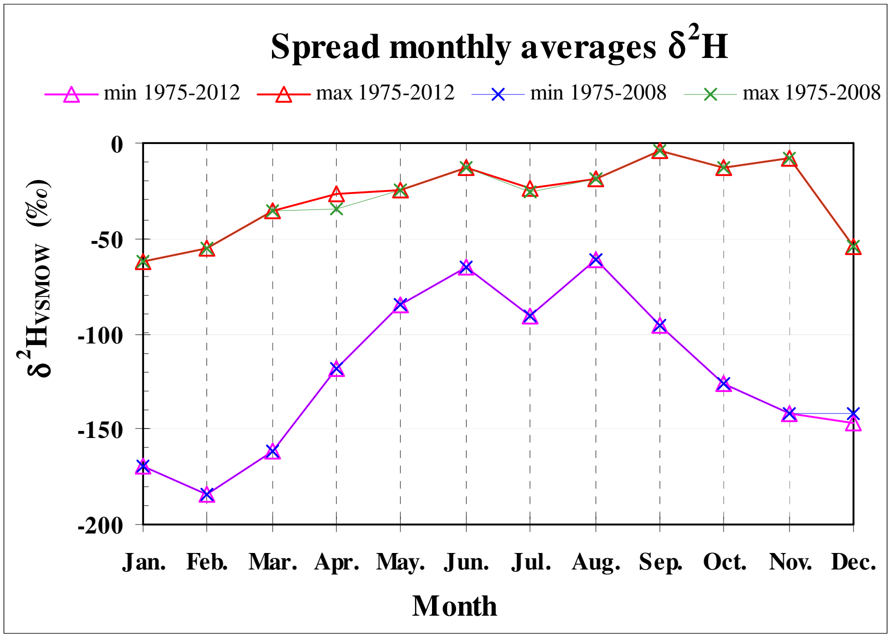


Fig. 25. The variation domain of the monthly average δ^2H values for rainfall in Cluj-Napoca.

The year 2009 from the last 4 years monitored was the year in which the variation domain of the monthly average values for the months April, July and December extended. Thus, for the entire monitored period, the average δ^2H values of -26,57‰ for April 2009 and of 23,24‰ for July 2009 have lifted the superior limit of the variation domain of the monthly averages for April and July, and the monthly average of December 2009 of δ^2H = -146,6‰ lowered the bottom limit of the variation domain (**Fig. 25**).

The variation domain of the multiannual monthly average δ^2H values for the 1975-2008 time period are between: $-119,31‰ < \delta^2H < -45,55‰$

For the 1975-2012 time period the variation domain of the multiannual monthly averages is : $-121,05‰ < \delta^2H < -45,00‰$

For the multiannual monthly average δ^2H values, the variation domain on the 1975-2012 intervals is slightly higher. The last 4 years have contributed to the movement of the bottom limit of the domain towards the negative values more than the movement of the higher limit towards the positive values. In the warm months δ^2H gas slightly higher values, in the cold months δ^2H has lower values (**Fig. 26**), which means in terms of phenomenology that, in the area around Cluj, the meteorological influences from the cold areas have been preponderant and more intense rather than those from warm areas.

The charts of the multiannual monthly averages (**Fig. 26, 27, 28**) and the time series of the monthly average values (**Fig. 29, 30, 31**) highlight very well the seasonal effect of the δ^2H values, of temperature and of the amount of rainfall, with high values in the warm season months and low values in the cold season months. The multiannual monthly average for δ^2H, temperature and amount of rainfall do not vary essentially for the two time intervals (1975-2008 and 1975-2012).

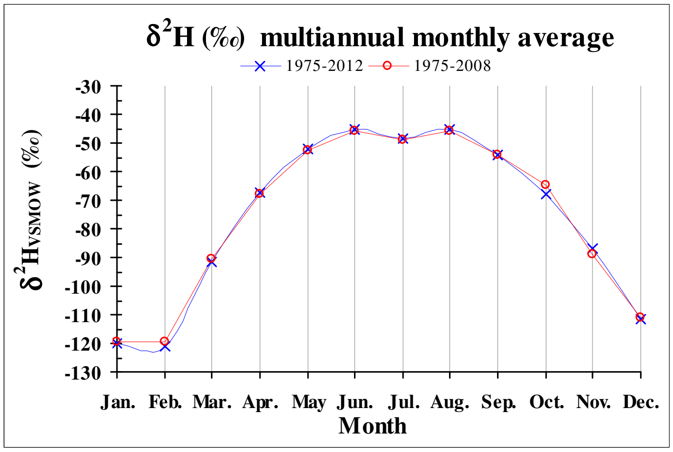


Fig. 26. The δ^2H values for the multiannual monthly averages recorded in rainfall from 1975-2008 and 1975-2012.

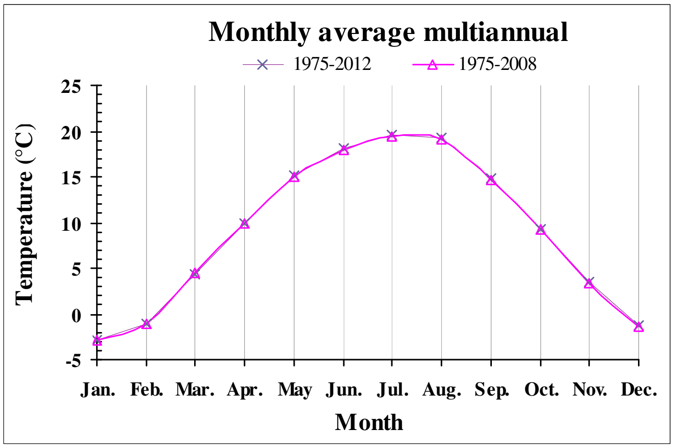


Fig. 27. The multiannual monthly averages of temperature for the 1975-2008 and 1975-2012 time periods.

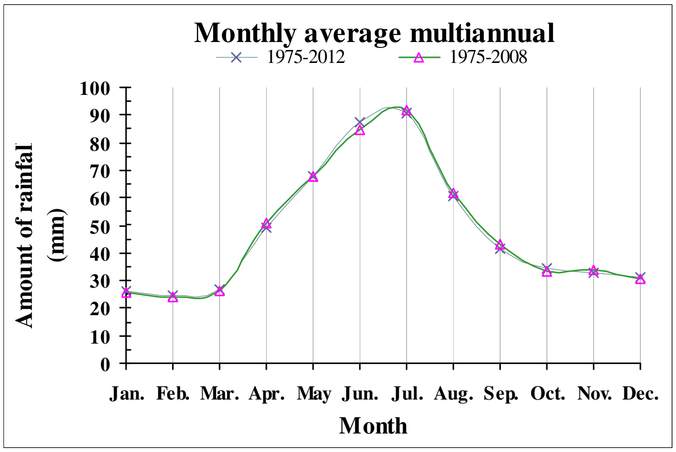


Fig. 28. The multiannual monthly average of the amount of rainfall for the 1975-2008 and 1975-2012 time periods.

The time series of the monthly average values (**Fig. 29, 30, 31**) highlight the months and the years in which the monthly averages present abnormal values, meaning the differences between the monthly averages and the multiannual averages are large.

The succession of maximum and minimum values follows the warm-cold succession of seasons. The profiles of the time series (**Fig. 29, 30**) highlight the fact that the monthly averages of δ^2H from rainfall do not always follow the evolutions of the monthly averages of local temperature, this being most likely because of the large share of extreme events (storms, ice, strong rainfall, very small amounts of rainfall during hot periods, rains in winter months). The extreme events usually have extreme δ^2H values and are not usually correlated to the local temperature, being due to the disruption of the atmospheric currents, but contributes to the weighted monthly δ^2H averages.

For the δ^2H monthly averages, in the cold season, the time series (**Fig. 29**) presents, with a cyclicity of a few years, minimum values situated under the multiannual monthly average. Usually, the lowest δ^2H monthly minimums correspond to the colder winters, with time intervals (longer or shorter) in which the temperatures were very low. Compared to the multiannual monthly δ^2H values, rainfall in the cold season, very depleted in deuterium from Jan. ’80, Jan. ’85, Dec. ’91 – Jan. ’92, Feb. ’93, Dec. ’99 – Jan. ’00, Jan. ’02, Feb. ’03, Jan. ’04, Jan. ’11 and Feb. ’12 correspond to the months with average temperatures lower than the multiannual average, these rainfalls presenting δ^2H values preponderantly correlated with the local condensation temperature. δ^2H minimums were recorded far below the multiannual average, and in other years, the local average temperature was not lower than the multiannual average (Jan.´81, Feb.´84, Jan.´89, Mar.´96, Feb.’´99, Feb.´09), the δ^2H values being preponderantly due to the discharge or the moist masses of air having a polar origin.

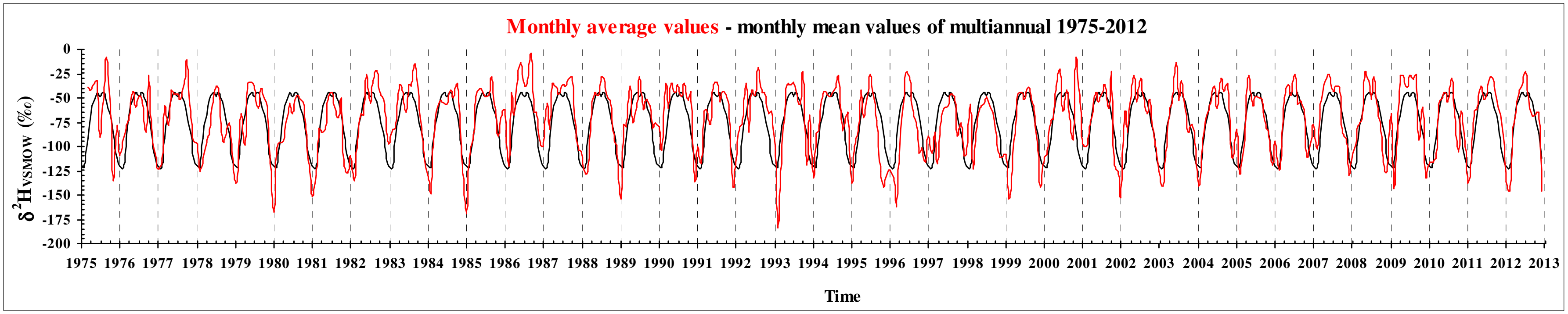


Fig.29. The monthly average δ^2H values compared to the multiannual weighted average values for the 1975-2012 time period.

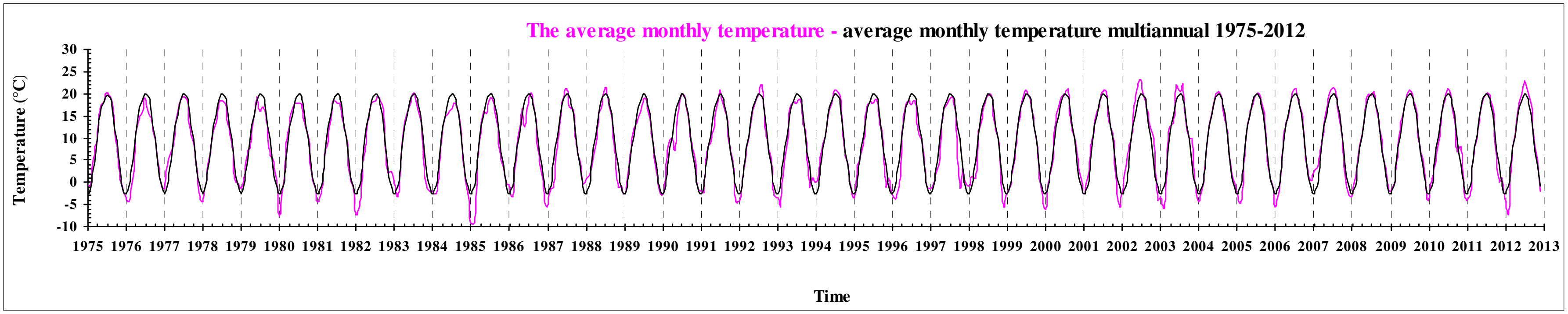


Fig. 30. The values of the monthly average temperature compared to the multiannual monthly values for the 1975-2012 time period.
(Data obtained from the meteorological station at the University of Agricultural Sciences and Veterinary Medicine Cluj-Napoca and [38, 39]).

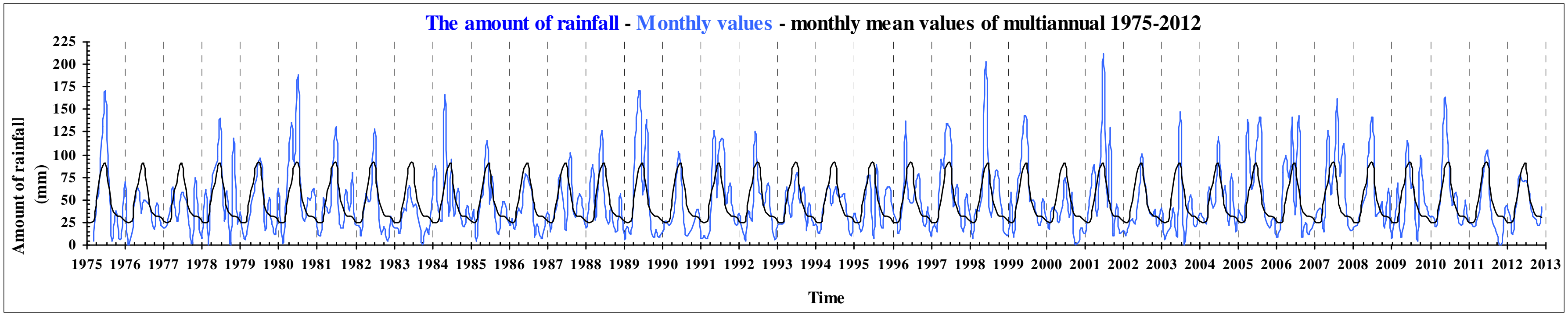


Fig. 31. The values of the amount of monthly rainfall compared to the multiannual average values for the 1975-2012 time period.

The winter monthly δ^2H averages with the highest values and which follow the evolution of the temperature correspond to the ‘82/′83, ′89/′90, ′96/′97, ′97/′98, ′00/′01, ′06/′07 winters. In these months the polar influences were minimal.

The δ^2H monthly averages for the warm season months present variations of different magnitudes from the multiannual averages. The δ^2H monthly average values for the summer months larger than the multiannual average and in correlation with the monthly temperature are recorded in the years with the hottest July months, which were , 1988, 2002, 2007, 2012, those without a clear correlation in the 1991-1996 period, which presented large variations of the temperature at la global level (**Fig. 22**), and after 2008 the δ^2H monthly average for the warm season were generally larger than the multiannual averages, which lead to a slight increase of the multiannual average of the summer months for the 1975-2012 time period, compared to the multiannual average for the 1975-2008 time period.

For the summer months, the δ^2H monthly averages which have the closest or the smallest values to the multiannual averages are recorded in the years with temperature values close to the multiannual averages (most frequently below these values) and with amounts of rainfall larger than the multiannual average (the rainy summer from 1975, 1978, 1980, 1981, 1984, 1989, 1997, 1998, 1999, 2001). For these periods the amount effect is obvious, compared to the rest of the monitored period.

<u>In the last 4 years</u> of the time series the δ^2H monthly averages for the warm season were larger than the multiannual average, but, the causes of these values are not because of the local condensation temperature of the air humidity, but rather because of the phenomena that caused movements of the hot and wet air masses from the mediterranean basin towards the N-E continental part of Europe. In this period the extreme meteorological phenomena had a larger frequency and variability of the intensity of the rainfall events, with the result being the δ^2H in rainfall did not follow strictly the temperature correlation.

Vladimir Petoukhov [44] explains the mechanism of the extreme events and the prolonged periods of warmth or cold as being due to the global warming, which is not uniform on Earth. The growth of the temperature in the polar areas amplifies the snow and ice losses which reduces the temperature differences between the Arctic area and Europe, which affects the air flux around the planet, whose driving force is the temperature difference.

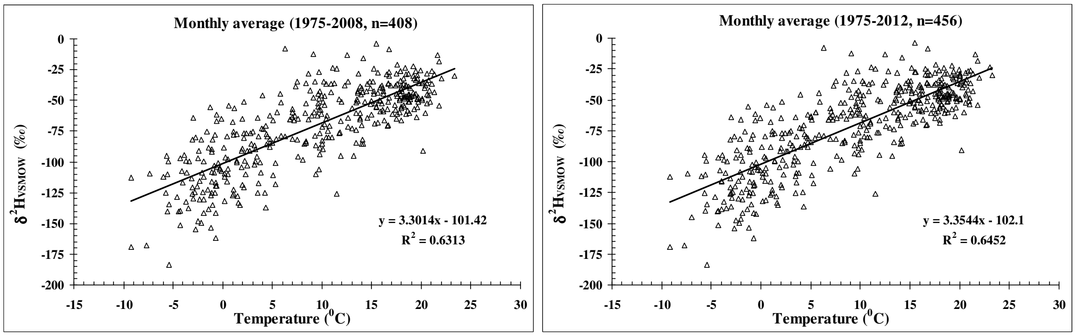


Fig. 32. The correlation of the δ^{2}H monthly average values – temperature for two time periods.

- The slopes of the regression lines show a change from larger values of 4,5‰ / °C to ~1‰ / °C for the local average temperatures of the air lower than 5°C respectively larger than 15°C. The larger slopes in the months with lower temperatures are due to a larger degree of rainfall of atmospheric moisture [36] and a substantial snow contribution which is accompanied at its formation by a isotopic fractionation effect which has a isotopic fractionation factor higher at lower temperature compared to the one at temperatures over 10°C.
- The δ^{2}H – temperature correlation (**Fig. 32**) for all the monthly average values (408 or 456 pairs of values) is good, the value of the slope is 3,30‰ / °C for the 1975-2008 period and 3,35‰ / °C for the 1975-2012 period, slopes close to the theoretic value of $\Delta\delta^{2}H/\Delta T=3$‰/°C [48]. The results for rainfall in Cluj-Napoca are very close to the values recorded on long term for rainfall in the central area of Switzerland for which was found $\delta^{2}H = 3.27*T-102.7$ [49] compared to the results in this thesis $\delta^{2}H = 3.35*T-102.1$, the period we monitored having data even after 2000 opposed to the data for Switzerland.
- For all the analyzed period (**Fig. 32**) the last 4 years have contributed to a slight increase of the slope and the correlation coefficient for the regression line δ^{2}H – Temperature of the monthly average values.
- The correlation of the multiannual monthly averages (**Fig. 33**) highlights the fact that at a large time scale the averaged values diminish the variations of the processes and increase considerably the correlation coefficient. The slope of the regression line is slightly larger than of the monthly averages and does not differ significantly for the two time periods. The correlation coefficients are close to 1, an almost perfect correlation.

The charts in **figures 33** and **34** highlight a positive correlation between the δ^{2}H monthly averages and the amount of rainfall, accordingly to the configuration of the time series (**Fig. 29, 31**) and to the multiannual monthly averages (**Fig. 26, 28**) for δ^{2}H and the amount of rainfall. For the multiannual monthly averages the correlation coefficients of the regression line δ^{2}H – amount of rainfall are large, compared to those of the regression line for the monthly average values. For Cluj-Napoca, an area with temperate continental climate, the amount effect is not highlighted.

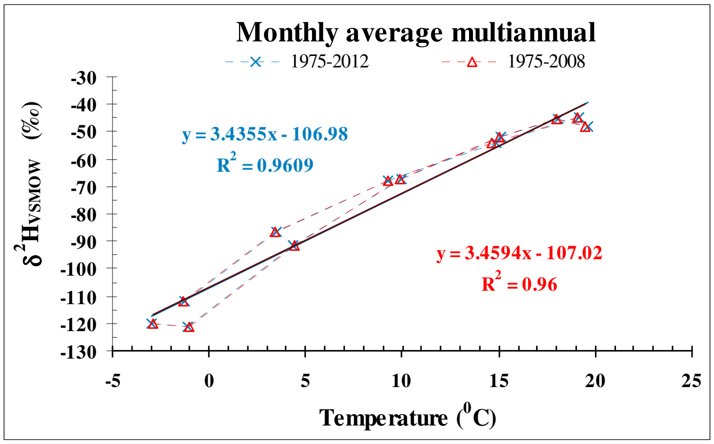


Fig. 33. The correlation of the multiannual monthly δ^2H averages – temperature for two time periods.

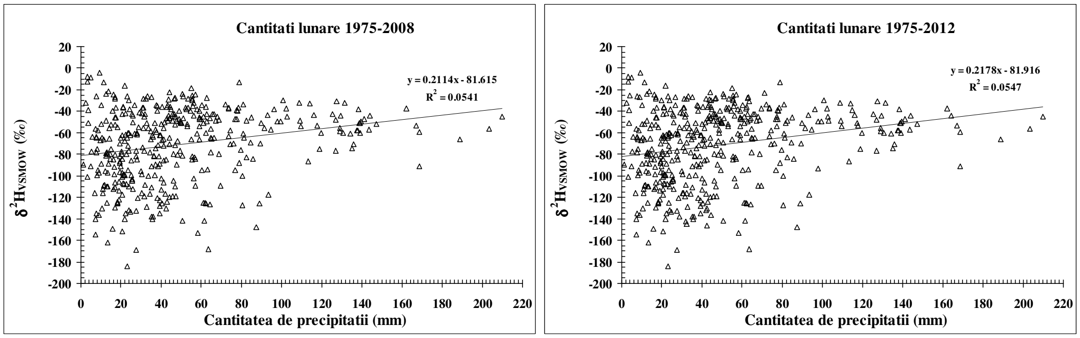


Fig. 34. The correlation of the δ^2H monthly average values - amount of rainfall for two time periods.

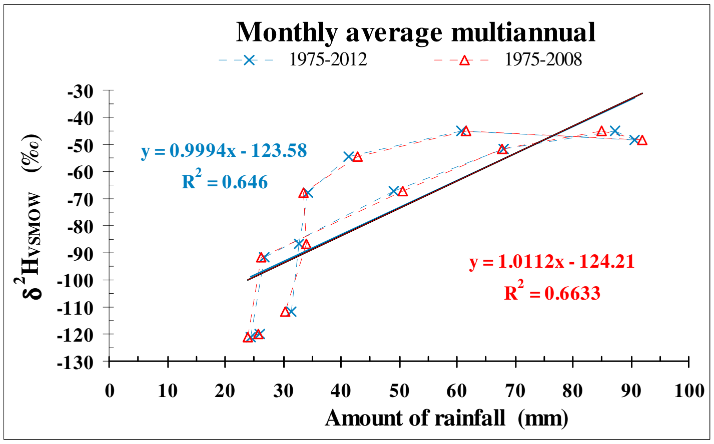


Fig. 35. The correlation of the multiannual monthly δ^2H averages – amount of rainfall for two time period.

4.2.2.2. Annual averages

The values of the annual average of the deuterium content in rainfall, temperature and amount of rainfall in Cluj-Napoca are represented in **figures 36, 37** and **39**, and the correlations between these parameters in **figures 40** and **41**. All the charts in **figures 36, 37** and **39** highlight a slightly growing trend of the annual average values for δ^2H, amount of rainfall, and temperature, but the variations from one year to another have a random character.

The variation domain of the δ^2H annual average values for the 1975-2008 period are between -85,59‰ $< \delta^2H <$ -45,52‰ and the variation domain of the annual average δ^2H of the same, in the last 4 years the annual δ^2H average having a small variation around the value of -64,55‰.

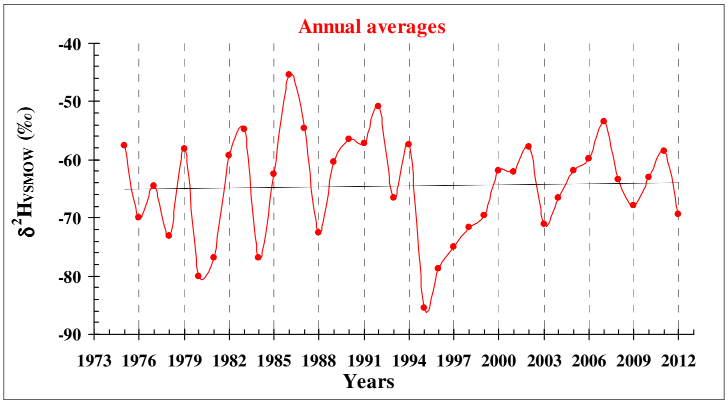


Fig 36. The annual averages for δ^2H from rainfall in Cluj-Napoca during the 1975-2012 period.

A large δ^2H annual average value shows us that the year was a year with rainfall from areas where the evaporation temperature of water is higher and/or local temperatures higher than normal, a year with annual average δ^2H values lower shows us that the year was a year with rainfall from areas where the evaporation temperature of water is lower and/or local temperature lower than normally.

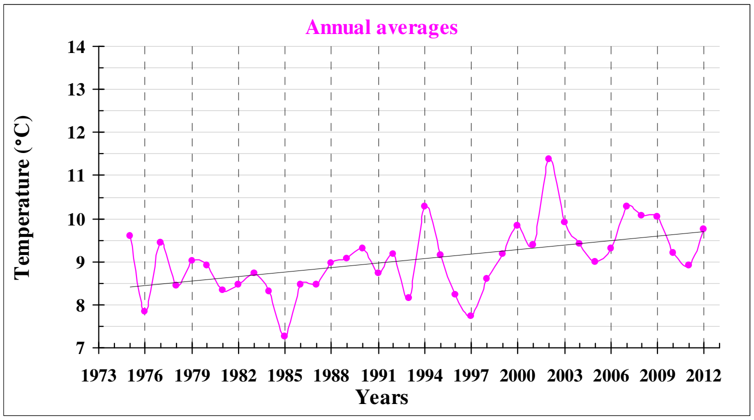


Fig. 37. The average year temperature in Cluj-Napoca.

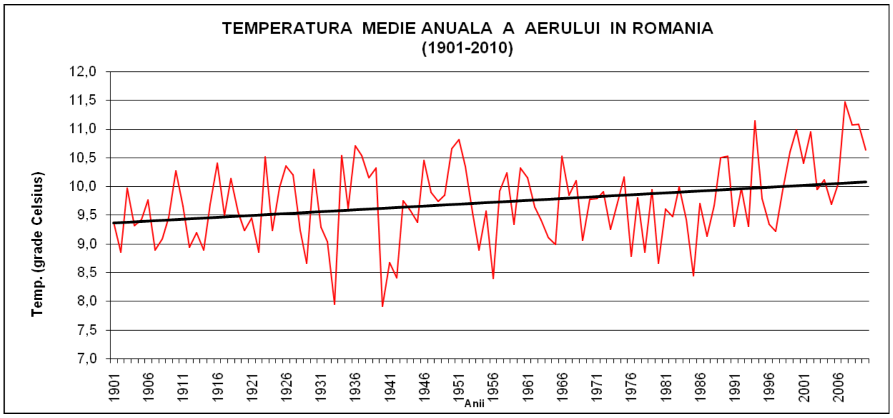


Fig. 38. The average temperature of the year for Romania [50]

From **figures 37** and **38** it can be observed that for the 1975-1988 periods there were alternations of hotter years with colder years but with a constant general tendency. For the 1988-1992 periods the variations from one year to another have been minor with a slight tendency of warming. In the 1992-1997 periods we had again an alternation of hotter years with more colder years, but this time a quite pronounced general cooling tendency appears. From 1997 until 2002 there is no alternation of hotter years with colder years, but a quite strong tendency of continuous warming, and then in 2003 the annual temperature variations are lower and have a warming tendency.

In terms of amount of rainfall in the time interval from 1975 to 2012 it can be observed that until 1991 there is an alternation of years with quantitatively more significant rainfall (over 500 mm) and more drought years 1983, 1986 and 1990 whose average does not exceed 378 mm. The 4 year period (1992-1995) is a time interval in which the annual average of rainfall is almost constant and at a low level. From 1996 the year alternation comes back with weak quantitative precipitations and years with quantitatively more average amounts with a slight tendency of growth of the annual average amount of rainfall. The year 2011 is a part of the series of years with low amounts of rainfall (448.3 mm). The multiannual average value of the amount of rainfall on the 1975-2012 time interval is 572,57 mm.

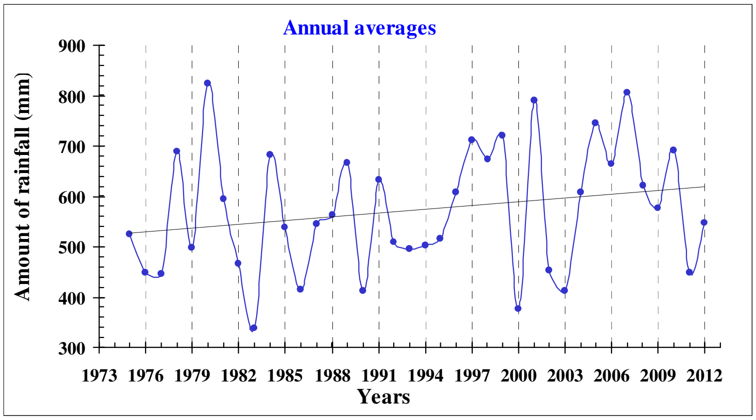


Fig. 39. The annual amounts of rainfall in Cluj-Napoca.

Between the annual δ^2H average values and temperature, respectively the annual δ^2H average values and amount of rainfall there is no correlation (**Fig. 40, 41**).

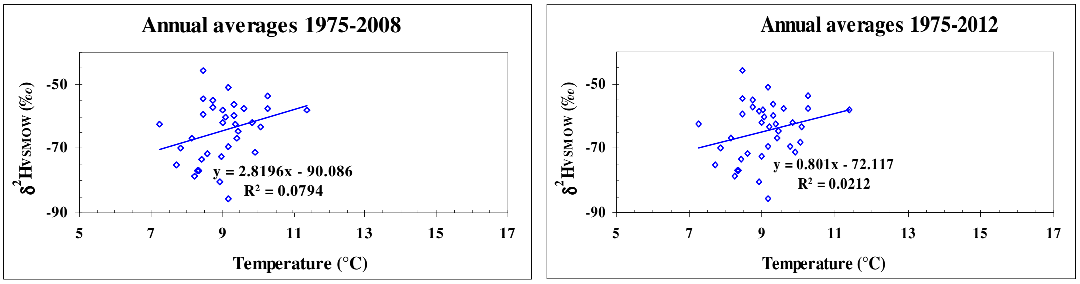


Fig. 40. The relation between δ^2H and temperature for the annual average values.

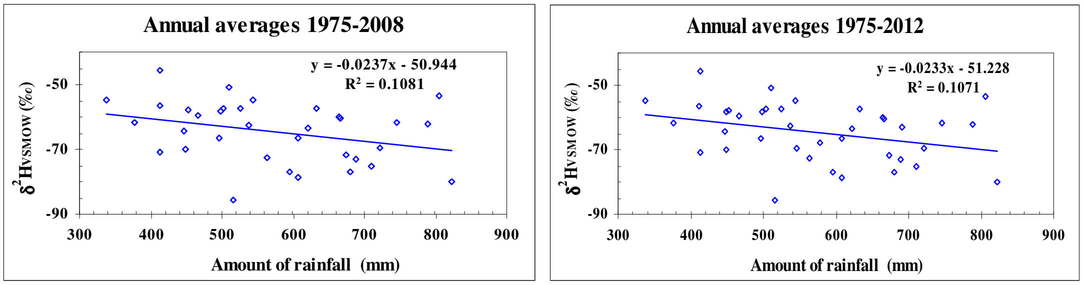


Fig. 41. The relation between the annual average δ^2H values and the annual average amount of rainfall.

For such a database to be used for climatic prognosis over average periods (from a few months to a year) it necessary to find some rigorous criteria for establishing the similarity with the former years. Also it is necessary to establish what the precise cyclicity of the major climatic factors is. The purpose of such a database is to make available for scientists an overview of past climatic evolution, to find clear similarity and cyclicity criteria's. When these goals will be achieved then we will have the efficient instruments for climatic forecasts which will cover periods of around one year and which will have a high degree of certainty.

Table 11. The values of the variation domain of the δ^2H values.

	The events		Monthly average		Monthly average multiannual		Annual averages	
	Min	**Max**	**Min**	**Max**	**Min**	**Max**	**Min**	**Max**
1975-2012	-221,88	65,74	-183,89	-3,90	-121,05	-45,00	-85,59	-45,52
Estimate maps [42]			-102	-30	-102	-30	-78	-54

Table 12. The values of the variation domain of the multiannual monthly average δ^2H values (‰).

	Data recorded 1975-2012		**Estimates of** [42]	
	minim	**maxim**	**minim**	**maxim**
January	-169,02	-61,61	-102	-78
February	-183,89	-55,50	-102	-78
March	-161,85	-35,86	-78	-54
April	-117,95	-26,58	-78	-54
May	-84,95	-24,50	-78	-54
June	-64,95	-12,89	-54	-30
Julie	-91,07	-23,24	-54	-30
August	-60,89	-18,28	-54	-30
September	-95,25	-3,90	-78	-54
October	-126,22	-12,58	-78	-54
November	-141,51	-7,61	-102	-78
December	-146,60	-54,53	-102	-78

Table 13. The multiannual monthly average values for δ^2H (‰) for the 1975-2012 period.

	Data recorded 1975-2012	**Estimates of** [42] **(median interval)**	**Estimates of** [43]
January	-120,03	-90	-80
February	-121,05	-90	-79
March	-91,62	-66	-63
April	-67,16	-66	-56
May	-51,91	-66	-46
June	-45,20	-42	-44
Julie	-48,18	-42	-36
August	-45,00	-42	-38
September	-54,24	-66	-46
October	-67,66	-66	-53
November	-86,81	-90	-70
December	-111,82	-90	-78

Table 14. The δ^2H values in rainfall at 46° latitude, 23° longitude, 360 m altitude: (CLUJ-NAPOCA) the annual average on long term.

	$\delta^2H_{V\text{-}SMOW}$ (‰)
1975-2012	-65,17
Estimates of [42]	-66,00
Estimates of [43]	-54,00

Comparing the data in **tables 11, 12, 13** and **14** for the δ^2H values in all rainfall in Cluj-Napoca in the 1975-2012 period, with the estimated data from maps and calculation programs based on global data recorded and interpolated, it can be observed that the minimum values of the isotopic composition recorded in Cluj-Napoca are more isotopically depleted, and the maximum values are more enriched isotopically than the values obtained from estimates. Only the annual average value on long term is close to the close to the isotopic value obtained from the isotopic maps. This highlights the fact that the continuing of these isotopic measurements is necessary in Cluj-Napoca, in order to have a more accurate estimate in meteorology, hydrology, hydrogeology, dendrology, agronomy, glaciology, paleontology studies which use the stable isotopes of water as natural tracers. These studies are necessary because the method brings an extra contribution in developing the scientific knowledge and/or validating some theories where classic study methods are limited. The data will need to be introduced in the scientific circuit and in the isotopic database of AIEA Vienna in order to be considered in creating calculating programs used for interpolating isotopic data which leads to the increase of the confidence degree of the isotopic maps for Europe.

4.3. THE CORRELATION OF THE δ^2H-δ^{18}O VALUES FROM ATMOSPHERIC HUMIDITY WITH LOCAL RAINFALL

The study of the isotopic composition of atmospheric humidity brings new information concerning the travel routes of water and the major changes of ongoing parameters of processes in which water participates in the atmosphere-soil-vegetation continuum.

The collection of the atmospheric humidity was done in the same perimeter with the rain gauge destined for collecting rainfall, and the time interval in which the collection was made was daily from Monday until Friday and corresponds to the collection period from May 2010 until December 2011, with the exception of vacations and legal holidays. In the same period rainfall was collected, according to collection program for rainfall. A number of 373 samples of humidity were collected, and the number of rainfall events in the monitored period is 153.

The analysis of the isotopic composition (δ^2H and δ^{18}O) for the time interval mentioned before shows what are the variation domain, the short term variations, the correlations between the isotopic values and other parameters, for humidity as well as for rainfall.

The variation domains of the δ^2H and δ^{18}O values from the humidity and rainfall samples collected in the monitored period are:

$-205{,}0‰ < \delta^2H_{umid} < -50{,}4‰$ $-34{,}1‰ < \delta^{18}O_{umid} < -0{,}20‰$

$-213{,}7‰ < \delta^2H_{precip} < -5.0‰$ $-28{,}3‰ < \delta^{18}O_{precip} < -0{,}57‰$

and the average values are:

$$\delta^2H_{umid} = -111{,}9‰ \qquad \delta^{18}O_{umid} = -17.9‰$$

$$\delta^2H_{precip} = -57{,}6‰ \qquad \delta^{18}O_{precip} = -8{,}3‰$$

The average δ^2H and $\delta^{18}O$ values for atmospheric humidity are much lower than the values for rainfall, but the variation domains are not bounded one by another, as there is no δ^2H and $\delta^{18}O$ value interval which could separate both domains during the entire monitored period.

The time series for the δ^2H and $\delta^{18}O$ values from humidity and rainfall are shown in **Fig. 42**, and for the monthly averaged values are shown in **Fig. 43**. It is found that the profile of the variation of the isotopic composition of rainfall follows the variation profile of the isotopic composition of humidity, but is delayed with at least 24 hours from the humidity (**Fig. 42**), meaning, isotopically depleted/enriched rainfall falls after a while from the collection of humidity with low/high values, the rainfall front being delayed from the atmospheric front of the air masses.

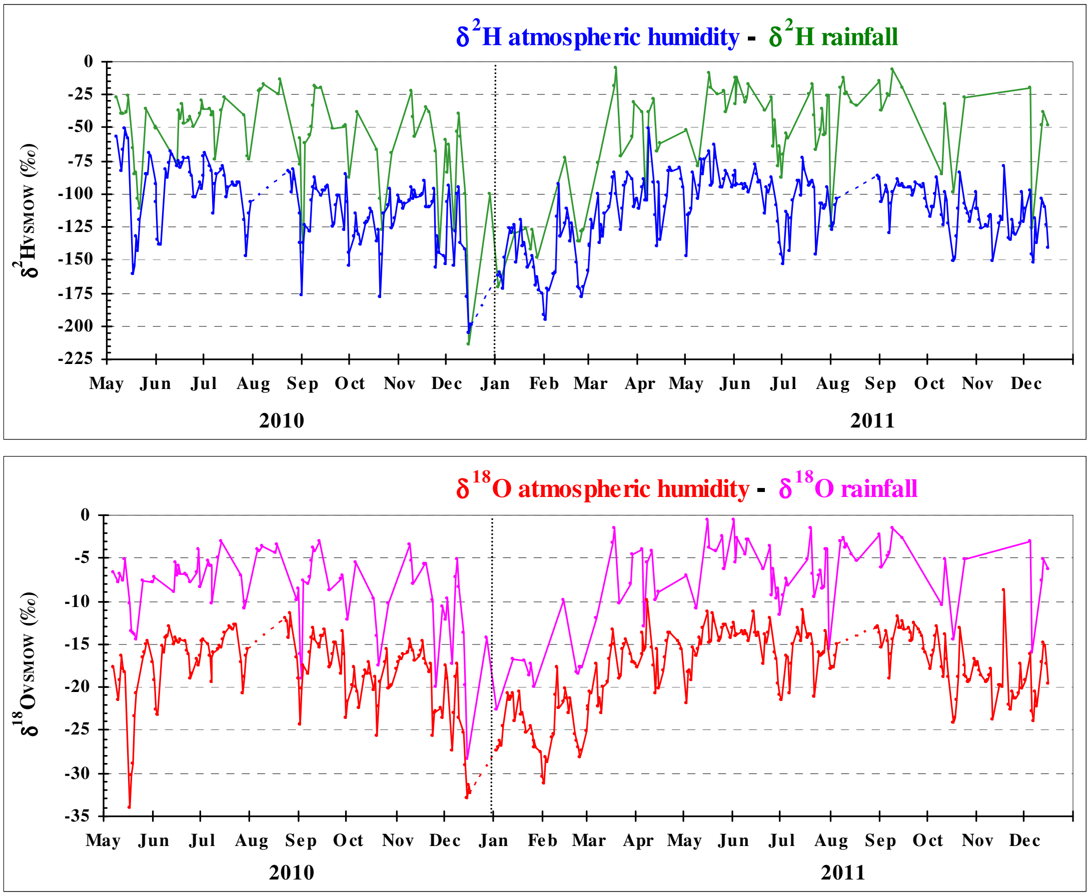
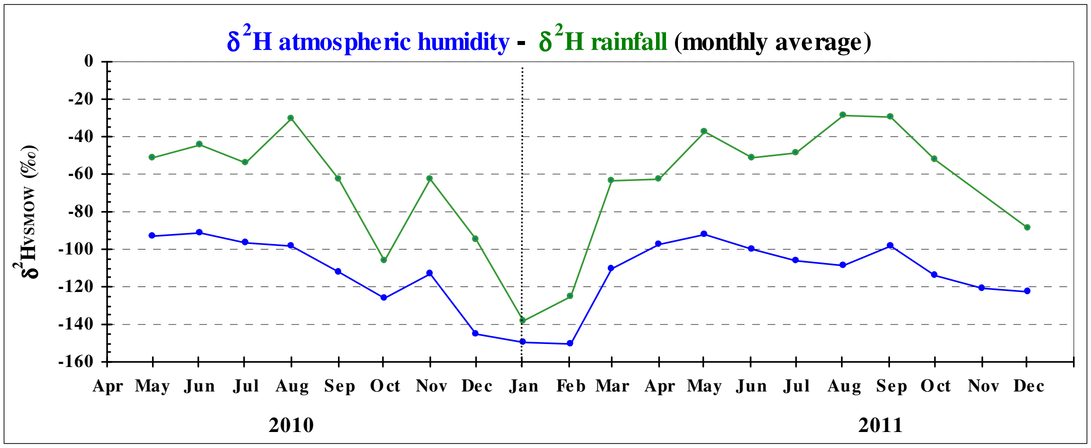


Fig. 42. The variation of the isotopic composition of atmospheric humidity and rainfall recorded during May 2010 until December 2011

The isotopic composition from humidity samples presents lower δ^2H and $\delta^{18}O$ values (an isotopic depletion) compared to the δ^2H and $\delta^{18}O$ values recorded for rainfall in the same period, according with the theory. On one side we have an isotopic depletion process of water left in clouds (vapors) after their discharge on the movement course of the atmospheric front (condensation process), the loss of water caused by the adiabatic cooling of the wet air masses leads to a progressive depletion of the heavier isotopes from the remaining water vapors, which can be described through the Rayleigh condensation formula. On the other side the atmospheric vapors are subjected to evaporation and/or mixing processes with the local sources of humidity as the atmospheric fronts advance towards the continental part of Europe. Both processes lead to the same result: the isotopic depletion of the atmospheric vapors on the travel route of the atmospheric fronts. In the monitored period a single exception was highlighted from this rule: a rainfall event in December 2010 (15.12.2010) presents a deuterium content of δ^2H_{precip}= -213,7‰ which is smaller than the deuterium content from the atmospheric humidity (δ^2H_{umid}= -205,0‰). This can be due to the incomplete isotopic exchange between the snow flakes and the isotopic humidity at soil level [51]. The daily variations of the isotopic composition of atmospheric humidity (variation of the isotopic composition of air humidity at a small time scale) show that the atmospheric fronts have steep changes in the movement direction, and the much lower δ^2H and $\delta^{18}O$ values recorded in humidity show atmospheric fronts from the NW direction.



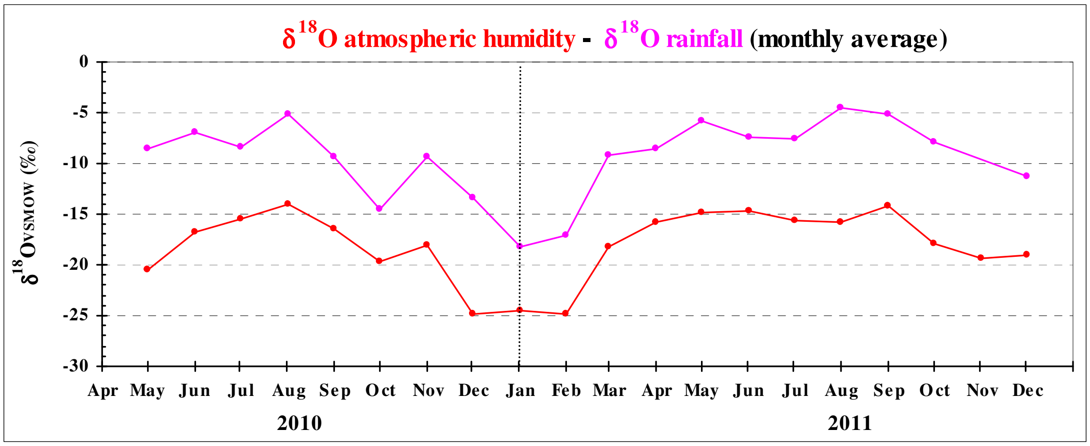


Fig. 43. The variation of the δ^2H and $\delta^{18}O$ monthly average values for atmospheric humidity and rainfall in the May 2010 – December 2011 period.

The profile of the δ^2H and δ^{18}O monthly averages for the atmospheric humidity follows very well the profile of the δ^2H and δ^{18}O monthly averages from rainfall in Cluj-Napoca in the May 2010 – Dec. 2011 time interval (**Fig. 43**).

The charts highlight the seasonal effect of the isotopic composition and the fact that the difference between the deuterium concentration from humidity and rainfall ($\Delta\delta^2$H) recorded in the winter months presents smaller values ($\Delta\delta^2$H ~ 30‰) than in the summer months when this difference is large ($\Delta\delta^2$H ~ 60 ‰). This is due most likely to the proximity towards the balance of the evaporation-condensation processes in the cold period, when the atmospheric humidity has low values and all the processes take place away from the balance between the two phases: vapors and liquid. Not the same thing can be said about oxygen 18, the difference between the oxygen 18 content from humidity and rainfall is approximately the same during the whole year ($\Delta\delta^{18}$O ~ 10 ‰). The δ^{18}O values determined for humidity and rainfall in the winter months present the same differences as in the summer months, this being due (most likely) to the isotopic exchange between nthe water vapors and the carbon dioxide released in the atmosphere by anthropogenic activities (the combustion of hydrocarbons for warming homes). In the summer, the isotopic exchange between the CO_2 in the atmosphere and the rainfall water more enriched in oxygen 18 transfers to the carbon dioxide the heavier isotope of the oxygen, this way the $\Delta\delta^{18}$O difference remains the same. The isotopic exchange of oxygen between CO_2 and H_2O is initially very fast, with an exchange rate of over 50% in the first half hour [52], deuterium being a more conservative tracer compared to oxygen.

From the data set of δ^2H and δ^{18}O values of atmospheric humidity and rainfall the following correlations can be made between the pairs of values.

$\delta^2H_{umid} - \delta^{18}O_{umid}$,	$\delta^2H_{precip} - \delta^{18}O_{precip}$
$\delta^2H_{umid} - \delta^2H_{precip}$,	$\delta^{18}O_{umid} - \delta^{18}O_{precip}$
δ^2H_{umid} – Temp	$\delta^{18}O_{umid}$ – Temp.
δ^2H_{umid} – Rh	$\delta^{18}O_{umid}$ – Rh.

From the δ^2H – δ^{18}O (**Fig. 44, 45**) correlation we obtain the parameters of the local meteoric lines (LMWL) which give indications about the processes which take place along the transport of the wet air masses.

The equations of the correlations lines for the δ^2H – δ^{18}O (LMWL) values in humidity and rainfall samples collected in the May 2010 – Dec. 2011 period are:

$$\delta^2H_{umid} = 5{,}61 * \delta^{18}O_{umid} - 10{,}92 \qquad R^2=0{,}8134$$

$$\delta^2H_{precip} = 7{,}67 * \delta^{18}O_{precip} + 6{,}23 \qquad R^2=0{,}9743$$

The local meteoric line of humidity has a smaller slope and the ordinate at origin is negative compared to the local meteoric line of rainfall (LMWL) for the same monitoring period, the smaller slope for humidity being due to the evaporation process of atmospheric humidity along the course of the atmospheric front. In **Fig. 44** are highlighted well the lower δ^2H and $\delta^{18}O$ values of humidity compared to those of rainfall, and the slopes of the distinct meteoric lines.

The equation of the local meteoric line of rainfall (LMWL) for monthly average δ^2H and $\delta^{18}O$ values is:

$$\delta^2H_{precip} = 8{,}06*\delta^{18}O_{precip} + 10{,}90 \qquad R^2=0{,}9892$$

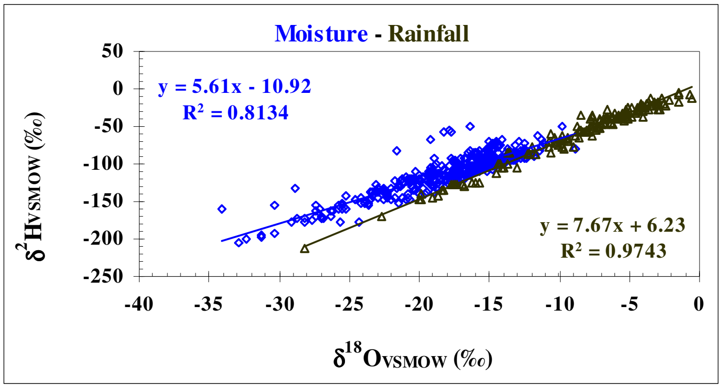


Fig. 44. The $\delta^2H – \delta^{18}O$ (LMWL) correlation for atmospheric humidity (n=373) collected and for rainfall events (n=153) in the May 2010 – December 2011 period.

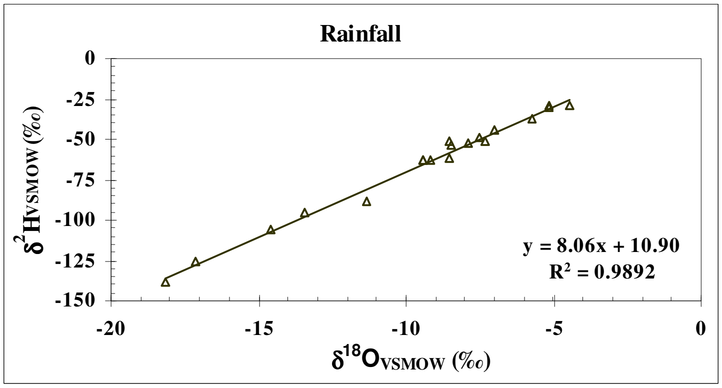


Fig. 45. The $\delta^2H – \delta^{18}O$ (LMWL) monthly average correlation from rainfall collected in the 2010 – 2011 period.

Compared to the local meteoric line for the weighted monthly average values of rainfall there is a difference of slope due to the isotopically high concentrations of light rainfall (small amounts of rainfall : in 18.03.2010the δ^2H= -13‰, $\delta^{18}O$= -3,5‰ values in amount of 0,2 mm; 13.09.2010 the δ^2H= -19,2‰, $\delta^{18}O$= -3,13‰ values in amount of 0,4 mm; 16. 05.2011 the δ^2H= -8,3‰, $\delta^{18}O$= -0,64‰ values in amount of 0,8 mm; 09.09.2011 the δ^2H= -6,5‰, $\delta^{18}O$= -1,53‰ values in amount of 0,1 mm). The local meteoric line for the monthly averages of rainfall has almost identical parameters with Craig's line parameters (GMWL), this being due to the evaporation – condensation processes that took place in balance conditions in the monitored period.

The relation between the isotopic composition and temperature is shown in **figures 46** and **47** and the one with humidity in **Fig. 48**.

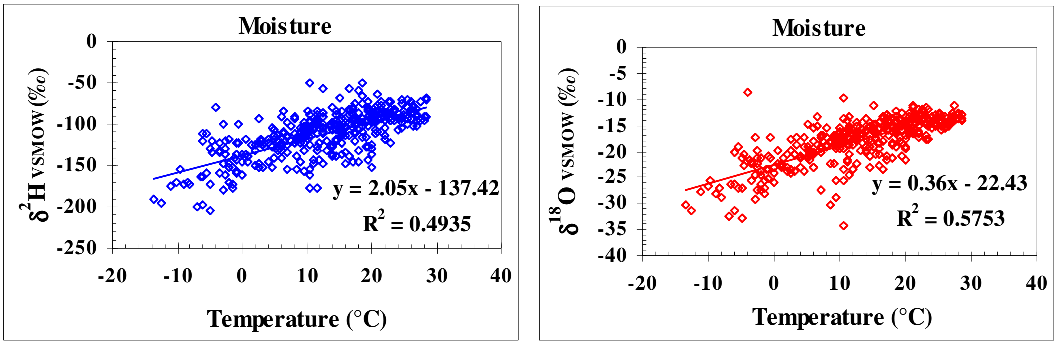


Fig. 46. The relation between local temperature and isotopic composition of atmospheric humidity collected in the March 2010 – December 2011 period n=373.

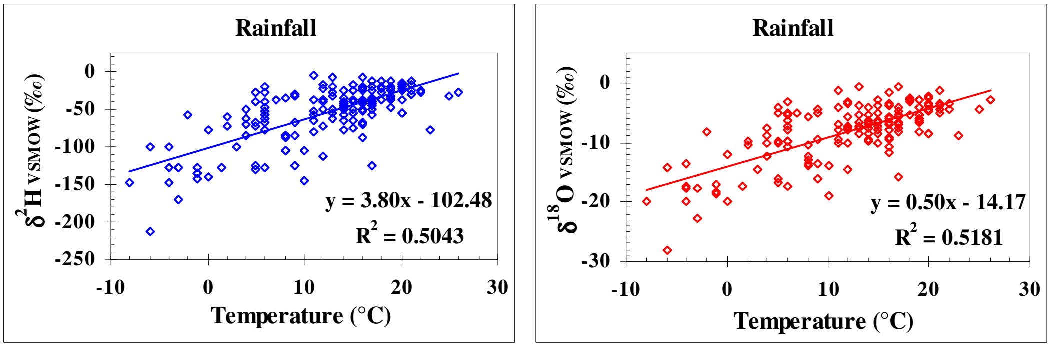


Fig. 47. The relation between the local temperature and the isotopic composition of rainfall events in the March 2010 – December 2011 period n=153.

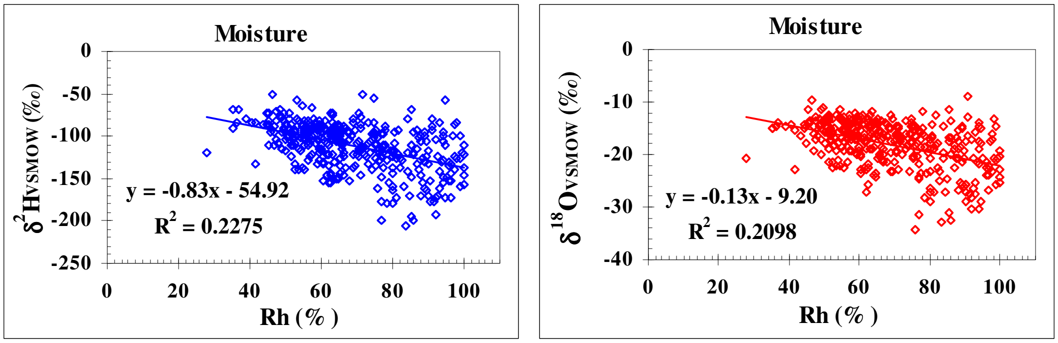


Fig. 48. The relation between the value of local humidity and the isotopic content of humidity (363 samples).

The equation of the δ^2H – T and $\delta^{18}O$ – T correlation lines for the atmospheric humidity samples collected in the May 2010 – December 2011 period and for rainfall events in the monitoring period of atmospheric humidity (**Fig. 46, 47**) are the following:

$$\delta^2H_{umid} = 2{,}05 \cdot T - 137{,}42 \qquad R^2=0{,}4935$$
$$\delta^2H_{precip} = 3{,}80 \cdot T - 102{,}48 \qquad R^2=0{,}5043$$
$$\delta^{18}O_{umid} = 0{,}36 \cdot T - 22{,}43 \qquad R^2=0{,}5753$$
$$\delta^{18}O_{precip} = 0{,}50 \cdot T - 14{,}17 \qquad R^2=0{,}5181$$

The slopes of the correlation lines are smaller for atmospheric humidity than the values measured in rainfall samples, namely at a variation of 1°C the isotopic composition of atmospheric humidity varies less than rainfall.

The dependency of the isotopic composition with relative humidity of the atmospheric air has a slight descending trend, while the isotopic composition of rainfall is not correlated with the amount of rainfall.

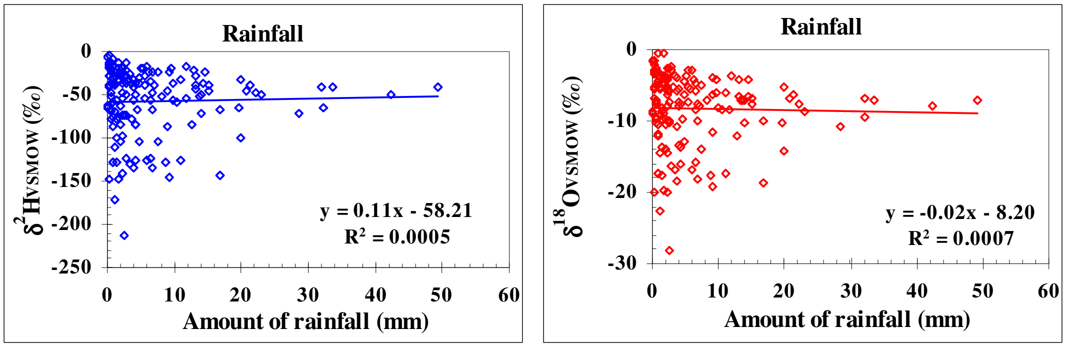


Fig. 49. The relation between the value of the amount of rainfall and the isotopic content of rainfall (153 samples).

The absence of the correlation between the values of the isotopic composition ($\delta^{18}O$ şi δ^2H) and the amount of rainfall (**Fig. 49**) is frequently reported in literature [41].

As integral constituents in water molecules, the environment isotopes ^2H and ^{18}O, are ideal tracers of water movement, because they are very sensitive to ambiental stress and to the reactions that take place in nature, and the isotopic time/space response of natural systems to any change is prompt.

The data connected to the isotopic composition of atmospheric humidity are given for establishing research methods for applying the natural isotopic tracers technique in investigating the isotopic transport in atmosphere-soil-plants structures, of translocation and accumulation of stable isotopes of water in plants, in the study of the impact of the exogenous and endogenous factors on the plant world.

The isotopic effects in rainfall show a natural isotopic marking process at a global scale. How the main element in waters cycle in nature is rainfall it is easily understandable that surface and underground waters will be tributary to the natural isotopic marking effect. The natural isotopic marking method used in the study of processes and components in waters natural cycle offers additional information of the intimate mechanism which take place in nature. Because they are inherent parameters, they are free, being available in nature, they are non-pollutant, non-invasive, are not limited in study by the amount of tracer used, are easily maneuvered and are not dangerous in working conditions, the stable isotopes of water are natural tracers in studies of:

- Climatology for the study of climate evolution and modeling of processes in atmosphere;
- Hydrology for the study of surface waters, infiltration waters, underground waters, glacier systems, humid areas, interactions in the hydrosphere, etc.
- Paleoclimatic studies from paleoarchives;
- Dendrology;
- Traceability studies in the food chain (milk [53], fruit juices [54-59], wine, bottled mineral waters);
- The study of transport, storage processes and water reactions in the components of the atmosphere-soil-plants system.

CONCLUSIONS

The results of the theoretical studies of the isotopic composition of rainfall (rain, snow, hail) allow the formulation of some general conclusions, according to these the isotopic composition of rainfall depends on:

1. The temperature and humidity at which the evaporation of the origin water of rainfall took place;
2. The history of movement of the vapor masses of water from when they left the evaporation reservoir (lakes, seas, oceans) until their condensation takes place;
3. The place in which the precipitations fell and the temperature at which the condensation of the vapors in the air masses takes place;
4. The evaporation and/or the isotopic exchange which take place in the time elapsed from the humidity precipitation to the collection of rainfall on the ground.

Because the isotopic composition of rainfall depends on the place and the formation conditions of these as well as the history of their movement, rainfall presents an isotopic distribution in space and time according to the isotopic effects caused by the evaporation – condensation processes and can be grouped after the scale at which they act: globally (the latitude effect and the continental effect) and locally (the seasonal effect, the altitude effect and the amount effect).

The analysis of the δ^2H and $\delta^{18}O$ from rainfall in the monitoring period from 2009 until 2012 leads to the following conclusions:

- The δ^2H and $\delta^{18}O$ values domain is between the domain of values obtained at a global level for a continental area, situated at great distances from an ocean or sea.
- The difference of the domain of δ^2H and $\delta^{18}O$ values for all events if larger than the one of the weighted monthly averages.
- The limits of the variation domain for the δ^2H and $\delta^{18}O$ values for events in a month of the year vary from year to year, due to the annual variability of the meteorological conditions.
- The large variability of the δ^2H and $\delta^{18}O$ values from one rainfall event to another, this being due to the short term changes of meteorological conditions.
- The evolution tendencies in time of the δ^2H and $\delta^{18}O$ values: similarity between the δ^2H – time and $\delta^{18}O$ – time profiles and seasonal oscillation with high amplitude, in correlation with local temperature, reflecting well the continental character of local climate.
- For the weighted monthly δ^2H and $\delta^{18}O$ averages, the parameters of the local meteoric lines are slightly higher than the parameters of the δ^2H and $\delta^{18}O$ lines for

all rainfall events, disagreeing with the global tendency. The opposite variation is due to the fact that there were a lot of rainfall events with extreme values of isotopic composition, but in small amounts of rainfall (<2mm).

- For the seasonal correlation, the local meteoric lines have different parameters: for the warm season they are smaller than for the cold season, according to the global tendency. The variation of the parameters is due to the amount of rainfall, the evapotranspiration and air temperature, different for the two periods mentioned before.
- For the monthly average δ^2H and δ^{18}O values the parameters of the correlation line for rainfall in Cluj-Napoca are very close to the parameters of the global meteoric line recorded at GNIP-AIEA.
- The correlation lines between the δ^2H and δ^{18}O values with temperature for rainfall in the 2009-2012 period in Cluj-Napoca have good correlation coefficients and the equations for the weighted averages show the values of the variation gradients of δ^2H and δ^{18}O overcome a little the maximum values of the recorded domain for the temperate regions of Europe.
- For rainfall in Cluj-Napoca, between the δ^2H and δ^{18}O values and the amount of rainfall there is no correlation, the amount of rainfall is not highlighted, the being frequently reported in scientific literature.

The comparative analysis of the δ^2H from all local rainfall in the 1975-2008 period with δ^2H data from the 1975-2012 period was done in order to see how the δ^2H data is influenced by dramatic climate changes in the last years.

- For rainfall events (3092 events) the limits of the variation domain have not altered through the contribution of data from the 2009-2012 period, the extreme values being recorded in March 2987 (the minimum) and October 1976 (the maximum).
- For the weighted monthly average the magnitude of the variation domain has not altered through the contribution of data from the 2009-2012 period, the minimum value being for February 1993, and the maximum for September 1986.
- For the multiannual monthly average the size of the variation domain for the values recorded in the 1975-2012 period is slightly higher than the one of the values from the 1975-2008 period, by moving the lower limit of the domain towards negative values more than moving the higher limit towards positive values, which means for the Cluj area that the meteorological influences from cold areas have been dominant and more intends than the ones from warm areas.
- For the annual averages the variation domain of the annual δ^2H is the same for the entire monitored period, the minimum value corresponds to the year 1995, and the

maximum to the year 1986, in the 2009-2012 period the annual δ^2H averages having a small variation around the -64,55‰ value.

- The variation domains of the δ^2H monthly averages for the 38 years monitored have different magnitudes for each month of the year and vary between $\Delta\delta^2$H = 42,61‰ for August and $\Delta\delta^2$H = 133,9‰ for November. The high spreading amplitude in the cold season months indicates the presence of rainfall fronts from different directions. The contribution of the 2009-2012 period was minor, the recorded values in 2009 have slightly extended the variation domain of the monthly averages for April (by 8‰) and July (2,7‰) by lifting the higher limit and for December (by 4,7‰) by lowering the inferior limit.
- The slopes of the regression lines for each long period for which the correlation δ^2H–T was done are closer as values, and the correlation is good for the monthly average values and very good for the multiannual monthly average values.
- The values of the correlation slopes for large time period are very close to the theoretical values due to the fact that at a larger time scale the averaged values diminished the variations of the processes and increase considerably the correlation coefficient.
- The correlations for the monthly averages of δ^2H and amount of rainfall for each month separately reveal a slight amount effect, but considering the bad correlation it can be stated that locally the amount of rainfall is not highlighted.

The analysis of the δ^2H and δ^{18}O values from collected humidity from May 2010 until December 2011 highlights the following conclusions:

- The average δ^2H and δ^{18}O values for atmospheric humidity are much lower than the values for rainfall collected in the same time period, but the variation domains are separated from each other.
- The profile of the monthly δ^2H and δ^{18}O averages for atmospheric humidity follows very well the profile of the monthly δ^2H and δ^{18}O averages from rainfall and highlights the seasonal effect of the isotopic composition.
- The local meteoric line of humidity has a much lower slope (5,61) compared to the local meteoric line slope of rainfall (LMWL) (7,67) for the same monitoring period.
- The equations of the correlation lines δ^2H – T and δ^{18}O – T for samples of atmospheric humidity have slopes of 2,05, respectively 0,36, smaller than for the slopes of the lines corresponding to the rainfall events in the monitoring period of the atmospheric humidity which are 3,8, respectively 0,5.

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