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Stable water isotopes in precipitation over western Cuba

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To my kids, César David and Dasiel Abraham: For all that you are, and all that you do

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“Science without religion is lame, religion without science is blind”.
(Albert Einstein)

“One of the things that is wrong with religion is that it teaches us to be satisfied with answers which are not really answers at all”.
(Richard Dawkins)

ABSTRACT

ALMOZA, Y. **Stable water isotopes in precipitation over Western Cuba.** 2017. 118 p. Tese (Doutorado) – Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, 2017.

The use of stable water isotopes as ^{18}O and ^{2}H are widely used in the last 50 years as tracer in climatic and hydrological studies. Stable water isotopes have slightly different physical properties and require different latent energy for phase changes, so the concentration of water isotopes varies during water phase changes, which is known as fractionation. Specifically in the tropics, the stable water isotopes have a very particular behavior unlike other regions, by the influence of large rainfalls amount, temperature and relative humidity. Cuba is an inland in the middle of the Caribe Sea, where studies about isotopic characterization of precipitations have never been made. In order to understand and explain some issues related to the isotopic behavior of precipitation in this inland, the research work was developed making use of data from that area. The general objective of this research proposal is to characterize the isotopic composition of rainfall in west of Cuba, including the demonstration of the vegetation influence in rainfall isotopic composition, and to determine mathematical models that describe the relationship between rainfall amount, intensity and isotopic composition for future paleoclimatic studies there. Data from the Global Network of Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA) were used. Thus, the thesis was developed in three chapters of contents. The first topic addressed was in relation to demonstrate the isotopic fractionation resulting from transpiration by a green canopy. As results, it was shown that transpiration is a fractional process with respect to water isotopes. The magnitude of this fractionation is determined by environmental factors, such as soil water content, rainfall amount, temperature, and the relative humidity. The environmental factors influence the behavior of such important variables as stomatal aperture, the different diffusion resistances, and the kinetic fractionation. Then were proposed eight mathematical models that describes the relationship between rainfall isotopic composition, amount and erosivity for paleoclimatic studies. The trend founded in this research is that months with highest rainfall erosivity were less heavy isotopically. $\delta^{2}H$ and $\delta^{18}O$ were negatively correlated with erosivity and with the rainfall amount. The rainfall amounts were the higher negative correlation with the isotopic composition for this tropical region. In the third chapter, finally, it was evaluated if even Cuba being an island could be seen the classic effects of the isotopic hydrology as, continentality, rainfall amount and seasonality. As results, rainfalls in western Cuba are in general isotopically enriched in $\delta^{18}O$ and $\delta^{2}H$ in comparison with other regions at higher latitudes. The annual mean values for $\delta^{18}O$ vary between (1 to -8) ‰ and for $\delta^{2}H$ between (15 to -40) ‰. Nevertheless, there is marked seasonal behavior, being the rainfalls heavier in winter and more depleted in summer, showing the established patterns for tropical region. The influence of the air masses movement on the rainfall isotopic behavior could be affirming the presence of the continental effect.

Keywords: Stable water isotopes. Transpiration. Rainfall. Paleoclimatic studies.

RESUMO

ALMOZA, Y. **Isótopos estáveis das precipitações sobre Cuba ocidental.** 2017. 118 p. Tese (Doutorado) – Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Piracicaba, 2017.

Isótopos estáveis da água como ^{18}O e ^{2}H foram amplamente utilizados nos últimos 50 anos como traçadores em estudos climáticos e hidrológicos. Os isótopos estáveis da água têm propriedades físicas ligeiramente diferentes, incluindo uma energia latente diferente para as mudanças de fase, de modo que a concentração de isótopos da água se altera em mudanças da fase aquosa, fenômeno conhecido como fracionamento isotópico. Especificamente nos trópicos, os isótopos estáveis da água têm um comportamento muito particular, contrário ao nas regiões temperadas, pela influência dos grandes acumulados da chuva, altas temperaturas e umidade relativa. Cuba é uma ilha no meio do mar Caribe, onde estudos sobre a caracterização isotópica das precipitações nunca foram feitos. Para entender e explicar algumas questões relacionadas ao comportamento isotópico da precipitação nesta ilha, o trabalho de pesquisa foi desenvolvido fazendo uso de dados da área. O objetivo geral desta proposta de pesquisa é caracterizar a composição isotópica das chuvas no oeste de Cuba, incluindo a demonstração da influência da vegetação na composição isotópica da precipitação e determinar modelos matemáticos que descrevem a relação entre a quantidade e intensidade da chuva com a composição isotópica para futuros estudos paleoclimáticos. Para isto foram utilizados dados da Rede Global de Isótopos em Precipitação (GNIP) da Agência Internacional de Energia Atômica (AIEA). Assim, essa tese se apresenta em três capítulos. O primeiro capítulo trata da demonstração do fracionamento isotópico resultante da transpiração através da folha de árvores. A magnitude desse fracionamento é determinada por fatores ambientais, como o teor da água no solo, a quantidade da precipitação, a temperatura e a umidade relativa do ar. Os fatores ambientais influenciam o comportamento de variáveis tão importantes como a abertura estomática, as diferentes resistências de difusão e o fracionamento cinético. No segundo capítulo propõem-se oito modelos matemáticos que descrevem a relação entre a composição isotópica da precipitação, sua quantidade e erosividade, úteis para estudos paleoclimáticos. A tendência encontrada nesta pesquisa é que meses com chuvas mais erosivas foram menos pesadas isotopicamente. Os valores de δ^{2}H e δ^{18}O foram negativamente correlacionados com a erosividade e com os acumulados de precipitação, sendo que os acumulados de precipitação foram os de maior correlação negativa com a composição isotópica nesta região tropical. No terceiro capítulo foi avaliado se em Cuba, uma ilha, podiam ser detectados os efeitos clássicos da hidrologia isotópica. Os valores médios anuais para δ^{18}O variam entre 1 e -8‰ e para δ^{2}H entre 15 e -40‰. No entanto, há um comportamento sazonal marcado, sendo as chuvas isotopicamente mais pesadas no inverno e mais leves no verão, mostrando os padrões estabelecidos para a região tropical. A influência do movimento das massas do ar sobre o comportamento isotópico da chuva pode afirmar a presença do efeito de continentalidade.

Palavras-chave: Isótopos estáveis da água. Transpiração. Chuva. Paleoclima

LIST OF FIGURES

LIST OF TABLES

TABLE OF CONTENTS

1 INTRODUCTION

There are several naturally occurring stable oxygen (^{16}O, ^{17}O, and ^{18}O) and hydrogen (^{1}H and ^{2}H or D) isotopes. The combinations of two of these hydrogen isotopes and one oxygen isotope into a water molecule forms a stable water isotopologue. The most common water isotopologue is the lightest one and is also called “light water”. It contains only the lightest isotopes to form $^{1}H_2\,^{16}O$. So-called “heavy water” contains heavier stable isotopes (e.g., $H_2\,^{18}O$, $H_2\,^{17}O$, or HDO) and occurs in regular proportions on Earth. Stable water isotopologues have slightly different physical properties, mainly regarding phase-change latent energy and diffusivity. For this reason, the concentration of water isotopologues may alter during water phase changes, a phenomenon called fractionation. Water phase changes occur at various spatiotemporal scales in the global hydrological cycle, resulting in relative changes in the spatiotemporal distribution of stable water isotopes. The stability of these isotopes and differences in fractionation properties make them very useful in hydological studies. The $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios in rainwater are determined by the occurrence of several effects such as latitude, altitude and seasonality effects, all related to temperature, as well as rainfall amount and continentality effect.

To give an example, hydrogen and oxygen heavy isotope contents of rainwater decrease with increasing altitude. This is attributed to the progressive condensation of atmospheric vapor and rainout of the condensed phase, which take place when air masses climb up along the slopes of high mountains and cool off due to adiabatic expansion. As the $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios are slightly higher in the liquid water or ice removed by precipitation than in the residual vapor, the latter becomes progressively depleted in heavy isotopes. A decreasing temperature should always lead to an increase in isotopic fractionation, making the water to become more depleted from heavy isotopes. Increasing altitudes (decreasing temperature) increases the fractionation.

The use of stable water isotopes in meteorological sciences deals with the complicated nature of water phase change in meteorological water cycles. Many processes or effects can influence meteorological isotopes, and information is limited to surface precipitation data with little temporal resolution (only monthly average data are available for most areas) using conventional mass spectrometry. In hydrological sciences, stable water isotopes have permitted a deeper understanding of terrestrial hydrological cycles at different scales, including the partitioning of total water transport.

Important studies were published during the 1970s about climatology and water recycling Dall'Olio et al. (1979); Salati et al. (1979), and then in the 1990s, Victoria et al. (1991) and Martinelli et al. (1995) and more recently by Jasechko et al. (2013), Sutanto et al. (2014b) and Galewsky et al. (2016). All of them include the hypothesis that transpiration is a non-fractionation process. The arguments for this affirmation are usually two: 1) when injecting deuterated water into tree roots and measuring the transport of deuterium in stem water from roots to leaves, no fractionation is observed and 2) measuring root water uptake isotopic fractionation gives similar results. Forgetting completely the physical processes that are carried out together with the biological ones in the plants leaf. In the leaf is where the physical processes (water phase changes) exist that allow seeing the process of fractionation, which will be discussed in chapter 2 of this dissertation.

Another important use of water isotopes is in paleoclimatic studies. Karstic environments are ubiquitous throughout the Caribbean and offer a variety of features that act as sediment sinks, such as sinkholes, blue holes and aquatic caves. These places are reservoirs of water isotopes from the past and very used to decipher previous climates (HODELL et al., 2004). In that situation is Cuba, which is an island in the middle of the Caribbean Sea, the climate is closely related to the direction of air mass movement, different in winter and summer and the precipitation amount vary between 1700 mm to 1300 as mean yearly. A relationship between the isotopic composition of rainwater and precipitation amount or intensity would help to reconstruct past precipitation. Gat and Matsui (1991) present such a relationship for tropical regions. As rainfall intensity is related to the kinetic energy of rainfall and erosivity (RENARD et al., 1997), understanding the relationship between rainfall isotopic composition, intensity and erosivity may allow interpreting the behavior of some hydro-meteorological features of the past-nature. Taking advantage, that the Network for Isotope in Precipitation by the International Atomic Energy Agency (IAEA) has data from Cuba in their website www.iaea.org and a rainfall isotopic characterization was never made in Cuba; it would be very interesting to determine these types of relationships between precipitation properties and isotopic composition for future paleoclimatic studies in the area.

In this context, the scientific problem of this study is: How rainfall will be characterized respect to water isotope in the western part of Cuba?

The following hypotheses are proposed:

- The deviation of the rainfall isotopic composition in Cuba is influenced by the processes of its formation, specifically distinct between frontal rainfalls with a heavier isotopic composition and predominating in winter, and convective rainfalls with a lighter isotopic composition predominant in summer.
- The isotopic composition of the convective rainfalls is influenced by the processes of soil evaporation and plant transpiration in the nearby region.
- Canopy transpiration is an isotopically fractionating process.
- There is an inverse relationship between rainfall amounts and rainfall intensity with rainfall isotopic composition.
- Mathematical modeling allows to determine a relationship between rainfall properties and rainfall isotopic composition that may allow to infer about paleo-rainfall properties.
- The different effects of isotopic hydrology can be manifested on an island like Cuba.

To corroborate the hypotheses, the general objective of this research proposal is to characterize the isotopic composition of rainfall in western Cuba, including the demonstration of the vegetation influence on rainfall isotopic composition, and determine mathematical models that describe the relationship between rainfall amount, intensity and isotopic composition for future paleoclimatic studies there.

The specific objectives are organized per chapter:

In Chapter 2, the specific objective is to demonstrate the isotopic fractionation resulting from transpiration by a green canopy.

In Chapter 3, the specific objective is to propose mathematical models that describe the relationship between rainfall isotopic composition, amount and erosivity for paleoclimatic studies in western Cuba.

In Chapter 4, the specific objectives are to characterize isotopically the precipitations in western Cuba and to evaluate if on a relatively small island, isolated from many continental processes, the classic effects of the isotopic hydrology as continentality, rainfall amount and seasonality can be observed.

1.1 INTRODUÇÃO

Existem naturalmente vários isótopos estáveis de oxigênio (^{16}O, ^{17}O, e ^{18}O) e hidrogênio (^{1}H e ^{2}H our D). A combinação de dois isótopos de hidrogênio e um isótopo de oxigênio é chamada de isotopólogo da água. Embora o isotopólogo normal ou leve, que inclui apenas isótopos de ($H_2\,^{16}O$), seja o mais comum, a água pesada que contém outros isótopos estáveis ($H_2\,^{18}O$, $H_2\,^{17}O$ e HDO) também ocorre em proporções regulares na Terra. Os isótopos estáveis da água têm propriedades físicas ligeiramente diferentes, requerendo uma energia latente diferente para as mudanças de fase, de modo que a concentração de isótopos da água varia durante as mudanças da fase aquosa, fenômeno conhecido como fracionamento. As mudanças de fase da água ocorrem em várias escalas espaciotemporais no ciclo hidrológico global, resultando em mudanças relativas na distribuição espaciotemporal dos isótopos estáveis da água. A estabilidade destes isótopos e as diferenças de fracionamento os tornam muito úteis em estudos de transporte da água. Desde Dansgaard (1964), numerosos estudos usaram isótopos estáveis da água em ciências hidrológicas e climáticas. O comportamento das razões ^{2}H / ^{1}H e ^{18}O / ^{16}O nas chuvas é determinado pela ocorrência de vários efeitos, tais como: latitude, altitude, efeitos sazonais (os três muito relacionados à temperatura), quantidade de precipitação e efeito de continentalidade.

Por exemplo, é bem sabido que o teor de isótopos pesados de hidrogênio e oxigênio da água da chuva diminui com o aumento da altitude. Isto é atribuído à condensação progressiva do vapor atmosférico e da precipitação da fase condensada, que ocorrem quando as massas de ar escalam nas encostas das altas montanhas e esfriam como consequência da expansão adiabática. À medida que as razões ^{2}H / ^{1}H e ^{18}O / ^{16}O são ligeiramente maiores na água líquida ou gelo removido por precipitação do que no vapor residual, este último se converte progressivamente à medida que evapora a agua em vapor com isótopos leves. À medida que a temperatura diminui, sempre deve aumentar o fracionamento isotópico e a água fica mais leve. Portanto, aumentar a altitude diminui a temperatura e aumenta o fracionamento.

O uso de isótopos estáveis da água nas ciências meteorológicas não é tão avançado devido à natureza complexa da mudança da fase da água nos ciclos meteorológicos. Muitos processos ou efeitos podem influenciar os isótopos meteorológicos e a informação é limitada aos dados de precipitação que têm pouca resolução temporal (somente dados médios mensais estão disponíveis para a maioria das áreas). Nas ciências hidrológicas, isótopos estáveis da água permitiram uma compreensão mais profunda dos ciclos hidrológicos terrestres em diferentes escalas, incluindo a partição do transporte total de água.

Resultados importantes foram alcançados durante a década de 1970 sobre climatologia e reciclagem da água, como Dall'Olio et al. (1979) e Salati et al. (1979), na década de 1990 com Victoria et al. (1991) e Martinelli et al. (1995) e mais recentemente por Jasechko et al. (2013); Sutanto et al. (2014b); Galewsky et al. (2016). Todos esses autores deixaram grandes contribuições, e todos utilizaram uma premissa questionável, "Transpiração é um processo de não-fracionamento". Os argumentos dos autores para isso são dois: 1) água deuterada foi injetada nas raízes das árvores, medindo o transporte de deutério na água do caule na direçao das raízes para as folhas como um traçador. A transpiração foi calculada com base na massa total do traçador administrado e na concentração na água do caule, provando que não houve fracionamento e 2) medindo no processo da extração da água do solo pelas raizes, obtiveram resultados semelhantes. Ignoraram os processos físicos que ocorrem juntamente com os biológicos na folha das plantas. É na folha onde ocorre a mudança de fase da água que resulta no fracionamento, como será discutido no capítulo 2 desta tese.

Outro uso importante de isótopos da água é em estudos paleoclimáticos. Os ambientes kársticos são onipresentes em todo o Caribe e oferecem uma variedade de características que atuam como sumidouros de sedimentos, como buracos e cavernas aquáticas. Esses lugares são reservatórios de isótopos da água do passado e frequentemente utilizados para decifrar os climas anteriores (HODELL et al., 2004). Nessa situação está Cuba, uma ilha no meio do mar Caribe. Seu clima está intimamente relacionado com a direção do movimento de massa do ar, diferente no inverno e no verão, e a quantidade de precipitação que varia entre 1700 mm e 1300 mm como média anual. Uma relação entre a composição isotópica da água da chuva e a quantidade ou intensidade ajudaria a reconstruir as características de sua precipitação passada. Gat and Matsui (1991) apresentam tal relação para regiões tropicais. Como a intensidade da chuva está relacionada à energia cinética das chuvas e da erosividade (RENARD et al., 1997), a compreensão da relação entre a composição isotópica da chuva, a intensidade e a erosividade pode permitir a interpretação do comportamento de algumas características hidrometeorológicas da natureza passada. A Rede de Isótopos em Precipitação pela Agência Internacional de Energia Atômica (IAEA) possui dados de Cuba no site www.iaea.org e nunca foi feita uma caracterização isotópica da chuva em Cuba. Assim, serão determinadas as relações entre propriedades de precipitação e composição isotópica para futuros estudos paleoclimáticos na região.

Neste contexto, o problema científico abordado no estudo é: como as chuvas serão caracterizadas isotopicamente na parte ocidental de Cuba?

Para resolver o problema científico, propõem-se as seguintes hipóteses:

- O desvio da composição isotópica da chuva em Cuba é influenciado pelos processos de sua formação, distinguindo-se especificamente entre as chuvas frontais que predominam no inverno e têm uma composição mais pesada e chuvas convectivas, predominantes no verão e com composição isotópica menos pesada.
- A composição isotópica das chuvas convectivas é influenciada pelos processos de evaporação do solo e transpiração das plantas na área.
- A transpiração das plantas é um processo de fracionamento dos isótopos da água.
- Existe uma relação inversa entre quantidades de precipitação e intensidade com a composição isotópica das mesmas.
- A modelagem matemática permite determinar uma relação entre propriedades das chuvas e sua composição isotópica que permitem inferir depois sobre propriedades paleoclimáticas das mesmas.
- Os diferentes efeitos da hidrologia isotópica podem-se manifestar em uma ilha como Cuba.

Para testar as hipóteses, o objetivo geral desta proposta de pesquisa é caracterizar a composição isotópica das precipitações no oeste de Cuba incluindo a demonstração da influência da vegetação na composição isotópica das mesmas assim como determinar modelos matemáticos que descrevem a relação entre a quantidade de precipitação, intensidade e composição isotópica para futuros estudos paleoclimáticos.

Para tal, os objetivos específicos são dispostos por capítulos:

No capítulo 2, o objetivo específico é demonstrar o fracionamento isotópico resultante da transpiração por um dossel verde.

No capítulo 3, o objetivo específico é propor alguns modelos matemáticos que descrevem a relação entre a composição isotópica da precipitação, quantidade e erosividade para estudos paleoclimáticos em Cuba.

No capítulo 4, objetiva-se caracterizar isotópicamente as precipitações no oeste cubano e avaliar se Cuba, sendo uma ilha, apresenta os efeitos clássicos da hidrologia isotópica como continentalidade, quantidade de precipitação e sazonalidade.

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2 ISOTOPIC FRACTIONATION OF WATER DURING TRANSPIRATION: A THEORETICAL DEMONSTRATION

Abstract

During the last three decades of the 20th century, a series of studies about the climate of the Amazon watershed were developed in the context of isotopic techniques. One of the questions these frequently cited publications deal with is the primary source of water vapor involved in cloud formation and subsequent rainfall. They agree, in one way or another, about the fact that regarding water isotopologues “transpiration is a non-fractionating process”. However, no explanation is given for this physically surprising fact. On the other hand, several publications report that transpiration from leaves increases the O^{18}/O^{16} ratio of water remaining in the leaves, corresponding to the expected isotopic enrichment in the leaf linked to the formation of isotopically lighter water vapor. This leaves us with the question: what are the underlying mechanisms of the non-fractionation reported for transpiration in the Amazon watershed? If evaporation is known to fractionate, is it possible to imagine transpiration as a non-fractionating process? Moreover, is there a miscommunication between plant-related scientists and those related to isotope hydrology? In this “Opinion paper”, we aim to elucidate the issue of isotopic fractionation resulting from transpiration by a green canopy, specifically applied to the environmental conditions of the Amazon watershed. To do this, we first show how transpiration deals with a very specific transfer of water from the inside of the stomata to the open air, comprising an evaporation stage followed by vapor diffusion, both notorious isotopic fractionating processes. Thus, transpiration can be expected to result in vapor depleted from heavy isotopes, whereas remaining liquid water in the leaves will enrich with heavier isotopes. We also demonstrate that the total diffusion resistance in the stomatal pathway is composed of three serial diffusion resistances that are influenced by the environmental conditions, essentially soil physical properties and relative humidity. The Amazon rainforest is a tropical humid broadleaf forest, with mean precipitation between 2000-2800 mm y^{-1}, most of its soils being Ferralsols. Refuting aforementioned publications, we conclude fractionation from transpiration is a fact, and will be larger under stressed conditions than under non-stressed conditions prevailing in the Amazon watershed.

Keywords: Transpiration, stomatal diffusion, water isotopes, plant, fractionating process

2.1 Introduction

Water molecules are composed of two hydrogen (H) atoms and one oxygen (O) atom. Several stable isotopes of both elements occur in nature. For H, ^1H (protium) is the most abundant (99.985%), being the remaining 0.015% composed of deuterium (^2H or D). For oxygen, its most abundant isotope (99.76%) is ^{16}O, followed by ^{18}O (0.20%) and ^{17}O (0.04%). Consequently, nine stable isotopologues of the water molecule exist, being the most abundant so-called “light” water: $^1H_2{}^{16}O$ (99.73098%). $H_2{}^{18}O$, $H_2{}^{17}O$, and $HD^{16}O$ exist in much smaller but still measurable quantities (0.199978%, 0.037888%, and 0.031460%, respectively) (SHARP et al., 2001; GALEWSKY et al., 2016). A heavier hydrogen isotope, ^3H or tritium, is unstable to β decay with a half-life of 12.32 years. As this half-life is compatible with the hold-up time in many subsurface reservoirs, it is sometimes used in hydrological studies (GAT, 2001).

Whereas there is no chemical difference between isotopologues, they have slightly different properties in some physical processes, notably diffusion and liquid-gas phase transitions (evaporation and condensation). In general, heavier isotopologues are expected to have a lower diffusivity and a lower vapor pressure, thus lagging behind their lighter counterparts during evaporation. During condensation, on the other hand, heavier isotopologues take the lead. From this, it is to be expected that the process of evaporation from natural water bodies, but also from soil surfaces or vegetation canopies, results in isotope fractionation, i.e., the isotope composition of source and sink tends to diverge over time. Evaporated water, like in atmospheric vapor and clouds, may be expected to have a lighter composition than the remaining water in the source (water bodies, soil or vegetation), which tend to enrich with the heavier isotopologues (GAT, 2001). During crop transpiration, involved diffusion processes through stomatal apertures may subtly affect this speciation, making it possible to infer about atmospheric or crop conditions during the respective process from the isotopic composition of sink or source.

Isotopic abundances may be expressed by the concentration ratio R, for instance $^2H/^1H$ or $^{18}O/^{16}O$. For practical reasons, instead of using R, isotopic compositions are generally given as the relative deviations (δ) of the ratio in a sample (R_{sample}) with respect to a standard value R_0, the stable isotopic composition of water

$$\delta = \frac{R_{sample}}{R_0} - 1 \tag{2.1}$$

R_0 is the International Atomic Energy Agency (IAEA) Vienna Standard Mean Ocean Water (VSMOW) ratio, which for the two main rare isotopes are $^2H/^1H = 155.95*10^{-6}$ and $^{18}O/^{16}O= 2005.2*10^{-6}$, close to the original standard of SMOW as defined by Craig (1961). As δ is a small number, it is usually expressed in ‰.

Within the hydrologic cycle, the variability in the isotope composition results primarily from mass-dependent isotope fractionation accompanying the phase transitions and transport processes in the cycle. The various individual isotope effects in evaporation were theoretically understood and correlated and summarized in a mathematical model (FARRIS et al., 1978). In the 1970s, the understanding of the isotopic composition of water in plants was accepted as: 1) heavy isotopes accumulate in leaves, 2) transpiration rate and isotopic enrichment are correlated, as evidenced by a diurnal pattern in the leaf isotopic concentrations, and 3) no isotopic fractionation of water results from the passage through roots and stem. This last finding may be expected to hold virtually always, as no phase transition or vapor transport is involved in this step. Exception could be made to root water uptake under very dry soil conditions, when vapor transport in the soil might become a dominating process (GIERKE et al., 1992; WARREN et al., 2011).

In the 1970s, a series of studies about the climate of the Amazon basin were developed in the context of isotopic techniques as Dall'Olio et al. (1979) and Salati et al. (1979), more than a decade later followed by publications on the same subject by Victoria et al. (1991) and Martinelli et al. (1995), standards in Brazil that focus on the hypothesis that part of the rainfall in the Amazon basin originates from the forest. These publications agree, in one way or another, about the fact that "transpiration is a non-fractionating process", however, without explaining this extraordinary claim which is in conflict with earlier papers by, e.g., Craig (1963) and Wershaw et al. (1966) who showed transpiration from leaves to increase the O^{18}/O^{16} ratio of the water remaining in the leaves, corresponding to the expected isotopic enrichment in the leaf linked to the formation of isotopically lighter water vapor.

The inconsistency, i.e., some authors considering leaf transpiration to lead to isotopic speciation while others state the opposite to corroborate their findings, is ongoing.

Supposing transpiration to be a non-fractionation process is common in isotopic hydrology, also in recent publications. Jasechko et al. (2013) state that the "physical process of evaporation enriches residual water in the heavy isotopes of oxygen and hydrogen, whereas the biological process of transpiration does not produce an isotopic fractionation, assuming an isotopic steady state over annual timescales". Schlaepfer et al. (2014) cite "We offer new data demonstrating that lakes do not consistently record H and O isotope signals from catchment-scale Evaporation and Transpiration (our main point) and that Transpiration is not the only non-fractionating isotopic process with significant water loss to the atmosphere".

In their review paper, Galewsky et al. (2016) state that "transpiration is not associated with fractionation relative to soil water because there is no fractionation during root extraction". The clue to the misunderstanding is in their sentence. It is plausible that root water uptake does not lead to fractionation, but root water uptake is only a part of the pathway of water from soil through plant to atmosphere. The isotopic fractionation occurs during the evaporation step taking place in the leaf. Therefore, water in the plant is expected to be heavier and transpired water to be isotopically lighter than soil water.

Until now, not much is known by hydrologists and climatologists about more biological aspects regarding the process of transpiration, and separate approaches are used by physicists and biologists.

In this opinion paper, we aim to elucidate the issue of isotopic fractionation resulting from transpiration by a green canopy, and apply it to the environmental conditions of the Amazon watershed. To come to an opinion, we first treat some topics essential for the understanding of the overall process.

2.2 Water phase transition: liquid to gas

The phase transition from liquid to gas is called evaporation, an endothermic process. Evaporation of water occurs when the surface of the liquid is exposed to unsaturated air, allowing molecules to escape and form water vapor. These gaseous water molecules (or vapor) represent the origin of clouds and rainfall (PENMAN, 1948).

Evaporation of water in the field can take place from plant canopies (mainly from stomata in green leaves), from the soil surface, or, more rarely, from a free-water surface (JONES; SUTHERLAND, 1991). Evaporation from plants is usually called transpiration, and it is the main mechanism of soil-water transfer to the atmosphere when the soil surface is covered with vegetation. When the surface is at least partly bare, evaporation directly from the soil may become important. Since these two interdependent processes are generally difficult to separate experimentally, they are commonly lumped together and treated as if they were a single process called evapotranspiration (HILLEL, 2003). Objections to the latter term exist, however, and some believe it to be both cumbersome and unnecessary. According to Monteith (1963), evaporation refers to all processes of vapor transfer to the atmosphere, both from the soil and from plant surfaces, making the term transpiration unnecessary from a physical standpoint of view.

For molecules of a liquid to evaporate, they must be located near the liquid-gas interphase, they should be moving in the proper direction, and have sufficient kinetic energy to overcome liquid-phase intermolecular forces (ISRAELACHVILI, 2011). The kinetic energy of molecules is temperature-dependent and described by the Boltzmann distribution, which states that the probability P_E of a molecule to have a kinetic energy equal or smaller than E is

$$P_E = 1 - \exp\left(\frac{-E}{kT}\right) \tag{2.2}$$

where k is the Boltzmann constant ($k = 1.38 \cdot 10^{-23}$ J K^{-1}) and T is the substance temperature. From Equation (2.2) it follows that the average kinetic energy of molecules in a substance ($P_E = 0.5$) is

$$\overline{E} = kT \ln(2) \tag{2.3}$$

It also follows that, at any temperature T > 0 K, molecules may have any kinetic energy, but the higher the temperature, the greater the abundance of high energy molecules. This explains why evaporation occurs at any temperature, and why evaporation proceeds more quickly at higher temperatures.

2.2.1 Factors influencing the rate of evaporation

At a liquid-vapor interface, high-energy molecules near the interface and with a velocity component in the right direction may escape from the liquid and form vapor. On a molecular scale, the escape consists of the transformation of kinetic energy in potential energy (TSURUTA et al., 1999; BUFFONE et al., 2005). On a substance scale, it is equivalent in transforming sensible heat into latent heat, quantified by the enthalpy of vaporization. In the reverse direction, vapor molecules near the surface may be captured by the liquid molecule´s binding forces and assume the liquid state (HIDE, 1953). Both processes occur simultaneously, but when the escape rate exceeds the capture rate, an overall evaporation is observed. In the opposite situation, we say the vapor is condensing. Moreover, when both processes occur at the same rate, there is no net evaporation or condensation.

From this, it is easy to see that the rate of escape depends on the kinetic energy (temperature) of the liquid molecules, whereas the rate of capture depends on the density of the vapor, in the case of water usually replaced by a related quantity, humidity. For a given temperature, a certain vapor density will result in equal escape and capture rates (no net evaporation nor condensation), and this vapor density (also expressed as the equivalent vapor pressure) is called the saturated vapor pressure. It corresponds to the relative humidity of 100%.

A very important factor defining the evaporation rate is the flow rate of the air near the evaporating surface. The process of evaporation leads to an increase in vapor saturation near the liquid-gas interface, reducing the net evaporation rate. The thickness of this boundary layer of air with increased humidity depends on the geometry, roughness and movement of air. If this more saturated air moves away from the surface and mixes with overlying air, the vapor concentration near the surface is kept low, maintaining evaporation at a higher rate. This mechanism explains the effect of wind speed on evaporation and transpiration.

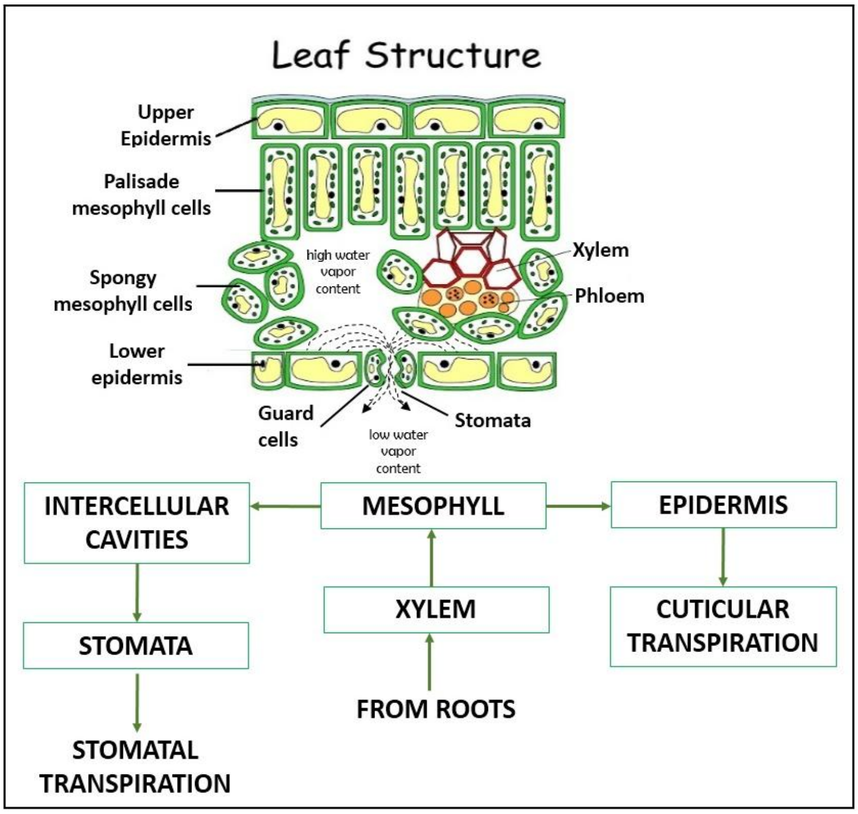
Besides temperature and relative humidity, the concentration of other substances in the air (or a high partial pressure of other components) is sometimes thought to affect evaporation of water. This is, per definition, a refutable hypothesis if the air is an ideal gas mixture, normally considered as such at common temperatures and pressure. In an ideal gas mixture, individual components of the mixture do not affect each other physically.

2.2.2 Transpiration

Transpiration is the process of evaporation from aerial parts of vegetation, mainly from the leaves. Transpiring water is replenished by a plant by root water uptake and water movement through the xylem vessels. Of all water taken up by the roots, only a tiny part is used for growth and metabolism (DAVIES; ZHANG, 1991). The remaining 97 to 99.5% is consumed by transpiration and guttation.

When dealing with transpiration on a leaf or canopy scale, the atmosphere is considered as sink for water vapor and ambient vapor pressure, boundary layer properties, incident radiation, wind and temperature are often lumped together in a quantity called evaporative demand. Higher plants use their stomatal complex (stomata bordered by guard cells and stomatal accessory cells) to regulate canopy conductance. It is through this complex that almost all transpiration occurs, and this loss of water can be thought of as a necessary “cost” associated with the opening of the stomata to allow the diffusion of carbon dioxide gas from the air for photosynthesis (NEALES; INCOLLL, 1968). Figure 2.1 displays the simplified proposed model for transpiration from Dongmann et al. (1974), showing two pathways, cuticular and stomatal.

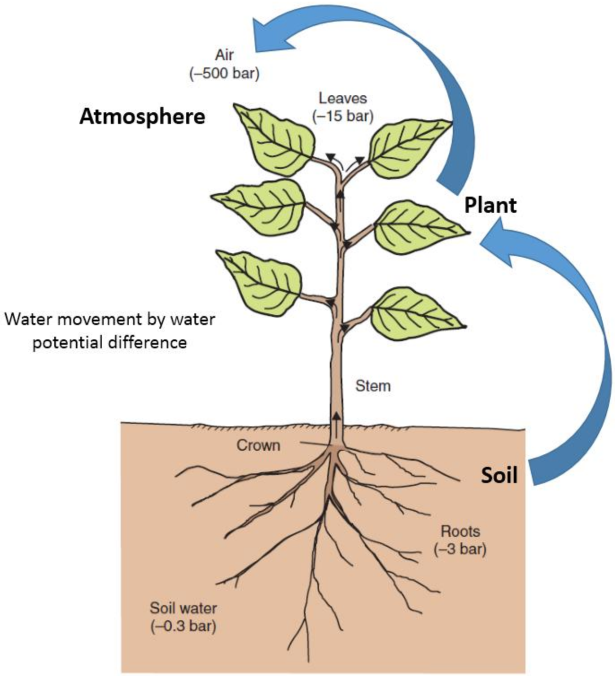
Figure 2.1 – Compartment model of the water movement until transpiration from a leaf, adapted from Dongmann et al. (1974)



Besides representing the major part of water consumption by plants, transpiration also cools the leaves, changes osmotic pressure of cells, and enables mass flow of mineral nutrients and water from roots to shoots (GATES, 1964). If the water potential in the ambient air is lower than the water potential in the airspace of the stomatal pore, water vapor will travel down the gradient and move from the leaf airspace to the atmosphere (Figure 2.2). This movement lowers the water potential in the leaf airspace and causes evaporation of liquid water from the mesophyll cell walls (Figure 2.1). This evaporation increases the tension on the water menisci in the cell walls and decreases their radius and thus the tension that is exerted on the water in the cells. Because of the cohesive properties of water, the tension travels through the leaf cells to the leaf and stem xylem where a momentary negative pressure is created as water is pulled up the xylem from the roots.

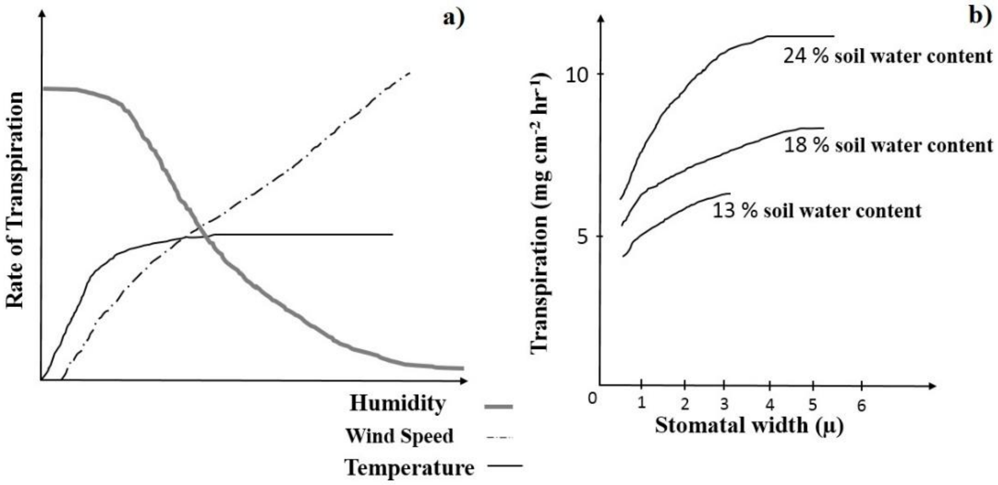
The potential evaporation rate within a leaf is substantially greater than that of a water surface with the same leaf area, since the total area of evaporation, i.e. the inner walls of the epidermis and the walls of the mesophyll cells, may be seven to thirty times greater than the leaf area (MEIDNER; SHERIFF, 1976).

Figure 2.2 – Water potential along the soil-root-shoot-atmosphere transpiration stream, adapted from Hillel (2003)



Along the soil-plant-atmosphere pathway, the soil is the source and the atmosphere is the sink for water. Soil water content determines soil water potential and hydraulic conductivity. If a soil becomes drier, root water uptake and transpiration shift from sink-limited (determined by the evaporative demand) into source-limited (determined by soil hydraulic and root system properties). Figure 2.3a illustrates the relationship between transpiration rate and external factors, highlighting the close to inverse relation with relative humidity, the linear relation with wind speed and the piecewise-linear relation with temperature. Figure 2.3b shows the importance of soil water content for stomatal opening shown by Gardner and Ehlig (1963).

Figure 2.3 – a) Relationship between transpiration rate and some environmental factors, and b) Transpiration as a function of stomatal width, at three soil moisture levels, adapted from Shimshi, (1963)



2.2.3 Isotopic fractionation during evaporation

Evaporation plays a crucial role in determining isotope ratios found in global precipitation and ice core records (CAPPA et al., 2003). In addition, isotope effects during evaporation from plants determine the isotopic composition of oxygen in atmospheric CO_2 and O_2 (FARQUHAR et al., 1993; BENDER et al., 1994).

Evaporation and condensation (or escape and capture) rates are determined by molecular binding energies. In the case of liquid water, molecules with heavier oxygen or hydrogen isotopes will have greater binding energies and lower diffusive velocities, which causes them to evaporate less readily than lighter isotopologues. As a result, when evaporation takes place, the resulting vapor has, by proportion, fewer of the heavy isotopes than the reservoir and a lower isotopic ratio, R_2. Conversely, the isotopic ratio R_1 of the (liquid) reservoir will increase due to the preferential evaporation of lighter isotopologues. On the inverse pathway, when net condensation occurs from a vapor reservoir, there is a preferential transfer of the heavy isotopologue to the condensate, resulting in fewer of the heavy isotopologue in the vapor and more of the heavy isotopologues in the condensate. This separation of different isotopologues during phase changes is called isotopic fractionation (GALEWSKY et al., 2016).

For phase equilibrium (e.g. between vapor and liquid), the proportion between isotopic ratios R_1/R_2 is proportional to thermodynamic temperature T (K) (DALL'OLIO et al., 1979):

$$\frac{R_1}{R_2} = \alpha_{1/2} T \tag{2.4}$$

where $\alpha_{1/2}$ (K^{-1}) is the isotope fractionation factor. From Eqs. 2.1 and 2.4 it follows that:

$$\alpha_{1/2} T = \frac{1+\delta_1}{1+\delta_2} \tag{2.5}$$

In the Rayleigh process (GAT, 2001), fractionation ε (commonly expressed in permil, ‰) is given by:

$$\varepsilon = \alpha - 1 \tag{2.6}$$

In research applications, the distinct behavior of isotopes during phase transitions allows the analysis of water flows on several time and space scales. Stable isotopes of water, both deuterium and ^{18}O, have been used to trace water through biophysical systems including aquifers e.g. Darling et al. (2003), continental water recycling e.g. Aemisegger et al. (2014) and identification of sources of plant water uptake e.g. Dawson and Ehleringer (1991). Models of water isotopic fractionation play a great role in the determination of sources of water vapor in the atmosphere, important in meteorology and hydrology.

2.4 Isotopic fractionation in precipitation

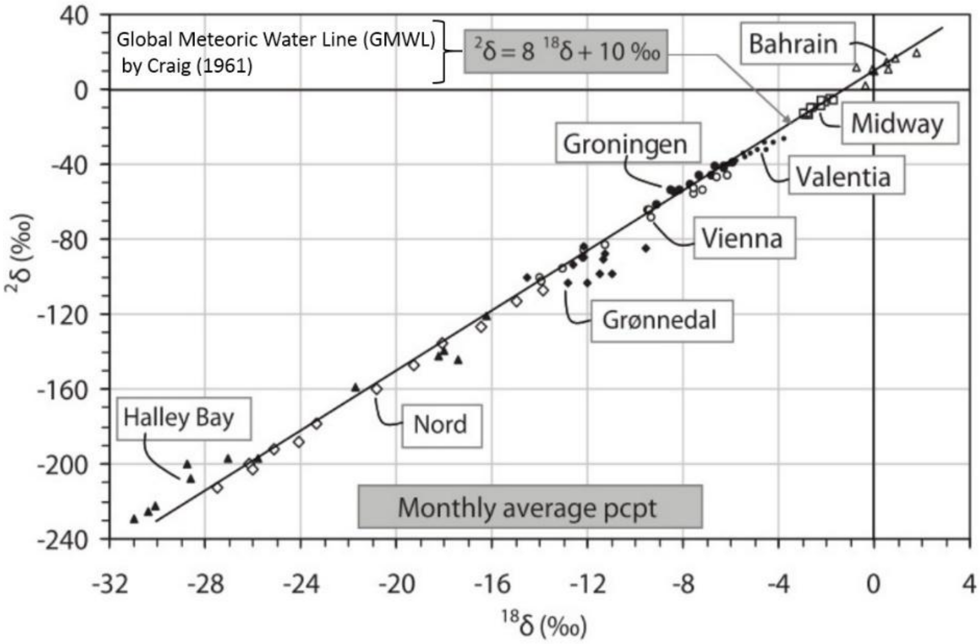
From the former, during evaporation the liquid source enriches, and the gaseous sink gets poorer in heavier isotopologues of water. From this, it is not surprising that $\delta^{18}O$ and δ^2H in meteoric water are correlated. A linear relation is commonly found, according to

$$\delta^2 H = r\delta^{18}O + d \tag{2.7}$$

with *r* being the slope and *d* the intercept, also called deuterium excess. Both *r* and *d* change according to the location and the characteristics of the rainfall formation. On the average global scale, the ratio $\delta^2H/\delta^{18}O$ turns out to be satisfactorily described by the Global Meteoric Water Line (GMWL) with $r = 8$ and $d = 10‰$ (Figure 2.4, CRAIG, 1961):

$$\delta^2 H = 8\delta^{18}O + 10 \tag{2.8}$$

Figure 2.4 – Seasonal influence on the $\delta^{18}O$ and $\delta^{2}H$ relation for average monthly precipitation at a number of stations, arctic, tropical, coastal and continental data by Gat (2001) and the Global Meteoric Water Line (GMWL) by Craig (1961)



Gat (2001) described many details about isotopic fractionation in precipitation, showing governing mechanisms related to latitude and temperature, seasons, altitude, amount and intensity, variations among years and continental effect.

2.5 The special case of transpiration

Transpiration from leaves of higher plants occurs in a relative complex geometry involving stomatal apertures and shoot architecture. Therefore, transpiration deals with a very specific transfer of water from inside the stomata to the open air involving evaporation followed by vapor diffusion. Both processes cause isotopic fractionation, depleting the transpiring water and enriching the water remaining in the leave with heavier isotopes.

The total diffusion resistance in the stomatal pathway to free outside air is composed of three serial diffusion resistances (NANGE, 1953):

1) The resistance in the stomata (see Figure 2.5), represented by cylindrical tubes with an elliptical section. This resistance r_s (T L^{-1}) may be represented by:

$$r_s = \frac{l_t}{kN\pi ab} \tag{2.9}$$

where l_t (L) is length of the tube, a (L) is the short radius of the ellipse, b (L) is the long radius of the ellipse, N (L^{-2}) is the number of stomata per unit area of leaf surface, and k (L^2 T^{-1}) is the diffusion constant which depends on the quality of the diffusing substance and of the diffusion medium and on the temperature. The short radius of the ellipse (a) is considered to represent stomatal aperture and may change due to water stress factors.

2) The resistance r_d (T L^{-1}) in the micro vapor cups over the individual stomata. The total resistance per unit area leaf surface of these vapor cups may be calculated by Brown and Escombe's formula cited by Nange (1953):

$$r_d = \frac{1}{4kN\sqrt{ab}} \tag{2.10}$$

where $\sqrt{ab}$ is radius of the circle with an area equal to the elliptical section of the stomata.

3) The resistance r_b (T L^{-1}) (sometimes referred to as *A*) in the macro vapor cup over the whole surface of the leaf (the hypothetical still air layer), depending on *k* and on the thickness of the still layer (l_s, L) cited by Nange (1953):

$$r_b = \frac{l_s}{k} \tag{2.11}$$

The diffusion rate i (M L^{-2} T^{-1}) cited by Nange (1953), equal to the transpiration rate, is then given by:

$$i = \frac{(c - c')}{r_s + r_d + r_b} \tag{2.12}$$

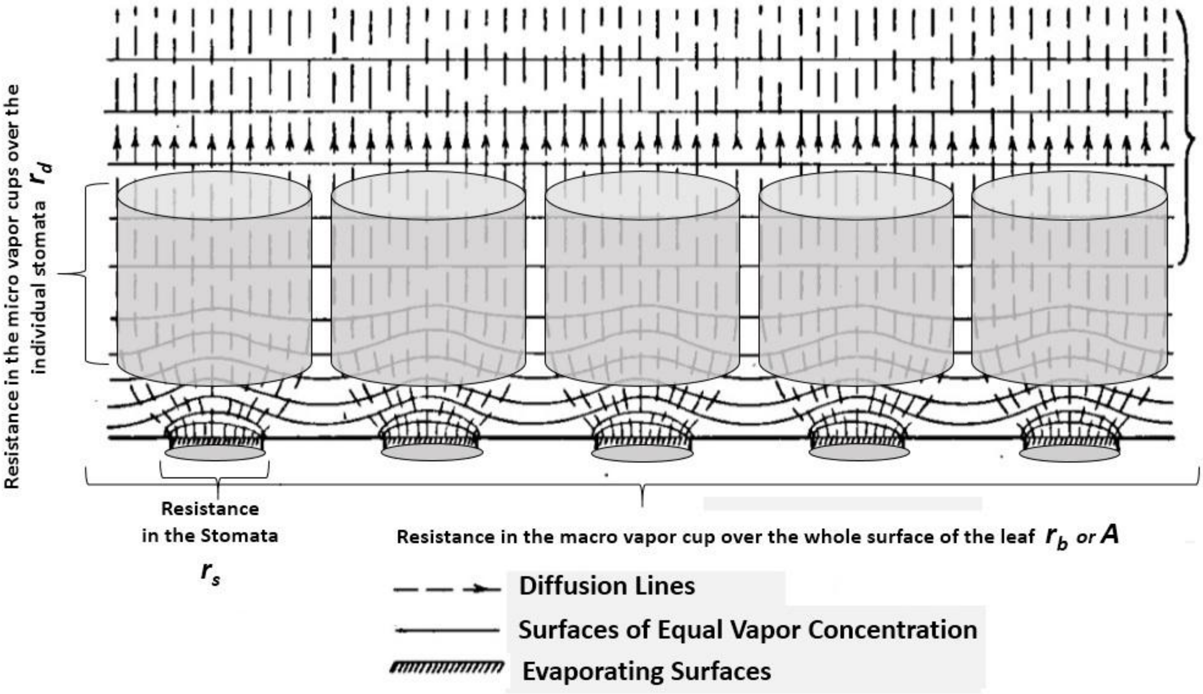
where c and c' (both in M L^{-3}) are the concentrations of water vapor in the substomatal space and in the surrounding air, respectively. The combination of eqs. (2.9) – (2.12) yields

$$i = \frac{abNk}{\frac{l_t}{\pi} + \frac{\sqrt{ab}}{4} + abl_sN}(c - c') \tag{2.13}$$

and

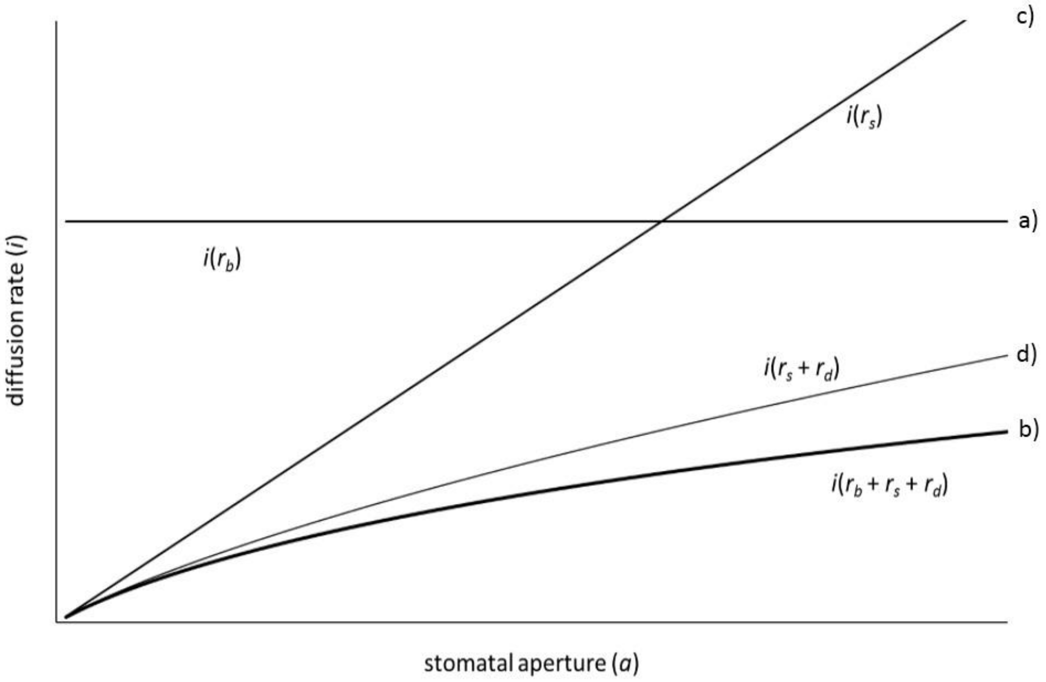
$$\frac{\partial i}{\partial a}=\frac{i}{a}\left[1-\frac{\sqrt{ab}+8abl_sN}{\frac{l_t}{\pi}+\frac{\sqrt{ab}}{4}+abl_sN}\right] \tag{2.14}$$

Figure 2.5 – Transition of micro vapor cups in adhering air layer (mutual interference of pores) adapted from Nange (1953)



Consequently, the transpiration rate increases faster with stomatal aperture at low stomatal apertures, becoming flatter as stomatal aperture increases (Figure. 2.6). It is important to emphasize that a lower atmospheric demand corresponds to a larger boundary layer resistance r_b. On the other hand, when wind speed is high, the boundary layer l_s is thinner and r_b lower (eq. 2.11). Boundary layer resistance thus depends on two factors, wind speed and relative humidity.

Figure 2.6 – Relation between diffusion (=transpiration) rate (*i*) and stomatal aperture as determined by the relative values of the resistance in the stomata (r_s), of the micro vapor cups (r_d) and of the macro vapor cup in the still air layer (r_b); inspired by Nange (1953)



In Figure 2.6, line a) shows that, for any stomatal aperture, transpiration rate (*i*) is the same, because the atmospheric demand will vary (r_b, boundary layer resistance) in function of the stomatal aperture or vice versa, the stomatal aperture would be just the necessary one to satisfy the atmospheric demand. Line b) represents the situation where all resistances in some magnitude are present and line c) shows the direct relationship between transpiration rate and stomatal aperture, without boundary layer resistance.

2.5.1 Fractionation in the leaf

Washburn and Smith (1934) measured water density in the branches and leaves of a willow tree (*Salix nigra*) and found a higher density than for river water near the tree. This triggered a discussion about isotopic enrichment in plant leaves. They attributed the higher density to a higher deuterium content in the tree water, although they did not analyze the hydrogen isotopic composition of water in the trees by the much more sensitive method of mass spectrometry. Later, Wershaw et al. (1966) showed that tree leaf water is enriched in deuterium related to phloem and xylem water. This is apparently due to isotopic fractionation that takes place during transpiration, and it appears that the amount of fractionation is a function of the transpiration rate.

Water moves through the xylem from the roots to the leaves, at a velocity which may be predicted by the distribution of xylem diameters and gradients in pressure and water temperature. Once water exits the xylem in the leaf, the pathways are less clear (RODERICK; BERRY, 2001). Water movement through leaves remains poorly understood, due to the complexity of pathways and lack of available measurement techniques (SACK; HOLBROOK, 2016; SCOFFONI et al., 2015). According to some authors like Barbour et al. (2017), it remains undetermined where the phase change from liquid to vapor occurs within leaves.

In the leaf, water moves through the xylem parenchyma and bundle sheath cells, and then through or around mesophyll cells via several potential pathways before evaporating from cell walls to finally exit as vapor through stomatal pores. Four parallel pathways are thought to exist for liquid water movement within the mesophyll according to Steudle (1993), specifically (1) apoplastic flow through the cell walls; (2) symplastic movement through plasmodesmata; (3) transcellular movement across membranes via aquaporins; and (4) vapor transport. Recent studies suggest that vapor phase transport is a significant fraction of total water transport within leaves, particularly in the presence of vertical temperature gradients as may be created by light absorption (BUCKLEY et al., 2015; ROCKWELL et al., 2014).

Besides fractionation in the leaf, leaf water isotope composition is also affected by the isotope composition of the source water taken up by plant. It is often overseen that, under dry soil conditions, the liquid film between two soil grains forms a gas-liquid-gas pathway for vapor transport. Water vapor in the soil may condense on one side of a liquid barrier and evaporate across the other side, thereby short-circuiting part of the liquid-filled pore space (JURY et al., 2004). This kind of state change may produce isotopic fractionation in the water taken up by the roots and transported to the leaf. On the other hand, the isotope composition of water vapor in the air surrounding the leaf and the ratio of the vapor pressures outside and inside the leaf also affects fractionation.

Variation in stable oxygen isotope composition can be expressed in two ways: using the mole ratio of the rare to the common isotope (R), relative to the Vienna Standard Mean Oceanic Water standard already explained above, or as an enrichment above the source water isotope composition (Δ, again in ‰).

The isotope ratio of liquid water at the sites of evaporation (R_e) were first described by Craig and Gordon (1965), and later adapted for transpiration from leaves by Dongmann et al. (1974); Farris and Strain (1978); Farquhar and Lloyd (1993); Harwood et al. (1998) as:

$$R_e = \alpha^+ \left[\alpha_k R_s \left(1 - \frac{w_a}{w_i} \right) + R_v \frac{w_a}{w_i} \right] \tag{2.15}$$

where R_s and R_v are the isotope ratios in source water and water vapor (the air water vapor), respectively, and w_a and w_i are the mole fractions (mol mol^{-1}; equal to the partial pressure ratio) of water vapor in the ambient air and inside the leaf, respectively. α_k (>1) is the kinetic isotope effect associated with the difference in diffusivities, and α^+ (>1) is the equilibrium isotope effect associated with the differences in vapor pressure.

The enrichment above source water can be expressed by Farquhar et al. (2007):

$$\Delta_e = \alpha^+ \left[\alpha_k \left(1 - \frac{w_a}{w_i} \right) + (1 + \Delta_v) \frac{w_a}{w_i} \right] - 1 \tag{2.16}$$

where Δ_v is vapor enrichment. Farquhar and Lloyd (1993) proposed a Péclet effect within leaves, in which convection of unenriched water via the transpiration stream is opposed by backward diffusion of enrichment from the sites of evaporation. The issue is treated in more detail by Barbour et al. (2017).

According to Farquhar et al. (2007), the maximum enrichment with $H_2{}^{18}O$ in leaves would occur in absolute dry air, with relative humidity (h) equal to zero, according to:

$$\Delta_e = (\varepsilon^+ + \varepsilon_k)(1 - h) \tag{2.17}$$

where Δ_e is the enrichment, in terms of the liquid-vapor equilibrium fractionation ε^+ $(= \alpha^+ - 1)$ (related to the process of evaporation inside the leaf), and kinetic fractionation ε_k $(= \alpha_k - 1)$ (related to the leaf diffusion process). Farquhar et al. (2007) proposed an equation for kinetic fractionation:

$$\varepsilon_k = \frac{32 r_s + 22 r_b}{1000 (r_s + r_b)} \tag{2.18}$$

where r_s is the stomatal resistance and r_b the boundary layer resistance.

If the source of variation is evaporative demand, it does, as can be seen by reducing relative humidity in the Eq. 2.17. Thus, the minimum enrichment corresponds to 100% of h (h =1).

2.6 The specific example of the Amazon watershed

2.6.1 Amazon watershed simple description

In the Amazonian ecosystem, the transpiration process from the point of view of isotopic fractionation in the leaf has a “non-standard behavior” in comparison to drier environments or other biomes in Brazil and around the world, for which possible causes will be discussed in the next session.

The Amazon rainforest is a tropical humid broadleaf forest in South America, mainly in Brazilian territory but covering also parts of neighboring countries. The basin encompasses 7 million square kilometers. It has an important value regarding global oxygen and carbon dioxide cycles and it is home to the most diverse and numerous arrays of plants species in the world. It has a tropical climate that is hot and humid throughout the year. The average temperature in the drier season is 27.9 °C and in the rainy season 25.8 °C. Air humidity is very high, 90% on average in the rainy season and 80% in the dry season. Mean precipitation is estimated between 2000-2800 mm y^{-1} (QUESADA, 2011). The geomorphological structure of the basin is plain with an altitude difference of only 120 m over a range of the 3400 km.

Although the Amazon basin appears, at first sight, to be a rather uniform hydro-meteorological unit, the isotope composition of rainfall and river water shows complex, with seasonal and geographic variability. This shows the basin to be inhomogeneous from the hydro-meteorological point of view (SALATI et al., 1979). The soils of the Amazon are maintained due to the climax of the ecosystem, most of them being Ferralsols. Despite common belief, sandy soils make up only 7% of the total area.

The trade winds that blow from the Atlantic Ocean account almost half of these rains according to several authors. The remaining part originates from evapotranspiration. Preliminary calculations on the water balance in the central Amazon watershed by Molion (1975) and Villa Nova et al. (1976) indicated more than half of the precipitated waters to be returned to the atmosphere through evapotranspiration, while about 45% are drained by the fluvial system. Isotopic analyses confirm evapotranspiration to be the dominant factor during the southern hemisphere winter months (SALATI et al., 1979).

2.6.2 Modeling a plant as an evaporating water reservoir in Amazon

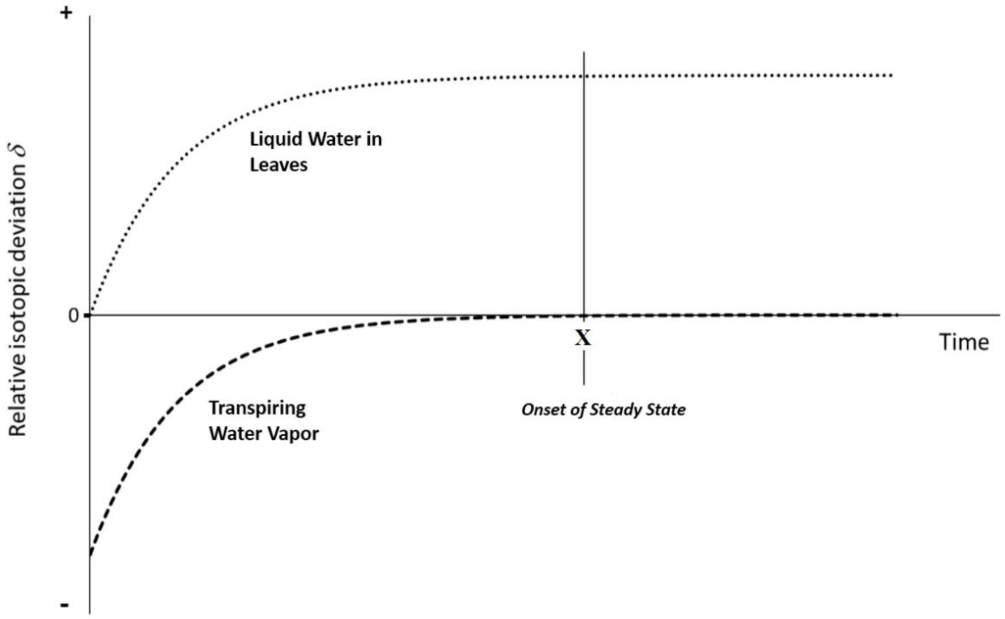
One could simply assume that there is no process of isotopic fractionation of water molecules anywhere in the plant. On the other hand, a plant (tree) in the Amazon could be modeled as an evaporating water reservoir which is replenished with (rain) water with a constant isotopic composition; the isotopic composition of evaporating water will tend to a steady-state in which it will be equal to the composition of the rainwater, over a long period of time (Figure 2.7) assuming that in the process of root water uptake is not associated with fractionation (ZIMMERMANN, 1966). Both ideas promote a direct recycling of water and argue the theory that transpiration is a non-fractionating process. The length of time to reach this equilibrium will depend on the anatomical characteristics of the plant and environmental conditions.

The same figure shows that, to compensate for the higher saturated vapor pressure and diffusivity of the lighter isotopologues, the relative concentration of the heavier isotopologues in the reservoir (plant) will be higher than in the rainwater; in a first period. If the liquid water isotope composition reaches the equilibrium level, so will the transpiring water vapor composition (Time “X” in Figure 2.7), and there will be no more isotopic fractionation in the transpiration cycle.

Under these steady-state conditions, the isotopic composition of rainwater and transpired water would be the same, and this situation might correspond to a tropical rainforest like in the Amazon, especially under humid conditions when the origin of rainwater is mostly the forest itself (SALATI et al., 1979). This is where some of the research work on isotopic hydrology carried out in the Amazon converges, but ignores the fact that physiological aspects of the plant make that this “steady-state” is never reached.

According to Jensen (1968) and Davies and Zhang (1991) the amount of water retained by plants is insignificant when compared to evapotranspiration. About 2% of water absorbed by roots is used by plants, the rest is transpired, and the permanence time of water inside the plant is very fast, most of the water being absorbed and transpired on the same day. This constant renewal of water makes that the steady-state from Figure 2.7 is never reached. As water is constantly circulating, the isotopic proportions in the system do not stabilize.

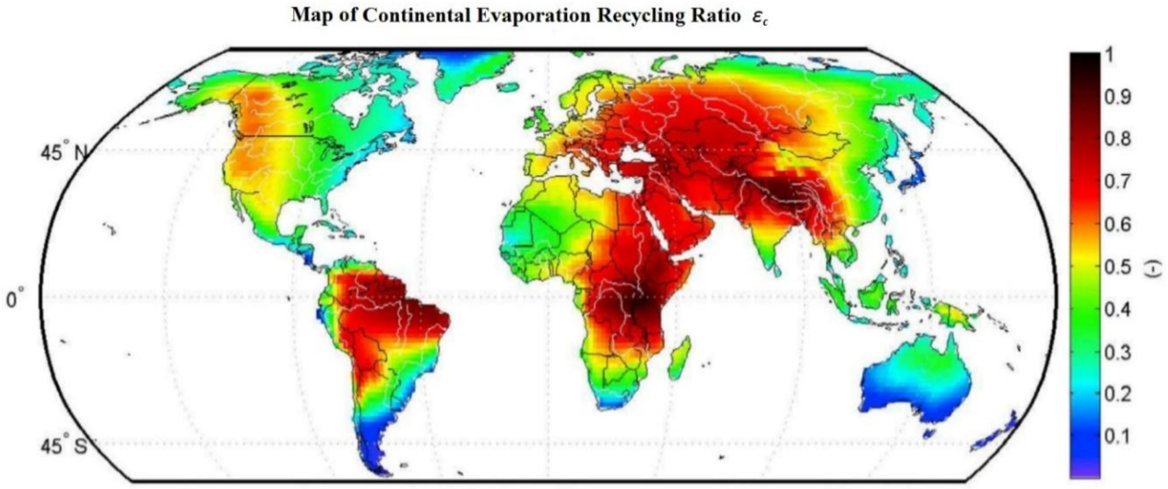
Figure 2.7 – Schematic representation of the isotopic deviation of plant water and transpired vapor relative to the isotopic composition of soil water



2.6.3 Water recycling in the Amazon basin

Water vapor isotopic measurements at continental sites have been used to identify the sources of boundary layer water vapor, including continental evapotranspiration, free tropospheric water vapor, or re-evaporated water from rainfall (WEN, 2010). Several studies as Noone (2011) and Lee et al. (2012) suggest that water vapor isotopic measurements could help characterize boundary layer mixing and associated structures, but quantitative estimates have not yet been done (GALEWSKY et al., 2016). Van der Ent et al. (2010) proposed a map of continental evaporation recycling, allocating the Amazon Basin within the largest evaporation recycling sites in the world (Figure 2.8), this evaporation including crop transpiration too.

Figure 2.8 – Continental evaporation recycling ratio ε_c (1998-2008) taken from van der Ent et al. (2010)



Quantitative estimates based on water vapor isotopic measurements have been more successful for the partitioning of the evapotranspiration flux into its different components, bare soil evaporation and transpiration (MOREIRA et al., 1997; WILLIAMS et al., 2004). When the isotopic composition of the total evapotranspiration flux is estimated, it can be partitioned into these two mechanisms if the isotopic composition of both components is known. For example, in the case of the partitioning into soil evaporation and transpiration, the isotopic composition of bare soil evaporation can be estimated using the equation of Craig and Gordon (1965) together with measurements of surface soil water isotopic composition, whereas the isotopic composition of transpiration can be estimated using isotopic measurements of water in leaf tissue (MOREIRA et al., 1997). The isotopic composition of transpiration in laboratory measurements using *in situ* water vapor analyzers can also be used (LEE et al., 2012).

At the continental scale, an important component of the water cycle is recycling, which is the partial return of continental precipitation back to the atmosphere through evapotranspiration. In some examples, the proportion of the precipitation arising from evapotranspiration over land can be as high as 85%, reported by Zimmermann et al. (2000) for Siberia during the summer season, or higher than 60% in the Congo basin all year long as reported by Yoshimura et al. (2004) and Gimeno et al. (2010).

In the context of the Amazon watershed, Dall'Olio et al. (1979) proposed to use the isothermal Rayleigh model to describe the average monthly isotopic distribution of rainfall; it was based on the almost constant temperature and constant relative humidity values in the basin along the year. The authors demonstrated that vapor from the ocean, entering the basin from east to west, was not the only vapor source. They concluded that vapor transpired by the Amazonian forest also had an important role in the cycle.

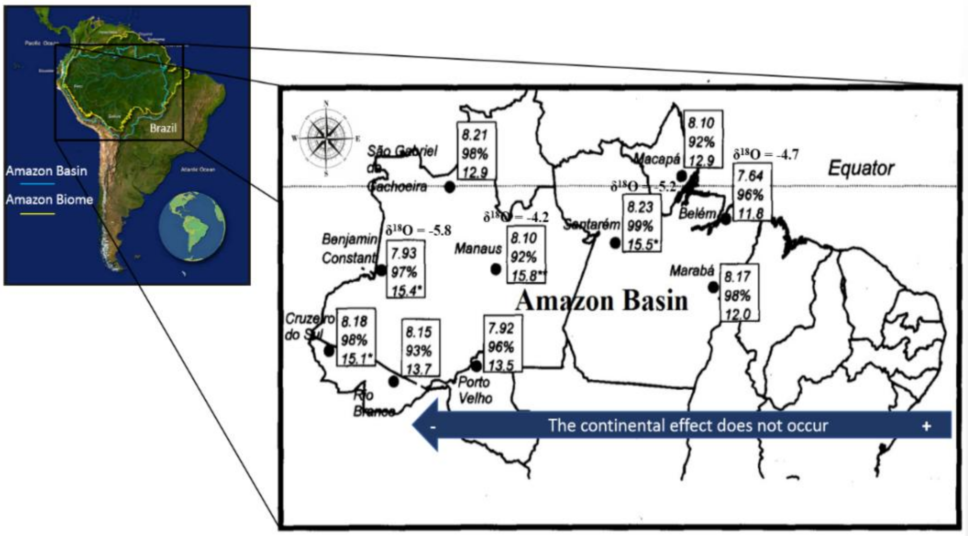
Dall'Olio et al. (1979) affirm that the relative isotopic enrichment of the vapor originated from evapotranspiration can be identified as the relative enrichment of the precipitation itself. They justify this by citing Zimmermann (1966) who stated that evapotranspiration does not induce isotopic fractionation. Although the statement by Zimmermann (1966) is plausible, i.e., root water uptake is not associated with fractionation because there is no phase change involved (WASHBURN; SMITH, 1934; BARNES; ALLISON, 1988; FLANAGAN; EHLERINGER, 1991), the subsequent transpiration of water in the stomata leads to isotopic fractionation, as detailed in previous sections. The publication by Dall'Olio et al. (1979) was used as a reference in some subsequent papers on related subjects (SALATI et al., 1979; VICTORIA et al., 1991) propagating the unproven and implausible assumption that the average isotopic composition of the vapor originated from transpiration is always equal to that of the soil water absorbed by the root system. These authors did not go into details of the topic, but simply assumed transpiration not to fractionate, thus ignoring the enrichment of heavy isotopes of the leaf water as a result of the phase change occurring in the stomata and affecting the isotopic properties of water in the hydrological cycle.

A landmark research paper about isotopic hydrology in the Amazon region was published by Salati et al. (1979), entitled "Recycling of Water in the Amazon Basin: An Isotopic Study". These authors affirm that there is a small inland gradient of the isotopic composition of precipitation, confirming the importance of the reevaporated moisture in the water balance on the area. According to the authors, the value of deuterium excess (*d*) can be taken as indicator of recycled water. A value of *d* greater than 10‰ indicates that the water recycling primarily occurs through evaporation. Salati et al. (1979) sustain that this information cannot be used for a quantitative measure of the reevaporation process in the basin, because the relative contribution of transpiration and free surface evaporation to the reevaporation flux is unknown. They confirm that "transpiration does not present isotopic fractionation", without a plausible explication for this extraordinary claim.

In a publication entitled “Mechanisms of Water Recycling in the Amazon Basin: Isotopic Insights”, Victoria et al. (1991) state that: “Evapotranspiration, which is a non-fractionating process with respect to isotopes, returns to the atmosphere water of isotopic composition similar to its source (rainwater)”. This affirmation seems, again, based on the apparently flawed Salati et al. (1979) model.

These publications show that the water vapor returns isotopically enriched to the atmosphere, making authors to conclude that transpiration is non-fractionating. The map in Figure 2.9 shows the maintained inland gradient of $\delta^{18}O$ and $\delta^{2}H$, without spatially significant variations. As shown, values of $\delta^{18}O$ are not decreasing when moving away from the coast. A decrease of $\delta^{18}O$ and $\delta^{2}H$ values in precipitation as air masses move inland is common, well known and has been named “continental effect” (DANSGAARD, 1964). The magnitude of the continental effect varies greatly over space, with a smoother decrease of vapor and precipitation ($\delta^{18}O$ and $\delta^{2}H$) values over tropical land forests such as Amazon basin. The continental effect, also referred to as the “distance from coast effect”, i.e. a progressive $\delta^{18}O$ depletion in precipitation with increasing distance from the ocean, varies considerably from area to area and from season to season, even over a low relief profile. It is also strongly correlated with the temperature gradient and depends both on the topography and the climate regime (GAT, 2001). Hence, the non-occurrence of this effect corroborates isotopically with water vapor returning enriched to the atmosphere. The mechanism behind this phenomenon is not yet understood.

Figure 2.9 – Map of the Amazon basin showing the location of the rainfall-sampling network (adapted from Martinelli et al. (1995)). For each station, from top to bottom, the slope and correlation coefficient of the regression line for $\delta^{18}O$ vs. $\delta^{2}H$ and the average *d* (deuterium excess) values are shown. There is no east-west pattern for *d* and slope. The values of $\delta^{18}O$ shown in the map were taken from Dall’Olio et al. (1979) demonstrating that there is no pattern of continental effect



Transpiration is the dominant process and evaporation may be responsible for up to 40% of the evapotranspiration flux according to Gat and Matsui (1991) and Victoria et al. (1991). On the other hand, according to Martinelli et al. (1995), transpiration is the largest component of the evapotranspiration flux, and has a clearly recognizable source, the dense vegetation of the Amazon region. However, this author calls attention to the high *d* values found in the central area of the Amazon basin that indirectly confirms the importance of evaporation in this area as a source of water vapor to the atmosphere.

2.6.4 Why is transpiration in the Amazon basin assumed a non-fractionating process?

As shown the Figure 2.9, the continental effect is almost absent in the Amazon basin and the $\delta^{18}O$ and $\delta^{2}H$ taken from precipitation do not vary significantly across the watershed, as confirmed isotopically by Salati et al. (1979), Victoria et al. (1991), and Martinelli et al. (1995). It seems plausible that plant transpiration is responsible for this non-continental effect. Then, refuting Salati et al. (1979) and cited subsequent papers, and considering transpiration a fractional process, how can the non-fractionation in the Amazon watershed be explained?

To understand the issue, it is important to firstly recall that in the Amazon watershed relative humidity is very high and almost does not vary over the seasons. The average rainfall is abundant, between 2000 to 3000 mm y^{-1}. These factors make the boundary layer resistance r_b to increase, reducing atmospheric demand. On the other hand, if r_s is large compared to r_b (at small stomatal apertures), r_s will practically determine the transpiration rate and it will be closely proportional to stomatal aperture. Soil water content is a determining factor in stomatal aperture (SCHULZE, 1986), which is reduced by plants when soil water becomes limiting. Therefore, water availability linked to soil and rooting properties in the watershed may play an important and overlooked role in isotopic fractionation.

Two major factors influence the rate of water flow from the soil to the roots: the hydraulic conductivity of the soil and the magnitude of the pressure gradient between soil and root through the soil (GARDNER, 1960; COWAN, 1965). Both factors influence the rate of bulk flow of water moving from the roots to the stomatal pores in the leaves through the xylem. Mass flow of liquid water from the roots to the leaves is driven by water potential differences.

Ferralsols are the predominant soil type in the central and eastern areas of Amazonia (QUESADA et al., 2011). Despite Ferralsols being chemically poor and with an acidic reaction, they mostly show favorable physical properties. They are deep, well drained soils which have low silt content, low bulk density, strong fine and very fine granular structure, and a high hydraulic conductivity (SANCHEZ, 1981). Ferralsols also have a considerable capacity to accumulate soil organic matter through prevalent organo-mineral interactions and their extensive depth (PINHEIRO-DICK et al., 2005). Although often with a low volumetric water holding capacity (due to their low silt content), because of their good physical structure and considerable depth, Ferralsols may be capable of storing much more water than other more common tropical soil types. This allows forests on these Amazonia soils to maintain physiological activity (i.e., maximum stomatal aperture) throughout extended dry seasons (LLOYD et al., 2009).

Therefore, with the high rainfall amount and high humidity in all seasons and a high available water content in the soil, the soil-water conditions are very favorable suitable, and stomatal resistance r_s will be low through most part of the year, making it easier to reach the isotopic water recycling. In the Amazon environment, the r_b resistance is higher than r_s resistance. If the atmospheric demand changes and the water content in the soil decreases, both resistances must be taken into account, as in case b) in Figure 2.6. On the other hand, case c) would only occur for very dry conditions with wind, when atmospheric demand would be so large that there would be no still air layer resistance ($r_b = 0$). However, the larger the stomata aperture, the more important r_b becomes and eventually it may constitute the main limiting factor in transpiration, especially in the case of the Amazon basin.

Correspondingly, according to Eq. 2.15, the minimum enrichment Δ_e in leaves would occur under high relative humidity. At the same time, Eq. 2.16 from Farquhar et al. (2007) shows the direct relation between kinetic fractionation and both resistances. In measurement performed by Cappa et al. (2003), the fractionation factor in the boundary layer was lower than in the stomatal pore (Figure 2.10). Consequently, when stomatal resistance increases, its fractionation tends to dominate and ε_k increases. In other words, leaf water should become more enriched by stomata closure and i reductions. This explains that fractionation due to transpiration occurs under certain conditions, that it is a component to take into account in the simulation models, and that it cannot be simply ignored. The duration of this isotopic imbalance may be important depending on the kind of study.

In the Amazon, the opposite happens: leaves are less enriched in ^{18}O and ^{2}H, and water vapor going to the atmosphere is isotopically almost equal to the water taken up by roots, given by environmental stability and ideal conditions. In Figure 2.11 this is explained stepwise. Figure 2.11a demonstrates the conditions of the Amazon basin. While transpiration demand is low, the stomata remain open because soil water is not limiting. Under these conditions, no significant fractionation occurs in the leaf by diffusion and the formed water vapor ends up in the atmosphere with almost the same isotopic composition as the water taken up from the soil. It produces the water recycling explained by Salati et al. (1979) and Victoria et al. (1991).

Figure 2.11b shows another extreme scenario with dry soil and lower relative humidity. This is a high evapotranspiration demand scenario and the stomata are more closed due to a low soil water availability. This leads to a large fractionation in the leaves, which become strongly enriched in heavy isotopes; the depleted water vapor formed in the leaf goes to the atmosphere, making resulting rainfall to have a depleted ("light") isotopic composition. As the rainfall in this type of environment are originated from different sources this also produces different water fractionation.

Figure 2.10 – Enrichment of leaf water versus relative humidity in five C_3 grass species. All grasses were grown in chambers where the isotope ratio of source water was held constant, leaf boundary layer development was minimized by high wind speeds, and only relative humidity varied across treatments taken from Cappa et al. (2003)

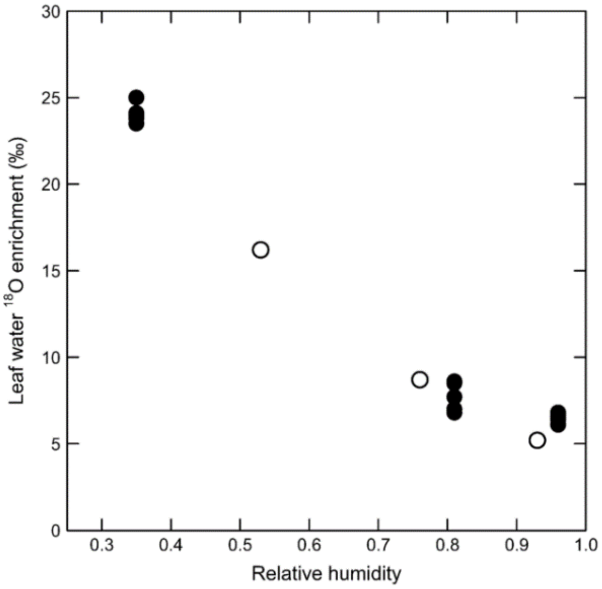
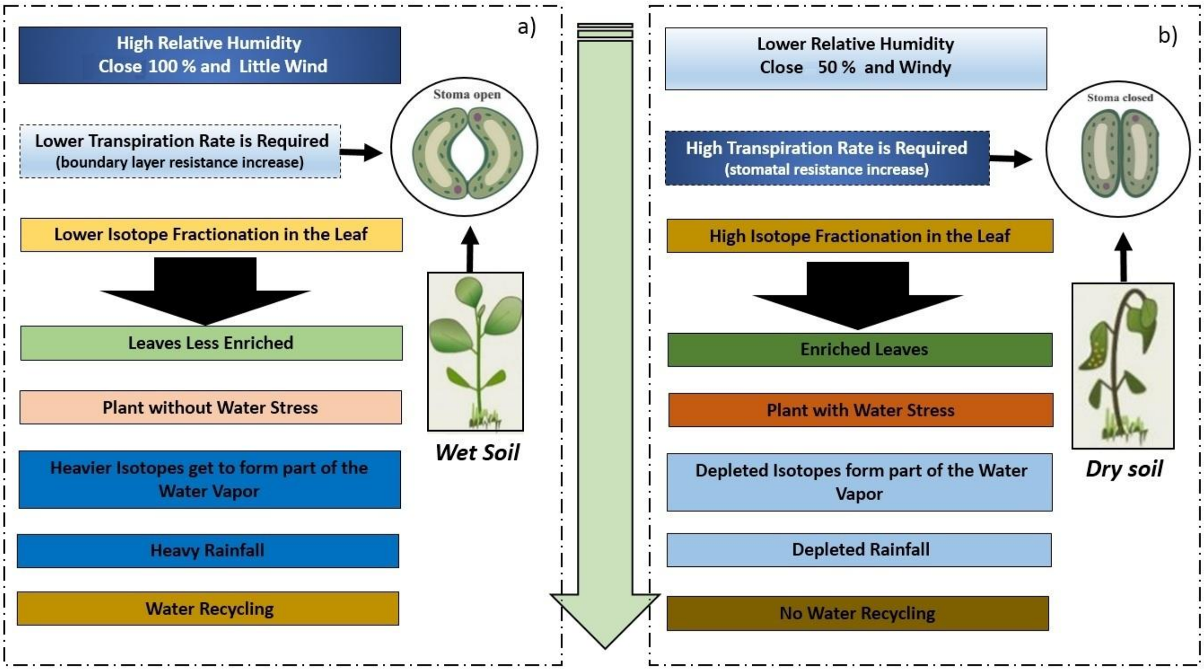


Figure 2.11 – Two representations of different environmental conditions and their response in terms of leaf fractionation under transpiration a) without fractionation, and b) with fractionation



2.7 Conclusions

In this study, we showed transpiration to be an isotopic fractionating process. The magnitude of this fractionation is determined by environmental factors, such as soil water content, amount of precipitation, temperature, and relative humidity.

The environmental factors influence the behavior of important system properties like stomatal aperture, diffusion resistances, and kinetic fractionation. This explains why several authors demonstrated the recycling of water vapor in the Amazon Basin using isotopic methods.

Different approaches are used by researchers in the branch of isotopic hydrology and those who study isotopes in plants, such as biologists and agronomists. More interdisciplinary work could benefit the understanding of isotopic behavior in the soil-plant-atmosphere hydrology.

Transpiration and evaporation physical involve the phase change of water from liquid to gaseous state. This implicitly leads to isotopic fractionation. The main difference between both processes is the pathway of the water vapor to the open atmosphere, more complex in transpiration than in evaporation. The complexity of this pathway increases with increasing stomatal resistance.

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3 RELATING RAINFALL ISOTOPIC COMPOSITION, AMOUNT AND EROSIVITY FOR PALEOCLIMATE RECONSTRUCTION IN WESTERN CUBA

Abstract

Knowing the relation between rainfall intensity and erosivity versus isotopic composition enables understanding the energetic behavior of precipitations in past eras; however, this relation is rarely established. In this study, we look for a relationship between the isotopic composition of rainfall ($\delta^{18}O$ and $\delta^{2}H$), amount and erosivity for the western part of Cuba. Based upon weighted-mean stable isotope values taken from the Global Network of Isotopes in Precipitation (GNIP) for three sites in Cuba, an isotopic study was made in combination with the determination of a mathematical model that describes the relationship between $\delta^{18}O$ and $\delta^{2}H$, amount and erosivity of rainfall. In addition, pluviographic data from the study area were used to calculate erosivity according to three models (*R* factor, Lal Index and Modified Fournier Index) which were then correlated to erosivity and isotopic composition. The isotopic characterization showed a seasonal variation: in summer, rainwater was depleted of heavy isotopes, whereas in winter it was enriched. The isotopically most depleted month was September with a $\delta^{18}O$ of -6.28‰ and a $\delta^{2}H$ of -35.5‰ at the El Salto location, related to an erosivity of 2205 MJ mm ha^{-1} h^{-1}, Lal factor of 130.3 cm^{2} h^{-1} and a Modified Fournier Index of 0.2 mm. June was the most erosive month, with a mean R_m value of 2753 MJ mm ha^{-1} h^{-1}, whilst $\delta^{18}O$ was -3.23‰ and $\delta^{2}H$ -13.5‰. $\delta^{2}H$ and $\delta^{18}H$ were negatively correlated with erosivity and with the amount of precipitation at the three investigated GNIP sites. Rainfall amount strongly and negatively correlated to the isotopic composition ($\delta^{18}O$ with r = -0.85 and $\delta^{2}H$ with r = -0.87 in the El Salto location). Regression equations to correlate monthly isotopic composition and *R* erosivity factor and rainfall amount were established for western Cuba.

Key words: erosivity, oxygen, hydrogen, rainfall amount, Cuba, paleoclimate

3.1 Introduction

Karstic basins have been used frequently to obtain paleoclimatic information (HODELL et al., 2004). Karstic environments are ubiquitous throughout the Caribbean and offer a variety of features that act as sediment sinks, such as sinkholes, blue holes and aquatic caves. These basins remain stable after their formation and may record sedimentation history from past geological eras when the sea level was sometimes lower and sinkholes deeper (BROWN et al., 2013). In Cuba, despite these advantages, karstic basins remain relatively unexplored in terms of environment and sediment studies. Recently, sediments from sinkholes have been used to examine hurricane incidence (BRADEN et al., 2014). Stalagmites show strong potential as high resolution records for paleoclimatic and paleoenvironmental reconstruction and stable isotopes of oxygen and hydrogen in stalagmites allowed to study the climatic changes during the Late Pleistocene-Holocene in Cuba (PAJON et al., 2006). These studies focused mainly on temperature changes.

A relationship between the isotopic composition of rainwater and rainfall amount or intensity would help to reconstruct past rainfall $\delta^{18}O$ or $\delta^{2}H$ found in stalagmites. Gat and Matsui (1991) present such a relationship for tropical regions. As rainfall intensity is related to the kinetic energy of rainfall and erosivity (RENARD et al., 1997), understanding the relationship between rainfall isotopic composition, intensity and erosivity may allow interpreting the behavior of some hydro-meteorological and geomorphic features of the past-nature. Knowing not only rainfall amount but also intensity would improve the interpretation of paleoclimatic data.

Variations of the isotopic composition of meteoric waters through time at a particular site may not always be an indication of past surface temperature variations but could, instead, reflect past changes in the precipitation amount. Observations of a qualitative, inverse relationship between precipitation $\delta^{2}H$ and $\delta^{18}O$ values and precipitation intensity in single storms suggest that intensity may be of importance (MATSUO; FRIEDMAN, 1967; MIYAKE et al., 1968; MOOK et al., 1974). Nevertheless, there are few papers addressing the relationship between rainfall amount, erosivity, and isotopic composition in tropical regions. Most observations indicate that the deuterium content and drop size are inversely correlated (WOODCOCK; FRIEDMAN, 1963). Furthermore, in tropical regions, rainwater in summer is observed to be isotopically less heavy than in the winter (GAT, 2001). To contribute to the understanding of the relationship between these variables, Yapp et al. (1982) developed a simple model to show that a relationship between isotopic composition and precipitation intensity may arise as a direct consequence of the condensation process.

Spatial and temporal variations in the $\delta^{18}O$ and $\delta^{2}H$ contents of rainwater are caused by the isotope fractionation effect accompanying evaporation from the ocean and condensation during the atmospheric transport of water vapor (GAT, 1996). Water isotope fractionation is a thermodependent process, therefore a correlation exists between $\delta^{18}O$ in rainwater and the environmental temperature at the occasion of evaporation (SIEGENTHALER; OESCHGER, 1980). Generally speaking, a higher temperature leads to a higher heavy isotope content (ANDREO et al., 2004), but this rule of thumb may lead to misinterpretations, and according to Dansgaard (1964), the behavior in the tropics is the opposite as in temperate climates due to the rainfall amount effects.

On the average global scale, the $\delta^{18}O/\delta^{2}H$ relation turns out to be satisfactorily described by the Global Meteoric Water Line (GMWL) (CRAIG, 1961). Regionally and for certain periods (such as seasons) Local Meteoric Water Lines (LMWL) may be found, depending on the conditions for forming the local water source in each region and time of the year. An interesting case to focus on is Cuba. In Cuba, the climate is closely related to the direction of air mass movement, different in winter and summer, strongly determining $\delta^{18}O$ and $\delta^{2}H$ of rainwater. Summer rains in Cuba, like in most tropical regions, are normally convective. Convective rainfall occurs when the surface, within a conditionally unstable or moist atmosphere, becomes heated more than its surroundings, leading to significant evaporation. Convective rain is characterized by high intensity showers of relatively short duration and with a limited horizontal extent.

No research has been dedicated to the isotopic characterization of Cuban rainfall or to its interpretation. In this study, we investigated the relationship between rainfall isotopic composition ($\delta^{18}O$, $\delta^{2}H$), amount and erosivity. In this context, some results on rainfall erosivity from Almoza et al. (2016) were used.

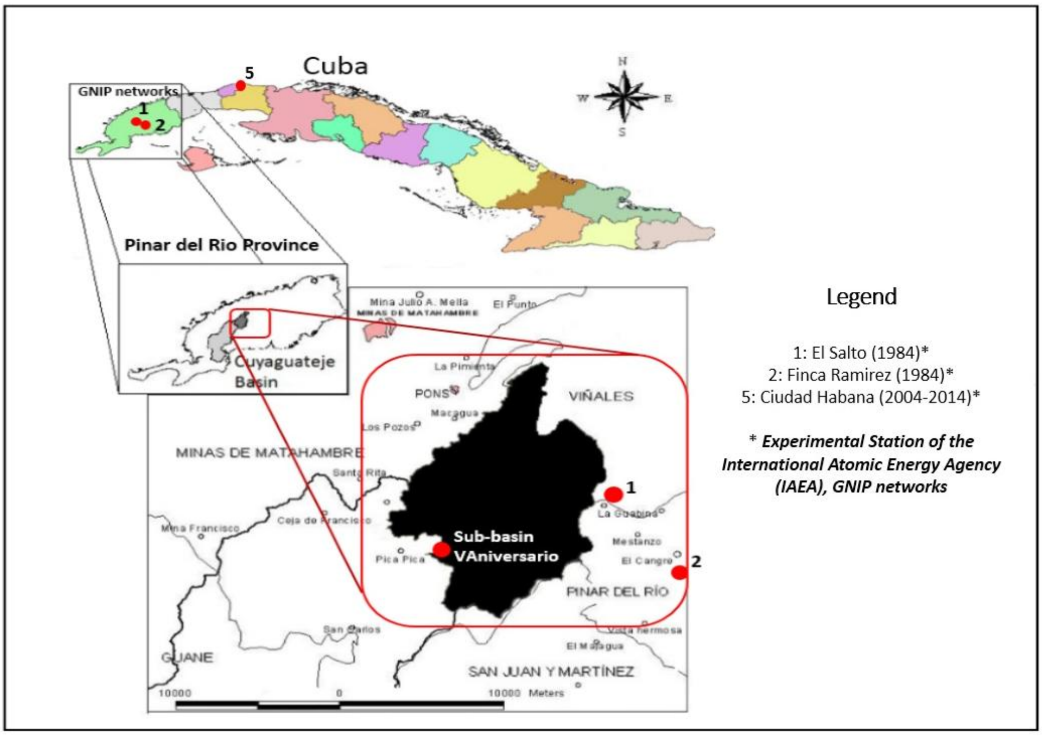
3.2 Material and methods

3.2.1 Study area

The study was performed around the 157 km² V Aniversario sub-watershed, part of the Cuyaguateje watershed, located in the Pinar del Rio province in western Cuba, latitude 22.5 °N and longitude 83.9 °W (Figure 3.1). The area is considered one of the most important karstic basins in Cuba, with underground caverns and rivers. The climate is subtropical with a well-defined dry season from November to April, and a tropical savanna climate (Aw) according to the Köppen climate classification. Mean yearly rainfall is 1700 mm and mean yearly temperature is 25.1 °C, with monthly means ranging from 22 °C in January to 27 °C in August. Relative air humidity is high, around 77% in the dry season and around 88% during the rest of the year. In this region, data from two experimental stations were used, part of the GNIP networks of the International Atomic Energy Agency IAEA and located at a few kilometers from the V Aniversario sub-watershed: El Salto (1) and Finca Ramirez (2).

The most recent data from these stations date from 1984. In Cuba, only the Ciudad Habana station (5), located at the northern side of Havana (23°N; 82°W; 50 m above sea level) has more recent data. Therefore, data from the Ciudad Habana station were also used for analysis. The Ciudad Habana station has a tropical climate that is tempered by the island’s position in the belt of the trade winds and by the warm offshore currents. Average temperatures range from 20 °C in January to 27 °C in August. Rainfall is highest in June and October and less from December through April, averaging 1 200 mm y^{-1}.

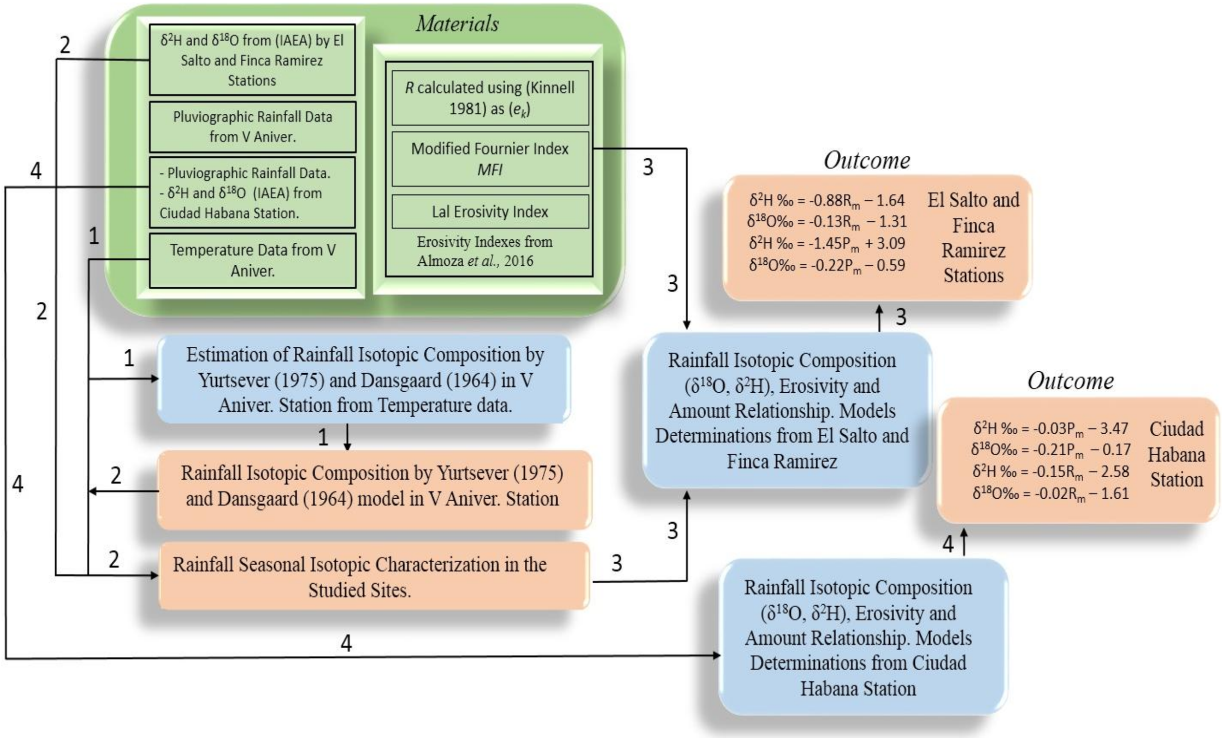
Figure 3.1 – Location of the V Aniversario sub-basin with the experimental stations El Salto and Finca Ramirez part of the GNIP networks of International Atomic Energy Agency and the Ciudad Habana station



3.2.2 Simplified description of the used methodology

Figure 3.2 shows a schematic diagram of the used methodology, subdivided in four steps. In Step 1, the temperature data from the V Aniversario sub-watershed and the models proposed by Yurtsever (1975) and Dansgaard (1964) were used to calculate de rainfall isotopic composition (δ^2H, δ^{18}O) in the sub-watershed, to be used in the regression models between rainfall (δ^2H, δ^{18}O), rainfall erosivity and rainfall amount. Models tended to overestimate the isotopic valor (see next sections for details). Step 2 deals with the general rainfall isotopic characterization for the El Salto and Finca Ramirez area near the V Aniversario sub-watershed. In step 3, the rainfall isotopic composition (δ^2H and δ^{18}O) for Finca Ramirez and El Salto were used in addition to rainfall erosivity indexes (*R* factor from RUSLE model, Modified Fournier Index *MFI*, and Lal Erosivity Index) and rainfall amounts obtained from Almoza *et al.*, (2016) to generate the respective regression models. In order to verify if there are spatial differences, other regression models between the same variables were calculated in step 4, using the data of isotopic composition and pluviographic rainfall from the Ciudad Habana station.

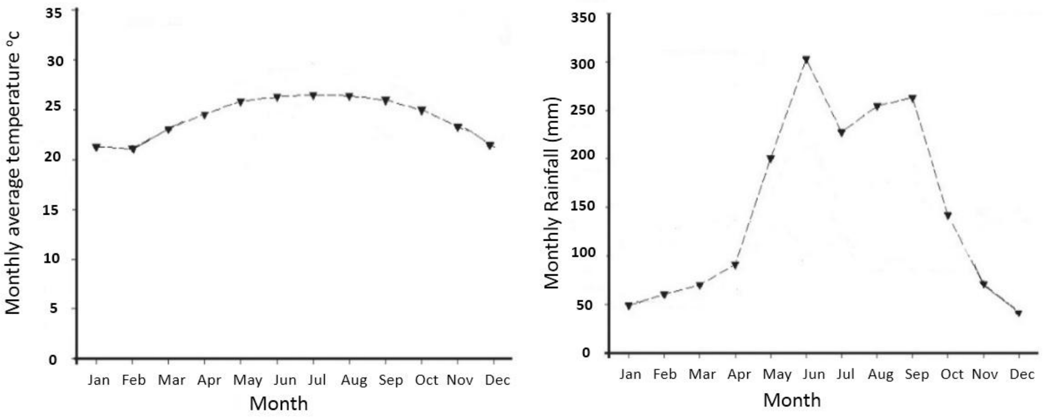
Figure 3.2 – Schematic diagram of methodology for this study



3.2.3 Rainfall and temperature data

Pluviographic rainfall data from the year 1984 in V Aniversario provided by the National Institute of Water Resources (INRH) were used. It is important to remark that regular measurements were interrupted in Cuba during the economic crisis in the 90s, and newer observations do not exist. Some meteorological data from V Aniversario are shown in Figure 3.3. In addition, temperature data were retrieved from the same source, years 1983 and 1984. On the other hand, pluviographic data from the Ciudad Habana station, obtained from the Cuban Institute of Meteorology, were used for the period between 2004 to 2014.

Figure 3.3 – Monthly rainfall distribution (left) and monthly mean temperature (right) for the V Aniversario sub-watershed



3.2.4 Data of isotopic composition of δ^2H and δ^{18}O

Data of δ^2H and δ^{18}O for El Salto and Finca Ramirez were retrieved from [websso.iaea.org], the official site of the Global Network of Isotopes in Precipitation (GNIP) of the International Atomic Energy Agency (IAEA). Available data comprised monthly mean values for 1984 and the summer months of 1983. Data from the Ciudad Habana station (available from the same IAEA website) were used for the period between 2004 and 2014.

Data from the stations participating in the GNIP originate from cooperation between WMO, Cuban national meteorological services, national authorities and scientific volunteers collecting precipitation samples for deuterium and ^{18}O analysis. The samples are mainly analyzed in the IAEA Isotope Hydrology Laboratory in Vienna, but are also measured in cooperating laboratories, usually by isotope ratio mass spectrometry and by laser absorption spectrometry for stable isotopes.

Isotopic abundances may be expressed by isotopic abundance ratios, for instance ^{2}H/^{1}H or ^{18}O/^{16}O. For practical reasons, instead of using the isotope ratio R, isotopic compositions are generally given as δ values (given in permil, equivalent to 10^{-3}), the relative deviations with respect to a standard value, as defined by:

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) * 1000(‰) \tag{3.1}$$

The accepted standard for the isotopes in water is VSMOW (Vienna Standard Mean Ocean Water), which is close to the original standard of SMOW as defined by Craig (1961). All data taken from GNIP were expressed as δ.

3.2.5 Erosivity indices

3.2.5.1 RUSLE-R erosivity factor for the pluviographic stations

Erosivity indices were calculated in several ways in Almoza et al. (2016) which will be used in the analysis for El Salto and Finca Ramirez station. At the same time, to obtain the R factor (rainfall erosivity from RUSLE) for the Ciudad Habana station, rainfall erosivity *R*, was calculated according to Renard et al. (1997):

$$R = \frac{1}{n}\sum_{i=1}^{n}\left(\sum_{j=1}^{m}(EI_{30})_j\right)_i \tag{3.2}$$

where *R* is the averaged erosivity in *n* years expressed in MJ mm ha^{-1} h^{-1}, *m* is the number of rain events each year, *i* is the year, *j* is a rain event and EI_{30} is the erosivity of a rain event expressed in MJ mm ha^{-1} h^{-1}.

Individual storm EI_{30} values were calculated according to:

$$EI_{30} = \left(\sum_{k=1}^{q} e_k \,\Delta V_k\right) I_{30} \tag{3.3}$$

where *E* is the total kinetic energy of an event expressed in MJ ha^{-1}, I_{30} is the maximum intensity of a rainfall event during 30 minutes in mm h^{-1}, *q* is the number of pluviophases of the rain event, e_k is the kinetic energy by unit of rain amount and surface in pluviophase *k* in MJ ha^{-1} mm^{-1}, and ΔV_k is the amount of rain in the pluviophase *k* in mm.

RUSLE *R* values per event (EI_{30}) were computed using a software that produces a file with: 1) event number, 2) event beginning, 3) event end, 4) rainfall by event, 5) maximum intensity of a rainfall during 30 minutes by event, 6) maximum intensity of a rainfall during 7 minutes, 7) kinetic energy by event and finally, 8) RUSLE *R* factor per event.

As shown in Almoza et al. (2016), there are different models for calculating kinetic energy, among these, several were tested and the Brown and Foster (1987) and Kinnell (1981) models were considered best for the region of Cuba.

3.2.5.2 Modified Fournier Index (MFI)

The Modified Fournier index *MFI* was defined according to Arnoldus (1977):

$$MFI = \frac{\sum_{i=1}^{12} \overline{p_i}^{\,2}}{\overline{P}} \tag{3.4}$$

where $\overline{p_i}$ is the mean rainfall in mm of month i, and $\overline{P}$ is the mean annual rainfall in mm.

3.2.5.3 Lal Erosivity Index

The Lal Erosivity Indexes were taken from Almoza et al. (2016) and calculated according to Lal (1976):

$$AI_m = 100 \sum_{i=1}^{12} \left(\sum_{j=1}^{N} (P_d \, I_{\max 7})_j \right)_i \tag{3.5}$$

where AI_m is rain erosivity, expressed in cm^2 h^{-1}, $I_{max\ 7}$ is the maximum rainfall intensity of 7 minutes in cm h^{-1}, n is the number of rain events in the respective period (month), and P_d is the daily rainfall in cm.

3.2.6 Models to estimate δ^2H and δ^{18}O for the V Aniversario station

The observed relation between monthly temperature and isotopic composition shows much scatter and is not linear. The correlation improves by taking the amount-weighted means. Based on north Atlantic and European stations from the GNIP network, Yurtsever (1975) reported the relation:

$$\delta^{18}O‰ = (0.521 \pm 0.014)t - (14.96 \pm 0.21) \tag{3.6}$$

where t is the surface temperature in ^{o}C. This equation is similar to another proposal by Dansgaard (1964) for the north Atlantic stations:

$$\delta^{18}O‰ = 0.695t - 13.6 \quad (3.7)$$

The relation is further improved if the surface temperature is replaced by the cloud-base temperature (RINDSBERGER et al., 1983). According to Dansgaard (1964), the relationship between δ^2H and δ^{18}O for tropical island rainfall is

$$\delta^2 H(‰) = 4.6(\delta^{18}O) \quad (3.8)$$

and the same author proposed the quantity *d* to be used as an index for non-equilibrium conditions, between δ^2H and δ^{18}O:

$$d = \delta^2 H - 8\left(\delta^{18}O\right) \quad (3.9)$$

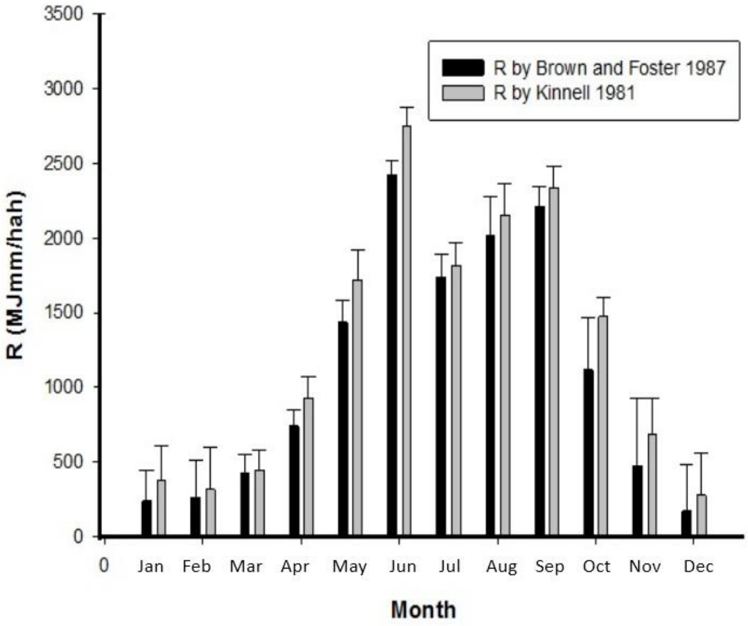
where *d* is the deuterium excess in ‰.

To develop the analysis of the relationship between rainfall isotopic composition, erosivity and rainfall amount, pluviographic data from 1984 for the V Aniversario station were used first. On the other hand, monthly values of δ^{18}O were estimated by equations (3.6) and (3.7), based on surface temperature. The δ^2H concentrations were calculated using the Dansgaard (1964) model for tropical island rainfall (3.8). The results for δ^{18}O and δ^2H for V Aniversario were compared with El Salto and Finca Ramirez station data from the GNIP network.

3.2.7 Temporal behavior of erosivity indices in the study area

According to the results of Almoza et al. (2016), monthly erosivity (R_m, MJ mm ha^{-1} h^{-1}) correlated to monthly rainfall distribution very well, with a correlation coefficient of r = 0.98. June is the most erosive month with a mean R_m value of 2753 MJ mm ha^{-1} h^{-1}, whereas December is least erosive (mean R_m = 280 MJ mm ha^{-1} h^{-1}) (Figure 3.4). The high erosivity of the June rainfall is not so much due to higher erosivity per mm of rain, but essentially related to the higher amounts of rainfall and thus the higher monthly kinetic energy. This kind of information is important in planning agricultural and irrigation activities for minimizing soil erosion. The monthly Lal Erosivity Index AI_m followed a similar pattern and was well correlated to monthly rainfall P_m (r = 0.90) and to R_m (r = 0.97). As explained in section 3.2.2, different kinetic energy models were tested in Almoza et al. (2016). Hence, Figure 3.4 shows R_m calculated using two of these models, one using Brown and Foster (1987) and the other one using Kinnell (1981).

Figure 3.4 – Representation of monthly R_m using kinetic energy models by Kinnell (1981) and by Brown and Foster (1987)



Mean annual R, calculated by Brown and Foster (1987) was 10 618 MJ mm ha^{-1} h^{-1}; using kinetic energy by Kinnell (1981) it was 12 514 MJ mm ha^{-1} h^{-1}. In the following we will use the factor R values calculated using the Kinnell (1981) model, which was developed for the region of Miami, state of Florida, USA, with climatic conditions very similar to Cuba.

According to the erosivity classification proposed by Carvalho (1994) (Table 3.1), rainfall erosivity in the sub-watershed is very high.

Table 3.1 – Classification of rainfall erosivity R (MJ mm ha^{-1} h^{-1} year^{-1}) according to Carvalho (1994)

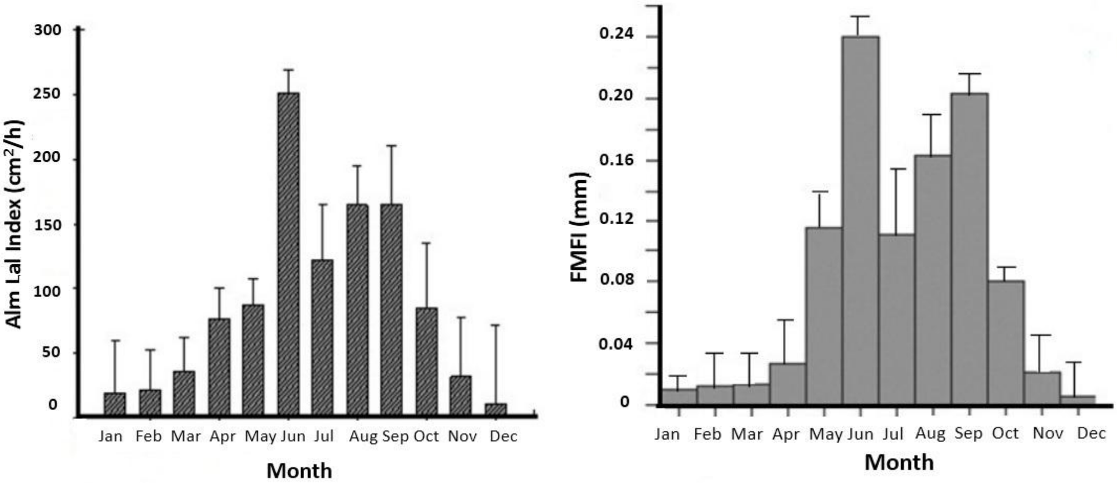
R	Classification
≤ 2452	low erosivity
2452 – 4905	medium erosivity
4905 – 7357	medium-high erosivity
7357 – 9810	high erosivity
> 9810	very high erosivity

Mean values of the monthly index AI_m by Lal (1976) changed together with the mean monthly R index. The correlation coefficient between monthly R_m and monthly AI_m was 0.97.

The maximum observed AI_m value was 251 cm^2 h^{-1} for June, and the lowest value was observed for December (11.6 cm^2 h^{-1}).

Regarding the modified Fournier index (MFI) by Arnoldus (1977), highest values were obtained also for June (MFI=0.240 mm) and lowest values for December (MFI=0.005 mm) (Figure 3.5). MFI correlated very well to R (r=0.98).

Figure 3.5 – Monthly analysis of AI_m (left) and the fraction of MFI (right) for the V Aniversario station taken from Almoza et al. (2016)



3.3 Results and discussion

3.3.1 Assessing $\delta^{18}O$ and δ^2H

Dansgaard (1964) was the first to recognize that the δ^2H and $\delta^{18}O$ composition of precipitation was negatively correlated with latitude, altitude, distance from the coast, and the amount of precipitation. Of those correlations, temperature and the continuous loss of moisture from an air mass as it moves away from its evaporative vapor source are considered to be overriding factors (YURTSEVER, 1975; GAT, 1996).

To establish a relationship between the presented erosivity indices and the isotopic composition of rainfall, a general description about the isotopic composition of rainfall for V Aniversario with the models of Yurtsever (1975) and Dansgaard (1964), and observed values at El Salto and Finca Ramirez stations data are shown in Table 3.2. Values using the Dansgaard (1964) equation in V Aniversario overestimate the $\delta^{18}O$ values by 0.30 to 7.25‰ and the δ^2H values between 1.38 and 33.35‰. This overestimation is probably due to the fact that the Dansgaard (1964) model was based on north Atlantic and European stations from the GNIP network with conditions very different from the Cuban climate. On the other hand, the Yurtsever (1975) model, also based on data from temperate climates, showed better results when compared to stations of the GNIP network in the area, deviating from -0.08 to -4.60 ‰ for $\delta^{18}O$, and from -6.81 to -21.16 ‰ for δ^2H. The Pearson correlation coefficient between $\delta^{18}O$ observed at El Salto and the $\delta^{18}O$ estimated for V Aniversario using Yurtsever (1975) is r = 0.60.

The dependence of the isotope variations on the local temperature or the closely related parameter of the precipitable water content (SONNTAG et al., 1983) appears as the overriding parameter (YURTSEVER, 1975; FRICKE; O'NEIL, 1999). Usually, the temperature dependence of both ($\delta^{18}O$, $\delta^{2}H$) values is smaller than exposed by the latitude effect, varying from about 0.5‰/°C for some higher-latitude stations to ultimately 0‰/°C for tropical ocean islands. In the case of Cuba, the latitude effect is apparently stronger than the effect of temperature.

Table 3.2 – Monthly weighted mean values of $\delta^{18}O$, $\delta^{2}H$ and *d* (deuterium excess) in rainfall in the study area (GNIP data for El Salto and Finca Ramirez stations and model-estimated data for V Aniversario station.

	El Salto			Finca Ramirez			V Aniversario					
	GNIP			GNIP			Yurtsever (1975)*			Dansgaard (1964)*		
Month (1984)	$\delta^{18}O$	$\delta^{2}H$	d ‰	$\delta^{18}O$	$\delta^{2}H$	d ‰	$\delta^{18}O$	$\delta^{2}H$	d ‰	$\delta^{18}O$	$\delta^{2}H$	d ‰
Jan	-1.02	-3.12	8.04	-0.89	-3.2	8.32	-0.08	-8.77	3.87	0.99	4.58	13.87
Feb	-1.22	-3.2	9.56	-1.02	-3.9	7.26	-0.34	-7.96	4.76	0.65	2.98	14.76
Mar	-1.41	-0.15	11.13	-2.02	-6.9	9.26	-1.04	-8.98	8.34	2.39	10.97	10.34
Apr	-1.51	-3.5	8.58	0.87	14.3	7,34	-2	-9.20	6.80	3.78	17.37	6.80
May	-1.29	-2.7	7.62	-2.34	-8.6	10.12	-3.48	-6.81	5.03	4.47	20.56	5.03
Jun	-3.23	-13.5	12.34	-3.1	-13.1	11.70	-3.44	-12.02	1.50	5.86	26.96	1.50
Jul	-2.21	-8.4	9.28	-5.31	-27.3	15.18	-3.08	-10.37	10.27	6.56	30.15	-0.27
Aug	-2.94	-15.2	8.32	-2.06	-9.3	7.18	-2.6	-12.76	12.04	7.25	33.35	-2.04
Sep	-6.26	-35.5	14.58	-6.59	-38.4	14.32	-0.96	-4.42	3.26	5.17	23.76	3.26
Oct	-3.19	-12.4	13.12	-3.49	-10.5	17.42	-1.48	-6.81	5.03	4.47	20.56	5.03
Nov	-2.16	-5.0	12.38	-2.44	-6.9	12.62	-3.04	-13.98	10.34	2.39	10.97	10.34
Dec	-1.01	-3.3	7.78	-1.32	1.2	8.76	-4.60	-21.16	15.64	0.30	1.38	15.64

* V Aniversario $\delta^{18}O$ values were determined according to the models of Yurtsever (1975) and Dansgaard (1964). The respective values of $\delta^{2}H$ were calculated by Equation (3.8)

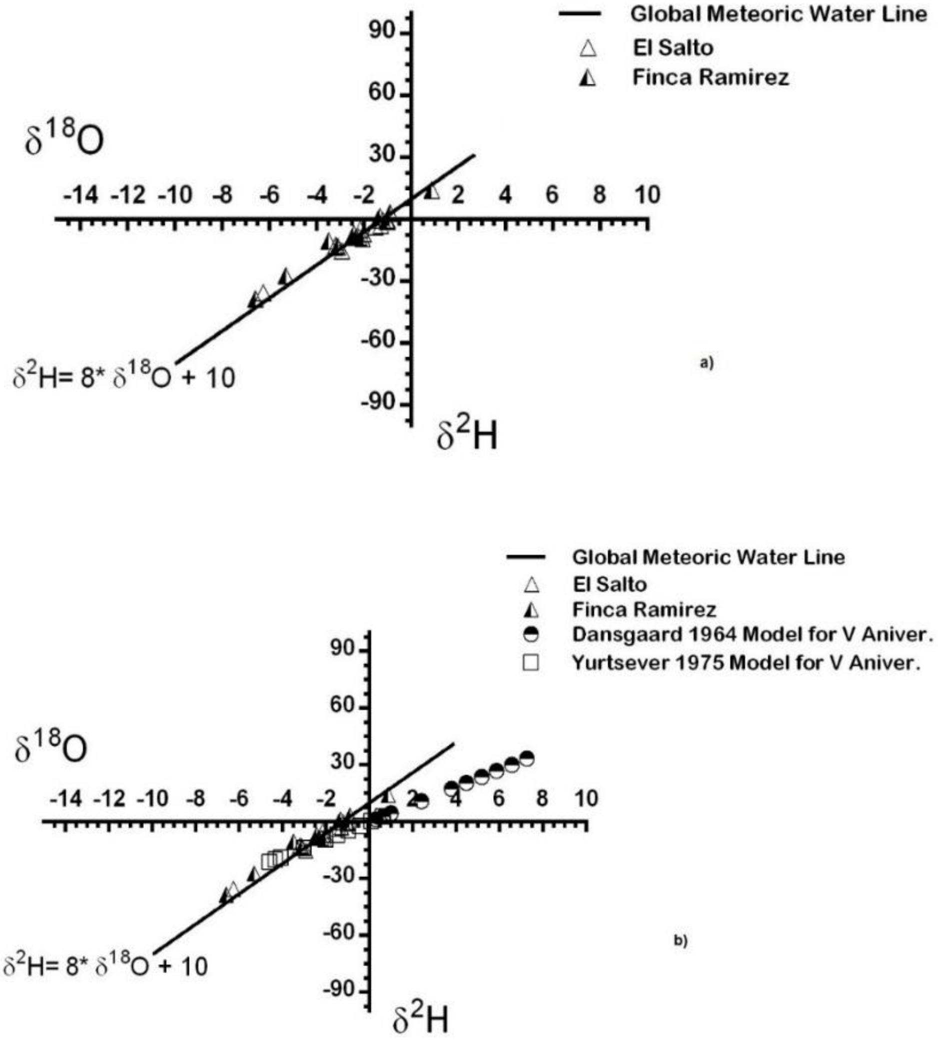
It is well established that, on the average global scale, $\delta^{18}O$ and $\delta^{2}H$ in natural waters are correlated according to the Global Meteoric Water Line (GMWL) (MARTINELLI et al., 1995). The relation between $\delta^{18}O$ and $\delta^{2}H$ values of total 1984 precipitation for El Salto and Finca Ramirez stations are represented in Figure 3.6a. Values are located near the GMWL with slope 8 and intercept of 10 as defined by Craig (1961). A least square regression of the data resulted in the equations for each individual site (Table 3.3). The slope is around 7, showing precipitation to be isotopically heavy. A slope of 7.4 was found in Florida at sites similar to the investigated Cuban locations (PRICE et al., 2008). Due to their proximity, the characteristics of both ($\delta^{18}O$, $\delta^{2}H$) equations for both GNIP network stations in Pinar del Rio showed similar behavior (Table 3.3).

Table 3.3 – Regression data for the isotopic composition of rainfall for 1984 in two stations in Western Cuba

Station name	El Salto	Finca Ramirez
	Linear Regression	
Equation	$\delta^{2}H = 6.78\delta^{18}O + 7.53$	$\delta^{2}H = 6.80\delta^{18}O + 8.23$
Slope	6.78 ± 0.32	6.80 ± 0.36
$\delta^{2}H$ –intercept (at $\delta^{18}O$ =0)	7.43 ± 0.87	8.23 ± 1.11
$\delta^{18}O$ –intercept (at $\delta^{2}H$ =0)	-1.097	-1.211
1/slope	0.1475	0.1471
R^2	0.9779	0.9733
	95% Confidence Intervals	
Slope	6.06 to 7.49	6.005 to 7.59
$\delta^{2}H$ –intercept (at $\delta^{18}O$ =0)	5.49 to 9.37	5.750 to 10.72
$\delta^{18}O$ –intercept (at $\delta^{2}H$ =0)	-1.282 to -0.88	-1.464 to -0.92

The isotopic rainfall composition estimated for V Aniversario together with both GNIP network stations is show in Figure 3.6b. Data points from Dansgaard (1964) are not on the GMWL. The models of Yurtsever (1975) and Dansgaard (1964) used to estimate in V Aniversario site show slopes of 5 and 4.6 respectively, demonstrating the overestimation of values. At tropical islands like Cuba, where the vapor source region essentially coincides with the region of precipitation, the temperature dependence may almost disappear, as is the case for data in this figure.

Figure 3.6 – Relationship between $\delta^{18}O$ and $\delta^{2}H$ weighted mean isotope values and the Global Meteoric Water Line a), and b) the same graph with the Yurtsever (1975) and Dansgaard (1964) estimated values added



As the model-generated values overestimate and El Salto and Finca Ramirez stations are close to the V Aniversario sub-watershed, in the following discussion about erosivity the station data will be used.

Although there are differences in the isotopic composition between El Salto and Finca Ramirez, their values are expected to be close due to the proximity. At both GNIP sites, rainwater in winter is isotopically heavy, whereas summer rains show depletion of heavy isotopes. The values of $\delta^{18}O$ in El Salto were concentrated between -1 and -1.5‰ in winter. Usually, May is considered a summer month, but its isotopic behavior (in both GNIP network stations) was more similar to the winter months. Regarding $\delta^{2}H$, its weighted mean values for winter were between -0.15 and -5.0‰, reflecting heavy isotopic precipitation in this season.

During summer (June to October), $\delta^{18}O$ was between -2.21 and -6.26‰ and $\delta^{2}H$ between -8.4 and -35.5‰.

During the same winter, in Finca Ramirez, $\delta^{18}O$ was between 0.87 and -2.44‰ and $\delta^{2}H$ between 14 and -3.2 ‰. On the other hand, in summer $\delta^{18}O$ was between -2.06 and -6.59‰ and $\delta^{2}H$ between -9.3 and -38.4‰, similar to the El Salto site.

3.3.2 Rainfall isotopic composition, erosivity and amount

Price et al. (2008) found that it is common for inland sites to have lower $\delta^{2}H$ and $\delta^{18}O$ values than coastal sites due to "rain-out" of air mass moisture as it moves inland. An intense recycling of water from within a watershed by evapotranspiration as observed in the Amazon basin by Martinelli et al. (1995) can reduce this effect. Therefore, high values of $\delta^{2}H$ and $\delta^{18}O$ in rainfall can occur for two reasons: proximity to the sea and low isotopic fractionation by evapotranspiration at the site. The latter closely relates to temperature, accumulated rainfall, water content, and relative humidity. However, mixing of different air masses from local vapor sources (GAT; MATSUI, 1991) as well as convective storm and frontal rainfall from the northern course (FRIEDMAN, 1962) also affect the isotopic signature of local precipitation.

One of the possible explanations for the isotopic depletion of Cuban summer rainwater is the occurrence of trade winds. The atmospheric circulation pattern Hadley cell, a closed circulation loop beginning at the equator, explains the trade winds. The rising air creates a low-pressure zone near the equator. As the air moves poleward, it cools, becomes denser, and descends at about the 30th parallel where it creates a high-pressure area. The descended air then travels toward the equator along the surface, replacing the air that rose from the equatorial zone, closing the loop of the Hadley cell. The poleward movement of the air in the upper part of the troposphere deviates toward the east due to the Coriolis acceleration. This is the source of the air masses movement from eastern in summer in Cuba, and may be one of the causes of depleted rainfall in this period because the rainfall trajectory inland is responsible for the kinetic losses in the rainfall isotopic composition.

Another important reason for this isotopic signature could lie in the fact that most precipitation in the tropical summer is convective, and convection occurs when the Earth's surface, within a conditionally unstable or moist atmosphere, becomes heated more than its surroundings, leading to significant evaporation from soil and plant surfaces.

Given the landscape conditions of the warm savannah in the study area, in summer the atmospheric demand is very excessive and the isotopic fractionating process from evapotranspiration increases returning lighter water vapor to the atmosphere.

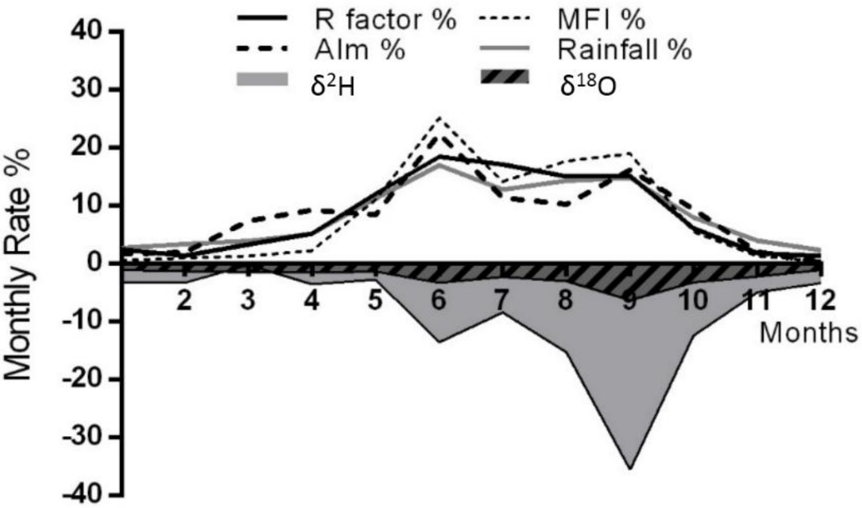
Monthly erosivity indices, the mean precipitation and the isotopic composition of rainfall ($\delta^{18}O$, $\delta^{2}H$) are shown in Figure 3.7. The most depleted month was September with $\delta^{18}O$ = -6.28‰ and $\delta^{2}H$ = -35.5‰ in El Salto, corresponding to R_m = 2205 MJ mm ha^{-1} h^{-1}, AI_m = 130.3 cm^2 h^{-1} and MFI = 0.2 mm. Nevertheless, June was the month with the highest erosivity, a mean R_m value of 2753 MJ mm ha^{-1} h^{-1} and with $\delta^{18}O$ = -3.23‰ and $\delta^{2}H$ = -13.5‰. The $\delta^{2}H$ and $\delta^{18}O$ were negatively correlated with rainfall erosivity (Table 3.4) with correlations r= -0.75 for $\delta^{18}O$ and r= -0.78 for $\delta^{2}H$. The rainfall amount showed the highest negative correlation with the isotopic composition, r= -0.85 for $\delta^{18}O$ and r= -0.87 for $\delta^{2}H$ in El Salto.

Gat (2001) found similar values for Pretoria, South Africa. They suggest these values to be correlated with a high precipitation intensity and low $\delta^{18}O$ and $\delta^{2}H$ during summer. The strong tropical rainfall at times of the passage of the Intertropical Convergence Zone (ITCZ) characterized by towering clouds and strong downdrafts, may be extremely depleted in $\delta^{18}O$ and $\delta^{2}H$, the former by as much as -15‰. Similar though smaller effects are observed in thunderstorm-engendered (hence: convective) precipitation. In north-western Europe, changes in $\delta^{18}O$ of -7‰ have been found within 1 hour during convective storms. Small amounts of rain are, as a rule, enriched in the heavy isotopes along typical evaporation lines. This effect obviously results, among other things, from the evaporation of rain droplets on their fall to the ground. However, no further consistent amount effect is noted for rain intensities more than about 20 mm/month (GAT, 2001).

Bolin (1958) calculated that only the heaviest showers with intensities above 10 mm/h represent the relatively unmodified composition of the precipitation at the cloud base, when that is up to an elevation of about 1000 m.

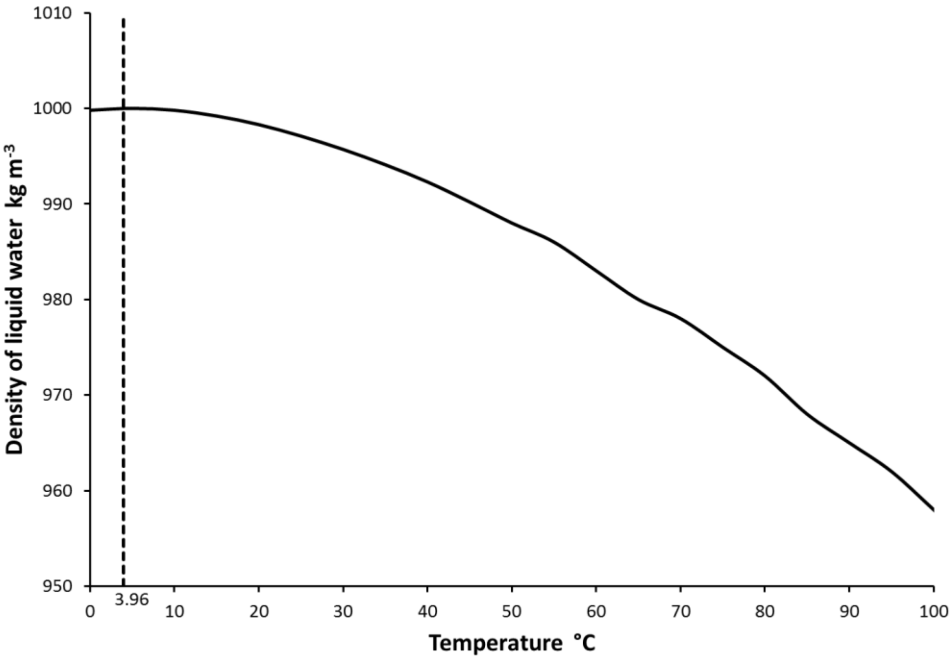
Taking into account that in the case of the Cuban winter the air mass movement comes from the north, and that it is collected at an island site not far from the coast (25 km from the north coast), it has the characteristics of a first condensate vapor, therefore isotopically heavier. Considering four months of summer data from 1983 at both GNIP sites as well as the 1984 data, we can conclude that for rainfall amounts higher than 110 mm the $\delta^{18}O$ is more or less -3‰.

Figure 3.7 – Monthly values of erosivity indices, rainfall amount and monthly composition of $\delta^{18}O$ and $\delta^{2}H$ at El Salto station, being (Alm) the Index of Lal and (MFI) the modified Fournier Index



Some criteria about the relationship between erosivity and rainfall isotopic composition in the tropics are based on the observed strongly negative correlation. Possibly, erosivity is negatively correlated to isotopic composition by transitivity, but it is not a causal relationship. In nature, heavy isotopes ($\delta^{18}O$ and $\delta^{2}H$) are in low proportion in water molecules, making that the mass of raindrops is not affected significantly by the abundance of heavy isotopes. In fact, water density is much more affected by temperature, but even this variation is relatively small, varying from 999.8428 kg m^{-3} to 992.2152 kg m^{-3} between 0 ºC to 40 ºC (TANAKA et al., 2001). Figure 3.8 show de relation between density and temperature. Regardless of whether the temperature affects the density more than the isotopic composition, neither of them reaches considerable alterations in the rainfall erosivity in Cuba. As the differences between the means of seasonal temperature in Cuba are not very large, according to Tanaka et al. (2001) in summer could be approximately the density of 996.5151 kg m^{-3} and in winter of 997.5408 kg m^{-3}, the variation being not significant to influence erosivity.

Figure 3.8 – Relationship between temperature and liquid water density (TANAKA et al., 2001)



As shown, there are many possible explanations, and the conclusion is that there is no simple generalization and that the local amount effect should be evaluated individually in each case, by running an extended planned sampling. Nevertheless, with the limited data set available, we established relationships between variables (Table 3.4).

Table 3.4 – Correlations between rainfall amount, erosivity with $\delta^{18}O$ and $\delta^{2}H$

Pearson Correlation Coefficient	Experimental Station, GNIP data network, (IAEA)	
	El Salto	Finca Ramirez
R_m and $\delta^{18}O$ [a]	-0.75	-0.72
R_m and $\delta^{2}H$ [a]	-0.78	-0.75
MFI and $\delta^{18}O$ [b]	-0.80	-0.82
MFI and $\delta^{2}H$ [b]	-0.82	-0.84
AI_m and $\delta^{18}O$ [c]	-0.70	-0.73
AI_m and $\delta^{2}H$ [c]	-0.73	-0.76
P_m and $\delta^{18}O$ [d]	-0.85	-0.83
P_m and $\delta^{2}H$ [d]	-0.87	-0.85

[a] correlation with the monthly factor R

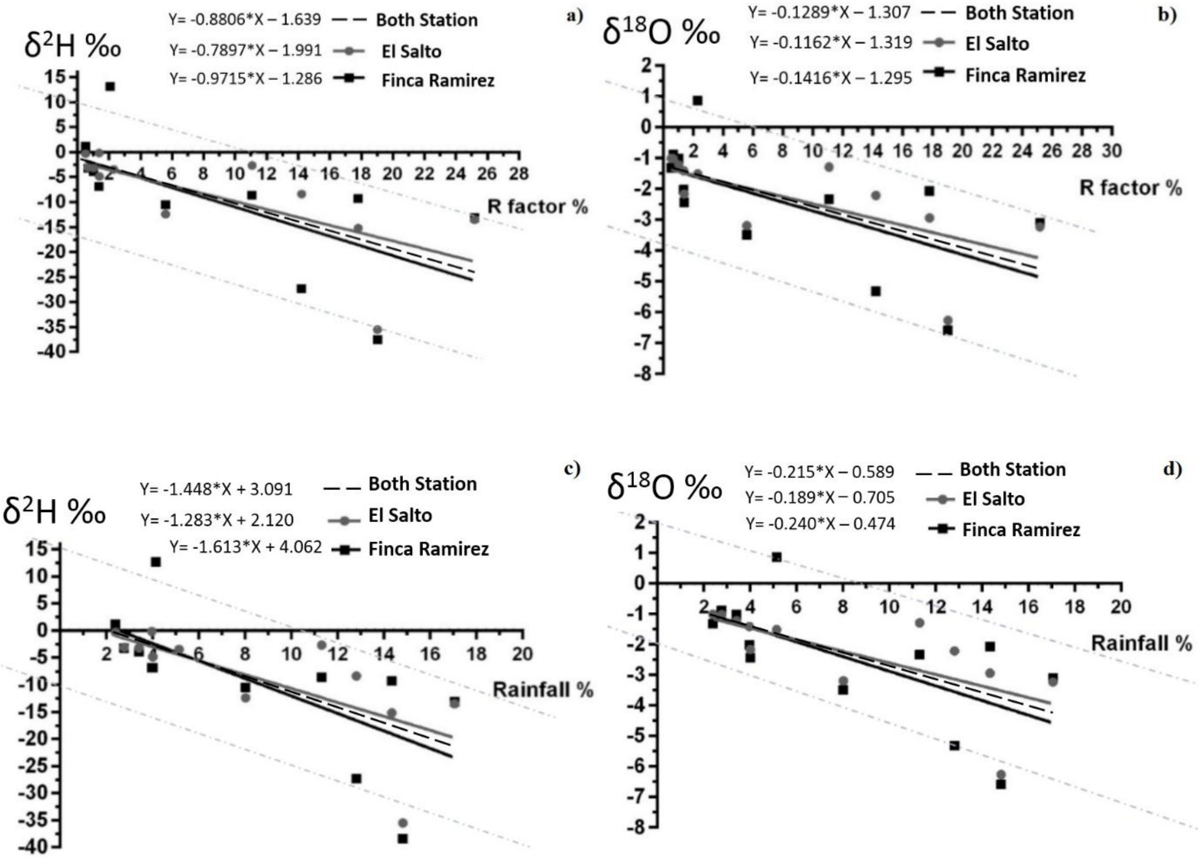
[b] correlation with the monthly Modified Fournier index

[c] correlation with the monthly Lal index

[d] correlation with the monthly rainfall, for both stations El Salto and Finca Ramirez

Regression equations that describe the relationship between Erosivity R_m and isotopic composition (δ^{18}O and δ^{2}H) are represented in Figure 3.9a and b. Figure 3.9b shows that both equations have an intercept of about -1.3 and slopes of -0.11 and -0.14 for El Salto and Finca Ramirez respectively in relation to δ^{18}O. In the association of δ^{2}H with Factor R_m (Figure 3.9a), the regression equations showed slopes close to 1 for both sites and intercepts of -1.99 and -1.28 for El Salto and for Finca Ramirez, respectively. The relationship between rainfall amount and δ^{18}O and δ^{2}H is shown in Figure 3.9c and d. The different monthly models obtained between (δ^{18}O, δ^{2}H), precipitation and factor R_m is displayed in Table 3.5 in next section. All data were collected and then the best model was fitted.

Figure 3.9 – Regression equations, a) and b) relationship between Rm factor and (δ^{18}O, δ^{2}H) and c) and d) relationship between monthly rainfall and (δ^{18}O, δ^{2}H) from El Salto and Finca Ramirez sites



3.3.3 Determination of the relationship between (δ^{18}O, δ^{2}H) and monthly rainfall and erosivity factor R for Ciudad Habana Station

The models proposed in the previous section were developed for Cuba or, more specifically, for the region near the El Salto and Finca Ramirez stations, based on the isotopic composition of the typical precipitations of Cuba and especially of the smaller study area in western Cuba. The rainfall composition depends on the process of water vapor formation, the movement of air mass and obviously of factors such as temperature and humidity. Knowing that air mass is the volume of air defined by its temperature and water vapor content and it is adapted to the characteristics of the surface below them, the isotopic rainfall behavior is very dependent on these local climatic characteristics. In addition, it is known that this area located in the Pinar del Rio province is characterized by large rainfall amounts with a high energy, different from other regions in Cuba. For example, in the province of Havana, at the Ciudad Habana station, yearly averages of 1200 mm with an erosivity of 15 000 MJ mm ha^{-1} h^{-1} have been reported.

In order to find out if there are differences in these relationships between (δ^{18}O, δ^{2}H), rainfall amount and R_m Factor for other regions in Cuba, the rainfall erosivity for the Ciudad Habana station was calculated and regression equations were determined as in the previous section.

Figure 3.10 shows the relationship between the three components, showing differences regarding the models of El Salto and Finca Ramirez. The differences between the equations are not very large; these can be given to the isotopic rainfall behavior in each region and in addition the difference between accumulated and rainfall erosivity. Another important aspect to consider is that the analyses in the Pinar del Rio region were performed based on 1984 only, whereas for the Ciudad Habana station 10 years were available. Finally, in Table 3.5, all the models are shown together.

Figure 3.10 – Regression equations, a) and b) represent the relationship between monthly rainfall and ($\delta^{18}O$, $\delta^{2}H$) and c), d) the relationship between R_m factor and ($\delta^{18}O$, $\delta^{2}H$) from Ciudad Habana station

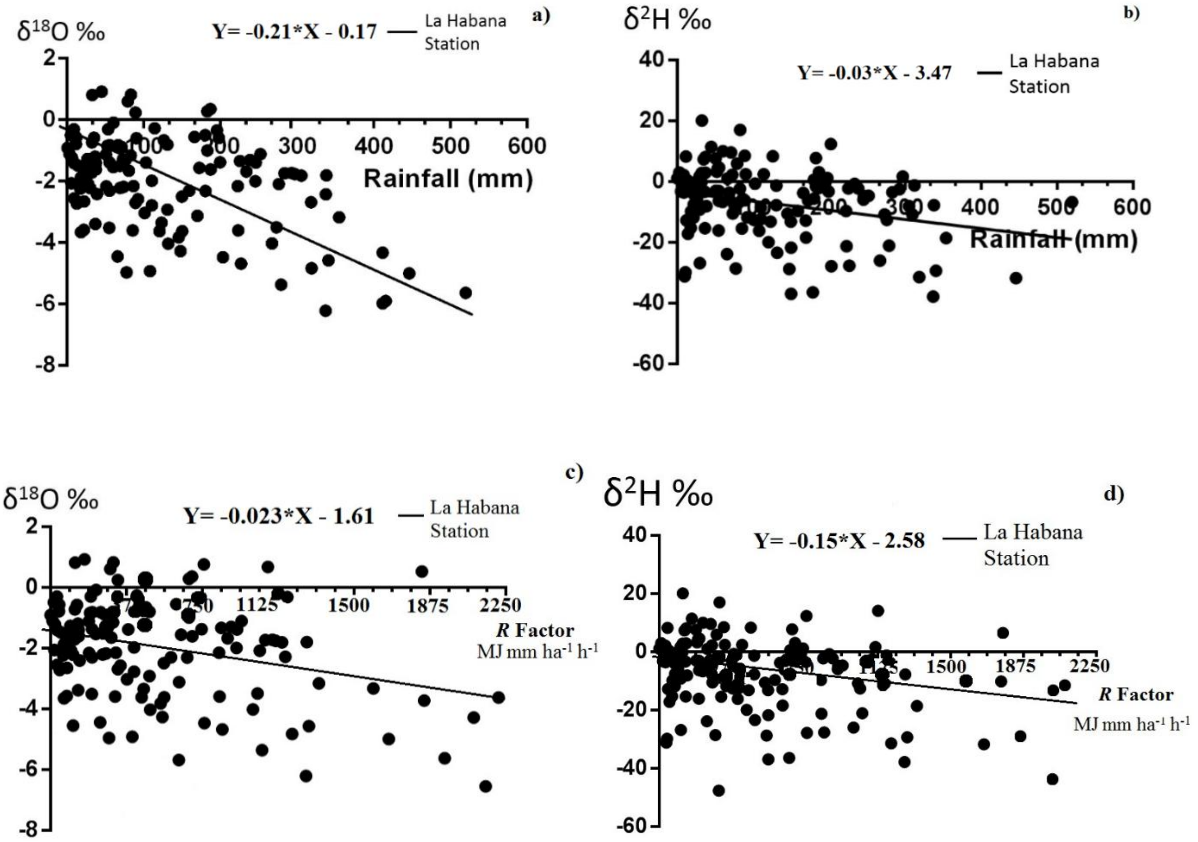


Table 3.5 – Representative models for the relationship between monthly rainfall isotopic composition and factor R_m, rainfall amount

Experimental Station Data	Equation	r^2	Years
El Salto and Finca Ramirez	δ^2H ‰ = $-0.88R_m - 1.64$	0.75	1984
	$\delta^{18}O$‰ = $-0.13R_m - 1.31$	0.71	
	δ^2H ‰ = $-1.45P_m + 3.09$	0.76	
	$\delta^{18}O$‰ = $-0.22^* P_m - 0.59$	0.73	
Ciudad Habana	δ^2H ‰ = $-0.03P_m - 3.47$	0.68	2004-2014
	$\delta^{18}O$‰ = $-0.21P_m - 0.17$	0.77	
	δ^2H ‰ = $-0.15R_m - 2.58$	0.68	
	$\delta^{18}O$‰ = $-0.02R_m - 1.61$	0.66	

3.4 Conclusions

Eight models that describe the relationship between rainfall erosivity, amount and isotopic composition were determined for western Cuba. They show that the models regionalization for areas outside the pattern of these rainfalls could lead to false results.

Regarding the isotopic composition, the slope of the relation between δ^2H and $\delta^{18}O$ is almost 7. Both GNIP network sites showed isotopically heavy precipitations, with a difference between seasons, the summer months with more depleted rainfall and the winter months less depleted. September was the isotopically most depleted month with $\delta^{18}O$ = -6.28‰ and δ^2H = -35.5‰.

In the study area, the use of models to estimate isotopic composition using ground temperature overestimates values, especially the Dansgaard (1964) model. The Yurtsever (1975) model shows better results for this area.

The overall trend indicated months with a high rainfall erosivity to correlate to isotopically less heavy water. The δ^2H and $\delta^{18}O$ values were negatively correlated with erosivity and with the rainfall amount. The rainfall amounts had the best negative correlation with respect to the isotopic composition.

The final criterion about the relationship between erosivity and rainfall isotopic composition is based as the erosivity sometime has a high correlation with the amount of rainfall, normally in the tropic regions, at this point, the erosivity has a good negative correlation with the isotopic composition, by transitivity, but it is not a causal relationship

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4 RAINFALL ISOTOPIC CHARACTERIZATION IN WESTERN CUBA

Abstract

Cuba, a large island in the middle of the Caribbean Sea, has unique and interesting conditions for isotopic studies of hydrological features. Classical effects of isotopic hydrology like continentality, rainfall amount and seasonality can be studied for Cuban coastal locations and compared to regions outside the direct oceanic influence sphere. In this study, we used data from the Global Network for Isotopes in Precipitation (GNIP) managed by the International Atomic Energy Agency (IAEA) from nine experimental stations in western Cuba, containing the isotopic characterization of rainfall. In general, rainwater in western Cuba is isotopically enriched with the heavy isotopes ^{18}O and ^{2}H. The annual mean values for $\delta^{18}O$ vary between +1 to -8‰ and for $\delta^{2}H$ between +15 to -40‰. There is a marked seasonal behavior, with isotopically heavier rainwater in winter and lighter in summer, in agreement with the common patterns for tropical regions. Even the Ciudad Habana station, located at the north coast of Cuba, presented seasonal differences with an annual mean $\delta^{18}O$ of -2.17‰ and $\delta^{2}H$ of -7.15‰. A high correlation between rainfall amount and rainwater isotopic composition was shown to exist, caused mainly by the predominant direction of air mass movement over the seasons. Concluding, even being an island in the middle of the Caribbean Sea, the classic effects of isotopic hydrology can be seen on Cuba.

Key words: Water isotopes, precipitation amount, western Cuba, seasonal effect

4.1 Introduction

The International Atomic Energy Agency (IAEA) supports research and development of isotope applications for climate studies and hydrology. The joint IAEA/WMO Global Network for Isotopes in Precipitation managed by the IAEA has provided the basic isotope data necessary for integrating stable oxygen and hydrogen isotopes in climate models for the last four decades. Furthermore, the use of water isotopes as climatic and hydrological tracers are widely used in recent times (PORCÙ et al., 2014). Stable isotope ratios of rainfall and water vapor exhibit much larger spatial and temporal variations than the ocean water (CRAIG; GORDON, 1965). The abundance ratios $^1H_2{}^{18}O/^1H_2{}^{16}O$ and $^2H_1H^{16}O/^1H_2{}^{16}O$ for Standard Mean Ocean Water (SMOW) are 0.0020052 and 0.00015576 respectively (HOEFS, 2008). SMOW is used as the standard of comparison for isotope ratios. Variations of isotope ratios in natural waters are described using δ notation in permil, where $\delta = (R_x/R_{SMOW} - 1)*1000‰$. The R_x is the isotopic content of any water sample and R_{SMOW} is the pattern. The $\delta^{18}O$ and δ^2H values of water vapor and precipitation near sea level range from about +5 to -50‰ and +40 to -400‰ respectively according to Lawrence et al. (2004), while $\delta^{18}O$ values of surface waters of the open oceans range between -0.5 to about 1.5‰ (BIGG; ROHLING, 2000).

In principle, variations in $\delta^{18}O$ and δ^2H are coupled according to Dansgaard (1964), Yurtsever (1975), Craig (1961); Friedman (1953) in one way or the other: under conditions of isotopic (and thus physical) equilibrium according to the Meteoric Water Line with slope 8, or under non-equilibrium conditions by a more complicated kinetic process. For less detailed hydrological surveys, it is generally assumed that $\delta^{18}O$ and δ^2H values are coupled as if in equilibrium. In the (δ^2H, $\delta^{18}O$) graph, the isotopic compositions of precipitation are aligned along what is referred to as a Meteoric Water Line (MWL) for which a global average is $\delta^2H = 8\delta^{18}O + 10‰$ (then called the Global Meteoric Water Line GMWL), where 10‰ in the equation is referred to as the deuterium excess (*d*) . The variations in $\delta^{18}O$ and δ^2H can be better understood if we consider the two main processes in the global water cycle 1) evaporation of surface ocean water and 2) the progressive raining out of the vapor masses as they move towards regions with lower temperatures, i.e. higher latitudes and/or altitudes (GALEWSKY et al., 2016).

Retaking the *d* explanation, there is a relatively large variability in the value of the deuterium excess especially notable close to the major source regions of the atmospheric moisture. Deuterium excess has shown specific potential in climate studies for tracing past and present precipitation processes (DELMOTTE et al., 2000). It is a measure of the relative proportions of ^{18}O and ^{2}H contained in water, and can be visually depicted as an index of deviation from the global meteoric water line (GMWL; $d = 10$) in $\delta^{18}O$ versus $\delta^{2}H$ space. In the early 2000s, *d* was demonstrated to be a useful, independent climatic parameter to calibrate atmospheric general circulation models (HOFFMANN et al., 2000) and to characterize atmospheric circulation in polar regions (PETIT et al., 1991).

The models that describe the relationship between $\delta^{2}H$ and $\delta^{18}O$ are influenced by different factors like temperature (linked to latitude, seasonal effect and altitude), continental effect and rainfall amount effect. Generally, the temperature dependence of both $\delta^{2}H$ and $\delta^{18}O$ values is smaller than shown by the latitude effect, varying from about 0.5‰/^{o}C for some higher-latitude stations to ultimately 0‰/^{o}C for tropical ocean islands (GAT, 2001). Stations situated in a mid-continental location normally represent a seasonal change in the rainfall isotopic composition. These variations are correlated with the temperature, in most cases. On the other hand, precipitation originating from ocean water, collected at island stations (as Cuba) or weather ships, has the characteristics of a first condensate of the vapor. The range of most $\delta^{18}O$ values is relatively small, between 0‰ to -5‰ with but little seasonal change in many cases, and a lack of a clear correlation with temperature (DANSGAARD, 1964; ROZANSKI et al., 1993). The same is true for the $\delta^{2}H$ values.

At tropical islands, where the vapor source region essentially coincides with the region of precipitation, the temperature dependence almost disappears as shown by Price et al. (2008) for the state of Florida, USA. For tropical regions, as is the case of Cuba, the most influential factor in the isotopic rainfall isotopic behavior has suggested to be the rainfall amount (YAPP et al., 1982). Dansgaard (1964) observed a relationship between the amount of precipitation and $\delta^{18}O$. For example, the very strong tropical rainfalls at times of the passage of the Intertropical Convergence Zone (ITCZ), characterized by tall clouds and strong downdrafts, may be extremely depleted in $\delta^{18}O$ and $\delta^{2}H$, the former by as much as -15‰. Similar but smaller effects are observed in thunderstorm-engendered precipitation. During convective storms, changes in $\delta^{18}O$ have been found of -7‰ within 1 hour in northwestern Europe (GAT, 2001).

In the specific case of Cuba, the predominant movement of air masses is different in summer and winter seasons, and the formed water vapor that originates the rainfall has a different formation process in both seasons. In the Cuban summer, normally, rainfall originates from convective storms, whereas winter rains are frontal. This difference between the seasons is likely to produce a different isotopic signature of the precipitation.

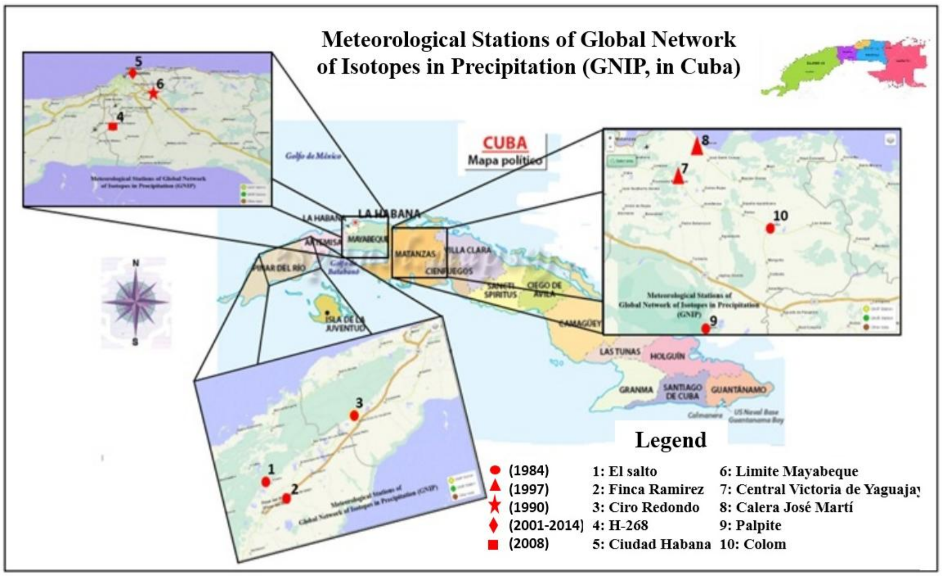
A question is if on Cuba, a relatively small island, the classic effects of the isotopic hydrology as continentality, rainfall amount and seasonality could be detected? To elucidate this question, the research work aimed the rainfall isotopic characterization in western Cuba. This characterization allows also knowing if the isotopic techniques are useful to determine changes in the climate and atmospheric circulation regimes.

4.2 Material and methods

4.2.1 The region of study

The Republic of Cuba has a surface area of 104 556 km². According to the Köppen-Geiger classification, Cuba's climate is Aw, a tropical climate with a dry season in winter and rainy in summer. The area selected for this study is located in the western part of the country (Figure 4.1), comprising the provinces Pinar del Rio, Artemisa, Mayabeque, Ciudad Habana and Matanzas, with a total area of 28 611 km^2. The selection of this area was motivated by the presence, in those provinces, of meteorological stations that yet recently were included in experiments of the International Atomic Energy Agency (IAEA). The area is located between the parallels 20.3° N and 23.3° N and the meridians 82.2° W and 87.2° W.

Figure 4.1 – Spatial location of the International Atomic Energy Agency stations data from Cuba



4.2.2 Data used

In the early 1960s, a precipitation sampling network was established by the International Atomic Energy Agency (IAEA) in Vienna and the World Meteorological Organization (WMO) in Geneva aiming to document the isotopic parameters, $^{2}H/^{1}H$, $^{18}O/^{16}O$ and ^{3}H, together with some meteorological parameters of the input into the hydrological systems. The network consisted of about 100 sampling sites worldwide, including marine, coastal and inland stations. Samples are still being collected monthly and analyzed, although the network has been slightly reduced and modified over the years. In addition, some local and regional networks and stations were added over shorter periods. For Cuba to be an island in the middle of the Caribbean Sea is very attractive for climate studies and it was therefore privileged with several stations from the IAEA.

The relevant data have been published regularly in the Technical Report Series of the IAEA, but have lately become available on Internet as Global Network of Isotopes in Precipitation (GNIP Data) (see <www. iaea.org/programs/ri/gnip/gnipmain.htm>).

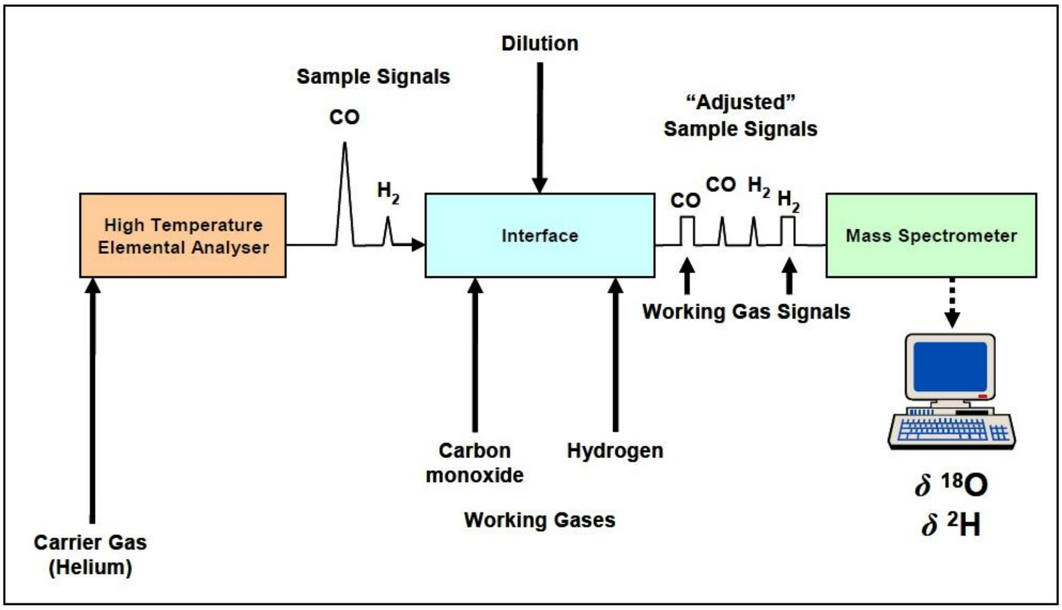
Data of $\delta^{18}O$ and $\delta^{2}H$ from nine experimental station in western Cuba (as shown in Figure 4.1) and several years were downloaded. To these data were added the values of station number 4 for the year of 2008 taken from Peralta et al. (2015), referring to the bordering region between the provinces of Artemisa and Mayabeque.

4.2.2.1 IAEA data measurement techniques

The IAEA provides data obtained from Isotope Ratio Mass Spectrometry (IRMS) instruments, specifically designed to precisely measure small differences in the abundance of isotopes such as $^{2}H/^{1}H$, $^{18}O/^{16}O$. Prior to analysis by IRMS, samples are converted to gases such as H_2, CO_2, N_2 and others depending on the composition of the material and the isotopes of interest. The IRMS measures the ratio of ions that correspond to these gases. Isotope rations, at natural abundance levels, are measured relative to international standards (primary materials) which define the measurement scale for particular isotopes. For the isotope ratios for unknown test samples to be traceable to the international standards, it is a prerequisite to use well-characterized standards (working gas and/or solid material) whose isotope ratios have been determined against the primary materials. According to Carter and Barwick (2011), there are two types of elemental analyzer available by IRMS, 1) for the analysis of carbon and nitrogen, the sample undergoes combustion in an oxygen atmosphere (known simply as Elemental Analyzer-IRMA) and 2) for the analysis of hydrogen and oxygen the sample undergoes high temperature thermal conversion referred to as High Temperature Conversion-IRMS. According to Figure 4.2, the analysis can be subdivided into four steps:

- Combustion or thermal conversion of the sample material using the elemental analyzer;
- Introduction of the evolved gases into the ion source of the mass spectrometer via the interface;
- Ionization of the gas molecules followed by separation and detection of the ions in the mass spectrometer;
- Evaluation of the raw data.

Figure 4.2 – Simple schematic diagram of a High Temperature Conversion-IRMS for the determination of $\delta^{18}O$ and $\delta^{2}H$, taken from Carter and Barwick (2011)



4.2.3 Principles of stable isotope meteorology

The large variations in atmospheric water vapor and precipitation result from isotopic fractionation that occurs during evaporation and condensation. As temperature decreases from 25°C to 0°C, the fractionation factor $\alpha = R_{liquid} / R_{vapor}$ under equilibrium conditions at relative humidity of 100% increases from 1.00937 to 1.0117 for ^{18}O and from 1.0793 to 1.111 for ^{2}H (MAJOUBE, 1971). Effective (kinetic) fractionation factors also increase as relative humidity decreases because the molecular diffusivities of the heavy isotopes are disproportionately slow (GAT, 1980; MERLIVAT; JOUZEL, 1979). This is particularly the case for ^{18}O, which is consequently more sensitive to humidity conditions than ^{2}H. It leads to a deuterium excess, *d*, which usually increases (by evaporative processes) as relative humidity decreases and has a global average value about 10 (DANSGAARD, 1964; CRAIG, 1961). While oxygen-18 ($\delta^{18}O$) and deuterium ($\delta^{2}H$) at moderate and high latitude continental areas are well correlated with the surface air temperature at the precipitation site, *d* is correlated with the physical conditions (humidity, air temperature and sea surface temperature) of the oceanic source area of the precipitation (MERLIVAT; JOUZEL, 1979). In addition, *d* reflects the prevailing conditions during evolution and interaction or mixing of air masses in route to the precipitation site.

In studies like Victoria et al. (1991), the *d* calculation is used to define water evaporation in the atmosphere, assuming primary recycling of water to occur through evaporation if *d* exceeds the classical value of 10. Assuming this, it is possible to detect if the vapor is part of the next precipitation event. On the other hand, other authors like Peralta et al. (2015) propose that a value of $d < 10$ represent the presence of oceanic vapor in precipitation formation.

Another important questioning related to $d > 10$ is about the influence of canopy transpiration in the rainfall isotopic behavior, ignored by many authors. Focusing on $H_2{}^{18}O$, water with heavier oxygen isotopes has a lower diffusivity than lighter ones (LUZ, 2009), resulting in a fractionation effect associated with stomatal and boundary resistances to water vapor flux (FARQUHAR et al., 1989). This has consequences for transpiration in relation to the environment condition like soil water content, relativity humidity, and solar radiation, which play a large role in the isotopic composition of precipitation.

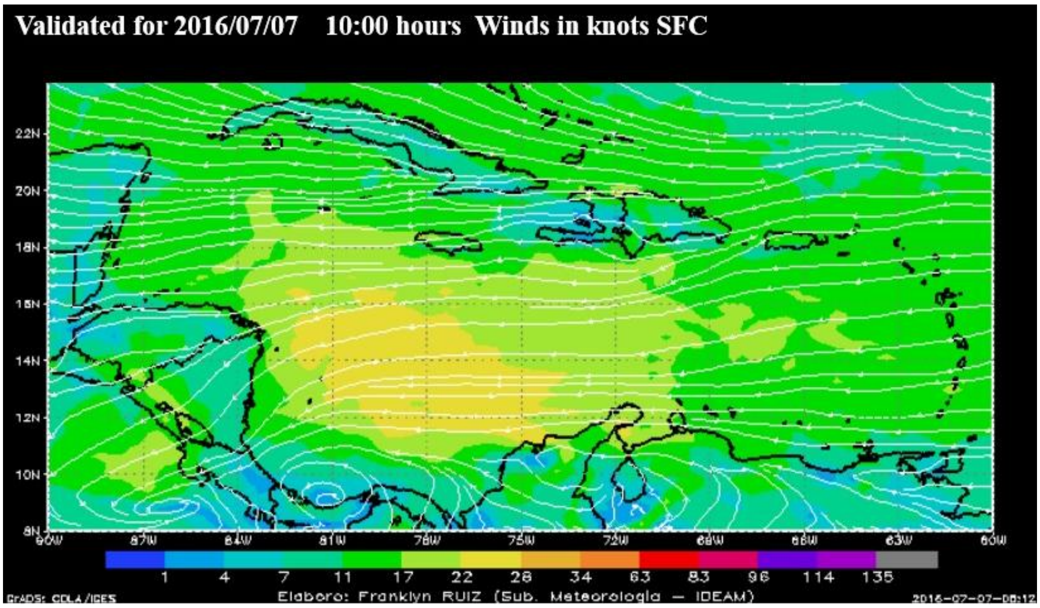
4.2.4 Analysis of air masses movement according to the seasons in Cuba

4.2.4.1 Air mass movement in the summer season

Two well-defined seasons can be recognized in Cuba differing in air mass movement direction: winter (from November to March) and summer (from May to October). Considering these seasons, the isotopic rainfall characterization was structured to describe $\delta^{18}O$ and $\delta^{2}H$ behavior.

The Cuban climate is mild subtropical, its narrow configuration, east-west oriented, receives the refreshing action of trade winds and marine breezes in summer. The trade winds are the prevailing pattern of easterly surface winds found in the tropics, within the lower portion of the Earth's atmosphere, in the lower section of the troposphere near the Earth's equator. The trade winds act as the steering flow for tropical storms that form over the Atlantic. In summer, the trade winds are stronger within the tropics and Central America (OLIVER, 2005). Figure 4.3 shows the trade wind trajectory on Cuba taken from the Institute of Hydrology, Meteorology and Environmental Studies (IDEAM) of Colombia.

Figure 4.3 – Image of air masses circulation in Cuba, July/2016, obtained from the Institute of Hydrology, Meteorology and Environmental Studies (IDEAM) of Colombia, showing the typical movement of air masses from southeast to northwest in summer



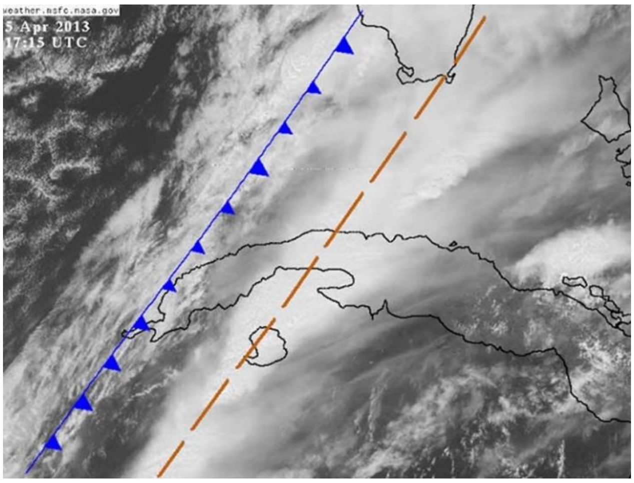
Another important factor influencing the vertical movement of water vapor in summer are the convective storms. Convective storms exist under a wide diversity of conditions and grow in an equally wide variety of ways. Storm behavior is inherently dependent on the environment in which the storm grows, including thermodynamic stability, vertical wind profiles, and mesoscale forcing influences. Convective precipitation is generally more intense, and of shorter duration, than stratiform precipitation (WEISMAN; KLEMP, 1986). The convective storms usually occur in flat areas or with small topographical irregularities, under a warm air ascent that goes to the encounter of cold air producing clouds of the cumulonimbus type with intense rainfalls and with short duration.

4.2.4.2 Air mass movement in the winter season

During the short winter, Cuba is influenced by cold air masses coming from the northern hemisphere. The cold front is defined as the leading edge of a cooler mass of air, replacing at ground level a warmer mass of air which lies within a fairly sharp surface trough of low pressure.

The cooler and denser air wedges under the less-dense warmer air, lifting it. This upward motion causes lowered pressure along the cold front and can cause the formation of a narrow line of showers and thunderstorms when enough moisture is present. On weather maps (an example is shown in Figure 4.4) the surface position of the cold front is marked with the symbol of a blue line of triangles/spikes (pips) pointing in the direction of travel (HOLTON, 2004). A cold front commonly brings a narrow band of precipitation that follows along the leading edge of the cold front. In Cuba, cold-front rains are characterized by low intensity.

Figure 4.4 – Image of a cold front approaching Cuba, April/2013, showing the movement of air mass from Northwest to Southeast, taken from https://weather.msfc.nasa.gov/



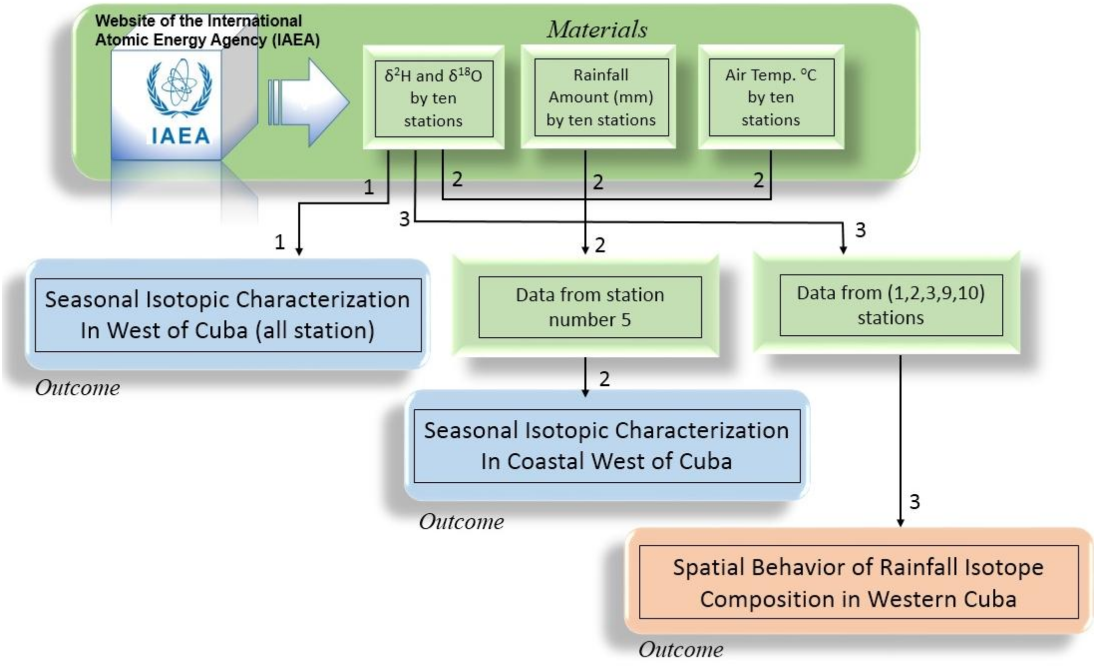
4.2.5 Rainfall isotopic characterization

Assuming that the air mass direction is different in summer and winter with possible repercussion in the rainfall isotopic composition, the following methodology was used (Figure 4.5): Initially at step 1, in order to be able to identify seasonal differences in rainfall isotopic signatures, the GMWL was plotted together with data from the summer months and the winter months separately, using all the experimental stations.

In step 2, to verify the influence of the air mass movement on the rainfall isotopic composition in Cuba, the data from Ciudad Habana station (number 5) were analyzed separately to determine seasonal differences for the conditions of a coastal station located in the north of Cuba. If this coastal station would not reveal a seasonal behavior, it could be concluded that in coastal stations the atmospheric vapor that originates rainfall is produced by the warm sea, therefore always with the same isotopic composition. To do so, winter and summer data were separated and the weighted mean of $\delta^{18}O$ was calculated together with the mean rainfall and the mean air temperature for each period and for each year.

In step 3, the spatial behavior was analyzed using data of ($\delta^{18}O$, $\delta^{2}H$) from stations number 1, 2, 3, 9 and 10 for which data were available for the same periods. For each station, the monthly isotopic signatures were determined and represented graphically to detect spatial differences. Finally, the deuterium excess was calculated using the Dansgaard (1964) equation ($d = \delta^{2}H - 8\ \delta^{18}O$), to be compared between western and eastern experimental stations.

Figure 4.5 – Flow chart showing sequence of operations to characterize the water isotope behavior in precipitations in western Cuba



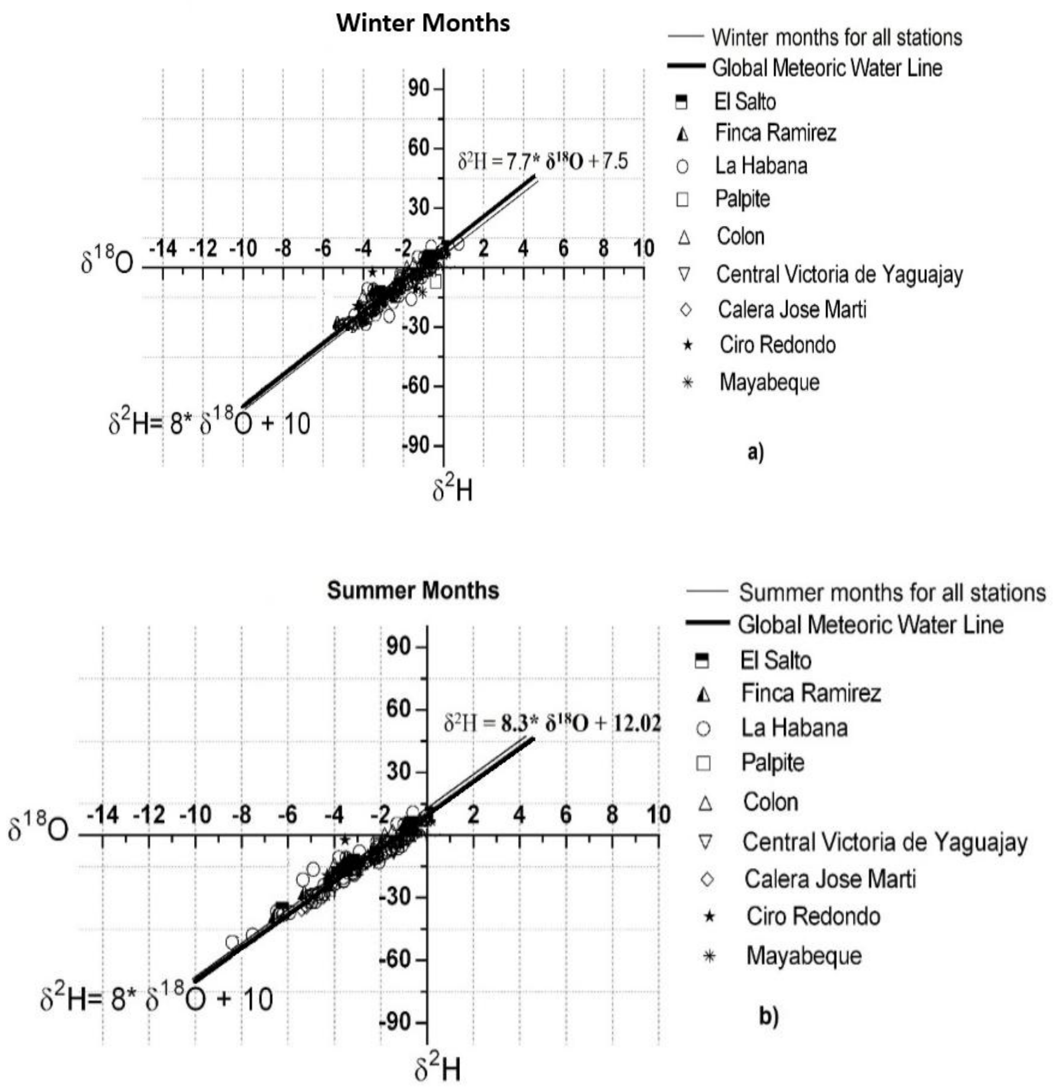
4.3 Results and discussion

4.3.1 Seasonal rainfall isotopic characterization in western Cuba

Precipitation over the ocean, collected at island stations, has the characteristics of a first condensate of vapor. The range of most δ^{18}O values is relatively small, between 0‰ and -5‰ with little seasonal change in most cases, and a lack of a clear correlation with temperature (DANSGAARD, 1964; ROZANSKI et al., 1993 and GAT, 2001). Obtained results from our study show a different behavior with seasonal effect (Figure 4.6).

Figure 4.6a shows winter rainwater data and the fitted equation for the relation between δ^{18}O and δ^2H with a slope of 7.7 and a *d* of 7.5, $r^2 = 0.97$. These values can be explained by a major influence of water vapor enriched by northern air masses with water vapor formed in the sea and with a direct influence on the island. In the western region, in winter, the air masses are coming directly from the coastal direction, representing the first isotopically enriched rainfall. These facts explain the slope lower than 8 for the winter equation. In winter months (Nov, Dec, Jan, Feb, Mar, Apr) the δ^{18}O value varied from -5 and -0.3‰ in relation to all experimental station, heavier in both isotopes.

Figure 4.6 – GMWL for ($\delta^{18}O$, $\delta^{2}H$) data from all stations for winter a) and summer months b)

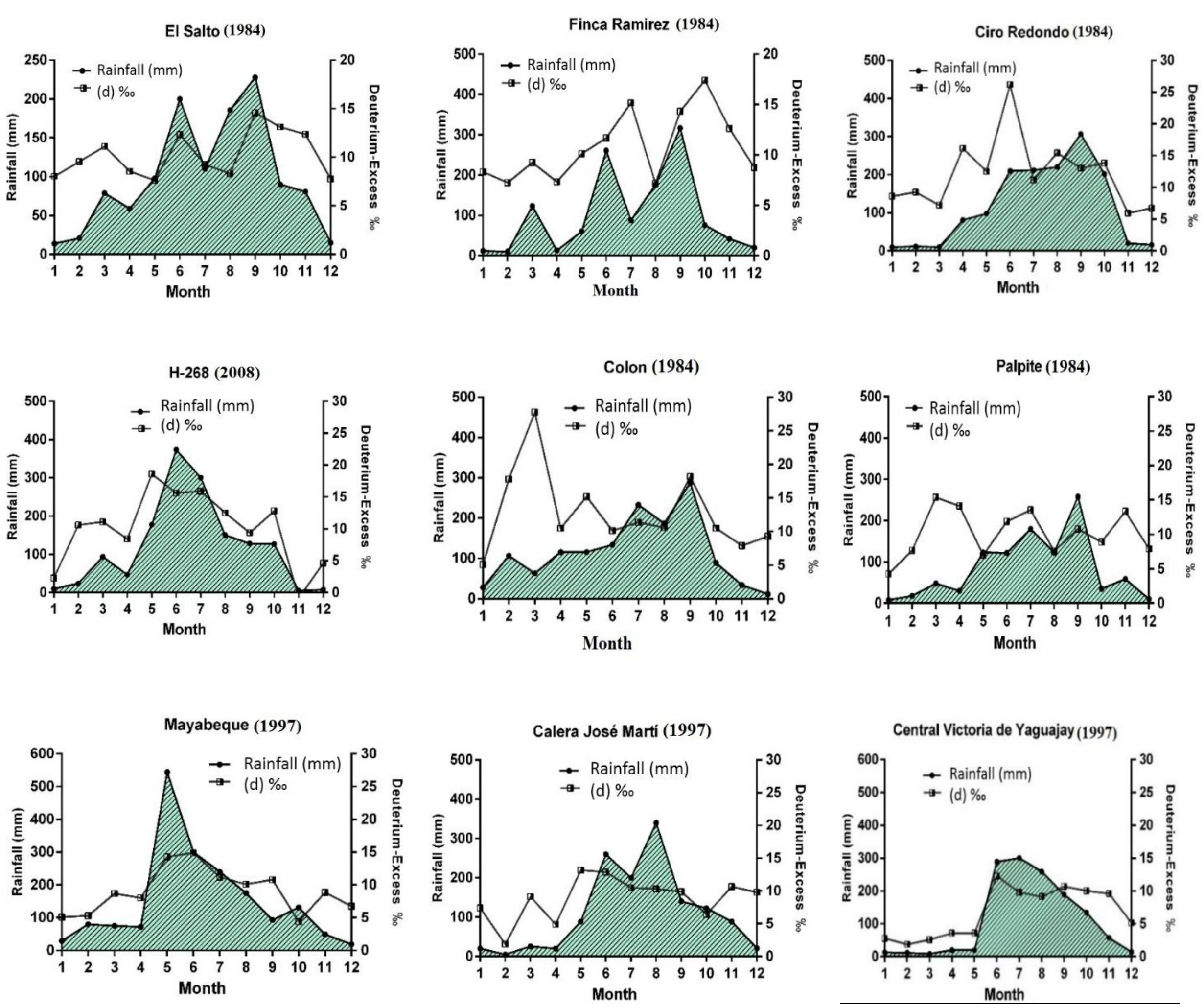


The fitted line for summer rainwater showed a slope of 8.3 and a deuterium excess *d* = 12 with r^2 = 0.98 (Figure 4.6b). This result shows that there is a general tendency to depleted rainfall in the summer months, with an excess of deuterium greater than 10‰. In addition to possible kinetic losses by the direction of the air masses (trade winds), there are two possible causes of fractionation: 1) direct evaporation from the surface of water bodies and soil (MARTINELLI et al., 1995), and 2) transpiration from vegetation (WERSHAW et al., 1966). In these two processes, the remaining water is enriched and the evaporating water will be more depleted.

In summer, the weighted mean isotope values for $\delta^{18}O$, considering all stations, ranged from 0.21 to - 8.12‰, which is clearly depleted if compared to the winter months.

On the other hand, the deuterium excess is positively correlated with rainfall amounts. During summer months, both rainfall and deuterium excess values are high (Figure 4.7), a common feature in the humid tropics. The high values of *d* in summer could indicate that the main source of water vapor is soil surface evaporation or evaporation from other water bodies together with canopy transpiration, justified by high temperatures and as consequence of convective rainfalls. Trade winds also play an important role, contributing to the existence of kinetic losses inland with the movement from the southeast to the northwest. The trade winds also cause precipitations formed over the sea at the southeast of Cuba not to be the first when they arrive to the western region; therefore, there are systematic losses (the heavy isotopes can be precipitated on the way) while the water vapor moves over the Cuban territory.

Figure 4.7 – Rainfall and deuterium excess *d* along the year for the evaluated experimental stations



El Salto (1984)

Finca Ramirez (1984)

Ciro Redondo (1984)

H-268 (2008)

Colon (1984)

Palpite (1984)

Mayabeque (1997)

Calera José Martí (1997)

Central Victoria de Yaguajay (1997)

Besides these small seasonal differences, in general, rainfall in western Cuba is isotopically heavy when compared to stations at other latitudes like Groningen, Vienna, Gronnedal, Halley Bay (GAT 2001; ROZANSKI et al., 1993). The same is true for the δ^2H values. The heavy δ rainfalls values may be caused by the specific Cuban island condition in the middle of the warm Caribbean Sea.

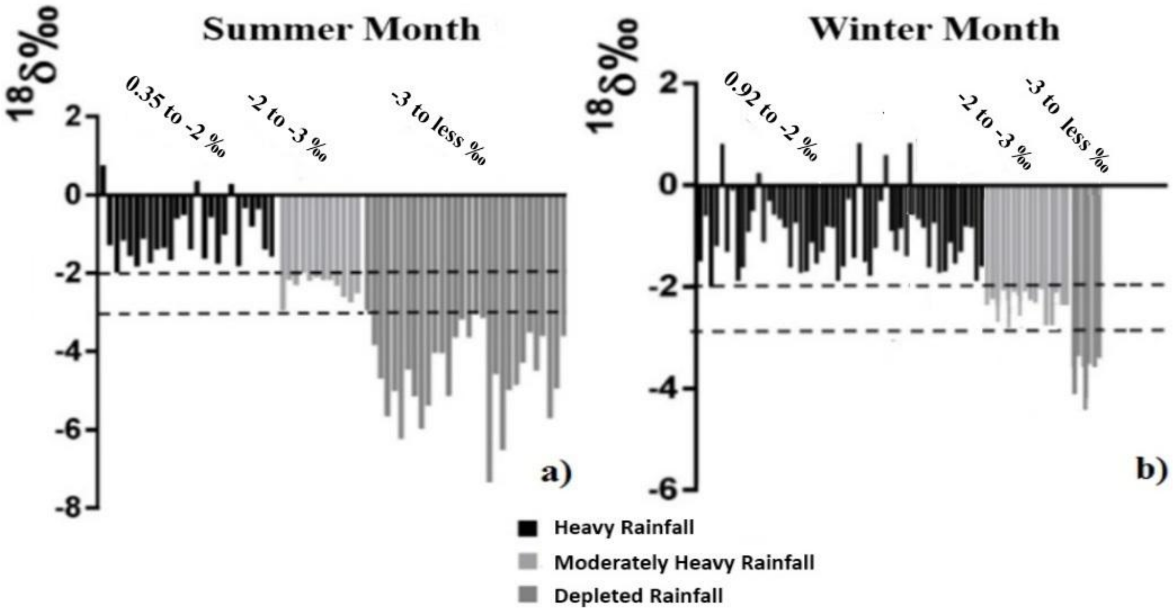
According to Gat (2001), some apparently anomalous features of rainfall isotopic composition, as in the case of Cuba, with relatively depleted values during summer, can be explained by the intense vertical mixing in the air column of tropical clouds in the presence of the Intertropical Convergence Zone, the area encircling the Earth near the Equator, where the northeast and southeast trade winds converge.

The amount effect, i.e. a correlation of the depletion of heavy isotopes with the amount of rain is explained by the preferential isotopic exchange of the smaller droplets, predominant in light rains and drizzle, with the near-surface moisture. Heavier rains on the other hand maintain the depleted isotopic values from within the clouds. This could be another cause of the isotopically heavier rains in winter in the tropics.

4.3.2 Seasonal isotopic characterization in coastal western Cuba

Data from station 5 (Ciudad Habana) were classified and grouped according to isotopic composition during summer and winter months. Isotopic rainfall composition was classified as "heavy rainfall" (δ^{18}O > -2‰), "moderately heavy rainfall" (-3‰ < δ^{18}O < -2‰) and "depleted rainfall" (δ^{18}O < -3 ‰). Summer months showed more rains in the depleted rainfall class (Figure 4.8), whereas winter rains were more likely to be in the heavy rainfall class.

Figure 4.8 – The seasonal representation for the $\delta^{18}O$ classes a) for summer months and b) for winter months over a period of 11 years (2004 to 2014) in Ciudad Habana station.



These results show that, although the Ciudad Habana station is located on the west coast, there are seasonal differences in the isotopic composition. This reinforces the idea that the rainfall isotopic composition during summer is under strong influence of the air mass movement from the Southeast (which includes kinetic losses).

Another factor that could be influencing this seasonal isotopic behavior in coastal regions is the sea temperature. The formation of atmospheric vapor by evaporation in regions with high surface ocean temperatures produces heavy rainfall, but for tropical regions, the relation is inverse (SONNTAG et al., 1983), analogous with the results found in this research work. Results of this type also were found in Pretoria, South Africa (GAT, 2001). According to this author, the opposite seasonal effect for tropical regions may be correlated with high precipitation intensity with often-low $\delta^{18}O$ values during summer.

Table 4.1 shows mean values for each seasonal period and year separately, inter-seasonal air temperature variations are between 4 to 5 degrees while summer average temperatures are around 27 °C. Summer rainfall is higher than winter rainfall. June was the most depleted month in this coastal station, with a mean $\delta^{18}O$ of -4‰ and $\delta^{2}H$ of -20‰ and coinciding with the month of accumulated highest rainfall (225 mm) reaching 446 mm in 2005. Nevertheless, December was the month of greatest isotopic enrichment with a mean $\delta^{18}O$ of -0.9‰ and $\delta^{2}H$ of 4.21‰ explaining the inverse correlation between accumulated, temperature, with rainfall isotopic composition.

The overall annual mean of rainfall isotopic composition for $\delta^{18}O$ was -2.17‰ and for $\delta^{2}H$ it was -7.15‰, showing that rainfall is generally heavy although there are seasonal differences.

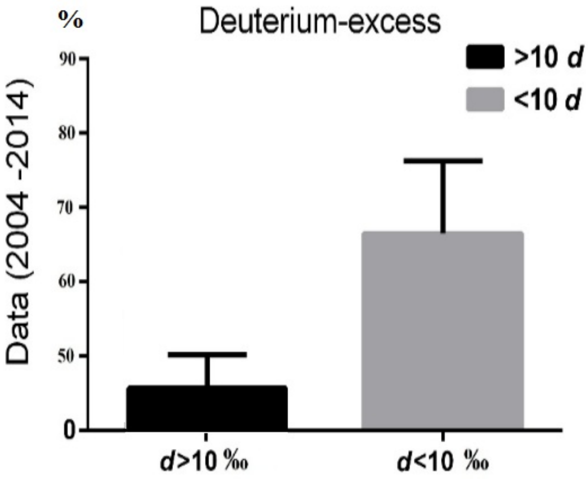
Table 4.1 – Mean climatic values for the Ciudad Habana station during winter months (November to April) and summer months (May to October)

Year	Weighted Mean $\delta^{18}O$ ‰ in Rainfall		Mean Rainfall (mm)		Mean Air Temperature (°C)	
	Winter	Summer	Winter	Summer	Winter	Summer
2004	-1.21$^{\bullet\wedge}$	-2.35	88.30	136.40	22.85	27.30
2005	-1.69$^{\bullet\wedge}$	-4.79*	35.43	281.43	22.52	28.28
2006	-1.03$^{\bullet\wedge}$	-3.03*	52.65	126.02	22.57	27.03
2007	-0.78$^{\bullet\wedge}$	-3.03*	52.27	207.33	22.51	27.25
2008	-1.82$^{\bullet\wedge}$	-2.76	71.93	210.82	22.57	27.05
2009	-2.16	-1.27	64.08	139.62	21.98	27.77
2010	-2.31	-3.19*	70.98	152.15	20.85	27.47
2011	-1.07$^{\bullet\wedge}$	-3.32*	42.82	205.7	22.67	26.23
2012	-2.53	-3.47*	78.60	189.63	22.92	25.87
2013	-1.02$^{\bullet\wedge}$	-2.41	53.53	210.55	22.58	27.38
2014	-0.84$^{\bullet\wedge}$	-3.28*	85.43	149.60	22.40	27.60

Note: * depleted rainfall class; •^ heavy rainfall class.

Figure 4.9 shows the deuterium excess (*d*) calculated by the Dansgaard (1964) equation from 11 years, presenting almost 70% of the values lower than 10‰ and almost 25% larger than 10‰. The latter means that in this coastal station there is a great influence of seawater on rainwater isotopic composition, as expected. Peralta et al. (2015) found similar results.

Figure 4.9 – Deuterium excess for the Ciudad Habana station



4.3.3 Spatial behavior of rainfall isotope composition in western Cuba

Using rainfall samples from many parts of the world, Craig (1961) found that the dispersion of most isotopic values was not large and were located along the Meteoric Water Line. In order to have an idea of the spatial data behavior in western Cuban and if there are significant spatial differences, data from five experimental stations with data from the same year (1984) were analyzed. Two of these are located in the Pinar del Rio province (stations 1 and 2), one in the Artemisa province (station 3) and two in the Matanzas province (stations 9 and 10). Figure 4.10 shows that the monthly means for $\delta^{18}O$ and $\delta^{2}H$ are located close to the GMWL. The tendency of monthly behavior in the five stations is similar and the figure does not show significant differences between the stations. In Figure 4.11, the trends for $\delta^{18}O$ and $\delta^{2}H$ were presented with September being the month with the lightest rainfall among the five sites, coinciding with one of the rainiest and warmest months of the year. June and September are the months with most rainfall (Figure 4.12).

Figure 4.10 – Global Meteoric Water Line with the rainfall isotopic values from stations number 1, 2, 3, 9 and 10

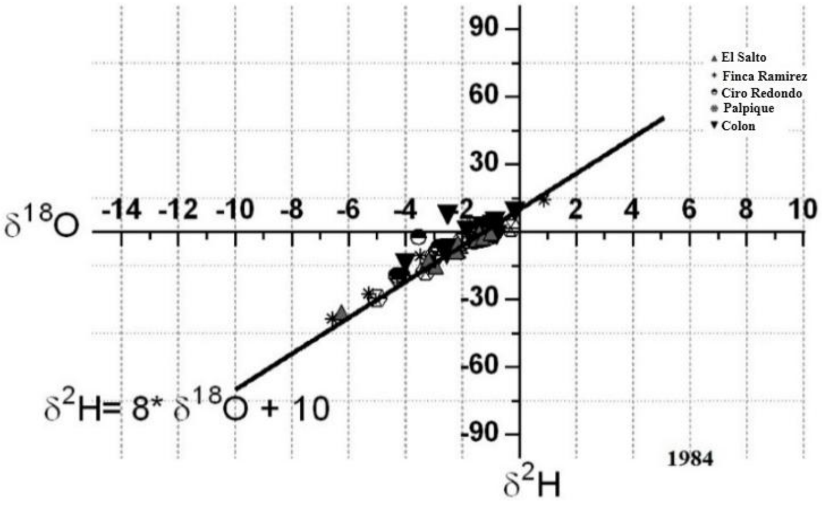


Figure 4.11 – Different rainfall isotopic compositions signatures $\delta^{18}O$ and δ^2H for stations 1, 2, 3, 9 and 10 separately

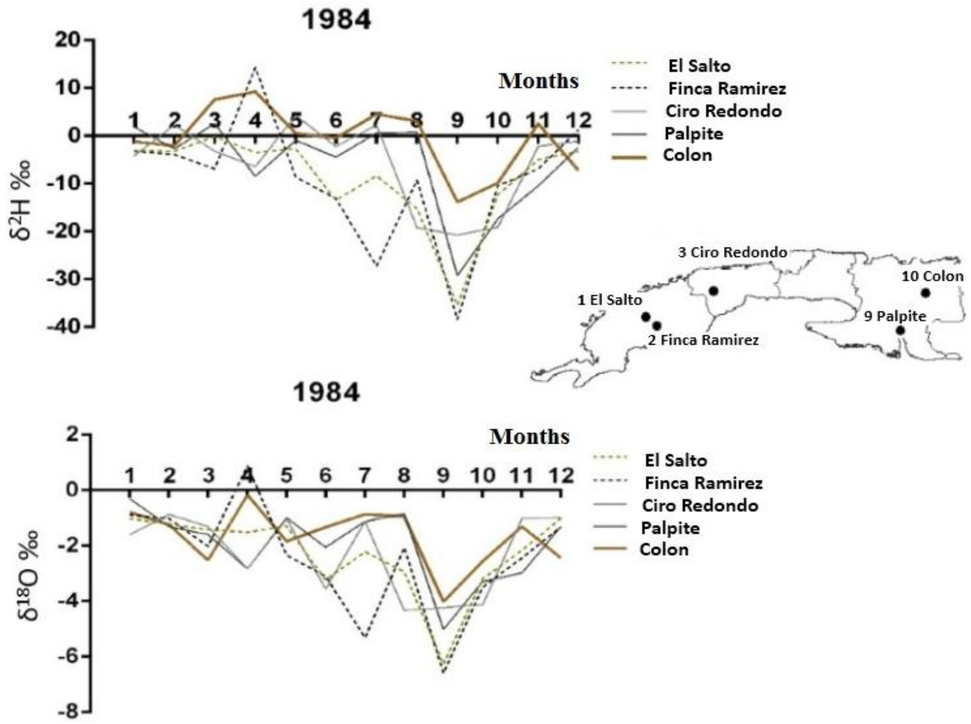
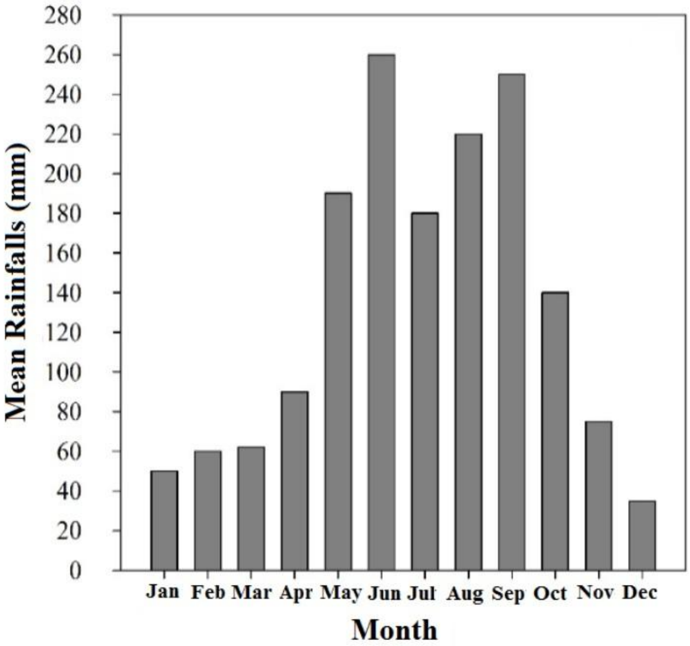


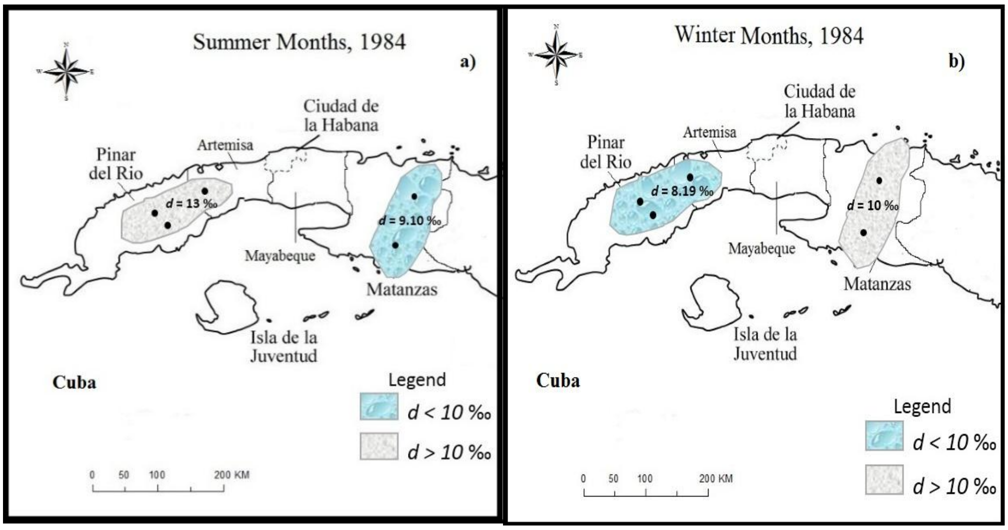
Figure 4.12 – Monthly average rainfall for stations 1, 2, 3, 9 and 10



Colon station (station number 10) shows a heavier isotopic signature, being maintained throughout the year. Finca Ramirez station (number 2) on the other hand, had the lightest rainfall signature for almost the entire year, except in April (Figure 4.11). Colon is the most eastern station with $\delta^{18}O$ between -0.16 and -4.1‰ and $\delta^{2}H$ between 9.2 and -13.9‰; however, the Finca Ramirez station is located more to the west with $\delta^{18}O$ between 0.87 to -6.59 ‰ and $\delta^{2}H$ between 14.3 to -38.4.

Excess deuterium averages from two easterly seasons (9 and 10) was compared with average *d* from westernmost stations 1, 2, and 3 in each seasonal period (Figure 4.13). The figure reveals that in winter the western stations had *d* equal to 8.19‰, less than 10‰, suggesting the direct influence of water vapor directed from the north (cold front) as already mentioned. In summer the opposite happens in western stations with an average *d* of 13‰, losing the direct influence of water vapor formed over the sea and with more influence of convective rainfall formed in the area and the trade winds trajectory.

Figure 4.13 – Geographical location of the analyzed *d* (deuterium excess), a) for summer months and b) for winter months of 1984



The fact that the western stations have more depleted rainfall in summer may relate to the continental effect, also referred to as the distance from coast effect. This effect refers to a progressive $\delta^{18}O$ depletion in precipitation with increasing distance from the ocean. Although the distance is not very large, the rainfall isotopic behavior varies considerably from area to area, even over a low relief profile. This last effect is highly correlated with topography, and only stations 1, 2 and 3 are located in a mountainous area, the Guaniguanico mountains, which may influence the kinetic losses in function of the air masses trajectory from the southeast to the northwest.

4.4 Conclusions

Rainfalls in western Cuba are in general isotopically enriched in $\delta^{18}O$ and $\delta^{2}H$ in comparison with other regions at higher latitudes. The annual mean values for $\delta^{18}O$ vary between +1 and -8 ‰ and for $\delta^{2}H$ between +15 and -40 ‰. There is marked seasonal behavior, with a heavier isotopic composition of winter rains, a common tendency in tropical regions.

Ciudad Habana coastal station presented the annual mean value for $\delta^{18}O$ of -2.17‰ and for $\delta^{2}H$ was -7.15‰ and despite being a coastal station, it showed seasonal differences too.

There is a strong relation between rainfall amount and rainfall isotopic composition in this tropical area: the months with highest precipitation amount were more isotopically depleted and vice versa.

It was demonstrated that the direction of air mass movement plays a very important role in the rainfall isotopic composition. This shows the importance of the use of isotopic techniques in the determination of the rainfall water vapor trajectories for hydrological cycle studies.

Even though Cuba is an island in the middle of the Caribbean Sea, the classic effects of isotopic hydrology such as latitude, seasonal effect, continental effect and amount effect are clearly present.

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5 CONCLUDING REMARKS

The hypotheses, general objective and specific objectives of this work were presented in chapter 1. In chapter 2 (“Water isotopic fractionation by transpiration: a theoretical demonstration”) transpiration was shown to be a fractional process with respect to water isotopes. The magnitude of this fractionation is determined by environmental factors, such as soil water content, amount of precipitation, temperature, and the relative humidity. The environmental factors influence the behavior of such important variables as stomatal aperture, the different diffusion resistances, and the kinetic fractionation. This explains that several authors demonstrated the recycling of water vapor in the Amazon Basin using isotopic methods.

Chapter 2 also treated the different vision of researchers working in the branch of isotopic hydrology and those who study isotopes in plants, mostly biologists and agronomists. More interdisciplinary work should be done inside the scientific community, as currently transpiration is regarded a fractionation process for water isotopes in the leave by biologists whereas climatologists and hydrologists consider it as non-fractionating because in the process of root water uptake no fractionation is involved, thus ignoring processes in the leaves.

In chapter 3 the study “Relating isotopic composition, amount and rainfall erosivity for paleoclimate reconstruction in western Cuba” deals with eight models that describe the relationship between rainfall erosivity, amount and isotopic composition in western Cuba. Extrapolate these models for another rainfall regime could lead to false results. In addition, the use of models to estimate isotopic composition in the area using ground temperature overestimates values, especially the Dansgaard (1964) model. The Yurtsever (1975) model shows better results in the area. The trend found in this research is that months with the highest rainfall erosivity were less heavy. The δ^2H and $\delta^{18}O$ values were negatively correlated with erosivity and with the rainfall amount. Rainfall amount had the highest negative correlation with isotopic composition.

Chapter 4 entitled “Rainfall isotopic characterization in western Cuba” showed that rainfalls in western Cuba are in general isotopically enriched in $\delta^{18}O$ and $\delta^{2}H$ in comparison with other regions at higher latitudes. The annual mean values for $\delta^{18}O$ vary between 1 and -8‰ and for $\delta^{2}H$ between 15 and -40‰. Nevertheless, there is a marked seasonal behavior, with heavier rainfalls in winter and more depleted in summer, showing the established patterns for tropical region.

Ciudad Habana coastal station presented an annual mean value for $\delta^{18}O$ of -2.17‰ and -7.15‰ for $\delta^{2}H$. Despite being a coastal station, it showed seasonal differences too. It was demonstrated that the direction of air mass movement plays a very important role in the rainfall isotopic composition. Even though Cuba is an island in the middle of the Caribbean Sea, the classic effects of isotopic hydrology such as latitude, seasonal effect, continental effect and amount effect are clearly present.