ALBERT-LUDWIGS-UNIVERSITÄT FREIBURG

MASTER THESIS

Combining soil water retention and pore water stable isotope data

Author:
Felix MÜLLER

Supervisor:
Prof. Dr. Markus Weiler
PD Dr. Christine Stumpp

A thesis submitted in fulfillment of the requirements
for the degree of Master of Science

in the

Chair of Hydrology

January 2, 2017

Declaration of Authorship

I, Felix MÜLLER, declare that this thesis titled, "Combining soil water retention and pore water stable isotope data" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Date:

"In the face of overwhelming odds, I'm left with only one option, I'm gonna have to science the shit out of this."

Mark Watney

ALBERT-LUDWIGS-UNIVERSITÄT FREIBURG

Abstract

Faculty of Environment and Natural Resources
Chair of Hydrology

Master of Science

Combining soil water retention and pore water stable isotope data

by Felix MÜLLER

The usage of stable isotopes extracted from soil is a common and trusted tool to determine water ages, flow paths, recharge rates and the circumstances that impaired the molecules on their way through the hydrological cycle. But once water is stored in small soilpores, processes influence the isotopes on an yet unknown scale.

In this work an effort is made to examine a relatively new method, the desorption solution method, regarding its capability to provide stepwise extracted soilwater for isotope analysis. That resulted in a need to improve the reliability and ideally its functional range.

An attempt was made to reproduce the characteristical isotope patterns, which made the lack of understanding for isotopic reactions in the soil matrix become apparent. It became clear, that the processes proceed in greater timespans, than applied in this work.

Due to the resulting small amount of datapoints the attempt to delineate the poresizes in witch the unspecified processes proceed came adrift.

ALBERT-LUDWIGS-UNIVERSITÄT FREIBURG

Zusammenfassung

Faculty of Environment and Natural Resources
Chair of Hydrology

Master of Science

Combining soil water retention and pore water stable isotope data

by Felix MÜLLER

Die Untersuchung der stabilen Wasserisotope ist ein weitverbreitetes und zuverlässiges Mittel zur Bestimmung von Fließpfaden, Grundwasserneubildungsraten und Altersdatierung. Befindet sich das Wasser jedoch in den kleinen Bodenporen, beeinflussen dort ablaufende Prozesse das Isotopensignal in noch unbekanntem Ausmaß.

In dieser Arbeit wird der Versuch unternommen, die relativ neue Methode der desorption solution method zu nutzen, um die Porenräume schrittweise zu entwässern. Hieraus ergab sich die Notwendigkeit einer weiteren Verbesserung der Methode bezüglich der Zuverlässigkeit. Eine Erhöhung der anwendbaren Drücke steht ebenfalls aus.

Auch sollten künstliche Bodenproben hergestellt werde, welche dieselben charakteristischen Merkmale aufweisen, wie die natürlichen Proben, anhand derer die Wissenslücke bezüglich der im Boden ablaufenden Prozesse deutlich wurde. Dieser vormals beobachtete Einfluss prägt sich jedoch erst nach längeren Zeiten, als den hier verwendeten aus.

Wegen dem daraus resultierenden geringen Probenumfang war auch der Versuch den Porengrößenbereich einzugrenzen, in welchem besagte Prozesse ablaufen, nicht von Erfolg gekrönt.

Acknowledgements

Acknowledgementss go to…
…Barbara Herbstritt and Dominic Demand for their support in the labor-intensive sampling process and the analysis.
…PD Dr. Christine Stumpp and Prof. Dr. Markus Weiler for support and evaluation.
…The Chair of Hydrology and the Faculty of Environment and Natural Resources for the profound education.
…The Chair of Soil Ecology for their unbureaucratic help

Contents

Declaration of Authorship **i**

Abstract **iii**

Zusammenfassung **iv**

Acknowledgements **v**

1 Introduction **1**
  1.1 Overview 1
  1.2 State of the Art 2
  1.3 Research Gap and Objectives 2

2 Theoretical Background **3**
  2.1 Stable Isotopes 3
    2.1.1 Notation 4
    2.1.2 Fractionation and Parameters 4
  2.2 Soilwater 5

3 Methods **7**
  3.1 Experimental Design 7
  3.2 Sampling 8
  3.3 Field Methods 8
  3.4 Desorption Solution 9
  3.5 Direct Equilibrium 10
  3.6 Cryogenic Extraction 10

4 Results **12**
  4.1 Performance of Desorption Solution Method 12
  4.2 Locating the borders of the two water worlds 14

5 Discussion **18**

6 Conclusion **20**

A Appendix **21**

List of Figures

2.1 scheme of soil drainage 6

3.1 pF-curve and experimental design 7
3.2 desorption chamber 9
3.3 cryogene extraction 11

4.1 natural values by chamber 13
4.2 natural values by method 14
4.3 heavy desorption values by pressure 15
4.4 cluster of heavy desorption values by pressure 16
4.5 absolute $\Delta\delta$ of ^{18}O and D 16
4.6 deuterium excess 17

A.1 natural values by chamber 21
A.2 light desorption values by pressure 22
A.3 cluster of light desorption values by pressure 22

Dedicated to…

…Minou, for being the reason to take all this with the adequate sobriety.

…Ignatz, for teaching me that one can act at full throttle without having a clue at all.

…my family, for all the support that afforded me to be what I am.

…the boys, for the hydrologically valuable and especially the hydrologically non-valuable talks and supports.

…my sisters, for the motivational and other pushes.

…Tanita, simply for being my wife.

Chapter 1

Introduction

1.1 Overview

Stable isotopes are widely used in Hydrology. As they are part of the water molecule, they participate in the hydrological cycle, without being absorbed or degraded. However they feature small differences in atomic mass, which cause a slightly different properties in the processes affecting them on their way through atmosphere and geosphere. Their presence and ratios give some indication about the circumstances of their history. Being ubiquitous, makes them a very strong tool for examination of surface and subsurface flowpaths, recharge rates, age dating and such like. But the application of stable isotopes comes with some uncertainties in terms of soilwater movement. These movements have long been described applying the theory of translatory flow, which says that isotope ratios from precipitation replace the stored isotope signals in the uppermost soil, pushing those downwards. The depth of this exchange is determined by the amount of precipitation.

But the complexity of soil fabric on every scale and the thereof resulting impacts on soilwater does not fit into modest models. Since McDonnell (2014) came up with his two water world hypothesis, a lack of understanding for isotopic reactions in the soil matrix became apparent. In his paper he indicated that, different to prior studies, soil water can be stored in two different reservoirs. The first reservoir is "normal" soil water, matching the translatory flow theory. The second reservoir, and this is new, is tightly bound water, that is subject to different processes and therefore feature different isotope signals. His paper is a confession of a lack of knowledge according to the processes that take place in the small pores of soils and is most widely unopposed with good reason. He ends his paper with the call to take effort in researching these unknown impacts.

1.2 State of the Art

As the border between the two water worlds runs among the poresizes in soils and each method used to extract soilwater samples a different poresize, several works are concerned with the obtained deviations of isotope values among the methods. Here the works of Sprenger, Herbstritt, and Weiler (2015) and Orlowski, Pratt, and Jeffrey J Mcdonnell () are to be mentioned. Those works help to assess the validity of a method for a specific issue, increasing the reliability of the results.

1.3 Research Gap and Objectives

The boundaries of the two water worlds are still undelineated. In this work I will take an effort to localize the poresizes in which yet unknown impacts on the isotope ratios occur. This effort contains following key objectives:

1. Examine the capability of the desorption solution method for stepwise sampling of soilwater for isotope examination.
2. Generating soilsamples containing isotope patterns with characteristics representing the two water worlds
3. delineate the borders between the two different pools of water

Chapter 2

Theoretical Background

2.1 Stable Isotopes

Isotopes are atoms whose nucleus contains the same number of protons, but a divergent amount of neutrons (Mazor, 2004). For oxygen fifteen isotopes are known so far (^{12}O - ^{26}O), but only three of them are stable and do not degrade. In case of Hydrogen, there are two stable isotopes occurring in nature, namely ^{1}H (also known as Protium) and ^{2}H (also known as Deuterium, written as D). The composition and abundance of those stable isotopes is given in table 2.1:

TABLE 2.1

Name	**Isotopic Abundance**[%]	**Composition/structure**
^{1}H - common hydrogen	99.985	1 proton, 0 neutrons
^{2}H - deuterium	0.016	1 proton, 1 neutron
^{16}O	99.762	8 protons, 8 neutrons
^{17}O	0.038	8 protons, 9 neutrons
^{18}O	0.2	8 protons, 10 neutrons

Therefore ^{16}O is considered to be the ′normal′ Oxygen-atom and the other two are called heavy isotopes. As ^{17}O occurs very rarely, its usage is extremely laborious compared to the usage of ^{18}O and thus uncommon. The isotopes show an almost identical chemical behavior, but also have tiny mass-differences. Molecules formed by at least one atom, that is not the common isotope are called isotopologues. Expect for isotopologues formed with ^{17}O the important isotopologues of water are consequently the ′normal′ or ′light′ H_2O, $H_2{}^{18}O$, DHO, $DH^{18}O$, D_2O and $D_2{}^{18}O$, ordered by increasing weight and decreasing abundance. As these isotopologues participate in the global water circulation, without being absorbed or degraded by surrounding processes, but even so being detectable, they are considered to be nearly perfect conservative tracers.

2.1.1 Notation

Isotopes are denoted as ratios between the amount of light isotope (X_l) and the amount of heavy isotope (X_h)

$$R_{X_h} = \frac{X_h}{X_l} \tag{2.1}$$

Since this leads to very small values, the isotope ratios are compared with a standard water with known concentrations of ^{18}O and D. These water is called Vienna Standard Mean Ocean Water (VSMOW) and is controlled by the International Atomic Energy Agency (IAEA) in Vienna.

$$\delta_X = \left(\frac{R_X - R_{STD}}{R_{STD}}\right) * 1000 = \left(\frac{R_X}{R_{STD}} - 1\right) * 1000[‰] \tag{2.2}$$

That means, that a positive δ of D or ^{18}O means a higher concentration of heavy isotopes in the probed water, than in the VSMOW (Clark and Fritz, 1997).

2.1.2 Fractionation and Parameters

The previously mentioned mass differences of the heavy isotopologues cause minimal deviations according to phase transitions. Heavy molecules tend to evaporate more slowly than common H_2O molecules, but condensate more rapidly. The less energy is present for this processes, the more effect is taken by the differences. These basic difference lead to some effects, as the continental effect, which describes the decrease of heavy isotopes with increasing distance to the sea (Dansgaard, 1964). With these effects conclusions about the conditions of origin and among the hydrological cycle can be drawn by examining collected water probes. The details of these so called fractionations are not necessary for understanding this thesis and can be found in numerous publications and standard references, such as Clark and Fritz, 1997 and Criss, 1999.

Isotope ratios from precipitation globally are in line with the **Global Meteoric Water Line (GMWL)**, which was first described by Craig, 1961 and is described by the following equation:

$$\delta D = 8 * \delta^{18}O + 10[‰] \tag{2.3}$$

Besides there are 'Local Meteoric Water Lines' (LMWL) for every region, defined by local data, which give back the influences of the mentioned effects. Deviations from these lines can be interpreted as indications of unregarded processes. One important indicator is the **d-excess** described by Dansgaard, 1964:

$$d = \delta^2H - \delta^{18}O * 8[‰] \tag{2.4}$$

Which can be understood as the intersection with the δ-axis if a line with the same slope as the GMWL is applied to the actual value. A low d therefore means a lower amount of D isotopes as usual. This (low d-values) can be found if evaporation takes place in surroundings with a low relative humidity (Pfahl and Sodemann, 2014).

2.2 Soilwater

Water in soils can be divided into adherent water and seeping water. The latter is also referred to as mobile water, since it moves through the soil towards groundwater or runoff. Adherent water is in contrast held in the soilpores against gravity either in capillaries or as hygroscopic water.

Solid soil particles feature electrical charges on their surface, which orient the dipoles of water molecules. These molecules form a thin layer of water around the soil particles, which is the hygroscopical water. As water molecules beyond this layer are also forced to orient due to cohesion and solid particles lie close together in the soil, menisci form in pores. Their pressure capacity exceeds gravitation if the pore diameter is below $10\,\mu m$. The narrower a pore, the more distinct are the occurring menisci-bends, which increases their pressure capacity. That implies, that a tighter pore binds water more tightly. Soils therefore cause tension on surrounding water, which is measured in $cm\ hydrostatic\ head$ or hPa and which is greatest at lowest water contents. In this work the desorption solution method is used, in which a increased air pressure flattens the menisci-bends, reducing their pressure capacity. This forces tightly bound water to drain off to larger pores and eventually off the soil, where it is collected. A completely dry soil shows tensions of approximately $10,000\,bar$. Water that is barely adhered in pores of a diameter of $10\,\mu m$ is bound with tensions of about $300\,hPa$. This wide range of pressures involved a parameter, that is feasible for describing the changes in soilwater, since biggest alterations take place in the higher water contents. This is accomplished by the nondimensional **pF**-value, which is defined as:

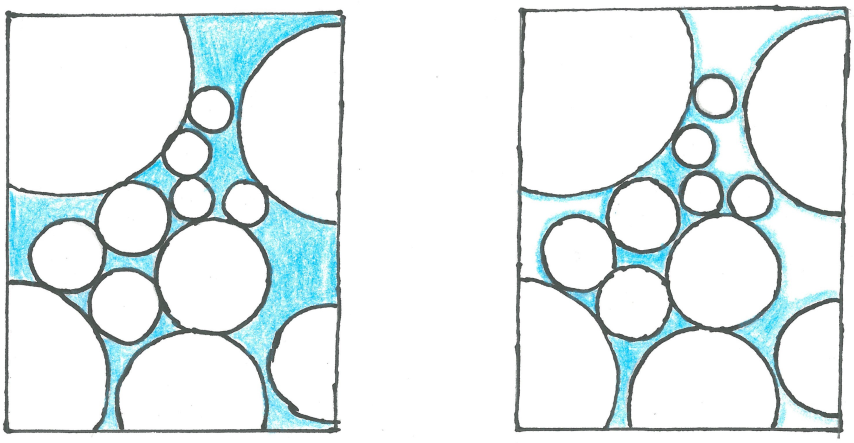

FIGURE 2.1: Scheme of soilpores. Fully saturated soilpores on the left side provide a high connectivity. As the water content declines (right side), small pores are separated.

$$pF = log\ cm\ hydrostatic\ head \tag{2.5}$$

A fully saturated soil runs dry in three steps. First mobile water moves down big pores, driven by gravity. Then water evaporates from capillaries after their diameter. Finally even the hygroskopic water evaporates. Air fills the emptied pores, causing gaps in connectivity of the soil water (see 2.1). These changes in connectivity have a huge influence on the mobility of the different isotopologues, since diffusion can only take place indirectly over the gaseous phase between the distinct water pools.

Chapter 3

Methods

3.1 Experimental Design

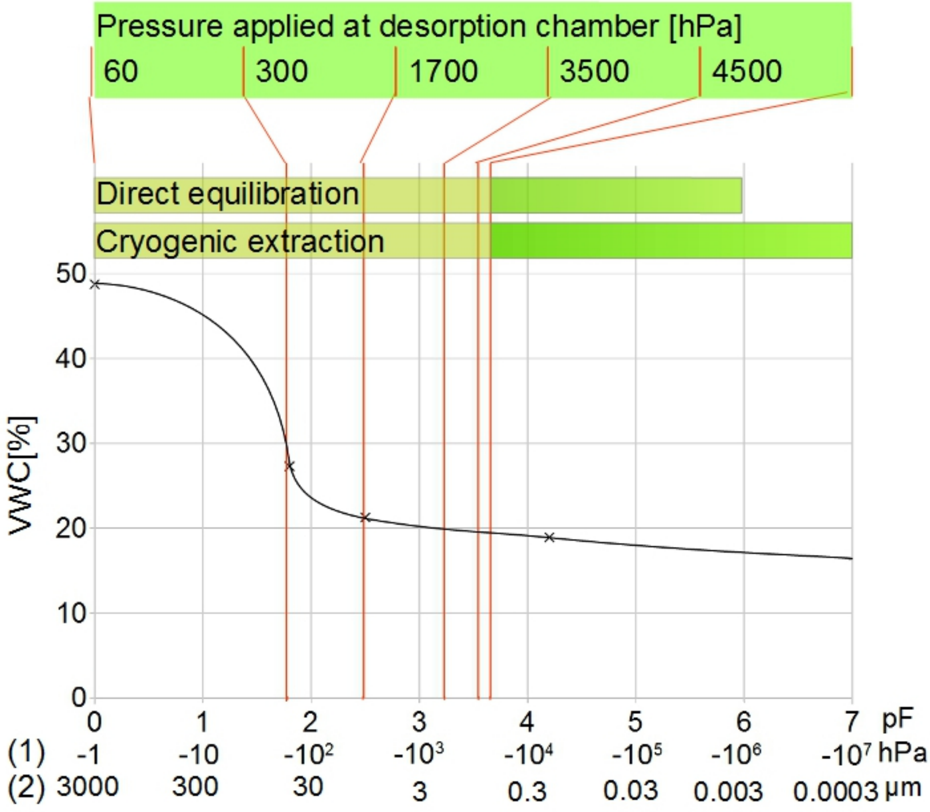

FIGURE 3.1: pF-curve of the used soil.The volumetric water content is plotted versus the pF-value, the matric potential (1) and the corresponding pore diameter (2). Above the methods and their ranges are given.

To get convincing data for propositions about the boundary lines of the two water worlds, soilcores labeled with a known isotope signal were drained successively by the desorption solution method. For extracting soilwater with water potentials exceeding the range of the desorption solution method, direct equilibrium and cryogenic extraction was used. Ten pressure chambers were used at once in each run, which consists of two parts. In the first part of a run, all ten chambers containing soilcores with a known isotope signal (natural, heavy or light signal) were drained successively by the desorption solution method. Then two cores of each label were separated from the other cores, cut in half and examined via cryogenic extraction and direct equilibrium. The remaining cores were dried at room temperature for two days and then rewetted with a known isotope signal, different than the one used in the first part. Afterwards the second part of the run was carried out similar to the first part, but with usage of direct equilibrium and cryogenic extraction on every probe at the end. In order to get an amount of data points as big as possible three runs were performed with two parts each. Each run was utilizing ten desorption chambers at once. In each of the six desorptions in total, it was attempted to obtain probes for five increasing pressures. In best case there should therefore result a data set of 250 values from the desorption solution and 60 values for the tightly bound water with potential greater than $4500\,hPa$.

3.2 Sampling

The soilsamples were taken at a vineyard in the Kaiserstuhl near Eichtstetten in february 2016. The silt loam was extracted in $60\,cm$ depth of the loess layer to prevent the presence of organic matter. Core cutters with matching size for the pressure chamber were driven into the soil, to obtain unimpaired soil samples, which were used for the first desorption run. Loose material was also collected to synthesize the labeled cores of the following two runs.

3.3 Field Methods

Three suction lysimeters were installed close to the dig side. Two of those were adjusted to extract mobile soilwater with a under-pressure of $700\,hPa$, one with $300\,hPa$. This samples were used to get an additional value for the actual isotope signal of the natural probes.

3.4 Desorption Solution

Blattner et al. first thought up the desorption solution method, which is used in this work, because it provides the opportunity to step wise drain the different porespaces (Blattner et al., 2000). Thus isotope ratios from certain sections of the pF-curve can be obtained. This method originally used to obtain the soil solution for researches of soluble ions. In this work the possibility to adapt this method on the mentioned issue is to be validated. It was additionally attempted to increase the functional rage of this method.

The soilcores from the field were put into brackets, which were then inserted into the pressure chambers as shown in Fig.3.2. As the chamber is tightly closed, the soil in the bracket is pressured by compressed air via a distribution unit, which gives the possibility to pressure 10 chambers at once. The porewater is drained over a cellulose acetate membrane, a porous HDPE disc and a cannula into vials. Originally this method is used for applying pressures up to 1700 hPa, which is equivalent to a pF of 3.2. By using cellulose acetate filters with a porespace of 0.02 μm instead of the originally used 0.47 μm an attempt was made to increase the usability of the pressure

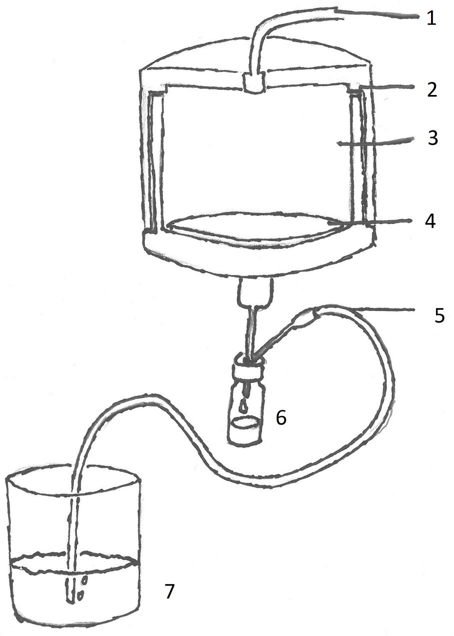

FIGURE 3.2: Scheme of the desorption chambers. 1. pressure supply, 2. inner sealing, 3. place for soilcores, 4. filter membrane with underlying HDPE disc, 5. excess compensating tube, 6. vial containing soilwater, 7. excess outlet

chambers to $4500\,hPa$ $(pF\ 3.6)$. Thus porespaces with a water potential of $60\,hPa, 300\,hPa, 1700\,hPa, 3500\,hPa$ and $4500\,hPa$ could be drained separately, giving the isotope values for $pF\ 1.78, 2.48, 3.23, 3.54$ and 3.65. Excess in the vial is compensated by a second cannula connected to a tube, which pipes the pressure into a jar slightly filled with oil. Thus excess is granted and isotopic exchange with the atmosphere is suppressed. An additional advantage of this excess is, that a dried out membrane is directly visible by the exceeding blistering at the corresponding excess tube. schreib doch ncoh was zur funktion. und auch was zum ueberdruck. The cores were then adjourned for about an hour in the closed pressure chamber, in order to give the new signal time to space out through the core, but preventing evaporation. As the new water seemed to be totally absorbed, pressure was applied. Ensuring the spans were about $30\,min$.

3.5 Direct Equilibrium

The direct equilibrium method was first indicated by Wasenaar (Wassenaar et al., 2008) and is very suitable for providing an additional data point with a very small porewater consumption. The soilsamples are put in heat-sealed bags, filled with nitrogen. Stored in an UV-opaque bag under constant room temperature, non-equilibrium fractionation processes should be prevented. The time to reach equilibrium conditions was set to two days. After equilibration the air in the headspace has the same isotope signal as the remaining water in the soilsample. The air is then sampled with the Picarro CRDS. Due to organisational problems in the laboratory equilibration times could not be satisfied for some batches and three different Picarro systems were used. As each batch was standardized with its own standards the use of different CRDS-units should not cause inaccuracy. The influence of exceeding equilibration times was tested and several values had to be discarded.

3.6 Cryogenic Extraction

Cryogenic vacuum distillation is a long used method for obtaining soilwater. Known since the late 1960s it is used with various parameters, but the principle remains the same. Orlowski et al. currently passed criticism on the missing standardizing of the method (Orlowski, Breuer, and Jeffrey J. Mcdonnell, 2016). The soil is placed in a vial, which has a connection to an empty one. With vacuum applied in the vials, the one containing the soil is heated, causing the watermolecules to distribute over the internal space. As the empty vial is cooled down vastly, it functions as a cold trap, bringing the water molecules to condensation (see fig.3.3). For this work a vacuum for $0.03\,mbar$ was applied, the soil was heated to $115\,°C$ and the cold trap was created with liquid nitrogen, which caused a temperature of approximately $-197\,°C$. About 40 minutes were given as extraction time. The soil was subsequently oven-dried for 24 hours at $130\,°C$. The weight of the soil before the extraction was compared to the weight of the extracted water and the dried soil, to check whether the water was entirely extracted. As every soilsample was divided into three probes and the three results were averaged, inaccuracies were minimized.

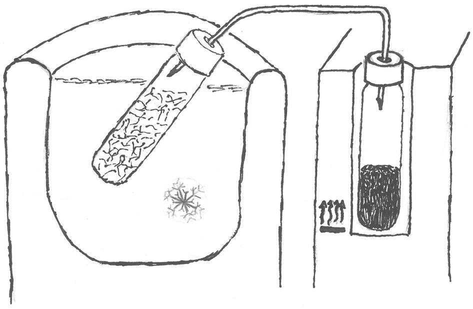

FIGURE 3.3: Scheme of cryogenic extraction setup, with heater element on the right and nitrogen-bath on the left

Chapter 4

Results

4.1 Performance of Desorption Solution Method

Experimental Design While performing the desorption runs a vast amount of outage occurred, since the cellulose acetate filters kept on running dry, loosing the air-tightness. Therefore the last desorption step ($4500\,hPa$) was omitted. Nonetheless outrage occurred frequently with the lower pressures, which is why only 69 instead of the anticipated 250 values could be obtained by the desorption solution method. As corrupted soilcores could not be used for the other methods, they provided 34 instead of 60 samples. So in total $58\,\%$ of data was lost.

Isotope values of the first runs Here the values are described, that were gathered from soilcores, that do not contain residual isotope signals or were collected directly in nature. The isotope values obtained from the natural soilcores via the desorption solution method plausibly map the heterogeneity of the natural soil (4.1). The δ^{18}O values also match the δD values. With the pressure ranging from $300\,hPa$ to $3500\,hPa$ (the soil moisture from the natural cores was too low to provide soilwater at the lowest pressures of $60\,hPa$), the values vary from -10 ‰ to -7.5 ‰ for δ^{18}O and from -71 ‰ to -63 ‰ for δD. Most chambers show a range less than 0.5 ‰ for δ^{18}O and 2 ‰ for δD, whereas values from chamber no. 25 nearly vary by the whole range. The suction lysimeters give average values of -10.2 ‰ for δ ^{18}O and -75 ‰ for δD, whereas the cryogenic extraction provides δ ^{18}O values of -9.79 ‰ and δD values of -72.74 ‰ for the whole soilwater and δ ^{18}O values of -10.02 ‰ and δD values of -75.51 ‰ if desorption solution method was applied beforehand.

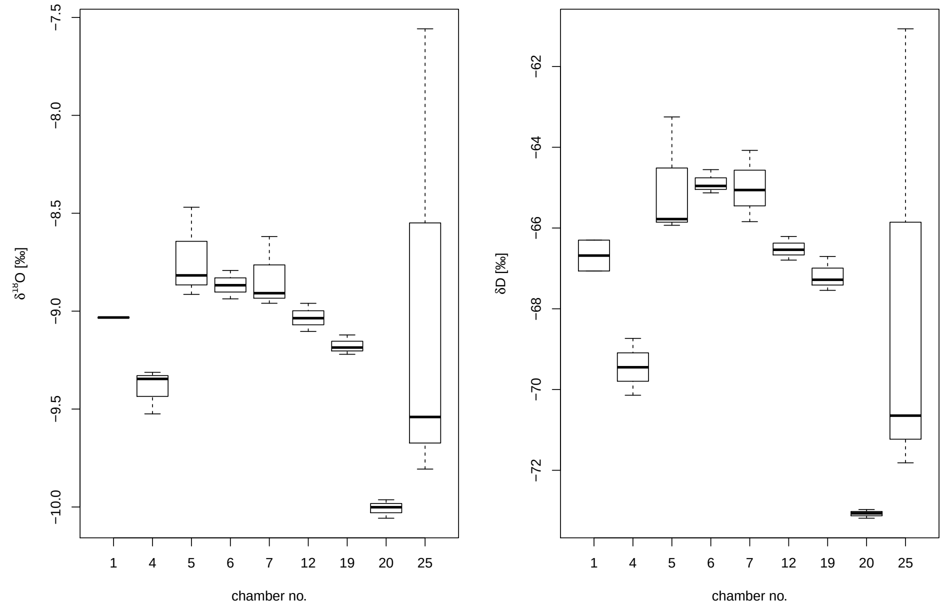

FIGURE 4.1: $\delta\ ^{18}$O and δD values from the natural soilcores by chamber

The spiked cores of following runs obtain similar patterns (fig. A.1 in Appendix) and frequently provided soilwater at $60\,hPa$. The overall δ^{18}O values from the soilcores spiked with the heavy standard (-0.45 ‰δ^{18}O, -2.22 ‰δD) and drained with the desorption solution method range from -0.7 ‰to -0.25 ‰, in case of chamber no.1. Most chambers provide values between -0.7 and -0.4 with a average range of 0.2 ‰. The mean value is -0.54 ‰. The δD values obtained by the heavy spiked cores vary between -4.5 ‰and -2.5 ‰with a range less than 1 ‰for each chamber. The mean value here is -3.36 ‰. Distributions of δ^{18}O and δD do not match entirely. Cryogenic extraction yielded δ^{18}O of -1.66 ‰and δD of -10.99 ‰. Direct equilibrium did not provide data from these soilcores.

δ^{18}O values obtained from the soilcores in the desorption chambers spiked with the light standard (-16.69 ‰δ^{18}O, -126.09 ‰δD) show a mean of $-16,11$ ‰. Here chamber no. 7 ranges from $-16,4$ ‰to -13 ‰. Whereas chambers 9, 20 and 25 only show a range of less than 1 ‰and values of chambers 12 and 19 even spread only over a range of approximately 0.3 ‰. δ^{18}O and δD again match rather good, with chamber no.7 showing a big range of δD values from -123 ‰to -108 ‰, whilst the other chambers show small ranges of less than 3 ‰. δD mean value is -122.09 ‰.

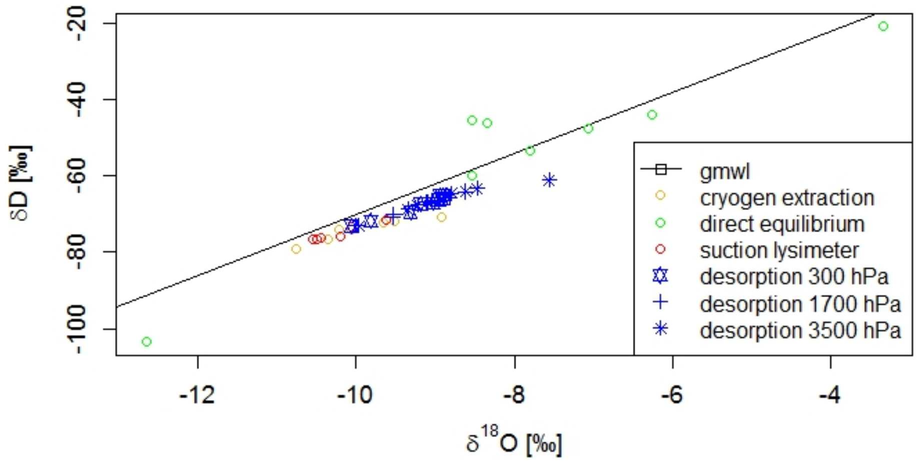

FIGURE 4.2: δ ^{18}O and δD values from the natural soilcores by method

The other methods applied after the desorption run obtained δ^{18}O values of -12.93 ‰(direct equilibrium) and -17.55 ‰(cryogenic extraction) and also δD values of -121.65 ‰(direct equilibrium) and -130.19 (cryogenic extraction).

4.2 Locating the borders of the two water worlds

For gathering data usable for delineating the borders between the two water worlds the air dried soilcores of the first run were rewetted and examined for residual isotope signals. To intensify the differences of the isotope signals, soilcores that were previously spiked with light water, were spiked with heavy water for the second run and vice versa. Here the isotope values of the second runs are described.

The study of the isotope values of cores from the second desorption run revealed that several datapoints are shifted from the new spikes origin towards the values of the former content. For the heavy spiked soilwater drained with the desorption method these range goes from the origin of the new label (-0.45 ‰δ^{18}O -2.22 ‰δD) down to values of approximately -7.84 ‰δ^{18}O and -60 ‰δD among the GMWL. Whilst some values from pressures of $60\,hPa$ to $1700\,hPa$ show these shift, the only available value from 3500 hPa ranges in the bulk close to the new label (see 4.3).

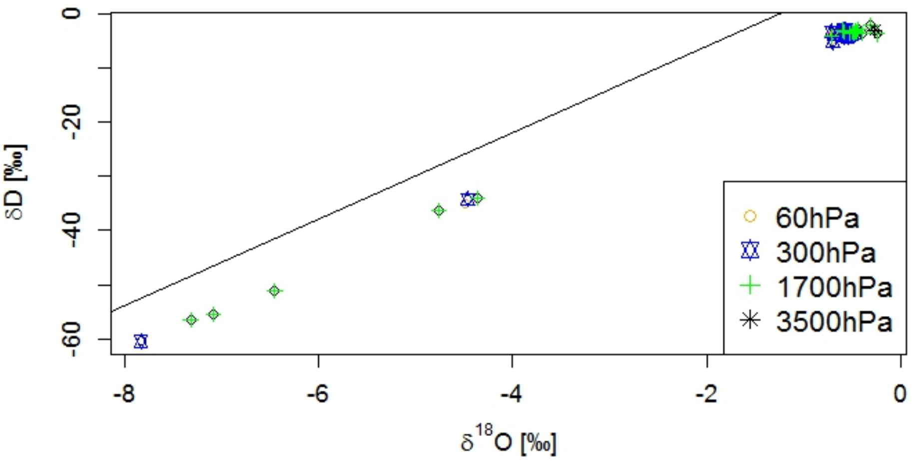

FIGURE 4.3: δ ^{18}O and δD desorption values from heavy spiked soilcores with GMWL

The same characteristics in the opposing direction can be found in the light spiked soilwater (A.2 in Appenix). Here some values obtained from pressures from 60 hPa to 1700 hPa range from -16.69 ‰δ^{18}O and -126.09 ‰δD (the new label) to -1.93 ‰δ^{18}O and -14 ‰δD. 3500 hPa values are not available for the light spiked soilcores.
Focusing on the values grouped near the new label, values obtained by 1700 hPa drainage tend to be located above the values from 3500 hPa. This can be noted for both heavy and light spiked probes. In case of the heavy spiked value-cluster the 60 hPa values all locate at the bottom edge of the cluster, showing a slight decrease of heavy isotopes (see fig. 4.4). The 60 hPa values from the light spiked probes have a wider range and do not show a distinct distribution (see fig.A.3 in Appendix).

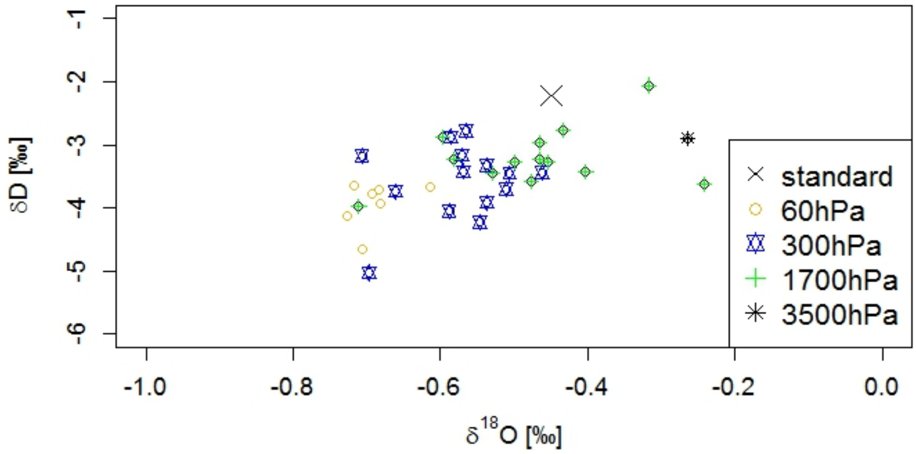

FIGURE 4.4: cluster of $\delta\,^{18}$O and δD desorption values from heavy spiked soilcores (cluster from 4.3) with the values of the standard

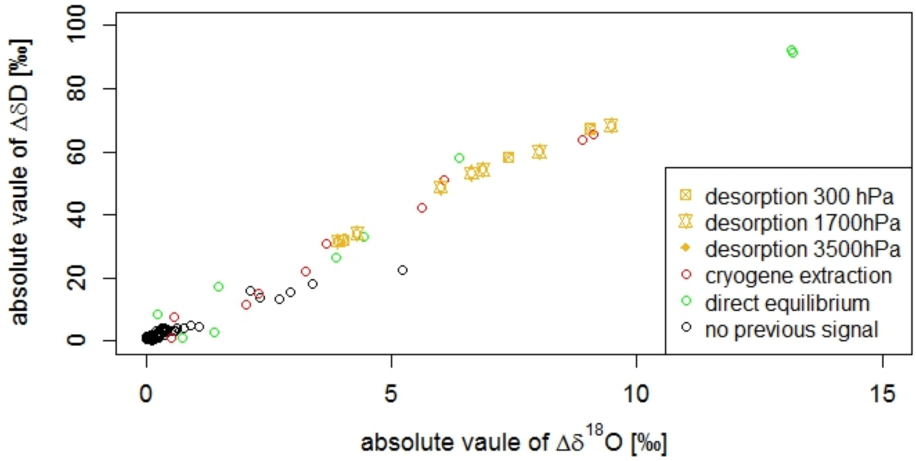

FIGURE 4.5: Absolute $\Delta\delta$ values of ^{18}O and D. Both standards are forming the neutral point

Regarding the other methods it can be observed, that values from direct equilibrium and cryogenic extraction mainly locate along the GMWL towards the former label. To plot values from heavy-labeled and light-labeled probes together the absolute value of variance from its actual label is used in figure 4.5. Therefore the absolute value of the subtraction of the actual value from the standard is used, written as $\Delta\delta\,^{18}$O and $\Delta\delta\,$D.

The distribution of the values taken by the direct equilibrium method show the widest range, reaching from the bulk near the original label sources (located at the neutral point) to $\Delta\delta^{18}$O of 13 and $\Delta\delta$D of 92. Besides these two aberrations the values evenly spread to $\Delta\delta^{18}$O of 6 and $\Delta\delta$D of 57. Cryogenic extraction provides values homogeneously spread from zero to $\Delta\delta^{18}$O of 9 and $\Delta\delta$D of 65. Soilwater drained via desorption solution plot from $\Delta\delta^{18}$O of $3, 9$ and $\Delta\delta$D of 31.

Values for the d-excess range from -24.67 ‰to 86.32 ‰, where all values

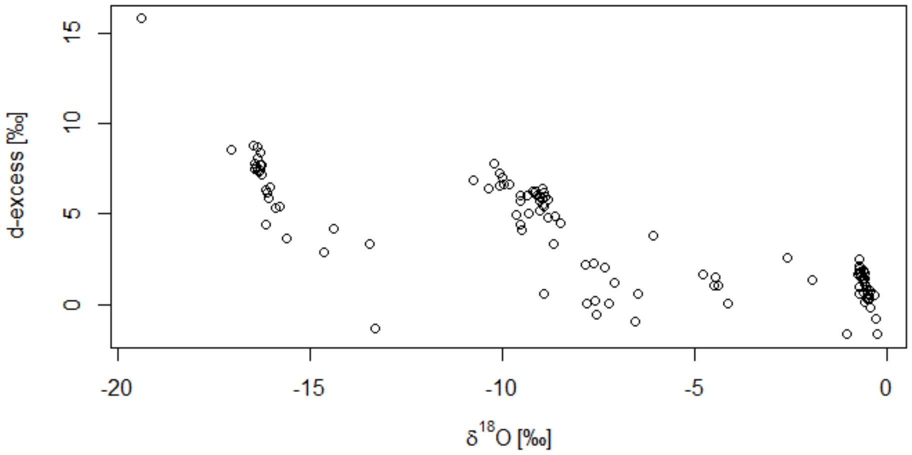

FIGURE 4.6: distribution of d versus δ^{18}O for all methods expect direct equilibrium

below -1.68 ‰and all above 8.77 ‰were obtained by the direct equilibrium method (expect for one cryogenic extraction value with a d of 15.81 ‰). The greatest deviations of deuterium from the GMWL occur in case of the soilcores with the natural soilwater, followed by cluster around the heavy spiked probes, that formerly contained the natural water(see 4.6). A coherence between the d-value and the used method or the applied pressure could not be found.

Chapter 5

Discussion

A major problem with the method occurred initially while using the desorption chambers, whose cellulose acetate membranes constantly ran dry. Thus the compressed air flowed through the soil, causing evaporation in the sample and making it unusable for further analysis via direct equilibrium or cryogenic extraction. The soilwater which was sampled in the vial as the leak occurred was also corrupted. Rewetting of the filter to restore tightness could not be performed, as it would have caused distortions of the isotope signal. Thus the last desorption step was omitted. Nonetheless outrages occurred frequently at the pressures from $60\,hPa$ to $3500\,$, leading to a major uncertainty concerning the gained values and notably reducing their amount.

The great ranges, that are exhibited by some of the pressure chambers show, that even with greatest care and continuous review for leaks, leakages occur imperceptibly. This causes a very negative impact on the reliability of this method. In this experimental design this method caused a wastage of nearly three out of four probes ($72.4\,\%$).

Remaining data without corruptions gained from the desorption runs, displays the expected values quite well. So δD -3.36 ‰and -0.54 δ^{18}O were measured as δD -2.22 ‰and -0.45 δ^{18}O were applied. The light spiked soilcores with a δD of -126.09 ‰and -16.69 δ^{18}O, obtained δD -122.09 ‰and -16.11 δ^{18}O. These deviations are acceptable compared to those of other methods.

The attempt to gain data useful for localizing the border between the two water worlds was not successful. Admittedly the values from soilcores containing a residual isotope ratio showed a clear shift towards the previous signal, but this trait was not limited to the higher pressures of the desorption runs or the methods describing the soilwater with an pF outraging desorption solution. Regarding the values from desorption solution method it is even rather perceivable, that higher pressures always lead to higher isotope values. A relative reduction of δD is also most likely to be found among these values, which indicates evaporation to have an effect as the soil is under pressure in the chambers for a longer time. This could also be a result of the connectivity in the soil, which is greatest for low pressures and therefore facilitates diffusion processes, which are than hindered as pressure increases and connectivity gets lost.

The examination of the d-excess showed, that the expected d-values appear most likely, if natural soils are used. They could not be reproduced by spiking cores with a residual signal as performed in this work.

Chapter 6

Conclusion

Despite the vast amount of losses the desorption solution method provides quite accurate data. The functional range could not be increased so far. Its reliability could be increased by taking considerably more care monitoring the process, by constantly checking the cores mass balance.

A further suggestion for subsequent work on this method is to vary the pressure steps, by starting with various pressures and comparing the results. A variation in the spans may also be of interest.

The examination of the boundaries of the two water worlds came adrift, since the spiked soilcores did not show the same features regarding d-excess as natural soilcores. An examination of the influence of varying rest spans, in which the new label can mix with residual signal, may fix this issue.

It is inexplicable what caused the values from the direct equilibrium method to show such bizarre deviations. Organic matter was prevented, samples with exceeded equilibration time where discarded and the device shift was adjusted by measuring standards with every batch.

A. *Appendix*

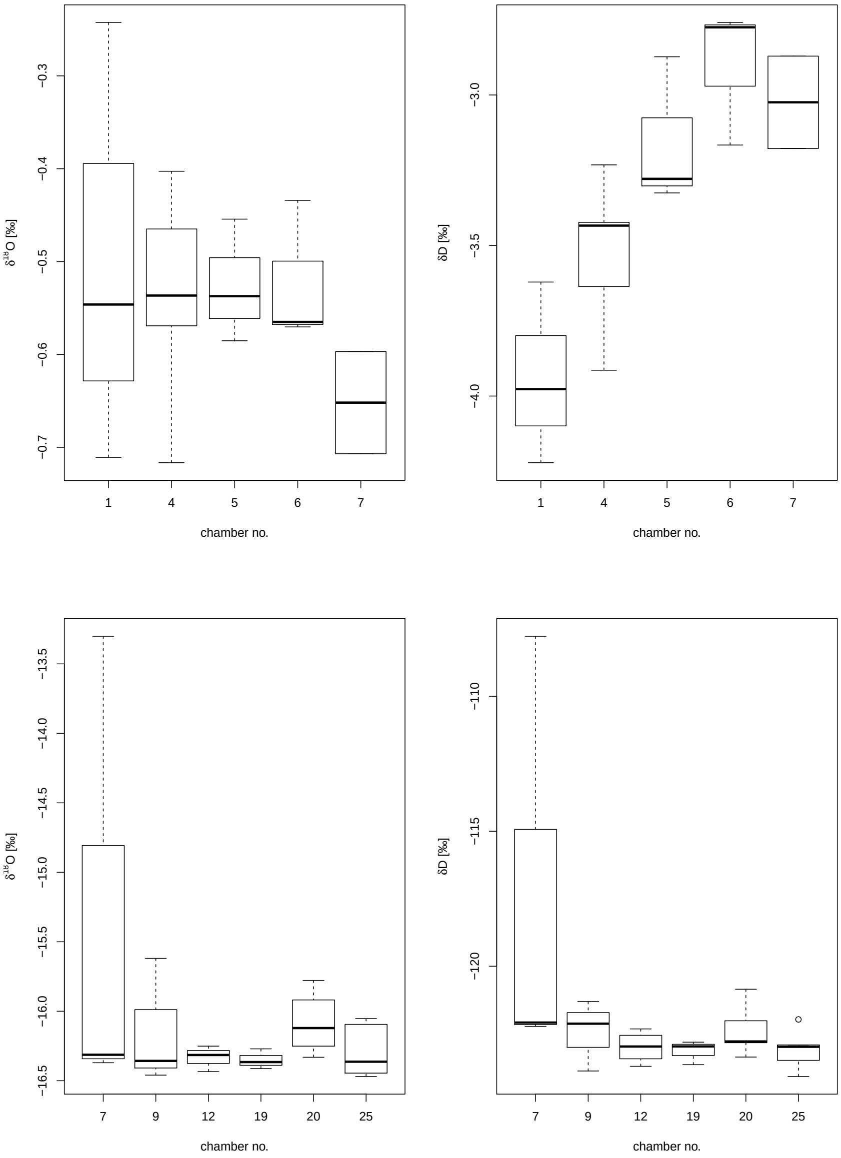

FIGURE A.1: δ ^{18}O and δD values from the heavy spiked soilcores (above) and light spiked soilcores (below) by chamber

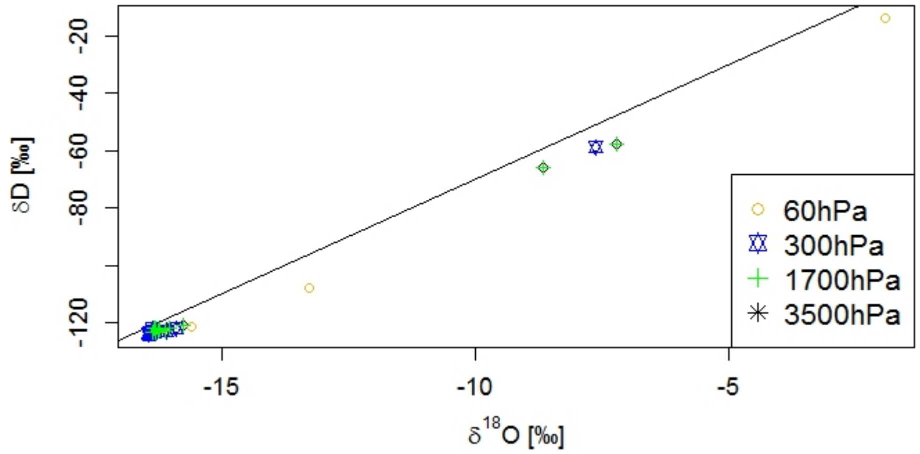

FIGURE A.2: δ ^{18}O and δD desorption values from light spiked soilcores.

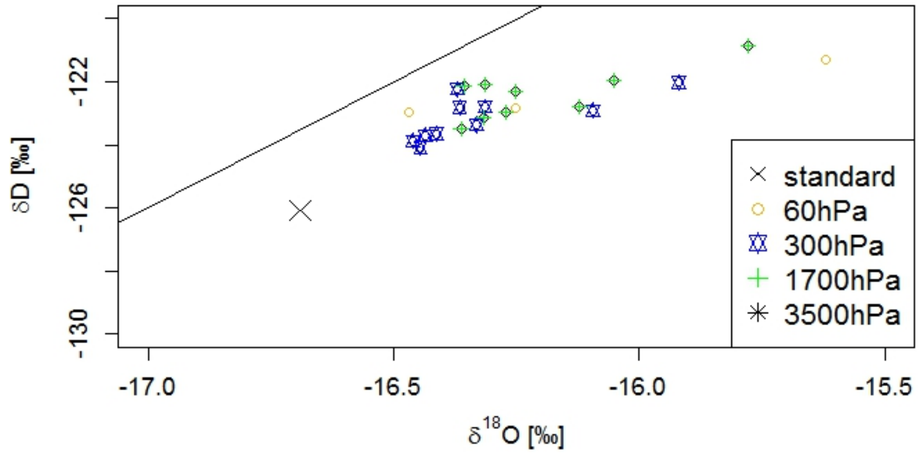

FIGURE A.3: cluster of δ ^{18}O and δD desorption values from light spiked soilcores (cluster from A.2)

Bibliography

Blattner, Mario S et al. (2000). "The desorption solution - an alternative approach to measure water soluble ions in soils". In: *Journal of Plant Nutrition and Soil Science* 163, pp. 583–587. DOI: `10.1002/1522-2624(200012)163:6<583::AID-JPLN583>3.3.CO;2-K`.

Clark, I D and P Fritz (1997). "Environmental isotopes in hydrogeology. Lewis Publisher." In: August, p. 328.

Craig, H (1961). "Isotopic Variations in Meteoric Waters." In: *Science (New York, N.Y.)* 133.3465, pp. 1702–1703. ISSN: 0036-8075. DOI: `10.1126/science.133.3465.1702`.

Criss, R.E. (1999). *Principles of Stable Isotope Distribution*. New York: Oxford University Pree, p. 264. ISBN: 9780195117752.

Dansgaard, W. (1964). "Stable isotopes in precipitation". In: *Tellus* 16.4, pp. 436–468. ISSN: 0280-6495. DOI: `10.3402/tellusa.v16i4.8993`.

Mazor, Emanuel (2004). *Chemical and Isotopic Groundwater Hydrology*. 4th ed. CRC Press, p. 352.

McDonnell, Jeffrey J. (2014). "The two water worlds hypothesis: ecohydrological separation of water between streams and trees?" In: *Wiley Interdisciplinary Reviews: Water* 1.4, pp. 323–329. DOI: `10.1002/wat2.1027`.

Orlowski, Natalie, Lutz Breuer, and Jeffrey J. Mcdonnell (2016). "Critical issues with cryogenic extraction of soil water for stable isotope analysis". In: *Ecohydrology* 9.1, pp. 3–10. ISSN: 19360592. DOI: `10.1002/eco.1722`.

Orlowski, Natalie, Dyan L Pratt, and Jeffrey J Mcdonnell. "Intercomparison of soil pore water extraction methods for stable isotope analysis". In: ISSN: 08856087. DOI: `10.1002/hyp.10870`.

Pfahl, S. and H. Sodemann (2014). "What controls deuterium excess in global precipitation?" In: *Climate of the Past* 10.2, pp. 771–781. ISSN: 1814-9332.

DOI: `10.5194/cp-10-771-2014`. URL: `http://www.clim-past.net/10/771/2014/`.

Sprenger, Matthias, Barbara Herbstritt, and Markus Weiler (2015). "Established methods and new opportunities for pore water stable isotope analysis". In: *Hydrological Processes*. ISSN: 10991085. DOI: `10.1002/hyp.10643`.

Wassenaar, L I et al. (2008). "High Resolution Pore Water δ2H and δ18O Measurements by Laser Spectroscopy". In: *Environmental Science & Technology* xxx.xx, pp. –5.