Porewater Stable Isotope Profiles: Similarities and its Implication for Vadose Zone Processes

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A Thesis presented for the degree of
Master of Science in Hydrology

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Dedicated to

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Abstract

To implicate the pore water stable isotope depth profile (PSIP) methodology 45 drill cores are taken in order to line out correlations and relationships between environmental and ground site characteristics like geology, land use, topographical position, exposition, canopy status, soil skeleton or water content and the hydrological response in the vadose zone of these sites in the Attert catchment, in the Grand Duchy of Luxembourg. The stable isotope relations of the pore water of the soil material which is extracted from the ground are used to generate the PSIP. The isotopic signal of the samples is measured with the direct equilibrium method, further a cryogenic vacuum extraction of pore water with a following isotope measurement of the soil pore fluid is made in order to compare the most frequently used measuring methods in this research field. The PSIP, depth profiles of the water content, the D Excess depth profiles as well as dual isotope plots (^{2}H and ^{18}O) of each site are generated in order to realise a descriptive statistical analysis to find out correlations between sites and their hydrological response in the unsaturated zone. The PSIP and the other graphics are used to create several variables which mainly describe the shape of the PSIP. Several groups due to similar shapes of the PSIP are made in order to figure out the origins of the site similarities which are regulating the similarities regarding the shapes of the PSIP. Hence a visual approach to work out similarities between the environments of the sites and their belonging PSIP is established. The geology, the land use as well as the topographical position

have the greatest influence on the hydrological processes of infiltration, evaporation, transpiration, mixing, soil storage and recharge of soil pore water in the vadose zone. Similar shapes of the PSIP can result from sites with similar environments as well as from sites with distinctive environments, therefore the similarity of the shape of the PSIP does not offer a great opportunity to line out functional units regarding the similar hydrological response of the sites. The PSIP methodology leads to good results in order to determine the dominant characteristics which influence the various hydrological processes in the vadose zone.

Zusammenfassung

Um die Anwendung von Bodenwasser Tiefenprofilen der stabilen Wasserisotope (^{2}H und ^{18}O) im Bezug auf die Bestimmung von möglichen Gemeinsamkeiten im hydrologischen Verhalten in der ungesättigten Zone von unterschiedlichen Standorten zu testen, werden 45 Bohrkerne im Attert Einzugsgebiet in Luxemburg entnommen, um 45 Bodenwasser Tiefenprofile mittels der direkten Equilibrierungsmethodik auf das Isotopenverhältnis des Bodenporenwassers bemessen. Ein Vergleich der herkömmlichen Messmethoden wurde bewerkstelligt, indem zusätzlich eine kryogene Vakuum Extraktion von Bodenporenwasser von 41 Teilproben mit einer gekoppelten Fluid Bemessung durchgeführt wurde. Neben den Bodenwasser Tiefenprofilen der stabilen Wasserisotope werden Tiefenprofile des Wassergehaltes, sowie Tiefenprofile des D Excesses und Duale Isotopen Grafiken verwendet, um beschreibende Variablen bezüglich der unterschiedlichen hydrologischen Prozesse wie Infiltration, Evaporation, Transpiration, Mischung, Bodenspeicherung oder Grundwasserneubildung in der ungesättigten Zone herzustellen. Diese Variablen werden dann im Rahmen einer deskriptiven statistischen Analyse verwendet, welche darauf abzielt, die Dominanz von unterschiedlichen Standortcharakteristika wie Geologie, Landnutzung, topographische Position, Exposition, Bedeckungsgrad oder Skelettanteil im Bezug auf die oben genannten Prozesse zu bestimmen. Des Weiteren werden die Tiefenprofile auf Gemeinsamkeiten überprüft, die auf ähnliches hydrologisches Verhalten der Standorte hinweisen. Gemeinsamkeiten in der Form der Bodenwasser

Tiefenprofile der stabilen Isotope haben mehre Ursachen und sind nur bedingt dazu geeignet auf ähnliches hydrologisches Verhalten in der ungesättigten Zone an den Standorten zu schließen, um eventuell funktionelle Einheiten mit gleichem hydrologischem Verhalten im Einzugsgebiet einzuteilen. Die Bestimmung der dominierenden Standortcharakteristika mittels der Tiefenprofile des Bodenporenwassers der stabilen Isotope (^{2}H und ^{18}O) führte zu guten Ergebnissen.

Declaration

The work in this thesis is based on research carried out at the CAOS Project in the gran duchy of Luxembourg, the Helmholtz Center in Munich and the Institute for Hydrology at the University of Freiburg, Germany. No part of this thesis has been submitted elsewhere for any other degree or qualification and it is all my own work unless referenced to the contrary in the text.

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PSIP Pore Water Stable Isotope Depth Profile

WPP Winter Precipitation Peak of the winter 2013/ 2014

VSMOW Vienna Standard Mean Ocean Water

CAOS Catchments As Organised Systems

IHF Institute for Hydrology Freiburg

CRDS Cavity Ring Down Spectroscopy

LMWL Local Meteoric Water Line

GMWL Global Meteoric Water Line

Chapter 1

Introduction

1.1 Literature review

The question of recharge of shallow aquifers is one of the most critical for groundwater management in dry areas [Darling and Bath, 1988]. Is recharge currently taking place and if so, at what rate? The amount of recharge of precipitation water to the groundwater always varies from site to site due to different geology and soils. If recharge is occurring, further important problems arise dealing with possible mechanisms of recharge which may occur through: (i) vertical (direct) infiltration of rains (ii) lateral seepage of river or flood waters, (iii) upward leakage from deep aquifers, (iv) lateral recharge from areas of higher rainfall [Fontes et al., 1986]. In addition, ground water recharge rates vary considerably due to topography, soil properties and vegetation types [Blume et al., 1968]. The knowledge of residence time of water in the soil is essential in order to understand contamination transport and examining catchment response to environmental changes [McGuire and McDonnell, 2010]. Mixing of different precipitation-, stream- and groundwater due to soil storage or seepage, evaporation, infiltration and recharge can be directly observed via a comparison of the pore water based stable isotope depth profiles (PSIP) which are used in this study in order to investigate vadose zone processes. In some cases PSIP can be directly used to measure water flux through the soil profile: If lateral flow is negligible vertical moving pore water will be the amount of recharge [McConville

et al., 2001]. Characteristic signals in the subsurface of a hill slope which not longer occur at the hill slope foot indicate mixing processes with stream- or groundwater [Garvelmann et al., 2012]. The relation of solute concentration to transit time of recharge water is strongly affected by the pathways of water in the unsaturated zone [Landon et al., 2000]. The applicability of the method which is used regulates the extent of the potential in order to investigate hydrological processes in the vadose zone. There are several studies using time dependent generation of PSIP at one spot using different observation methods like suction cups, lysimeters, wells or drill cores and also using different water extraction methods like distillation, centrifugation or direct equilibrium and different mass spectrometers for the isotope signal measurement [Darling and Bath, 1988, Geake and Foster, 1989, Maloszewski et al., 1995, Landon et al., 2000, O'Driscoll et al., 2005, Lee et al., 2007, Kabeya et al., 2007]. Many studies also led to great conclusions via the generation of time independent PSIP and offer a quicker way for higher resolated information about the hydrological response in the unsaturated zone [McConville et al., 2001, Kelln et al., 2001, Garvelmann et al., 2012, Mueller et al., 2014]. In general PSIP investigations have great potential for all scales. This thesis deals with 45 time independent PSIP which are used to figure out the influence of the environmental characteristics of a site on the hydrological processes at this site. Hence it carries out the degree of similarity of the hydrological response in the vadose zone in different environments which all belong to the same catchment. Forty five drill cores are taken in a meso-scale ($10^1 - 10^3$ $[km^2]$) catchment, in the Grand Duchy of Luxembourg at various sites. Analytic determination of the stable isotopic compositions of ^{18}O and ^{2}H in the soil pore water via cavity ringdown spectroscopy has to be done in order to create 45 PSIP. The shapes of these 45 PSIP are analysed to carry out variables which describe the degree of the hydrological processes that occur at the specific site. These variables further are used for a descriptive statistical analysis which has the goal to enhance the understanding of the hydrological response in the unsaturated zone of these 45 sites. As all these sites belong to one catchment also an effort is made in finding functional units in the catchment which can be separated and grouped due to a similar hyrological response and, as a consequence improve hydrological models in

the future (CAOS Project). This section delivers the first information belonging to the research field of the PSIP methodology and gives the reader a first impression of the research topic.

1.2 Hypothesis

PSIP contain information which explain the local hydrological processes in the vadose zone [Wassenaar et al., 2008, Garvelmann et al., 2012]. In order to develop a better understanding of vertical infiltration, evaporation, soil storage, mixing, transit time or recharge of water in the unsaturated zone the PSIP can be used as an important and very helpful tool. The dominant environmental characteristic of a site can be detected via a comparison of the shapes of the 45 time independent PSIP which are created through drill cores taken at the well instrumented sensor cluster sites in the catchment. Due to a reasoned selection of the sites a big range of various environmental characteristics like land use, topographical position or canopy status and a big range of ground characteristics like geology, type of soil, skeleton, soil texture or rooting depth is present. All these possible dominant site characteristics could strongly influence the hydrological response at the site compared to the other environmental or ground characteristics at the site. Areas with a similar hydrological response due to similar vadose zone processes are to be detected and distinguished in order to improve the hydrological models and to upgrade our understanding of how hydrological catchments work in general. Furthermore the following hypothesis are to be substantiated in this thesis: (i) Similarities in the shape of PSIP taken at different sites show that the hydrological processes at these sites are similar. (ii) If the environmental characteristics of a location are similar the local hydrological response shows a similarity too and therefore the shape of the PSIP belonging to these sites also show similarity. (iii) There are specific environmental characteristics which influence the local hydrological processes more than others. This section explains the hypothesis of this thesis which are to be tested and answered, the conclusions include these answers.

1.3 Research Questions

Soils play an important role regarding the water cycle of an hydrological catchment: Soils act as a buffer and as a reservoir for precipitation water and nutrients in the vadose zone. Characterizing the spatial variability of soil properties is essential for the understanding of how the land management influences the soil functions and associated ecosystem services, including those involving water quality, carbon (C) sequestration and biodiversity [Glendell et al., 2014]. The hydrological processes in the unsaturated zone are to be understood in order to manage and reduce contamination problems caused by humanity [Wösten et al., 1999]. This thesis deals with several research questions relating to the hydrological processes in the unsaturated zone. These research questions support the argumentation with reference to the hypothesis. Usage of 45 PSIP taken in a well instrumented catchment in the Grand Duchy of Luxembourg makes this possible. All the information about hydrological response which is included in the samples is extracted, illustrated and statistically analysed in order to answer certain study questions. The research topic is the understanding of (i) what are the site characteristics that govern similarities in the shapes of the PSIP and do these similarities belong to a similar hydrological response at these specific sites? (ii) How does the topographical position, the type of geology, the land use class or the exposition as well as the canopy and the soil skeleton affect the shape of the PSIP? (iii) Which environmental or ground characteristic at the site do effect the hydrological processes most? (iiii) How can functional units in space be delineated from each other via PSIP? This section is related to the hypothesis as well and the certain research questions should help the reader to understand the approaches which are done in order to answer these questions.

1.4 Objectives

As Wassenaar et al., 2008 concluded that PSIP are a powerful tool with respect to hydrological investigations in the unsaturated zone. This study refers to the investigation at a hill slope in the black forest [Garvelmann et al., 2012] using the

same methodology and similar graphics. Worldwide there are several studies which are working on the same or similar research questions. In order to understand the spatio temporal behavior of hydrologically separable areas Thomas et al., 2013 used PSIP or knowledge of isotopic relations of the stable isotopes ^{18}O and ^{2}H of precipitation-, stream- and soil pore waters to estimate the hydrological response in the vadose zone. The aim of this study is to create, analyze and compare various PSIP belonging to 45 locations with different environmental characteristics like for example geology, soil, canopy status, position, exposition, land use and soil texture. The study area is located in a meso-scale watershed in Luxembourg where natural conditions still are pre-existing and a lot of various environmental characteristics are present. Comparison of the different shapes of the PSIP leads to an understanding of how the various hydrological processes like infiltration, evaporation, mixing, dispersion and recharge can be detected in the visualisation of the PSIP. Consequently the shape of the PSIP belongs to the hydrological behavior of the site and therefore the shape is depending on the environmental characteristics which are present at the site. Descriptive statistics is used to find out relations between the hydrological response and the environmental properties. Scatter plots and Box-Whisker plots are created in order to express and outline significant correlations of the site characteristics which are controlling the hydrological processes. The uniqueness of the study corresponds to the large spatial temporal range of the distribution of the sensor cluster sites in the totally natural catchment with a large range of environmental characteristics. The resulting data is time independent because the drills were all done in two weeks of fieldwork whereas the hydrological processes in the unsaturated zone are seen to happen slowly [Thomas et al., 2013]. During the fieldwork there was no large precipitation event. One small precipitation event has been sampled during the fieldwork and could serve as additional reference for a recent infiltration event if it appears in the PSIP. In addition a comparison of the measuring methods of the isotopic compositions of the stable isotopes ^{18}O and ^{2}H is made in order to validate the frequently used methodologies (direct equilibrium measurement or fluid measurement after cryogenic vacuum extraction) in this research field. Thereafter the generation of the PSIP is completely achieved using the direct equilibrium

measurement method which is developed by [Wassenaar et al., 2008]. This section outlines the objectives and approaches of the study, the reader gets a first insight into the way the PSIP methodology works.

Chapter 2

Methods

2.1 Fieldwork

2.1.1 Study Area

The study area lies in the Attert catchment which is located in the western part of Luxembourg close to the border of Belgium. Forestal and agricultural use of the land is predominant. The hilly landscape of the study area in the Grand Duchy of Luxembourg is poorly cultivated. Several regional geologic processes like the Variscian orogeny (Paleozoic), the Eifel depression (Mesozoic) and the Alpine orogeny (Cenozoic) led to the development of the geologic complex which is underlying and therefore generating the soils in the catchment. Three main types of geologic strata and soil are present. Shist, sandstone and marl are underlying the cambisol, podsol and stagnosol of the research area. Figure 2.1 shows that the shist is mainly located in the north, the marl is situated in the center and the sandstone appears in the south of the study area. Younger alluvial sediments have developed in the valley bottoms of the valleys with different orientations and inclinations [Juilleret et al., 2011]. Due to the power of erosion which is regulated by the topography of the area three types of soils are shaped with different thicknesses and hydrological behaviours. Vegetation also is adapted to the geology and therefore to the mineralogical conditions of the ground. Investigations of hydrological processes in the vadose zone have to be

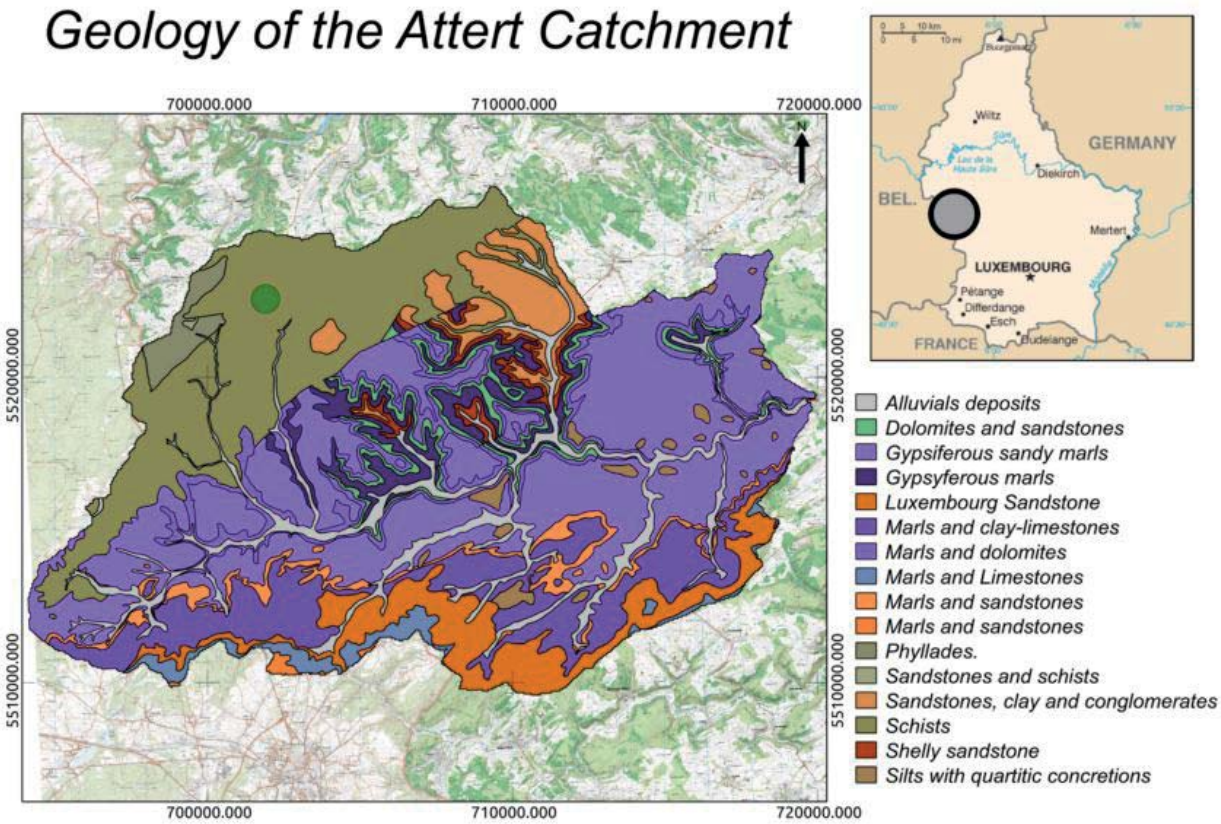

Figure 2.1: Superficial geology of the Attert catchment, Luxembourg. Ministere du Developement durable et des Infrastuctures, Service geologique du Luxembourg, Administration de ponts et chaussees, 1998.

accompanied with investigations in the soil and the rock or the regolith [Juilleret et al., 2011].

Table 2.1: Overview of Ground Characteristics of the Sensor Cluster Sites located in the Marl Area, with Thickness A - and B_1 - Horizon in [cm]; Skeleton A, B_1 in [%]; The Soiltexture A, B_1 [-] with C: Clay, Si: Silt, SSi: Sandy Silt, L: Loam, SL: Sandy Loam, S: Sand; Appearance of Hydromorphy in the Profile; Roots Appearance A, B_1, Rooting Depth and Drill Depth in [cm]. [-] illustrates that there is no data or no roots/ hydromorphical occurrence in the core.

Site ID	Thickness A; B_1	Skeleton A; B_1	Texture A; B_1	Hydromorphy	Roots A; B_1; Depth	Drill Depth
M-A	4; 38	3; 5	LS; -	Fe - Oxides B_2	many (fine); few (fine-gross); 90	193
M-B	8; 41	1; 1	SSi; CL	Fe - Oxides B_1	many (fine-gross); - ; 72	128
M-C	30; -	2; 20	-; -	-	many (fine); - ; -	126
M-D	27; 71	1; 1	-; -	Anoxic Areas	many (fine); many (gross); 43	166
M-E	19; 23	7; 5	-; -	-	many (fine); - ; -	95
M-F	28; 73	8; 40	SSi; CL	-	many (fine); few (fine); 62	128
M-G	40; 30	5; 55	LS -	-	many (fine); - ; -	105
M-H	22; 134	4; 1	LS; -	-	many (fine); few (fine); -	178
M-I	4; 36	2; 1	LS; S	Fe - Oxides	many (very fine); few (fine-gross); -	186
M-J	8; 21	3; 1	Si; LS	-	many (fine); few (very gross); 45	123
M-K	4; 23	3; 5	LS; SSi	Fe - Oxides	many (fine-gross); few (gross); 86	145

Table 2.2: Overview of Ground Characteristics of the Sensor Cluster Sites located in the Sandstone Area, with Thickness A - and B_1 - Horizon in [cm]; Skeleton A, B_1 in [%]; The Soiltexture A, B_1 [-] with C: Clay, Si: Silt, SSi: Sandy Silt, L: Loam, SL: Sandy Loam, S: Sand; Appearance of Hydromorphy in the Profile; Roots Appearance A, B_1, Rooting Depth and Drill Depth in [cm]. [-] illustrates that there is no data or no roots/ hydromorphical occurrence in the core.

Site ID	Thickness A; B_1	Skeleton A; B_1	Texture A; B_1	Hydromorphy	Roots A; B_1; Depth	Drill Depth
Sa-A	8; 16	3; 2	LS; S	-	many (fine); few; 90	190
Sa-B	7; 40	3; 5	LS; S	Fe - Oxides B_1	many (fine-gross); few ; 85	205
Sa-C	30; -	2; 3	S; S	-	many (fine); few; 60	190
Sa-D	4; 17	2; 1	S; S	Mn/Fe - Concretion B_2	many (fine); many; 150	196
Sa-E	9; 12	-; -	LS; S	-	many (fine); few; 75	198
Sa-F	6; 12	2; 1	LS; S	Mn - Concretion B_2	many (fine); few; 55	191
Sa-G	7; -	4; 1	S; S	-	many (fine); few; 93	195
Sa-H	3; 8	3; 3	S; S	-	many (fine); many; 80	195
Sa-I	5; 19	3; 5	S; S	-	many (fine); many; 135	155
Sa-J	24; 112	3; 1	S; LS	Mn - Concretion B_1	many (fine); few; 45	201
Sa-K	12; 43	3; 5	- ; -	-	many (fine-gross); -; 52	196
Sa-L	30; 95	1; 1	SSi; LS	-	many (fine); -; 40	203

Table 2.3: Overview of Ground Characteristics of the Sensor Cluster Sites located in the Shist Area (S_A - S_K), with Thickness A - and B/G_1 - Horizon in [cm]; Skeleton A, B/G_1 in [%]; The Soiltexture A, B/G_1 [-] with C: Clay, Si: Silt, SSi: Sandy Silt, L: Loam, SL: Sandy Loam, S: Sand; Appearance of Hydromorphy in the Profile; Roots Appearance A, B_1, Rooting Depth and Drill Depth in [cm]. [-] illustrates that there is no data or no roots/ hydromorphical occurrence in the core.

Site ID	Thickness A; B_1	Skeleton A; B_1	Texture A; B_1	Hydromorphy	Roots A; B_1; Depth	Drill Depth
S-A	6; 44	2; 15	LS; Si	-	many (fine); -; 87	183
S-B	5; 43	3; 35	LS; S	-	many (fine); few; 83	152
S-C	8; 42	3; 25	Si; Si	-	many (fine); few; 30	170
S-D	10; 75	2; 30	SSi; Si	-	many (fine); many; 60	196
S-E	8; 45	2; -	Si; SSi	Fe - Oxides B_3	many (fine); -; 75	192
S-F	10; 33	2; -	LS; S	Fe - Oxides G_1	many (fine); many; 60	114
S-G	9; 19	3; 25	LS; SSi	-	many (fine); -; 43	195
S-H	22; 43	2; 30	-; -	-	many (fine); -; 37	158
S-I	25; 20	5; 20	LS; Si	-	many (fine); few; 32	197
S-J	28; 22	3; -	LS; CL	Fe - Oxides G_1	many (fine); -; 39	142
S-K	27; 77	5; 40	LS; Si	-	many (fine); few; 41	173

Table 2.4: Overview of Ground Characteristics of the Sensor Cluster Sites located in the Shist Area (S_L - S_W), with Thickness A - and B/G_1 - Horizon in [cm]; Skeleton A, B/G_1 in [%]; The Soiltexture A, B/G_1 [-] with C: Clay, Si: Silt, SSi: Sandy Silt, L: Loam, SL: Sandy Loam, S: Sand; Appearance of Hydromorphy in the Profile; Roots Appearance A, B_1, Rooting Depth and Drill Depth in [cm]. [-] illustrates that there is no data or no roots/ hydromorphical occurrence in the core.

Site ID	Thickness A; B_1	Skeleton A; B_1	Texture A; B_1	Hydromorphy	Roots A; B_1; Depth	Drill Depth
S-L	16; 30	4; 35	Si; -	Fe - Oxides $G_{1,2}$	many (fine); -; 42	189
S-M	22; 24	4; 15	LS; -	-	many (fine); few; 70	180
S-N	13; 26	6; 15	SSi; Si	Fe - Oxides B_2	few (fine); -; 39	128
S-O	27; 38	3; 60	LS; SSi	-	many (fine); few; 122	150
S-P	28; 23	10; 95	Si; Si	-	many (fine); few; 34	176
S-Q	25; 28	10; 20	LS; Si	-	many (fine); few; 45	170
S-R	15; 15	5; 55	SSi; Si	Fe - Oxides $G_{1,2}$	few (fine); few; 30	148
S-S	26; 75	5; 80	LS; SSi	-	many (fine); -; 55	182
S-T	20; 30	5; 20	-; -	-	many (fine-gross); few; 40	203
S-U	12; 52	10; 50	LS; SSi	Fe - Oxides G_1	many (fine); few; 45	173
S-V	7; 55	5; 30	LS; Si	-	many (fine-gross); many; 75	184
S-W	12; 46	6; 35	- ; SSi	-	many (fine-gross); few; 45	152

Tables 2.1., 2.2., 2.3. and 2.4. illustrate the ground information of the sites where the drills are made. The determination of the soil texture was done after a simple hand analysis, some samples are missed out in this analysis due to disappearance after measurement in the laboratory. The appendix includes the details of how the soil texture was determined. The soils are loamy, silty or sandy. And the thickness of the horizons vary due to the topographical position of the site. Just the first two horizons are described in the tables because these two horizons were found in all profiles. The sites with a gleyic G - Horizon often are located in a valley bottom or are close to a stream where very fine material possibly is washed into the horizons in the ground through ground- or streamwater flow. The hydromorphical occurrences are indicating mineral reactions of stored soil pore water with the mineral environments. Roots in the upper horizons are considered to play an important role for example for the process of infiltration, this is the reason why the appearance of roots in the first two horizons was estimated before pack in the soil material. The drill depth refers to the compactness of the ground which delivers additional information regarding the hydrological processes in the vadose zone. The ground in the marl area shows greater bulk densities of the soil compared to the grounds which belong to the sandstone area.

Table 2.5: Overview of the amount of the precipitation input, the mean of the yearly precipitation from 2010 to 2014 is shown.

Area	Annual Precipitation from June 2010 to June 2014 [mm]
Sandstone	752.3
Shist Area	669.2
Marl Area	648.88

Table 2.5 summarises the amounts of precipitation throughout the years from June 2010 to June 2014. There is just a small difference regarding the different areas of the catchment.

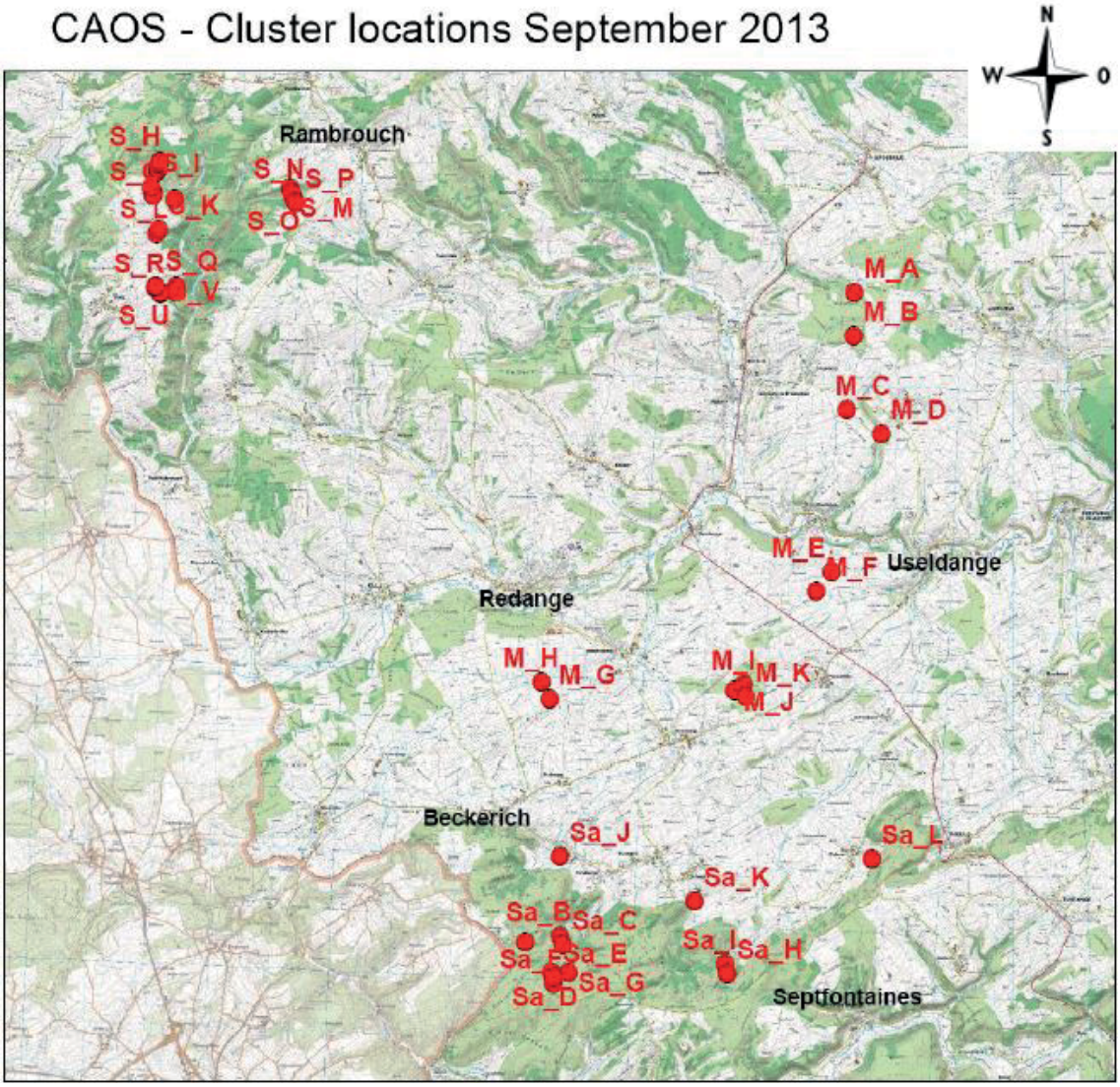

Figure 2.2: Map of the positioning of the Sensor Cluster Sites in the catchment, note that the geology is the characteristic which mainly leads to this distribution.

2.1.2 Spatial Distribution of the Sensor Cluster Sites

The main target of the CAOS (Catchment As Organized Systems) project in the Grand Duchy of Luxembourg is to understand the way a hydrological catchment works as an organised system and to develop or to enhance hydrological models based on functional units in the catchment (www.caos-project.de). One common problem of transferring the experimental results from one site to another is that either the soil properties change or the slope geometry is different [Weiler and McDonnell, 2006]. The target of this study is basically to find out how several similar or different

environmental characteristics of a site lead to a possible distinctness of a functional unit in the catchment with specified, distinguishable hydrological response in the unsaturated zone. An attempt to measure at sites where the difference of the site characteristics between themselves can be delineated via a range of the ground or the environmental characteristics is made in the CAOS project and this thesis also tries to work out the efficiency of the attempt in order to line out functional units in the catchment which show similar hydrological response in the vadose zone. Figure 2.2 shows the distribution of the 45 sensor cluster sites. It is visible that the geology has a great influence on the site selection, please compare this figure with the figure 2.1 where the geological strata are shown. Land use and topographical position were also very important when the selection of the sites was done, in order to be able to statistically compare the degree of a process which takes place at a site a certain number of sites which belong to the same group of characteristic is needed. In the end the work was done with 21 sites in the shist area, 12 sites in the sandstone area and 11 sites in the marl area. Whereas the land use and topographical position had to be considered as well. Further the work was established with 29 sites which are located in the forest and 15 which are located in the grassland. Researches [den Bos and Hoffmann, 2006] also made research on hydrologically homogeneous meso-scale areas (known as HRU's) and their runoff regime in the same study area. The topographical position is divided into hill slope, riparian zone and sites which belong to a plateau or a plain. Regarding this predictor the work is done with 19 sites which are located at a hill slope, 9 sites which belong to a plateau and 16 sites which belong to the riparian zone.

The sensor cluster sites in the study site literally measure the air temperature, the air moist, the air pressure, the wind strength, the wind direction, the precipitation amount, the soil moist, the groundwater fluctuations in the piezometers and if a stream is close the discharge is measured and sampled automatically. Forty five sensor cluster sites are installed in the field at various spots with well considered environmental characteristics. It is assumed that there are environmental characteristics which influence the hydrological response more than others. To be able to line out which characteristics have a high relevancy a big range of characteristics

Table 2.6: Overview of the Environmental Site Characteristics of the Sensor Cluster Sites located in the Sandstone and Marl Area, with Geology, Landuse, Topographical Position, Exposition (just North or South is considered) and the Canopy status in [%].

Site ID	Geology	Landuse	Topography	Exposition	Canopy [%]
Sa-A	Sandstone	Forest	Slope	S	80
Sa-B	Sandstone	Forest	Riparian	-	80
Sa-C	Sandstone	Forest	Slope	N	90
Sa-D	Sandstone	Forest	Slope	S	85
Sa-E	Sandstone	Forest	Riparian	-	85
Sa-F	Sandstone	Forest	Slope	N	80
Sa-G	Sandstone	Forest	Riparian	-	80
Sa-H	Sandstone	Forest	Slope	S	85
Sa-I	Sandstone	Forest	Slope	N	80
Sa-J	Sandstone	Grassland	Plateau	-	85
Sa-K	Sandstone	Grassland	Plateau	-	100
Sa-L	Sandstone	Grassland	Plateau	-	90
M-A	Marl	Forest	Plateau	-	80
M-B	Marl	Forest	Plateau	-	80
M-C	Marl	Grassland	Plateau	-	100
M-D	Marl	Grassland	Plateau	-	95
M-E	Marl	Grassland	Slope	S	95
M-F	Marl	Grassland	Plateau	-	95
M-G	Marl	Grassland	Plateau	-	100
M-H	Marl	Grassland	Slope	N	100
M-I	Marl	Forest	Plateau	-	80
M-J	Marl	Forest	Plateau	-	85
M-K	Marl	Forest	Plateau	-	90

Table 2.7: Overview of the Environmental Site Characteristics of the Sensor Cluster Sites located in the Shist Area, with Geology, Landuse, Topographical Position, Exposition (just North or South is considered) and the Canopy status in [%].

Site ID	Geology	Landuse	Topography	Exposition	Canopy [%]
S-A	Shist	Forest	Riparian	-	85
S-B	Shist	Forest	Slope	S	80
S-C	Shist	Forest	Slope	N	80
S-D	Shist	Forest	Slope	N	80
S-E	Shist	Forest	Slope	N	85
S-F	Shist	Forest	Riparian	S	85
S-G	Shist	Forest	Slope	S	75
S-H	Shist	Forest	Slope	S	60
S-I	Shist	Grassland	Plateau	-	100
S-J	Shist	Grassland	Riparian	-	95
S-K	Shist	Grassland	Slope	S	100
S-L	Shist	Grassland	Riparian	S	100
S-M	Shist	Forest	Slope	S	85
S-N	Shist	Forest	Riparian	-	70
S-O	Shist	Forest	Slope	N	70
S-P	Shist	Grassland	Plateau	-	95
S-Q	Shist	Grassland	Slope	S	100
S-R	Shist	Grassland	Riparian	S	95
S-S	Shist	Forest	Plateau	S	80
S-T	Shist	Forest	Slope	S	60
S-U	Shist	Forest	Riparian	S	60
S-V	Shist	Forest	Riparian	N	90
S-W	Shist	Forest	Slope	N	90

has to exist. The most important characteristics are geology, type of soil, land use, topographical position, exposition, canopy status and maximal rooting depth. Ta-

bles 2.6 and 2.7 summarise the environmental characteristics of the sensor cluster sites in the attert catchment. The great complexity in the vadose zone leads to a large range of factors on which the hydrological processes depend on. [Bachmair and Weiler, 2012] lined out the great variance of hill slope characteristics which play a role and affect the shallow subsurface flow of precipitation water. Regarding the vadose zone in a whole it has to be expected that even greater ranges of environmental or ground characteristics which influence the hydrological processes occur because the characteristics change from horizon to horizon. The vegetation affects the hydrological response due to the appearance of roots which basically intervene into the vadose zone water balance. The amount of coniferous- and deciduous forest plays a large role when considering the hydrological process of transpiration. As [Blume et al., 1968] lined out that transpiration does not take place during winter time. It is assumed that the hydrological response shows great differences regarding the seasonality as well as the location of the site that is regarded. However, the full potential of stable water isotopes to quantitatively characterize water dynamics is yet to be unfolded. This particularly holds with regard to complex and heterogeneous processes, such as infiltration and shallow subsurface flow in the vadose zone subject to strong gradients and fluxes of energy and matter, demanding stable isotope data with high spatial and temporal resolution to complement traditional observations [Volkmann and Weiler, 2014]. [Volkmann and Weiler, 2014] worked with a special measurement tool which allows in situ measurements of the stable isotope relations of the soil pore water. The great temporal and spatial variability of the stable isotope relations of the soil pore water leads to a great complexity as a great difficulty to work out significant correlations between the processes and the site characteristics. Nevertheless we do have to consider that a great number of findings will lead to better understanding of even these complex correlations of natural processes.

2.1.3 Drilling

The drills were done in a time period of nine days in the first two weeks of June 2014 at the 45 sensor cluster sites which are measuring natural parameters since 2011. The local drill spot is considered to be close to the piezometers which are installed at each cluster site in order to be able to amplify the soil moisture and groundwater information measured in the piezometers. Attention to not disturb the other experiments, the steepness of the hill slope and the representativeness of the drill point for the whole cluster site were criteria of the selection of the drill spot. Two drill cores (length: 100 [cm], diameter: 7 [cm]), a hydraulic jackhammer, a hydraulic pullout machine with a small generator and several useful tools like large screwdrivers to extract the geologic media from the ground are used during fieldwork action. The cores where then pictured, a first soil identification was made before the soil was sampled into zip logged aluminum bags. The first quick soil analysis and the sampling were done in the shade in order to reduce fractionation effects due to evaporation of the fresh soil material above the ground. The zip log bags were stored in stable plastic boxes and were transported after several days to the IHF institute in Freiburg. Drilling depth varied due to different soil types. The deepest drilling was 205 [cm] under top ground surface. Compression of the soil material in the soil core occurred at all sites and is considered when generating the PSIP.

2.1.4 Sampling

Immediately after pulling out each core each 5 [cm] of the first core and each 10 [cm] of the second core was bagged. To be sure that there remains enough pore water in the soil material for the equilibrium of the pore water stable isotope signal of the soil with the dry air in the head space of the bag at least 3 [cm] of the core as a minimum sampling interval is needed. Partly we had to sample 3 [cm] as a minimum or 13 [cm] as a maximum in order to have enough head space in the bag. Spoons to fill the bags and screwdrivers to loosen the material from the core are used. Most of the air was pressed out manually before closing the zip log of the bag. The sample boxes always had been stored in the shade during fieldwork action.

Additionally to the mechanically sampled depth profile samples disturbed samples of the first two horizons (A- and B-horizon) were taken with a simple spade at each site. These samples are used to calibrate the measurements in the laboratory with waters of committed isotopes signals. When the site was situated close to a stream and when ground water was present in the piezometers of the site water samples were taken manually. There was one rainy day during the fieldwork campaign, at this day the precipitation water is sampled immediately during the event into a small sample bottle in order to be able to check the possible influence of this event on the vadose zone hydrological processes. The fieldwork section is divided into the most important subsections which are the most important working steps referring to the gain of the soil samples. The study area is just explained briefly, the distribution of the sensor cluster sites has a great importance for the whole research because the site environments are related to the site characteristics.

2.2 Laboratory Work

2.2.1 Fractionation

Fractionation of the pore water stable isotope signal basically affects this research. Fractionation leads to an enrichment of heavier isotopes due to the favored evaporation of the lighter isotopes in general. The isotopic composition of precipitation is dependent upon several factors including the isotopic composition of its vapor source (typically from oceanic regions), fractionation that occurs as water evaporates into the air mass (sea-surface-temperature controlled), precipitation formation processes, and air mass trajectory (i.e., the influence of vapor source and rainout processes along the pathway of the air mass) [Fritz and I. Clark, 1997]. Most of these factors are related to isotopic fractionation caused by phase changes [McGuire and McDonnell, 2010]. Fractionation between water and vapor is fundamental to the hydrological cycle and plays an important role in partitioning ^{18}O and ^{2}H between the various reservoirs [Fritz and I. Clark, 1997]. The fractionation of the stable isotope signals between the water and vapor phase is caused by evaporation

in the upper centimeters of the soils and happens immediately at the surface when precipitation happens. At 20[°C] the vapor pressure of $^2H^{18}O$ is 1[%] lower than the vapor pressure of $^2H^{16}O$ therefore evaporation leads to an enrichment of $^2H^{18}O$ in the fluid and a depletion of $^2H^{18}O$ in the vapor. This effect gets stronger when the temperature is higher [Fritz and I. Clark, 1997]. All this also is applicable for the ^2H, although the magnitude of the isotope effects are different [Fritz and I. Clark, 1997].

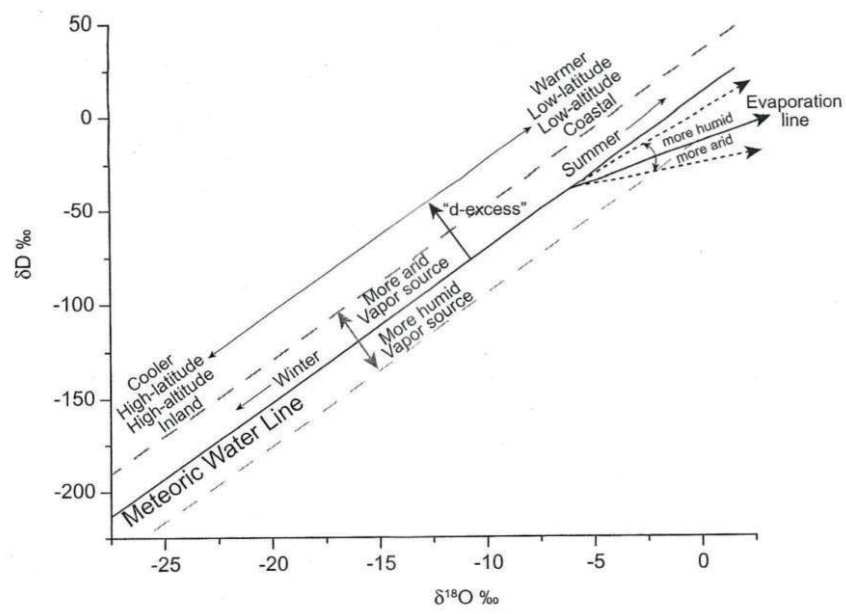

Figure 2.3: Schematic meteoric water line showing factors leading to deviations of $\delta^{18}O$ - δ^2H relationship (modified by Sahra, 2005).

$$\delta D = 8 \cdot \delta^{18}O + 10$$

The meteoric water line (MWL) which is illustrated in figure 2.3 was first published by Craig (1961) and is a convenient reference for understanding and tracing water origin. It is a linear relation in the form of: where d, the y-intercept, is the deuterium-excess (or d-excess) parameter when the slope = 8. Craig's MWL, referred to as the Global MWL, with d = 10 and a slope of eight, was based on approximately 400 samples representing precipitation, rivers, and lakes from various countries [McGuire and McDonnell, 2010].

2.2.2 Direct Equilibrium

Figure 2.4: Picture of the measuring set up in order to measure the relationship of δ^{18}O - δ^{2}H in [‰] of the vapor of the soil pore water in the head space of the bag after 48 h of equilibration time.

In order to measure the stable isotopic composition of pore water [Wassenaar et al., 2008] developed a method which works with uses evaporation and equilibration of the fluid and the vapor phase as main processes. The institute of hydrology in Freiburg, Germany (IHF) made several investigations using and improving this method [Gralher, 2009, Garvelmann et al., 2012, Mueller et al., 2014]. A special laser spectroscopy machine was developed to measure the isotopic composition in the head space of the bag. The isotopic relations of the stable isotopes ^{18}O and ^{2}H evaporated (until equilibrium is reached) from the fluid phase in the soil material to the vapor phase into the head space of the bag where the vapor is sucked into a needle and transported via a thin plastic tube into the cavity ringdown laser spectrometer (Picarro). Via cavity ringdown spectroscopy the isotopic compositions of the stable isotopes ^{18}O and ^{2}H are measured and monitored on a special screen. After measuring six minutes each sample the needle has to be removed from the bag and in order to exclude carry-over effects from one measurement to the next measurement the needle has to suck in room air for at least two minutes. The calibration has two considerations because of the relatively long time spread (six

- nine hours) of measuring one depth profile the isotopic compositions of known standard waters at each start and end of the measurements has to be measured. These standard waters represent a light, a medium and a heavy water in sense of the isotopic relations of the stable isotopes ^{18}O and ^{2}H. The calibration line is used to create the worldwide comparable [VSMOW - ‰] values which are used for the generation of the PSIP. The other consideration of the calibration is to calibrate the measurements with aid of the known standard waters in combination with the dried standard soil samples in order to find out how the fractionation during the evaporation in the bag affects the isotopic signal which is ultimately measured. In order to do the measurement and to be able to calibrate the measurements the samples had to be prepared. Dry air is pressed into soil samples in the zip logged bags and the zip log is in order to dismiss air and vapor loss. The samples need at least 48 hours until the equilibrium of the isotopic relations in the fluid and in the vapor phase is reached. The spot where the needle is to be stitched in is to be consolidated with a small silicon dot. The preparation of the standard soil samples is basically the same but they additionally have to be oven dried at 110[°C] for 48 hours in order to remove the pore water. The water content of the samples has to be lined out by weighing before and after the drying in order to know how much of the standard water is needed to reach the same water content like before. The bags which only include the standard waters are treated the same way like the soil samples of the depth profiles, 10 [ml] of the standard water are put into the bags. During the measurement the displayed values were manually selected and written off into excel files (Figure 2.4). Obviously this method of measuring the isotopic composition of the stable isotopes ^{18}O and ^{2}H contains potential sources of errors. It remains to clarify if just the surface of the soil material evaporates into the head space and therefore it is unknown if the isotopic signal in the head space is representing the whole isotopic composition of the pore water soil sample. Under equilibrium conditions, the heavy isotopes are always enriched in the more condensed phases by an amount known as the fractionation factor. Majoube, 1971 made research on that topic and worked out a correction formula which calculates the fractionation factor α with the room temperature and three specific coefficients

for ^{18}O and ^{2}H.

$$\alpha = \exp\left((a \cdot (10^3/T^2)) + (b \cdot (1/T)) + (c/1000)\right)$$

The coefficients are $a = 1.13$, $b = -0.41$ and $c = -2.06$ for ^{18}O and $a = 24.84$, $b = -76.24$ and $c = 52.61$ for ^{2}H. Before the calibration leads to the transformation from the measured values to the [VSMOW - ‰] values the correction is realised.

2.2.3 Cryogenic Vacuum Extraction

Vacuum extraction is the most commonly used technique for water extractions from unsaturated soil samples [Ingraham and Shadel, 1992, West, 2006, Koeniger et al., 2011]. In order to validate the direct equilibrium measurements of the stable isotope relations of the pore water cryogenic vacuum extraction of 37 sub samples was done at the Helmholtz center in Munich, Germany. The Method makes use of the different vapor pressures of water which correspond to different temperatures in order to extract the pore water from the soil during vacuum extraction. Technically this is achieved by a cold trap (liquid nitrogen) which acts as a water-vapor sink and water diffuses rapidly under low-pressure conditions from the substrate into a sample vessel [Koeniger et al., 2011]. The system includes a vacuum generation pump (Edwards rotary vane vacuum pump type E2M2,Crawley,UK), special heaters and several metallic capillary tubes which connect 10 pairs of extraction modules. Each module can be used separately due to a possible decoupling from the system. The pump is able to create a vacuum of 50 [Millitorr] as a maximum value. Each module contains two tubes which are connecting two special vials (Schott, GL 18) one vial contains the sample and the other vial catches the extracted pore water. The method uses freezing, melting and condensation of the pore water as main processes. Under isolation from the vacuum system the sample has to be clicked in and shockfreezed with liquid nitrogen (approx. -196[°C]). The frozen sample has then to be reconnected to the vacuum system. After a vacuum of circa 60 [Millitorr] is achieved the distillation can be started via an isolation of the module

Figure 2.5: Picture of the extracting machine, vials are clicked in at both ends, after extraction the vacuum pump creates a new vacuum in the tubes.

from the system. The second vial has to be cooled down and the sample has to be heated up to create a temperature gradient. In order to extract the pore water from the frozen sample the vials are now connected with each other via metallic tubes. After a time period of 90 [min] to 240 [min] the low pressure values of circa 60 to 300 [Millitorr] are achieved and all the pore water is extracted and stored as ice in the second vial. The septum and cap should not be cooled because the septum will leak if frozen. Leaks, if present, can be recognized because it will be

impossible to evacuate the vials sufficiently [Koeniger et al., 2011]. The method is inexpensive and allows a rapid extraction of large numbers of samples, and has been demonstrated to recover water of known isotopic composition from spiked soil and tree core samples [Koeniger et al., 2011]. After evacuation, the water samples were stored in a cooled box, transported to the IHF Laboratory in order to measure the isotopic compositions of ^{18}O and ^{2}H just a few days after extraction. Figure 2.5 shows a part of the tube system of the extraction machinery.

2.2.4 Cavity Ring-Down Spectroscopy Measurements

Cavity Ring-Down Spectroscopy (CRDS) leads to the determination of the stable isotopic composition of all samples. The equilibrated vapor phase in the head space of the bags as well as the extracted pore water via the cryogenic vacuum extraction is measured with CRDS machine from Picarro. In CRDS, the beam from a single-frequency laser diode enters a cavity defined by two or more high reflectivity mirrors. Picarro analyzers use a three-mirror cavity, as in the figure below, to support a continuous traveling light wave. This provides superior signal to noise compared to a two-mirror cavity that supports a standing wave. When the laser is on, the cavity quickly fills with circulating laser light. A fast photo detector senses the small amount of light leaking through one of the mirrors to produce a signal that is directly proportional to the intensity in the cavity.

When the photo detector signal reaches a threshold level (in a few tens of microseconds), the continuous wave (CW) laser is abruptly turned off. The light already within the cavity continues to bounce between the mirrors (about 100,000 times), but because the mirrors have slightly less than 100[%] reflectivity (99.999 [%]), the light intensity inside the cavity steadily leaks out and decays to zero in an exponential fashion. This decay, or "ring down", is measured in real-time by the photo detector, and the amount of time it takes for the ring down to happen is determined solely by the reflectivity of the mirrors (for an empty cavity). Consider that for a Picarro cavity of only 25 [cm] in length, the effective path length within the cavity can be over 20 kilometers. Now, if a gas species that absorbs the laser light is

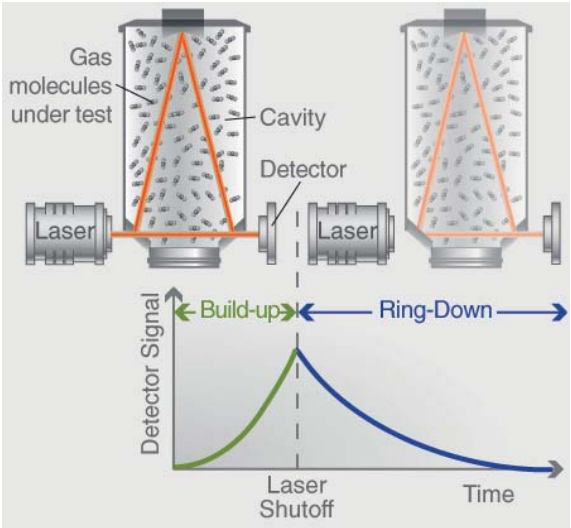

Figure 2.6: Schematic of Picarro CRDS analyzer showing how a ring down measurement is carried out.

introduced into the cavity, a second loss mechanism within the cavity (absorption) is now introduced. This accelerates the ring down time compared to a cavity without any additional absorption due to a targeted gas species. Picarro instruments automatically and continuously calculate and compare the ring down time of the cavity with and without absorption due to the target gas species. This produces precise, quantitative measurements that account for any intra-cavity loss that may be changing over time, and it allows the discrimination of loss due to absorption from losses due to the cavity mirrors (www.picarro.com). The injection needle has a diameter of 1 [mm] and sucks 35 [ml/min] into the analyzer. It is really important to work accurately and to make sure that there is no small slot between the bag, the silicon dot and the needle. Measurements are very precise there is just a small drift of 0.025 [‰] and 0.1 [‰] for the δ^{18}O and δ^{2}H measurements (www.picarro.com). The fractionation has great effect on the whole laboratory work, the subsections in this chapter refer to the most important working steps in the laboratory. The explanation of the direct equilibrium measurement method is the most detailed part because all the PSIP are generated with the data which is carried out with this measuring method.

2.3 PSIP Analysis

In order to analyze the PSIP data various graphs are established to determine similarities which could further be used to classify functional units in the catchment which can be separated due to their hydrological response in the catchment (CAOS Project). In order to have a look on similarities with reference on the shapes of the PSIP the search for distinction criteria leads to the problem of the great differences in the shapes of the PSIP. The PSIP which do not show a distinctive peak are considered to be grouped as well as the PSIP which show a peak. Further the PSIP which show the winter precipitation peak (WPP) of the winter 2013/ 2014 are subdivided into groups which belong to the various shapes of this peak. The peak extension in the horizontal or the vertical direction has to be considered. The big difficulty refers to the great number of processes which all are affecting the soil pore water movements and therefore the isotopic composition of the soil pore water at the same time. Approaches of generation of graphs which explain the PSIP via the calculated measurements which are used for the descriptive statistical analysis did not lead to well comparable diagrams. Therefore the PSIP themselves with their belonging dual isotope plots are used in order to show similarities or dissimilarities of the PSIP.

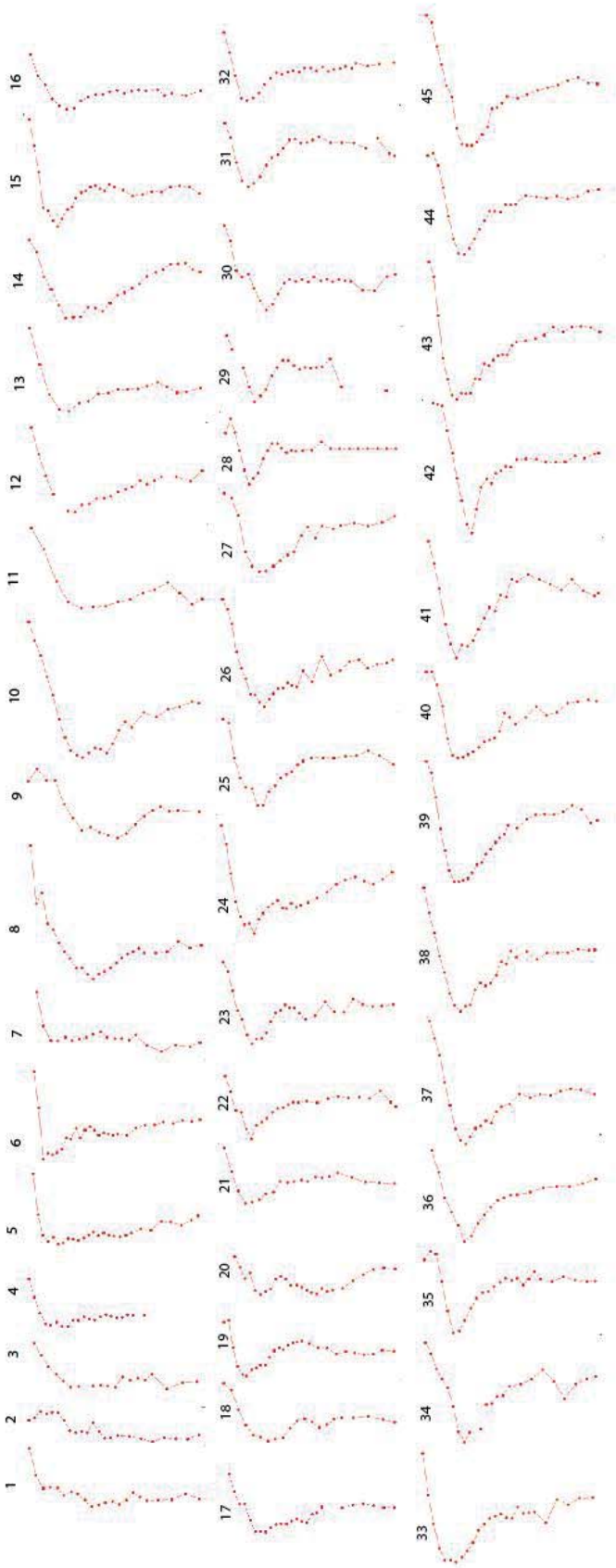

Figure 2.7: Overview of all 45 δ^2H - PSIP. The graph considers the great variance in the shapes of the PSIP, there is no relation between the depth or the isotopic values, the shape of the PSIP is the only criteria which is used to order them in a distinguishable way. All information related to this approach is explained in the text.

Figure 2.7 shows all 45 δ^2H - PSIP which were worked out, the preexistence of the WPP and its shape as well as the upper and the downer part of the PSIP have to be considered in order to list them up in a certain way. The δ^{18}O - PSIP show a greater instability and are not as suitable as the δ^2H - PSIP for visual comparisons. The way they are listed up refers to their shape as unique criteria, number one to three do not show the certain WPP at all, theses sites all belong to the riparian zones and the ground water level does raise that high that the soil pore water do not show a distinguishable WPP due to mixing of the soil pore water with groundwater which does not change the composition isotopically throughout the year [**?**]. The sites four to ten do not show a distinctive peak, their peaks are either vertically stretched or their shape does not offer great interpretations regarding the hydrological response at the site theses PSIP belong to. Errors which result from the measurements also could lead to these shapes. Site 10 to 45 all show the WPP, but all these peaks have different shapes. The PSIP with the most distinctive WPP are mainly located in the third row of the graph. This graph expresses the great variance of the PSIP shapes and gives the reader a first impression regarding the PSIP analysis.

2.3.1 Site Similarity versus PSIP Similarity

In order to implicate the PSIP analysis with the ability of determining functional units in the catchment where the hydrological response is similar the sites are grouped due to similar shaped PSIP. The shape of the PSIP is dominated by the appearance and shape of the WPP in the PSIP. Distinctive similar shaped positions in the psip make it possible to assign several PSIP to several groups. The shape of the PSIP is additionally described by means of the calculated variables which are also used to line out correlations between the sites and the hydrological processes (see chapter 2.4). Additionally the figures in chapter 3.3 (PSIP Similarities) show different possible shapes of PSIP which are used to show the relation between a certain PSIP similarity and their similarity regarding the hydrological response at the sites. The attempt to create groups of similar shaped PSIP is done visually, most of these PSIP obviously belong to one of the groups which are explained below but

some of them have similar shapes without belonging to sites with similar characteristics. Functional units which can be separated due to similar sites in the catchment are supposed to react similar when they are surrounded by a similar environment. It is assumed that these sites should show a similar hydrological response in the unsaturated zone. In order to express this correlation in a graph several groups of similar environmental characteristics are made. In order to show site similarity specific similar environmental characteristics which dominate the hydrological functionality of the sites are grouped. There are made groups due to the land use class and the topographical position of the site as well as land use class and geology of the site. This is because there should be at least five sites of a group to show a site similarity.

2.4 Statistical Analysis

Table 2.8: Summary of Significance Codes - Significance is established via a simple one way variance analysis (anova) with GNU R.

Significance	Value	Symbol (R)
very significant	0.0001	***
strongly significant	0.001	**
significant	0.01	*
poorly significant	0.1	.
not significant	1	

The descriptive statistic is established with the open source software GNU R. This statistical software offers a wide range of powerful tools and a great range of possible plots in order to line out various relations between classifiable and non classifiable parameters. The hydrological vadose zone processes of vertical infiltration of precipitation water through the soil pores (matrix) into the unsaturated zone, evaporation of soil pore water, transpiration of soil pore water, mixing of soil pore water in the upper part of the profile, vertical dispersion of soil pore water, soil storage of soil

pore water at the bottom of the profiles and recharge of soil pore water into the aquifer are described via calculated measurements with reference to the PSIP. The environmental and ground characteristics of the sensor cluster sites where the soil cores are taken out are the type of geology, the land use class, the topographical position, the main exposition (south or north), the soil skeleton of the A and B horizon, the canopy status and the mean rooting depth. Significant interrelations between the hydrological response and the site characteristics are carried out using various calculations and descriptive statistic tools like box-whisker-plots and scatter-plots. In order to illustrate and show the significance of several relationships between the hydrological response in the unsaturated zone and the environmental as well as the ground characteristics of each site simple one way variance analysis (anova) supports each box-whisker-plot. The anova tests the significance of a relation between all boxes which occur in the graph. All processes have been tested against all characteristics and a large range of graphs expresses the significant correlations. The graphs which are not significant partly are listed in the appendix. The most powerful results are illustrated in chapter 3 and discussed in chapter 4. Table 2.7 summarizes the significance codes i used in order to show the degree of significance, these symbols appear in every legend of each box-whisker-plot, the significance is also visible when regarding the position of each box in the box-whisker-plot.

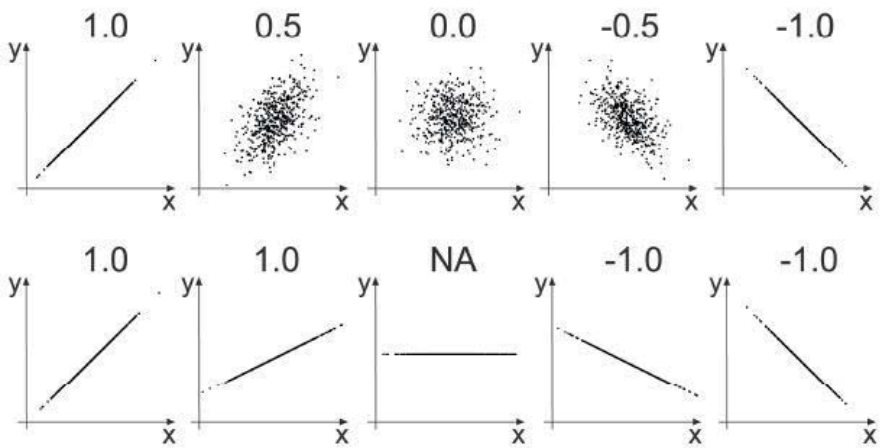

Figure 2.8: Correlation analysis - if there is a correlation between the predictor and the data, R writes out a certain value.

To work out correlation between the non classifiable ground parameters and the

hydrological processes scatter-plots are used. If there is a significant correlation of a certain predictor and a process the correlation analysis of GNU R expresses this correlation via a value which describes the distribution of the data and in this context the degree of correlation between the predictor and the process (Figure 2.8). These values are expressed in each legend of each scatter-plot. Additionally a regression line expresses the trend if there is a positive or negative correlated interrelation. Further groups of PSIP which belong to selected sites are made in order to be able to point out the natural correlations and the importance of several characteristics for the different hydrological processes. For each description or graph just the best PSIP are picked out to demonstrate and work out statistical significant facts regarding the various hydrological processes. Results contain just the best plots, graphs and tables. Furthermore an attempt is made to show significant similarities of similar shaped PSIP which belong to sites which have similar characteristics and vice verse, these similar sites could be seen as functional units in a catchment. This is expressed via graphs where the PSIP and the belonging dual isotope plots are shown next to their belonging descriptive parameters in a way that offers an easy comparison between the sites and their processes.

2.4.1 Infiltration

In order to determine the degree of infiltration of precipitation water through the soil pores into the unsaturated zone at a site the precipitation winter peak (WPP) of the season 2013 and 2014 is used. This soil pore water has isotopic values of $-11 \sim -9$ [VSMOW - ‰] for the δ^2H and $-80 \sim -65$ [VSMOW - ‰] for the δ^{18}O which varies remarkable from the isotopic signal of the soil pore water which is detected in the upper and lower part of the PSIP and contains pore water with isotopic values of $-8 \sim -6$ [VSMOW - ‰] for the δ^2H and $-60 \sim -35$ [VSMOW - ‰] for the δ^{18}O . Infiltration of precipitation water into the unsaturated zone can be detected via the existing WPP in the PSIP. In order to work out the peak depth of the WPP in the PSIP a visual determination is performed. These peak depths are listed up in a big table (Microsoft Excel) which is then used to establish the descriptive statistic.

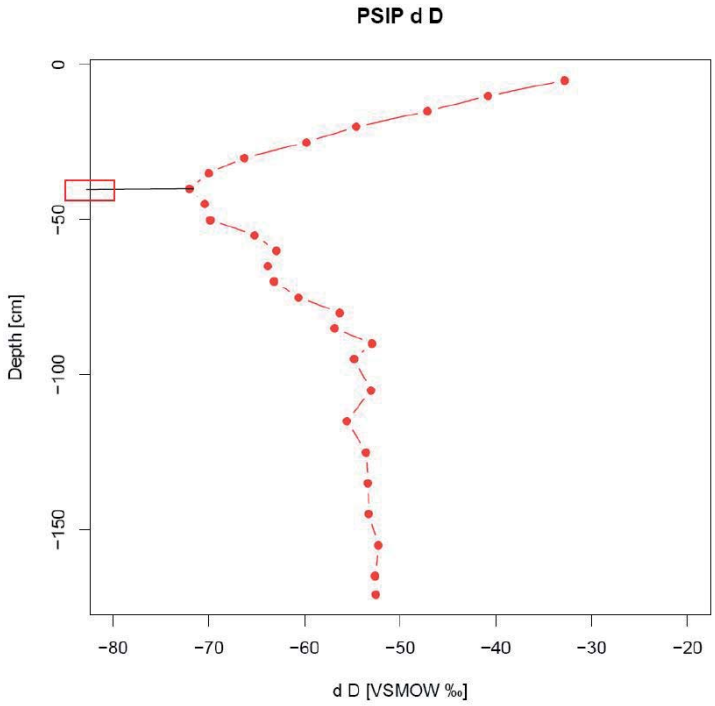

Figure 2.9: PSIP of the δD, schematic graph shows the determination of the peak depth [cm] in order to describe the hydrological process of infiltration in the unsaturated zone at each site.

All sites which show a detectable WPP are used for the statistical investigation here. The process of infiltration of precipitation water through the soil pores in the unsaturated zone is great if the peak depth is deep and vice verse. Figure 2.9 shows the peak depth of a PSIP, these peak depths are used to describe the degree of the process of infiltration of precipitation water into the unsaturated zone.

2.4.2 Evaporation

As evaporation leads to fractionation [Fritz and I. Clark, 1997] and therefore to a detectable change within the isotopic signal of the soil pore water of the upper part of the PSIP. Depth profiles of the deuterium excess are used to demonstrate the effect of the evaporation visually. The PSIP also shows the effect of the evaporation in the upper part but in order to work out reasonable values the deuterium excess is used.

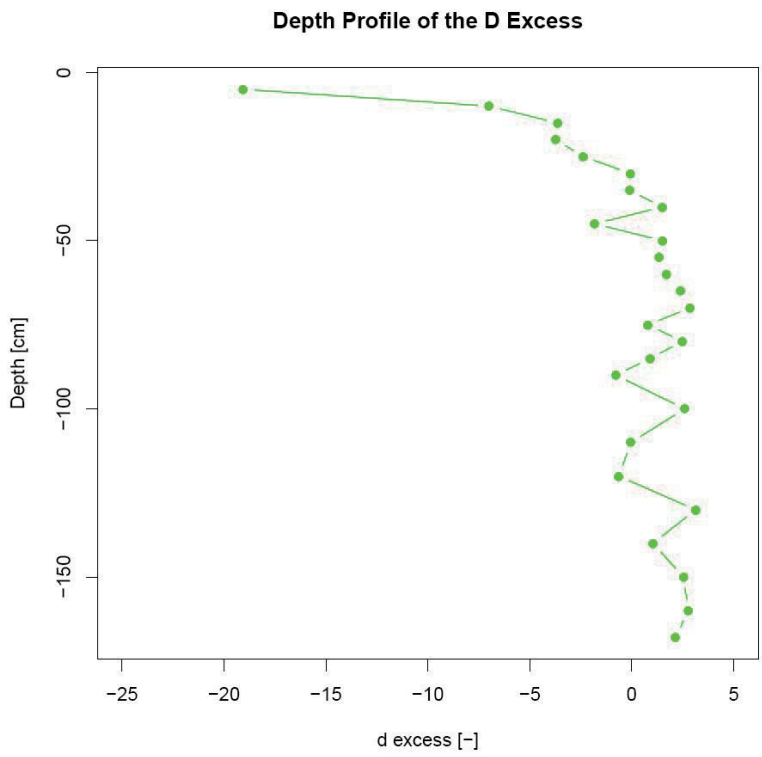

Figure 2.10: Depth Profile of the D Excess Deviance [-] between the mean of the upper three samples and the mean of the rest of the PSIP. This deviance is used as measurement for the hydrological process of evaporation at each site in the descriptive statistic.

The deviance from the mean deuterium excess value of the upper 15 [cm] and the mean deuterium excess value of the rest of each PSIP is used as measurement degree which describes the process of evaporation in the descriptive statistical analysis. This measurement is chosen due to the assumption that evaporation mainly affects the first 15 [cm] of the soil column at the site. As far as the sun radiation and therefore the local air temperature should be the main force which is leading to evaporation of the soil pore water of the upper soil layer. The difference between the mean of the upper part and the mean of the rest of the soil column should therefore be high if a lot of evaporation happens at a site. Figure 2.10 shows a depth profile of the deuterium excess, the deviation of the mean value of the first three data dots and the rest of the data dots in the profile is used in order to describe the degree of the hydrological process of evaporation at each site.

2.4.3 Transpiration

The transpiration of the soil pore water through the preexisting vegetation at a site is supposed to have a great influence with reference to the water balance of the unsaturated zone in summertime. It is to be explained if the vegetation does suck in light ($^{1}H_2{}^{16}O$) and heavy ($^{2}H_2{}^{16}O$) water molecules without any preference. If the vegetation does not differ between heavy or light water the isotopic signal will not change that much due to transpiration compared with the process of evaporation where fractionation always leads to an enrichment in heavy water isotopes in the soil pore water (see 2.2.1.). Therefore an attempt is made in order to find a measurement for the process of transpiration many assumptions regarding the PSIP and its originated shape have to be made: (i) The peak in the PSIP refers to the WPP of the season 2013/2014. (ii) During this time of the year the evaporation is negligible and the only possible change in the isotopic signal is to be described by the process of transpiration which happened after February at each site. (iii) The vegetation does extract lighter water with a certain preference. We do not call this process evapotranspiration because we want to try to just explain the transpiration here, evaporation is described via another measurement in this research (see 2.3.2). The isotopic signals of the weighted precipitation inputs over the last three years of the three distinguishable geographical areas of the shist, the sandstone and the marl geological unit (in the sense of isotopic variability in the precipitation input) have been available. As it is expected that the peaks in the PSIP belong to the winter precipitation of the season 2013/2014 the mean of the isotopic values of each peak (peak value $\pm$ 2 samples) and the difference between the mean isotopic signal of the precipitation of the winter months January and February. If the difference is big the site tend to be influenced a lot by the processes of transpiration.

2.4.4 Mixing

In order to be able to work out relationships between various sites and the hydrological process of mixing of lateral moving soil pore water or stored precipitation water in the soil pores the width of the WPP of the season 2013/ 2014 is used as

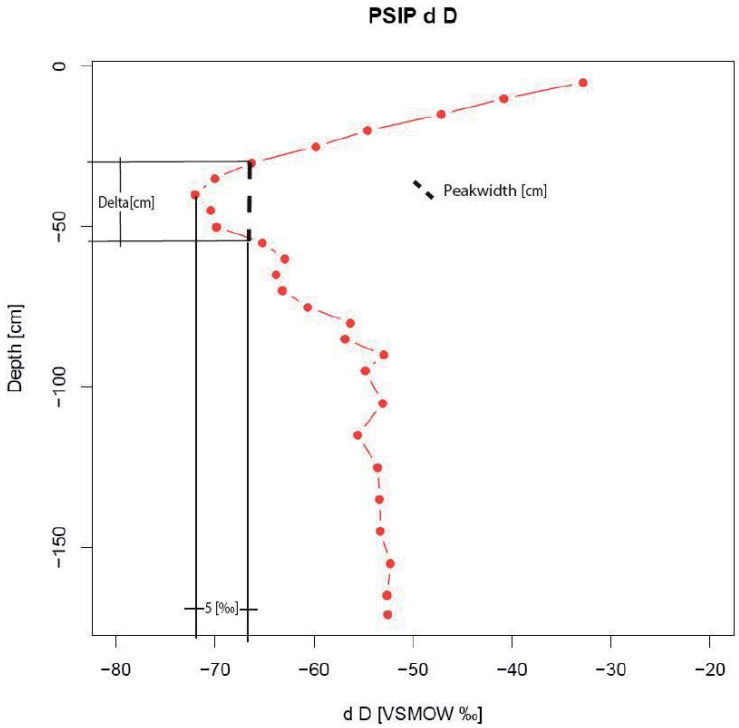

Figure 2.11: PSIP of the δD, schematic graph shows the determination of the peak width [cm] in order to describe the hydrological process of mixing of soil pore water in the unsaturated zone at each site.

degree for the statistical analysis and comparisons (Figure 2.11). The peak width is determined by the dimension of the peak which results after a subtraction of 5 [‰] of the minimum peak value for the δ^2H. This minimum refers to the maximum peak value, please note that the work is done with negative axes. The determination of the peak width (vertical extension of the WPP) is made visually and manually with a ruler. The depth scale is used in order to calculate the real peak width. The result after this specific calculation is the peak extension which has to be scaled using the depth scale (y-axis). If the 5 [‰]- line crosses the PSIP between two data dots, a linearity between the data dots in the PSIP is estimated. It is assumed that the greater the peak width the stronger is the influence of mixing processes at the specific site. As the PSIP for both stable isotopes δ^2H and δ^{18}O are lined out both peak widths are estimated but only the peak width of the δ^2H is used for the descriptive statistic. PSIP without a peak were not regarded.

2.4.5 Dispersion

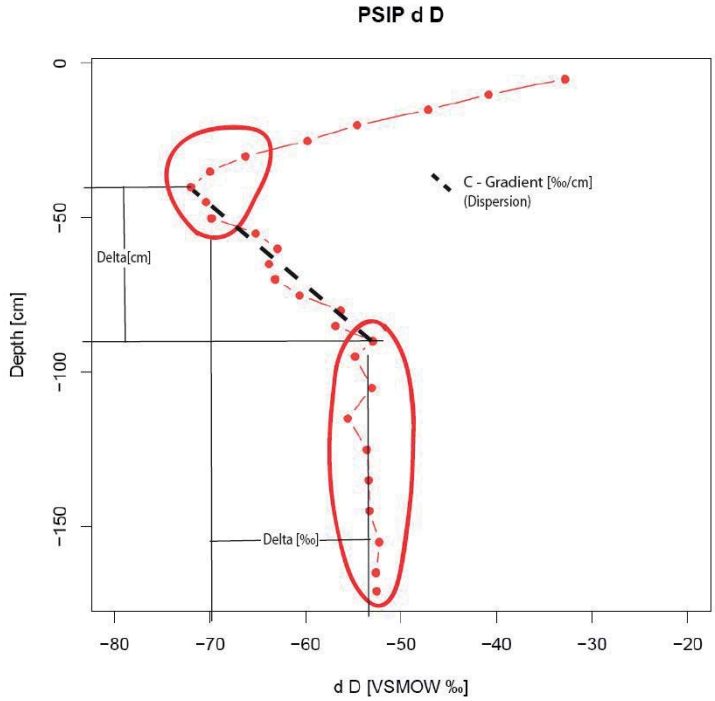

Figure 2.12: PSIP of the δD, schematic graph shows the determination of the C Gradient [[‰]/[cm]] in order to describe the hydrological process of dispersion in the unsaturated zone at each site.

As a statistical measurement value for the description of the hydrological process of the vertical dispersion in the unsaturated zone the concentration gradient of the peak in downwards direction is used. Therefore the difference from the mean isotopic composition [VSMOW - ‰] of the peak (peak value ± 2 samples) to the mean isotopic composition [VSMOW - ‰] of the lower part of the PSIP (y-component of the gradient) and the distance from the peak depth [cm] of each peak to the certain depth where the lower mean of the PSIP is reached [cm](x-component of the gradient) is used (Figure 2.12). The y-component of the gradient is calculated with R. The 39 PSIP which show a distinctive peak are considered whereas the x-component of the gradient is determined visually due to complex differences between the peak shapes. This concentration gradient has [VSMOW - ‰/ cm] as unit and

can be used for an explanation of the vertical dispersion of soil pore water at the sites. As we are only available of punctual information of the ground just the vertical component of the dispersion process can be regarded. The gradients which are used for the final statistical analysis result just from the δ^2H PSIP because of the greater stability compared to the δ^{18}O PSIP. A small gradient refers to a small occurrence of the dispersion process at the site because the WPP isotopic signal is not stretched due to a strong dispersion of soil pore water at the specific site. Vice verse a high gradient value refers to sites where the hydrological dispersion of the soil pore water is strongly affecting the PSIP. This also becomes visible by just looking at the shape of the PSIP because these PSIP have a great downwards extension of the WPP.

2.4.6 Soil Storage

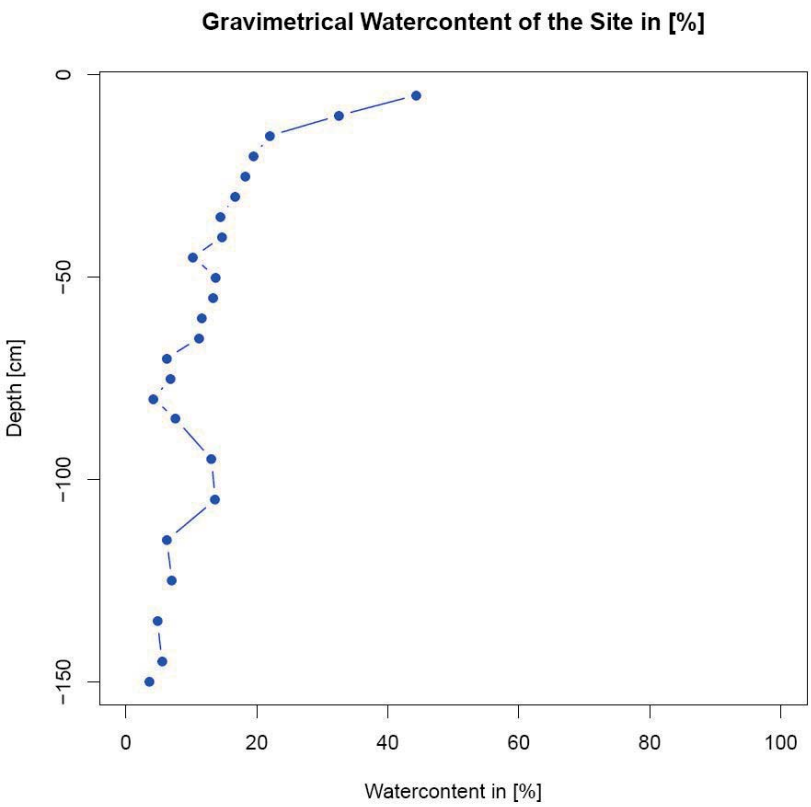

Figure 2.13: Depth profile of the water content. Bottom mean of the water content [%] is used as measurement for the process of soil storage of soil pore water in the vadose zone.

The gravimetrical water content of the samples was determined via 48 h oven drying at 110[°C] (Figure 2.13). The degree of moist of the samples in [%] obtains information about the soil storage of pore water at each site. It is assumed that the upper part of the soil pore water is most affected by the hydrological processes of evaporation, transpiration, mixing and dispersion, therefore the upper part of the water content depth profiles is not used neither. The mean of the second drill core from 1,20 [m.u.g] is used as measurement for the hydrological process of soil storage, the resulting box plots and anovas which are established with GNU R are expressing the correlations and influences of possible environmental or ground characteristics on the hydrological processes. The gravimetrical water content of four sites could not be determined. The goodness of this measurement for the determination of the process of soil storage is discussed in the fourth chapter of this thesis.

2.4.7 Recharge

The mean rooting depth is used as measurement for the hydrological process of recharge of soil pore water into the aquifers. This measurement was determined in the field when the cores were extracted from the ground immediately before pack in the soil material into the sampling bags. Sites with a great rooting depth are meant to belong to areas where the recharge rate is not as high as at sites where the mean rooting depth is not as deep as. All the water which arrives to the area where no more roots exist is considered to recharge the aquifer sooner or later. This measurement is not accurate, many errors remain hidden when using this variable as measurement for the hydrological process of recharge in the vadose zone because the amount of water which is sucked back in the upwards directions also depends a lot on the proportion and the type of the preexisting vegetation at each site. The process of transpiration influences the amount of soil pore water which could be recharged into the aquifer at each site. The great complexity of the hydrological processes and their influencing characteristics at a site leads to big difficulties in the process of finding good measurements which can be used to interpret the degree of the processes in the unsaturated zone which interact with certain amounts of soil

pore water. Nevertheless the mean rooting depth delivers information in order to interpret the degree of recharge at a site which can be used in a prudent way.

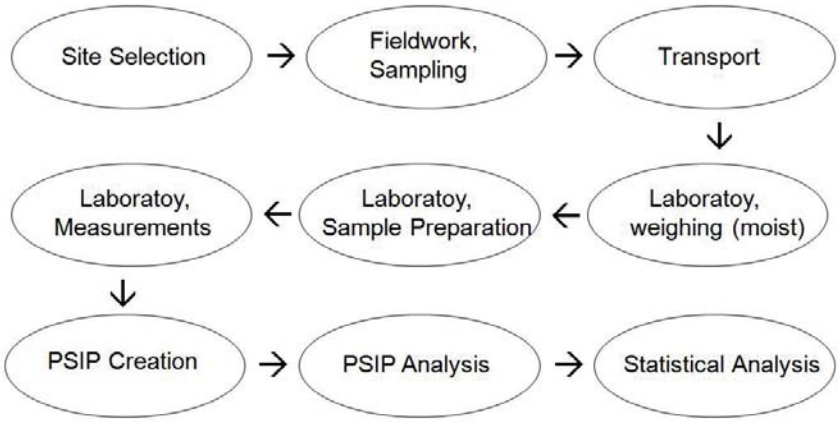

Figure 2.14: Schematic flipchart of the steps which have to be done in order to establish a PSIP analysis. Just the main steps are mentioned.

The flip chart figure 2.14 summarises the main working steps which have to be accomplished in order to carry out a PSIP analysis study, there is great potential for errors belonging to the fieldwork as well as belonging to the laboratory work. Work has to be done accurate, quick and it is very important not to change the working machinery during the whole research.

Chapter 3

Results

3.1 Cryogenic Vacuum Extraction vs. Direct Equilibrium

A comparison of the measuring methods was done in order to determine the accuracy of the main measuring method, the direct-equilibrium-method, which is frequently used and further developed at the IHF for the generation of PSIP in several other studies [Gralher, 2009, Garvelmann et al., 2012, Mueller et al., 2014]. Therefore 41 sub samples were taken out of the originals sample bags. These sub samples where then packed into small bags in 100 [g] or 50 [g] portions and transported to Munich. There a cryogenic vacuum extraction of the pore water of the sub samples was made. Afterwards the extracted pore water was measured at the IHF with a Picarro (fluid measurement). Figure 3.1 shows that the extraction leads to different results compared to the measurement after direct equilibrium. The blue stars represent the calibrated data which resulted after the fluid measurement with the Picarro after the cryogenic pore water extraction, the green stars represent the calibrated data which resulted after the isotopic measurement of the vapor in the head space of the bag after direct equilibrium of the moist soil material and the dry air in the head space of the bag. Regression lines are not parallel but the results all plot close to the local meteoric water line (LWML) of Trier, Germany which was

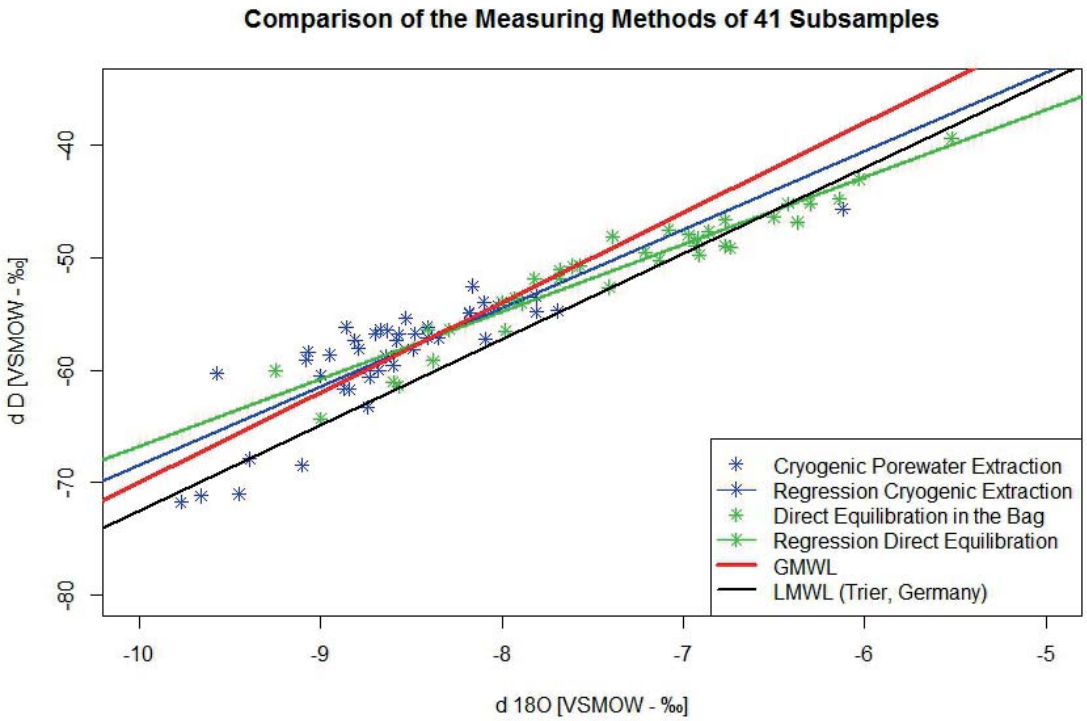

Figure 3.1: Graph of the Measuring Method Comparison - Direct Equilibrium vs.Cryogenic Vacuum Extraction. GMWL and LMWL as well as the regression lines are shown.

worked out by [Stumpp et al., 2014].

Table 3.1: Summary of Regression lines, LMWL and GMWL - Measuring Method Comparison

Data	Slope	Intercept
Cryogenic	5.9	-6.8124
Direct E.	6.9	1.4293
LMWL	7.6	3.9
GMWL	8	10

The intercepts and slopes of the regression lines, the LMWL and the GMWL are illustrated in table 3.1. The creation of PSIP exclusively was made with the direct equilibrium measuring method, if there exists a measurement bias the descriptive statistic fully takes this bias into consideration because all the measurements were

done with the same machinery in the same laboratory and if there is a certain bias this bias will be the same for all PSIP.

3.2 PSIP Analysis

3.2.1 Site Similarity

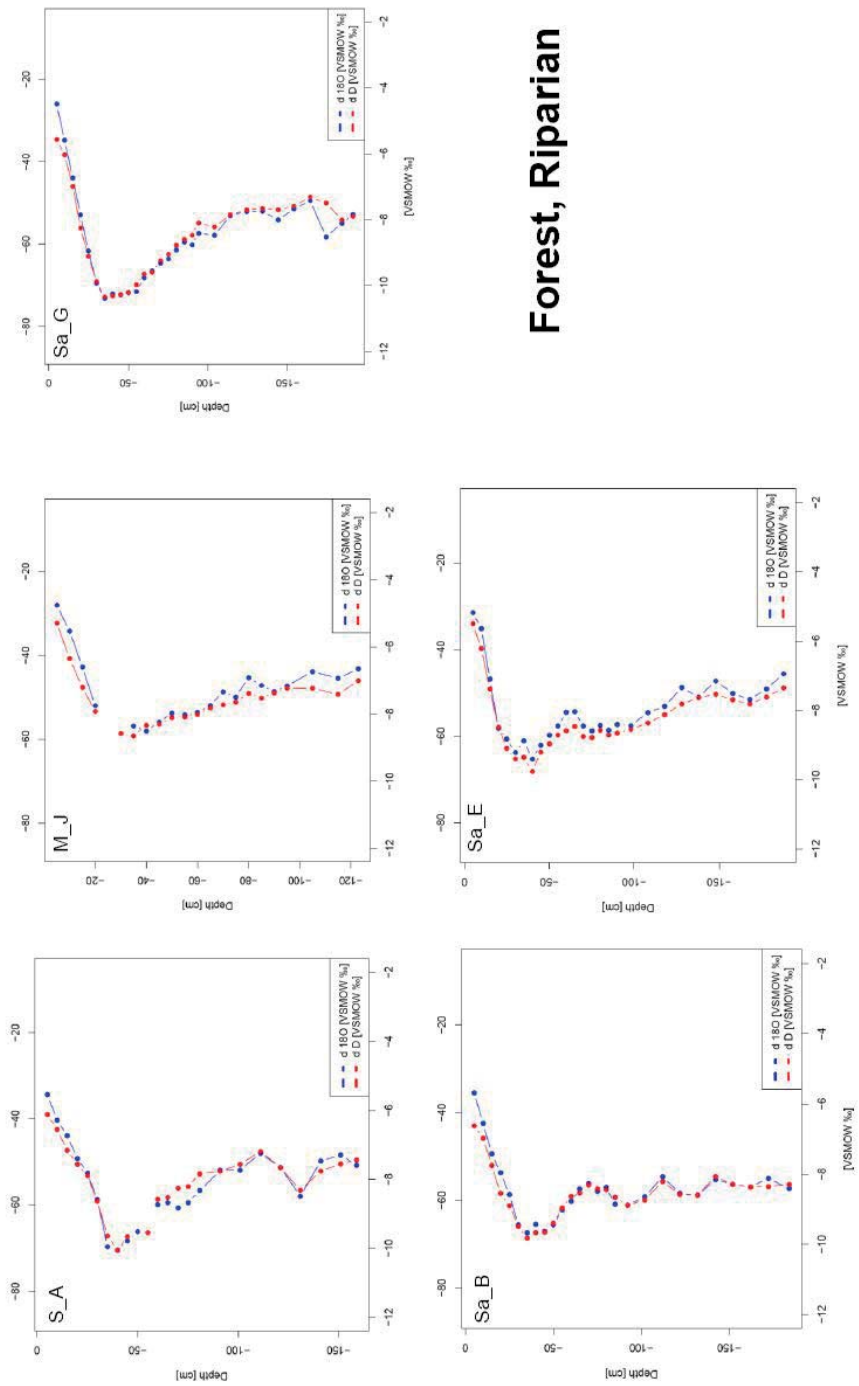

Figure 3.2: The sites $Shist_A, Marl_J, Sandstone_G, Sandstone_B$ and $Sandstone_E$ which belong to a forest and to the riparian zone, the blue dots of the dual - PSIP refer to the δ^{18}O and the red dots refer to the δ^{2}H data. They all show different types of peaks and are not to be classified as similar.

Figures 3.2 and 3.3 show the PSIP grouped after the dominant predictors land use and topographical position. It has to be concluded that sites with similar environmental characteristics refer to various shapes of the PSIP. There are distinctive similarities and certain dissimilarities regarding the shape of the PSIP, variation in the upper, the middle or the downer part of the PSIP are to be considered. The results of the statistical analysis show that the type of geology, the land use class and the topographical position are the most dominant predictors, therefore we expected similar shapes when we consider these predictors during the process of group building. The lack of very similar shapes leads to a great difficulty and hypothesis one and two therefore are not true. Graphs which we grouped due to the geological units do not show similar PSIP either.

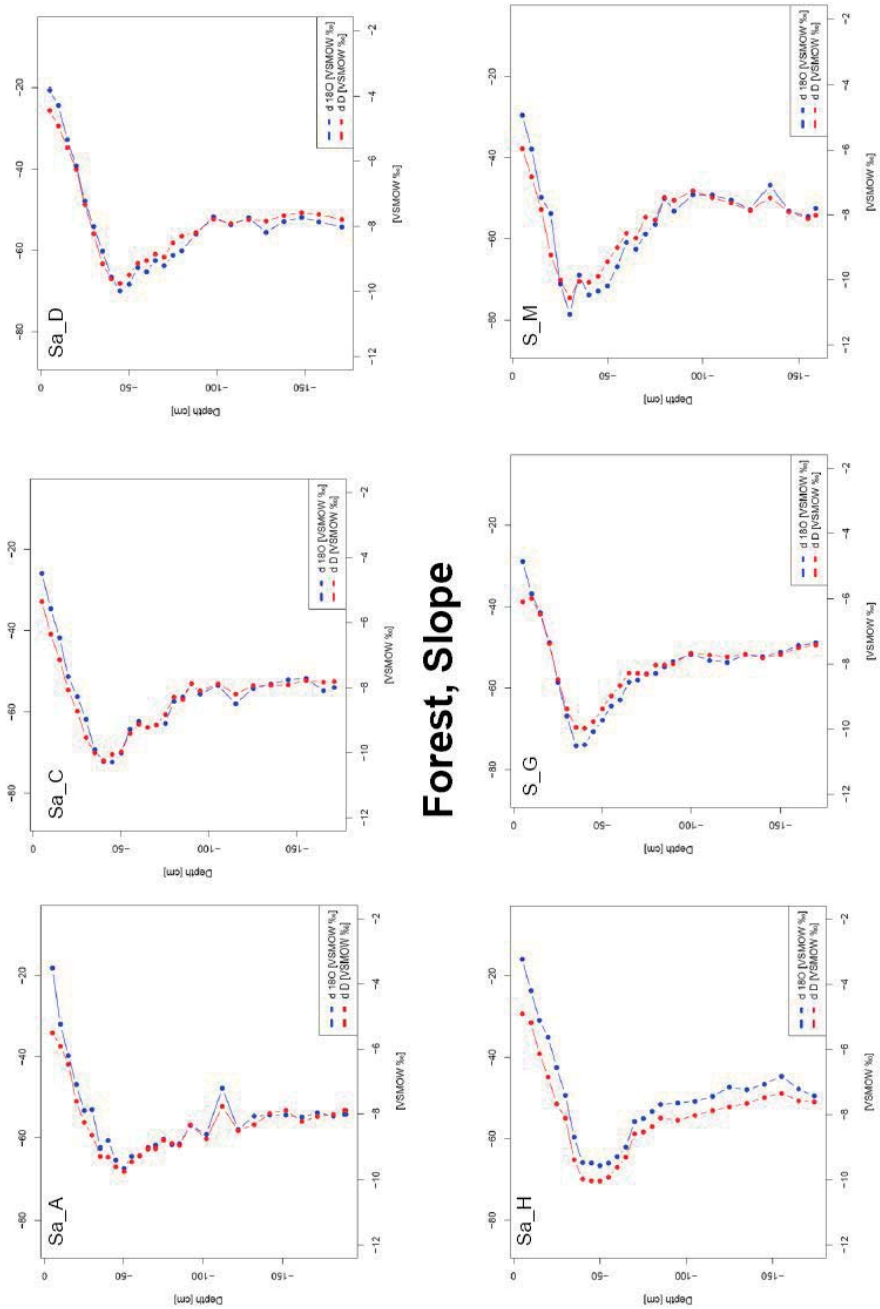

Figure 3.3: The sites $Sandstone_A, Sandstone_C, Sandstone_D, Sandstone_H, Sandstone_G$ and $Shist_M$ which belong to a forest and to a hill slope, the blue dots of the dual - PSIP refer to the δ^{18}O and the red dots refer to theδ^2H data. They all show different types of peaks and are not to be classified as similar.

3.2.2 PSIP Similarity

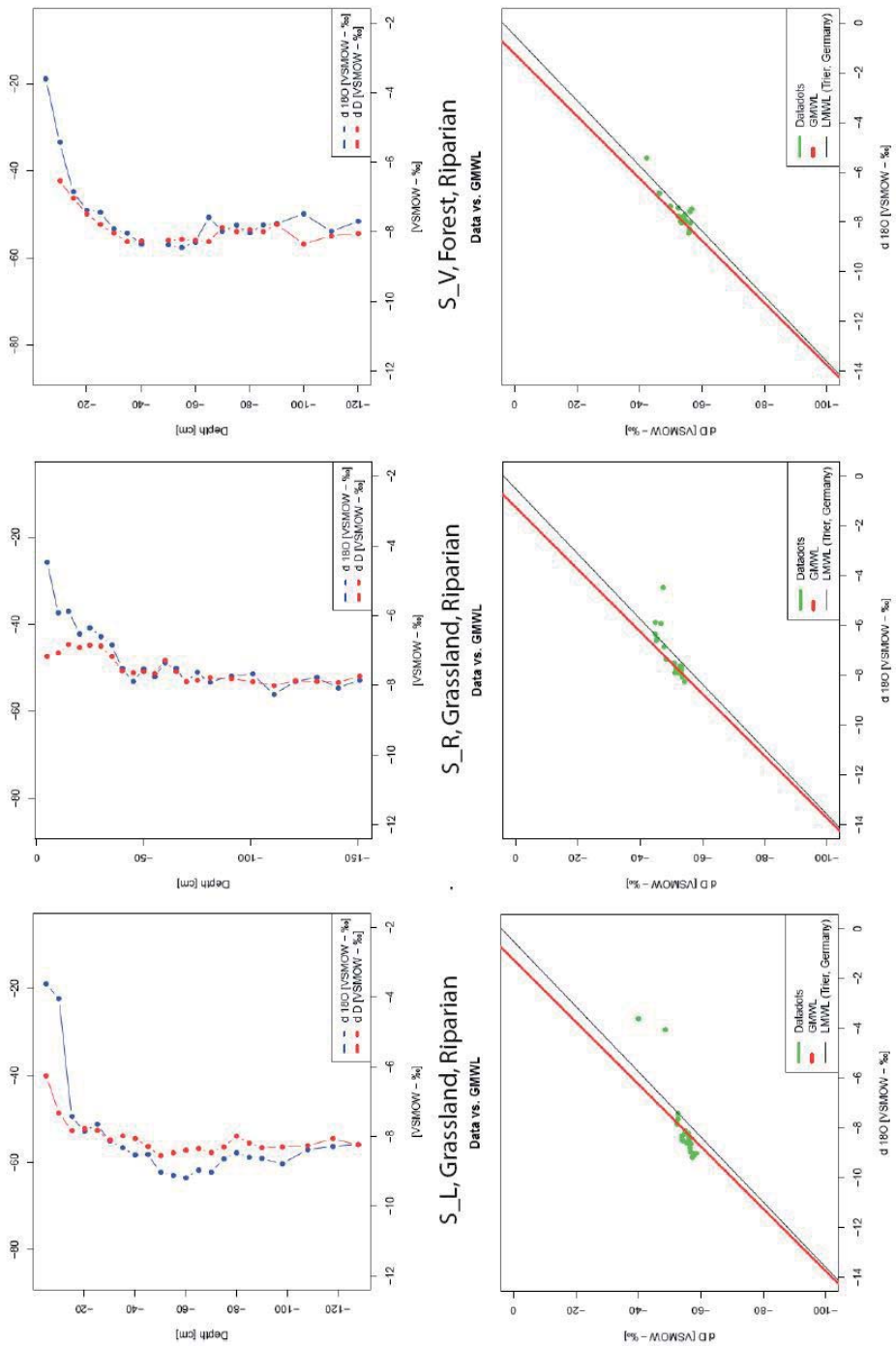

Figure 3.4: The graph shows the dual PSIP and the dual isotope plots of the sites $Shist_L$, $Shist_R$ and $Shist_V$ which belong to the riparian zone, the blue dots of the dual - PSIP refer to the δ^{18}O and the red dots refer to theδ^2H data. They all do not show a peak and are to be classified as similar. The dual isotope plots also show similar positioning of the data dots.

Figures 3.4 and 3.5 show the results of the approach to order and group similar shaped PSIP and their belonging dual isotope plots. The distinction criteria is the existence and the shape of the WPP. Figure 3.4 shows all three PSIP which do not show a peak at all, all these sites belong to the riparian zone and are isotopically affected by the groundwater or stream water. The dual isotope plots all show a accumulation of the data dots and all PSIP do not show a great range of variability regarding the [δ‰] - values. The environmental characteristics are not exactly the same but they are similar, the topographical position has the biggest influence as a predictor on the hydrological response at these sites. Figure 3.5 shows the sites with one of the most distinctive WPP of all 45 sites. Not just the shape of the PSIP is similar, the dual isotope plots also show a similar up lining of the data dots along the LMWL, this is due to the similar variance of the data dots throughout the whole profiles (from top to bottom). The environmental characteristics of these sites are exactly the same, they all belong to the sandstone area, are located at a hill slope and do all belong to a forest. Nevertheless do exist similar shaped PSIP which do not belong either to a forest or are not belonging to the same type of geology. The degree of similarity is very hard to measure, there are always small differences in the shapes of the PSIP.

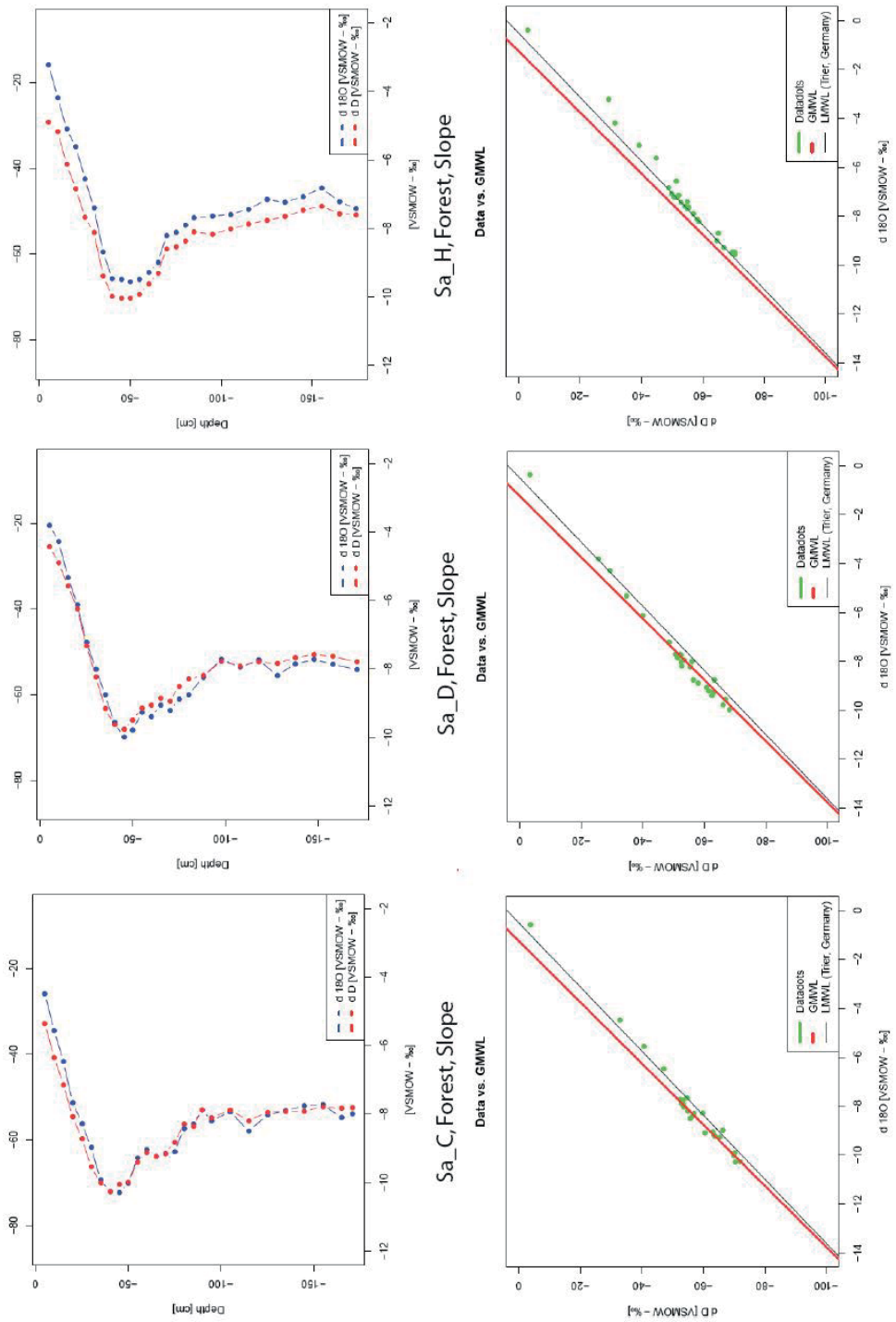

Figure 3.5: The graph shows the dual PSIP and the dual isotope plots of the sites $Sandstone_C$, $Sandstone_D$ and $Sandstone_H$ which belong to the sandstone area, a forest and are located at a hill slope, the blue dots of the dual - PSIP refer to the δ^{18}O and the red dots refer to theδ^{2}H data. They all do show a distinctive peak with a similar shape and are to be classified as similar. The dual isotope plots also show similar positioning of the data dots.

3.3 PSIP - Implication for Vadose Zone Processes

3.3.1 Infiltration

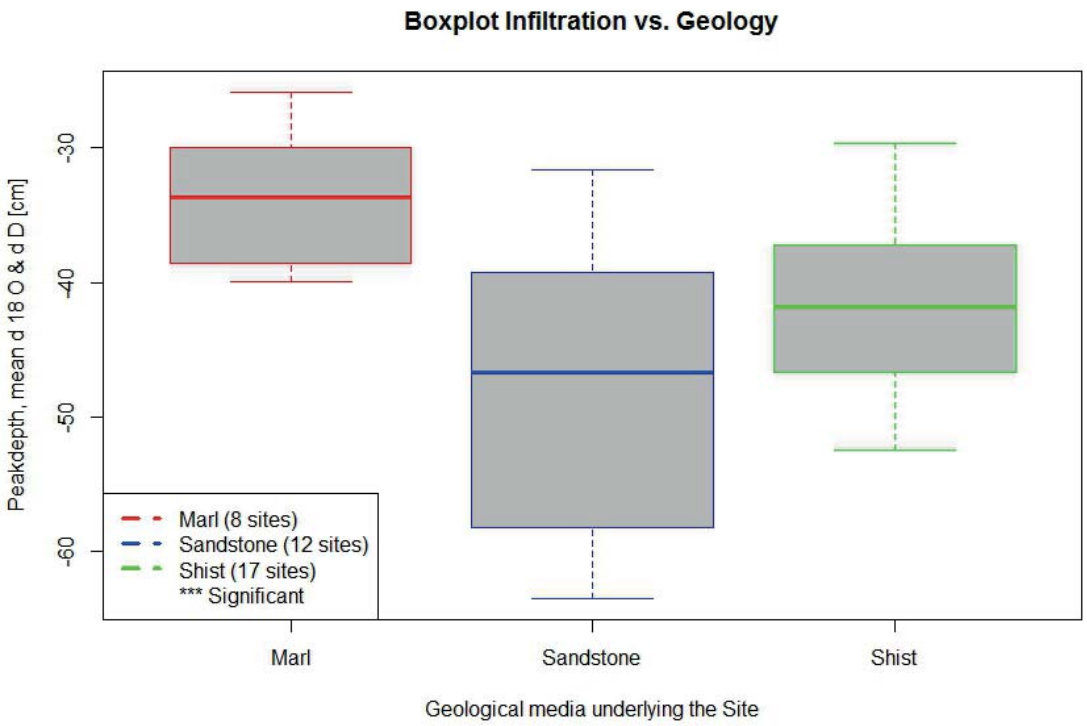

Figure 3.6: Peak depth [cm] of the mean of the δ^2H - and the δ^{18}O - PSIP of each site belonging to the marl, the sandstone or the shist area.

Figure 3.6 expresses the relation between the hydrological process of vertical infiltration of precipitation water through the soil pores in the vadose zone and the geological media which is underlying the site as single predictor. The winter precipitation peak (WPP) of the season 2013/ 2014 offers an accurate measurement for this process. We work with both the δ^2H PSIP and the δ^{18}O PSIP in order to consider all information of both stable isotopes depth profiles. Peak depths have not been different at every site, just few sites showed different peak depths of the the δ^2H PSIP and the δ^{18}O PSIP. However, the significance refers here to the whole plot, it is obvious that the sites which belong to the marl area show less infiltration depths, followed by the sites which belong to the shist area. The sites which belong to the sandstone area show the deepest infiltration depths. Without distinguishing

between the land use or the topographical position as additional predictors it has to be concluded that the sandstone in general offers an easier way for the infiltrated precipitation water through the soil pores to infiltrate vertically into the ground.

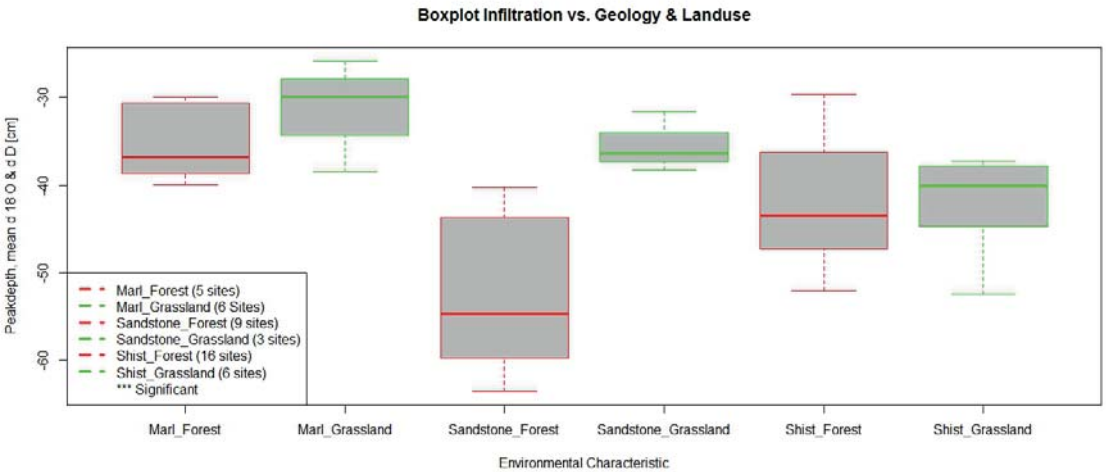

Figure 3.7: Peak depth [cm] of the mean of the δ^2H - and the δ^{18}O - PSIP of each site belonging to the marl, the sandstone or the shist area they are further subdivided into groups of the different land use class which expresses the influence of the land use on the process of infiltration.

Figure 3.7 offers even more insight when regarding the influence of the characteristics which could dominate the process of vertical infiltration. Here the interrelation becomes visible that the sites which belong to a forest always show a deeper infiltration depth compared to the sites which belong to the grassland areas. Further it becomes clear that the relations which are expressed in figure 3.6 also appear in this graph. The degree or the velocity of the vertical infiltration of the precipitation water through the soil pores depends mainly on the characteristics of the upper part of the soil column, here the soil texture, the root occurrence and therefore the size of the grains, which also determines the size of the pores and furthermore affects the connectivity among themselves, play the biggest role. It has to be concluded that the sites in the forest generally let the precipitation water infiltrate more easy than the sites which belong to grassland areas and in general the sites which belong to a sandstone area in a forest let the precipitation water infiltrate a lot better than the sites which belong to the marl areas belonging to grasslands, here the vertical

infiltration of pore water does happen really slowly.

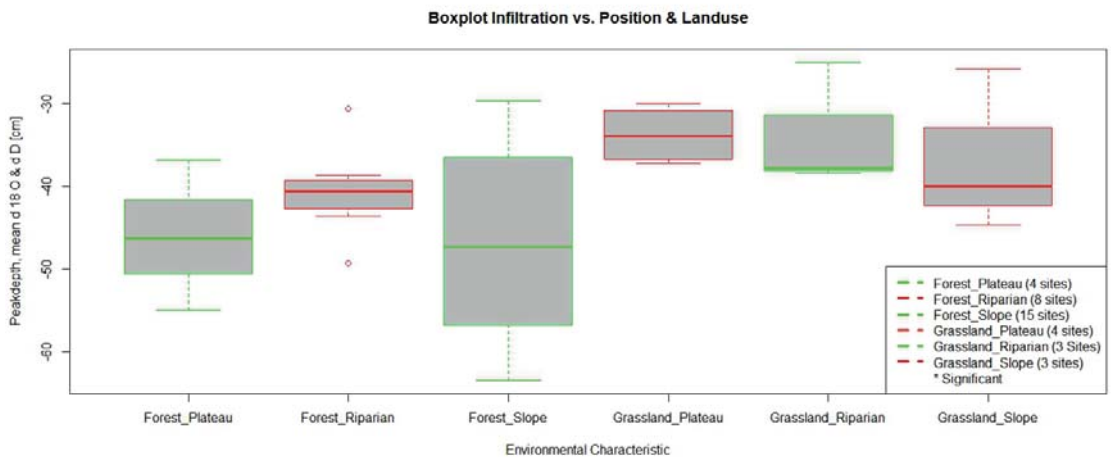

Figure 3.8: Peak depth [cm] of the mean of the δ^2H - and the δ^{18}O - PSIP of each site belonging to either the riparian-, the slope or the plateau area. They are further subdivided into groups of the different land use classes which additionally expresses the influence of the land use and the topographical position on the process of infiltration.

If one regards the data divided into groups after the land use classes and the topographical positions literally the correlation between these two predictors and the hydrological process of vertical infiltration through the soil pores becomes clear. It is expressed that all sites which belong to a grassland show minor infiltration rates. The soil pore water infiltrates more easy at sites which belong to a forest. The greatest variance of infiltration depths occurs at the sites which belong to a hill slope in a forest. Figure 3.8 tells us that the land use has a greater influence on the infiltration than the topographical position. Whereas the topographical position also plays a role regarding the process of vertical infiltration of soil pore water through the soil pores. Please note that the number of the sites which belong to each group is not that big, therefore the statistical relevance is not that big either. There is no significant relation of the main exposition (south or north) of the site and the infiltration of precipitation water into the unsaturated zone.

Figure 3.9 illustrates the correlation between the infiltration and the environmental characteristic of the canopy status. It becomes obvious that there is a positive

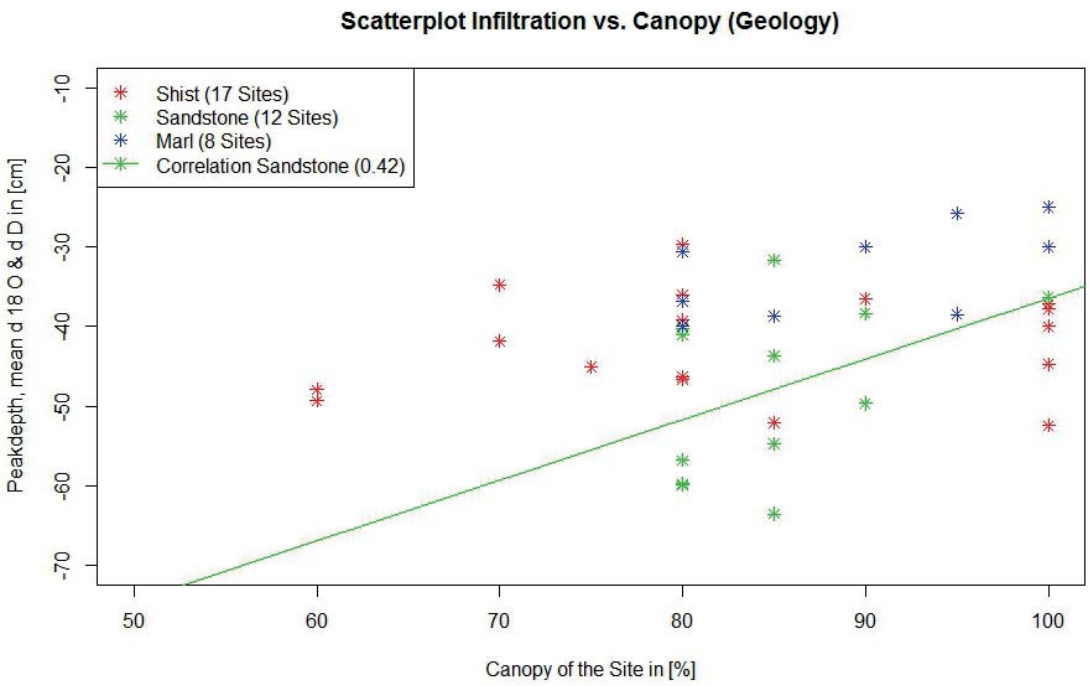

Figure 3.9: Peak depth [cm] of the mean of the δ^2H - and the δ^{18}O - PSIP of each site belonging to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The canopy status of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the sandstone (green line), correlation value is expressed in the legend of the plot.

correlation of the data carried out in the sandstone area, the more canopy is present the less deep infiltrates the precipitation water vertically through the soil pores. The data which belongs to the shist or the marl area does not show any correlation. It has to be concluded that the canopy status can affect the process of infiltration but is not a dominant predictor for this process. The graphs which illustrate the infiltration depth data against the soil skeleton of the horizon A and B does not show correlation, therefore these plots are just shown in the appendix.

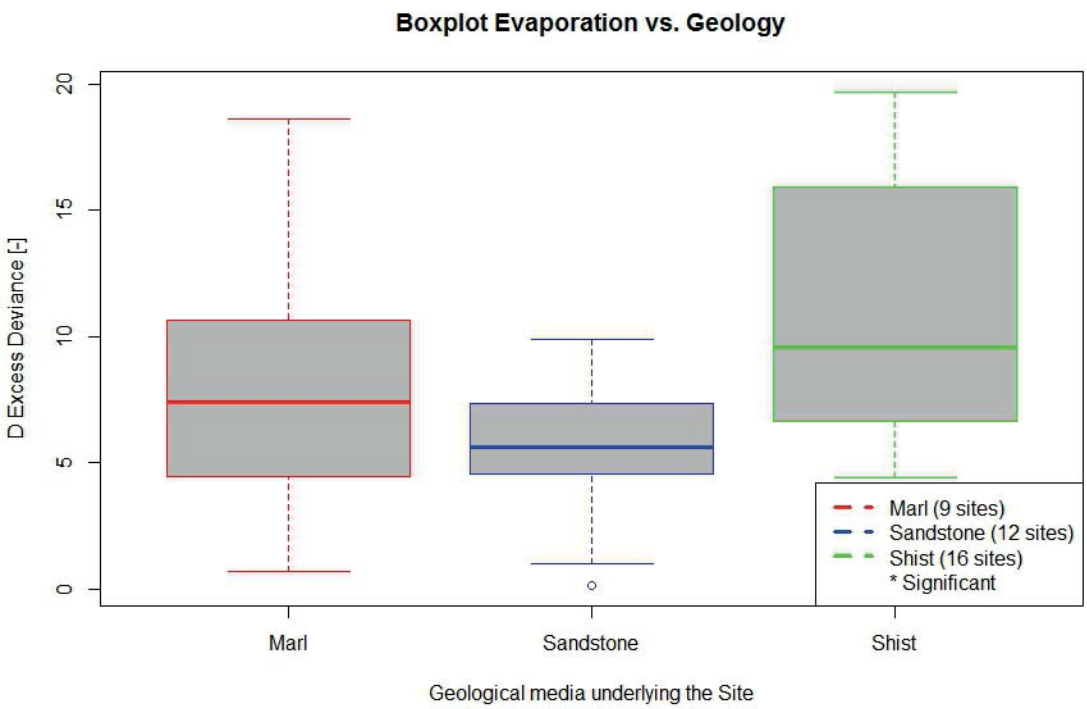

Figure 3.10: D Excess Deviance [-] of the mean of the upper three data dots and the rest of the D Excess depth profile generated via the [VSMOW- ‰] - values of the δ^2H - and the δ^{18}O - PSIP and the GMWL formula (see 2.2.1) of each site belonging to the marl (red box), the sandstone (blue box) or the shist (green box) area.

3.3.2 Evaporation

Figure 3.10 provides insight into the relations between the hydrolgical process of evaporation and the geological media which underlies the sites. It is visible that there is a significant interrelation between the sites which belong to the sandstone environment and the sites which belong to the shist environment. Sites in the shist area tend to show a greater evaporation compared to sites which belong to the sandstone area. The sites which belong to the marl area show the greatest variance and therefore are not to be regarded as significant towards the other data groups. The land use, the topographical position and the exposition do not show any significant relation with reference to the evaporation.

The soil skeleton of the A horizon is a dominant ground characteristic which influences the process of evaporation of soil pore water in the catchment. Figure 3.11

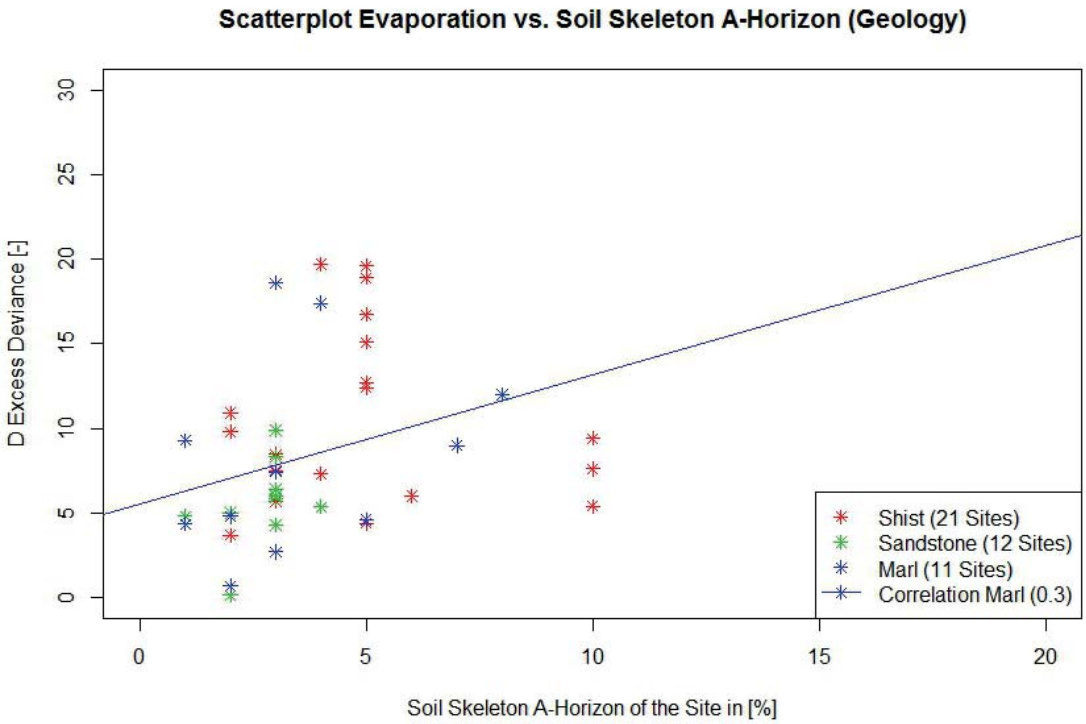

Figure 3.11: D Excess Deviance [-] of the mean of the upper three data dots and the rest of the D Excess depth profile generated via the [VSMOW- ‰] - values of the δ^2H - and the δ^{18}O - PSIP and the GMWL formula (see 2.2.1) of each site belonging to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The soil skeleton [%] of the A horizon of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the marl area (blue line), correlation value is expressed in the legend of the plot.

shows that the higher the soil skeleton the more evaporation happens at a site. Whereas this correlation is not expressed within the shist and the sandstone data this could be due to faster infiltration at the sandstone and shist sites (see above).

The sites which belong to the land use class grassland also show a correlation with reference to the hydrological process of evaporation and the soil skeleton of the A horizon. Figure 3.12 supports the result from the other scatter-plot where the geology is the predictor (above). The soil texture and the soil skeleton of the upper part of the soil column regulates the degree of evaporation at each site, sites with

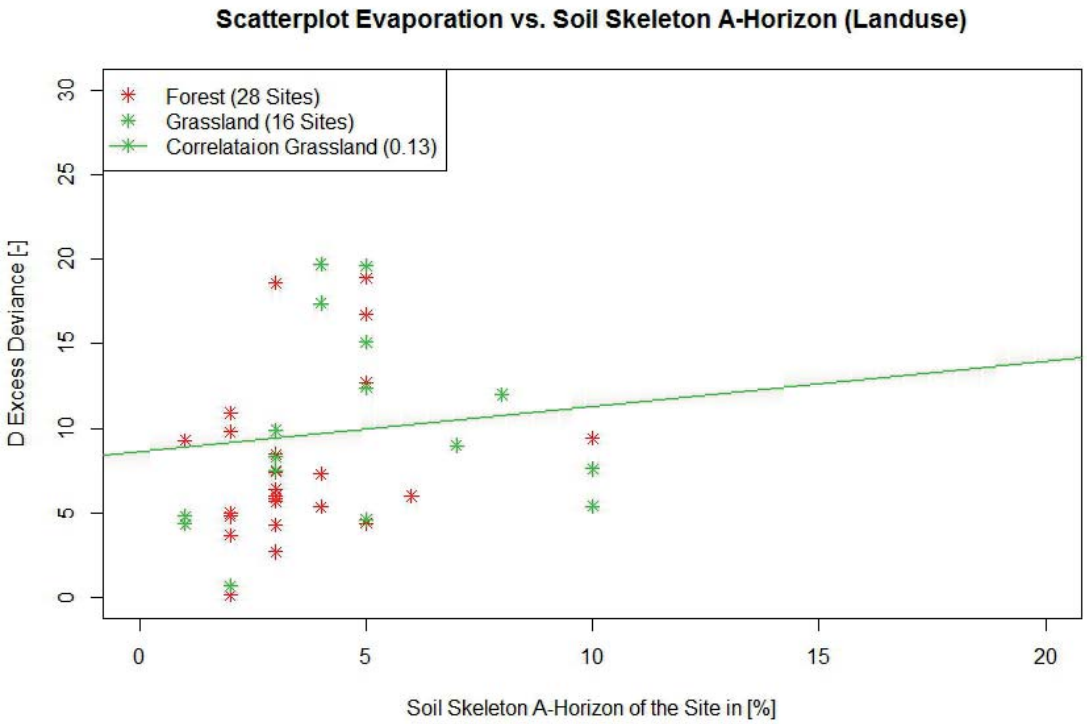

Figure 3.12: D Excess Deviance [-] of the mean of the upper three data dots and the rest of the D Excess depth profile generated via the [VSMOW- ‰] - values of the δ^2H - and the δ^{18}O - PSIP and the GMWL formula (see 2.2.1) of each site belonging to either the forest (red stars) or the grassland (green stars) area. The soil skeleton [%] of the A horizon of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the Grassland area (green line), correlation value is expressed in the legend of the plot.

a higher soil skeleton percentages show more evaporation than sites with lower soil skeleton percentages.

Figure 3.13 supports the results above, a greater soil skeleton in the A horizon is related to a higher evaporation at the sites. Exclusively the north facing sites show this correlation, the regression line in the graph expresses this correlation. The south facing sites do not show a significant correlation. The sites without a southern or northern exposition are not considered here, most of the sites which are more or less exposed also belong to hill slopes there are just a few sites which belong to a

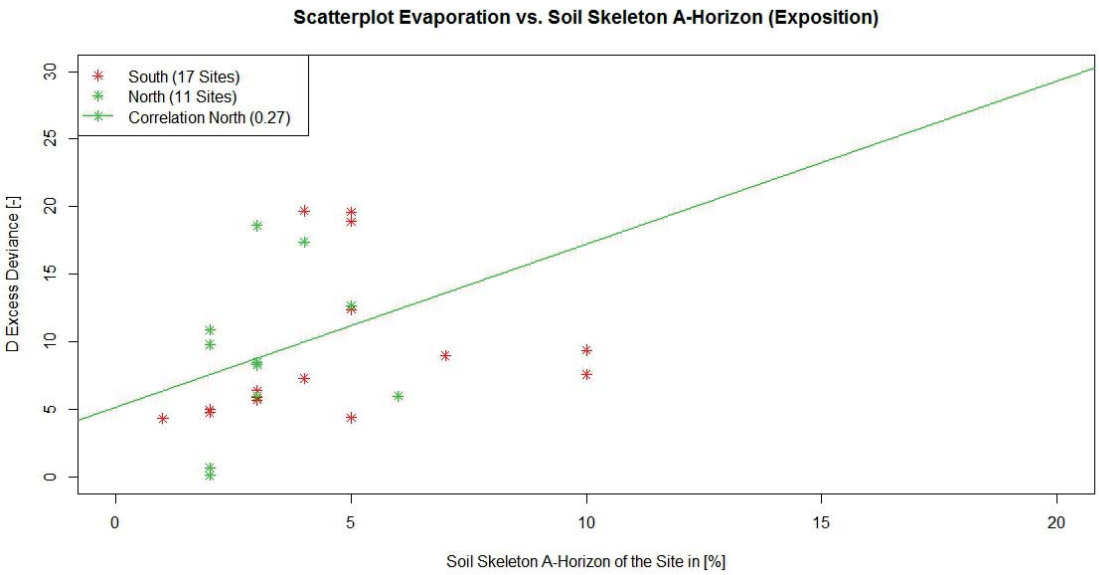

Figure 3.13: D Excess Deviance [-] of the mean of the upper three data dots and the rest of the D Excess depth profile generated via the [VSMOW- ‰] - values of the δ^2H - and the δ^{18}O - PSIP and the GMWL formula (see 2.2.1) of each site belonging to either the south facing sites (red stars) or the north facing sites (green stars). The soil skeleton [%] of the A horizon of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the north facing areas (green line), the correlation value is expressed in the legend of the plot.

plateau which is also taken into account here due to a slight northern or southern exposition.

Figure 3.14 expresses the correlation between the evaporation and the soil skeleton of the B horizon. This graph shows an interesting context with reference to the dominating characteristics on the process of evaporation. Above we saw that the soil skeleton of the A horizon has to be high in order to allow more evaporation at a site. Obviously this is not the case for the soil skeleton of the B horizon. If the soil skeleton of the B horizon is big the process of evaporation tends to be lower than when the soil skeleton of the B horizon is low. This could be due to a favored accumulation of soil pore water in the A horizon (which will lead to a greater evaporation rate) when the soil pore water can not infiltrate easily through

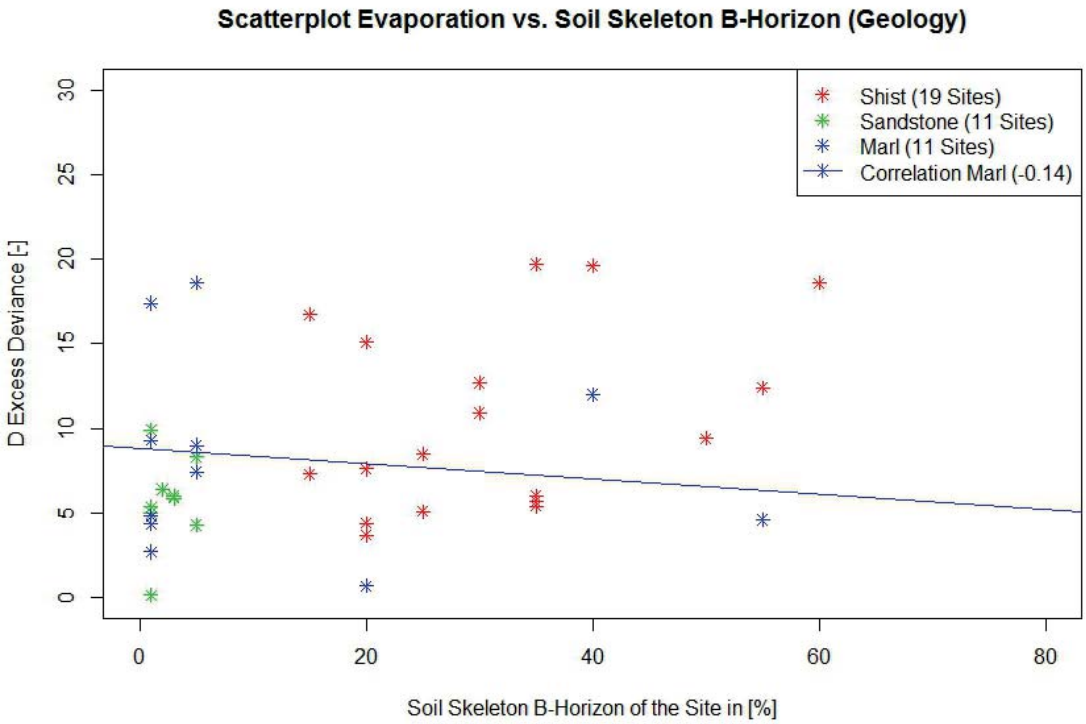

Figure 3.14: D Excess Deviance [-] of the mean of the upper three data dots and the rest of the D Excess depth profile generated via the [VSMOW- ‰] - values of the δ^2H - and the δ^{18}O - PSIP and the GMWL formula (see 2.2.1) of each site belonging to either to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The soil skeleton [%] of the A horizon of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the marl area (blue line), correlation value is expressed in the legend of the plot.

the B horizon due to a low soil skeleton.

Figure 3.15 expresses the interrelation between the canopy status in [%] and the evaporation at each site offers insight into another stunning correlation regarding the hydrological process of evaporation. The more canopy is present the less evaporation happens at the sites. This correlation belongs to north facing sites. The south facing sites do not show this correlation. The canopy at the north facing sites is supposed to create a certain shadow which regulates the air temperature and the solar radiation contact with the ground. I expected this correlation also for the south facing sites

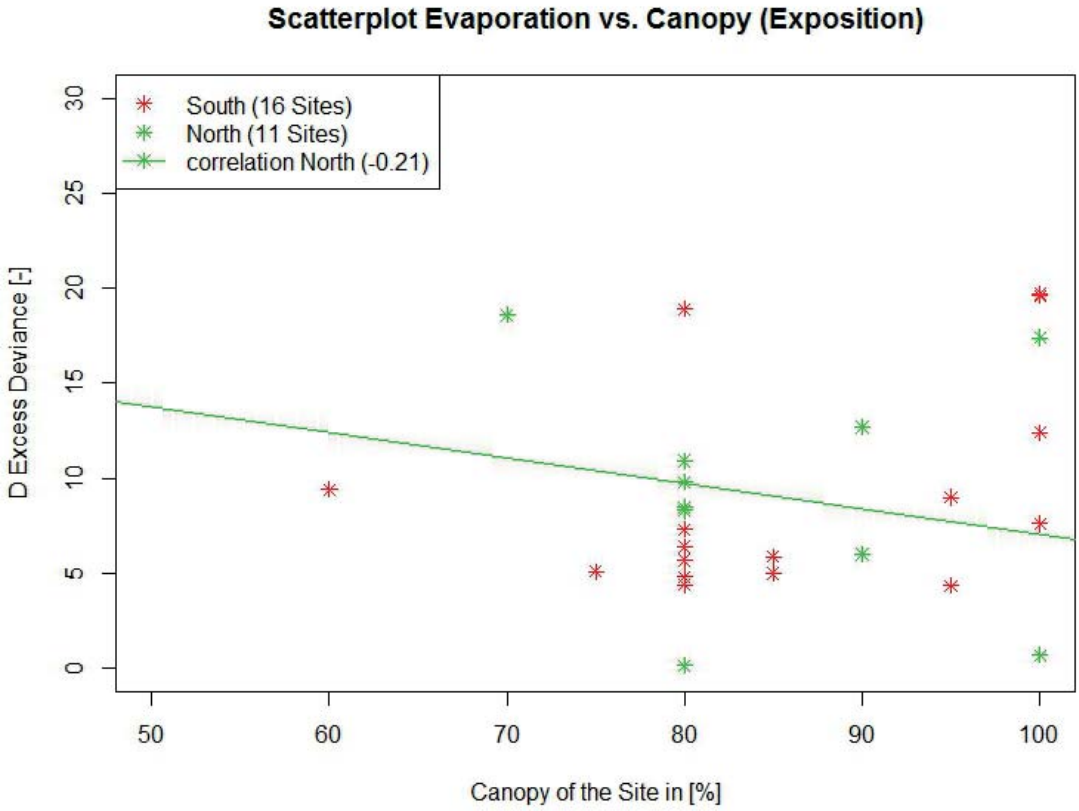

Figure 3.15: D Excess Deviance [-] of the mean of the upper three data dots and the rest of the D Excess depth profile generated via the [VSMOW- ‰] - values of the δ^2H - and the δ^{18}O - PSIP and the GMWL formula (see 2.2.1) of each site belonging to either to either the south facing sites (red stars) or the north facing sites (green stars). The canopy status [%] of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the north facing areas (green line), correlation value is expressed in the legend of the plot.

but other predictors seem to be even more important for this process (soil skeleton). Descriptive statistical analysis shows that the ground parameter of the soil skeleton and the canopy status are dominating the process of evaporation in the catchment, the influence of the characteristics of the land use, the topographical position, the exposition seem to play a minor role regarding this process. The type of rock which is underlying the site and therefore the type of soil which is present at the site seem to have a general influence on this process too.

3.3.3 Transpiration

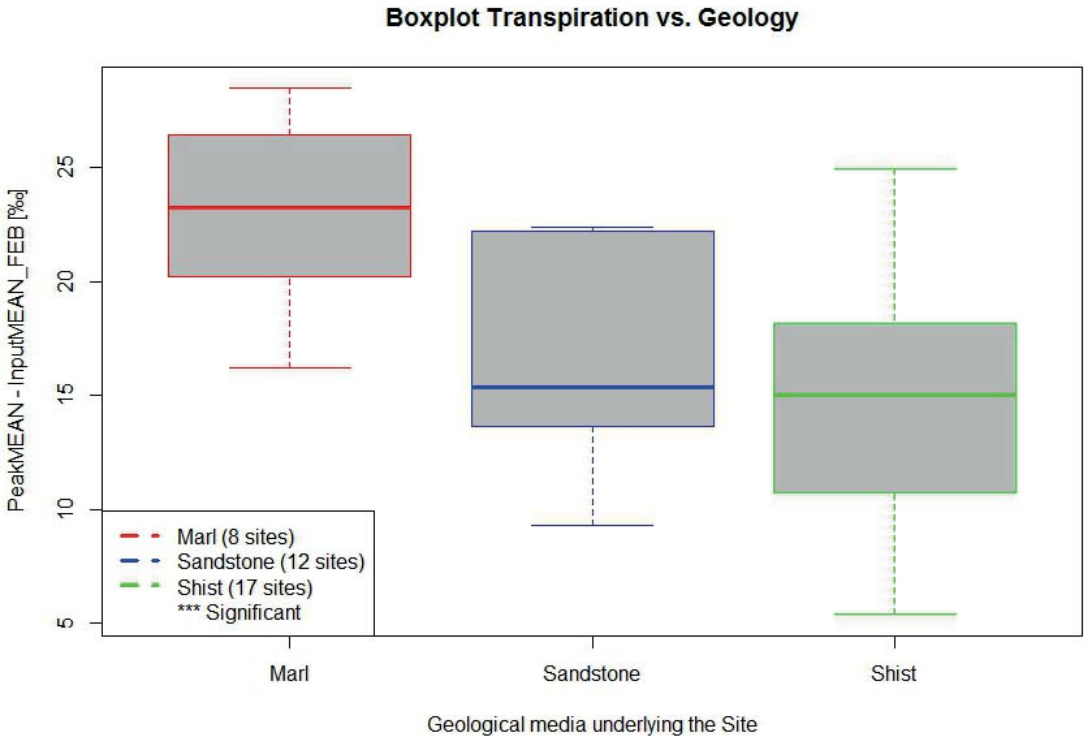

Figure 3.16: Deviance of the input mean of the February precipitaion and the peak mean [‰] of each δ^2H - PSIP belonging to the marl (red box), the sandstone (blue box) or the shist (green box) area.

Figure 3.16 shows the graph belonging to the hydrological process of transpiration of soil pore water through the vegetation. It is expressed that the sites which belong to the marl show the greatest transpiration followed by the sites which belong to the sandstone and shist area. There is a very strong significance in the variance of the data. The data which belongs to the shist area differ significantly from the data which belongs to the marl area.

Figure 3.17 shows the interrelation between the process of transpiration and the soil skeleton of the A horizon. The greater the soil skeleton percentage the more transpiration happens at a site of the sandstone area. This correlation is not shown in the shist and marl data.

Figure 3.18 shows the relation between the canopy and the process of transpiration

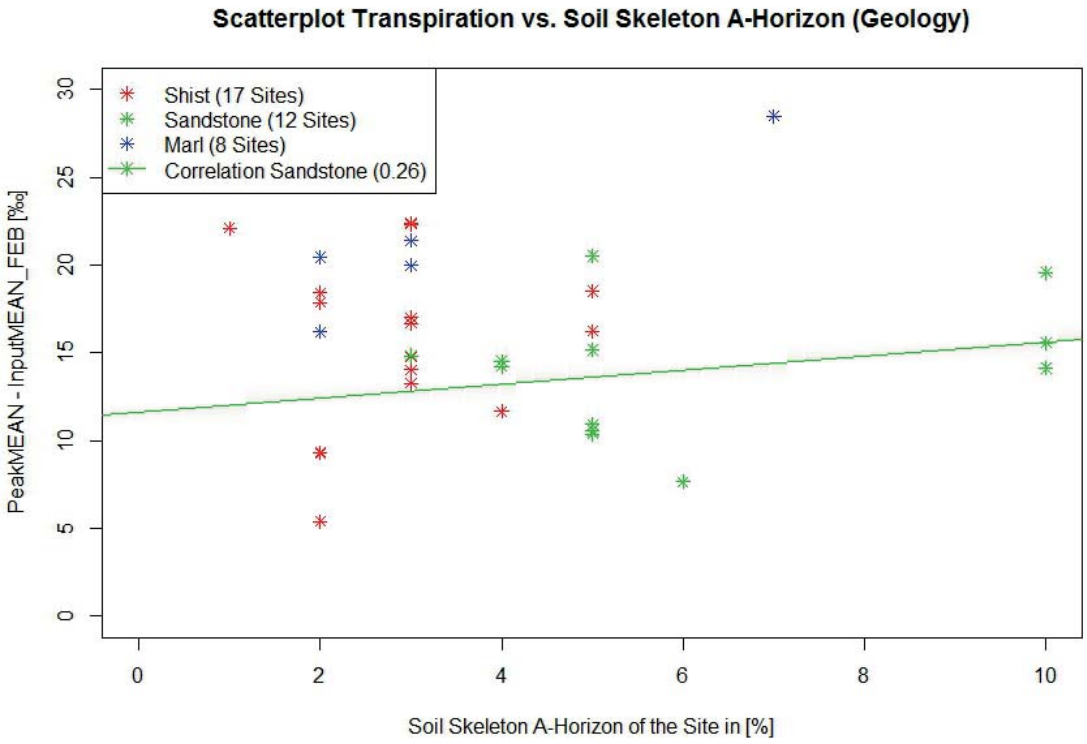

Figure 3.17: Deviance of the Input mean of the February precipitation and the peak mean [‰] of each δ^2H - PSIP belonging to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The soil skeleton [%] of the A horizon of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the sandstone area (green line), correlation value is expressed in the legend of the plot.

at a site. The data belonging to the canopy status in the field contains forest data as well as grassland data whereas the grassland data has extreme high percentages of the canopy status (from 95 - 100 [%]). This information should be considered in order to interpret this graph properly. Less canopy leads to higher transpiration rates for the data which belongs to the sandstone area. The other data does not show a significant correlation.

Figure 3.19 expresses the interrelation between the land use classes and the geology with reference to the hydrological process of transpiration of soil pore water in the vadose zone. The influence of the land use class gets visible when one regards the

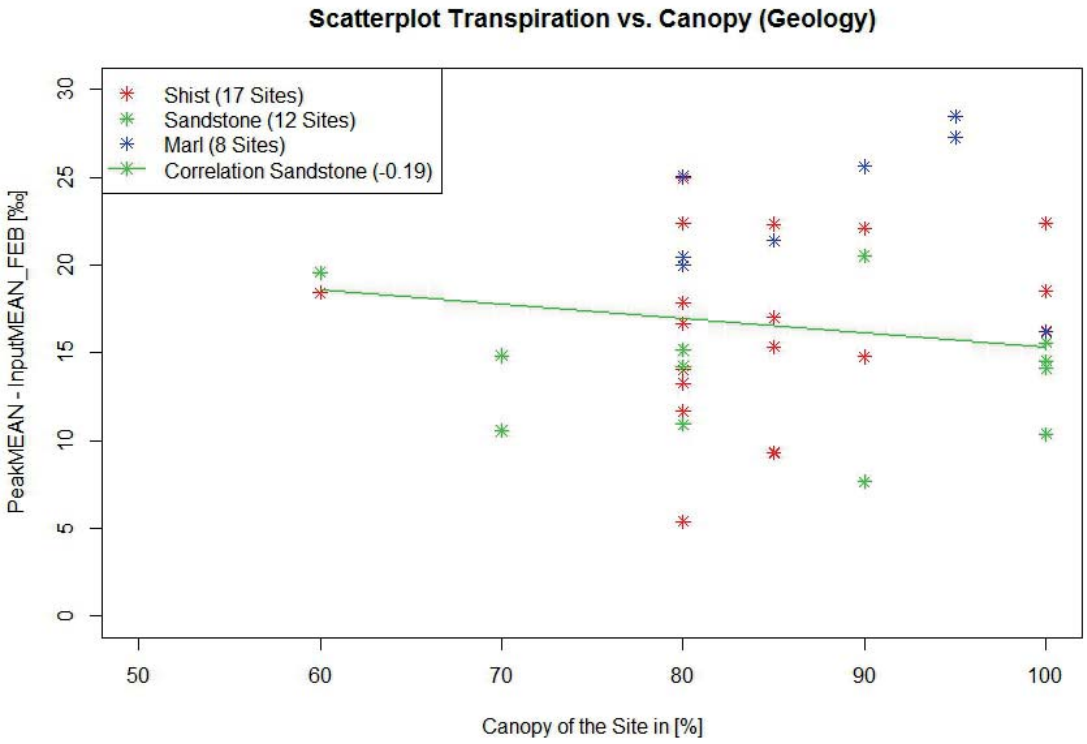

Figure 3.18: Deviance of the Input mean of the February precipitation and the peak mean [‰] of each δ^2H - PSIP belonging to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The soil skeleton [%] of the A horizon of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the sandstone area (green line), correlation value is expressed in the legend of the plot.

graph, all medians of the grassland data plot higher than the medians of the forest data. It has to be concluded that the transpiration is higher at sites which belong to grassland areas compared to sites which belong to forests. The canopy does not play a dominant role regarding the transpiration of soil pore water. The transpiration is most affected by the geology and the land use class. The soil skeleton of the upper soil horizon also affects the transpiration. Topographical position, Exposition, canopy and soil skeleton of the B horizon do not affect the process of transpiration in a significant way.

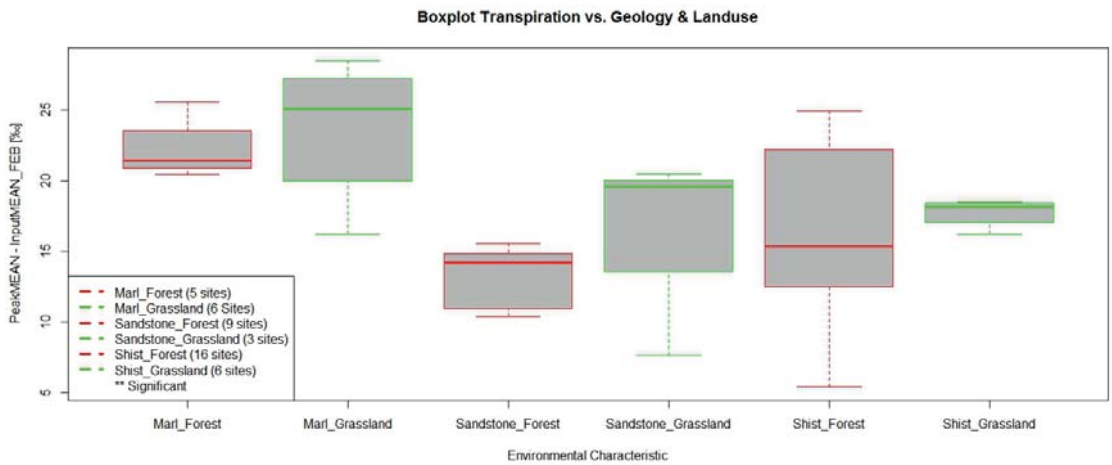

Figure 3.19: Peak depth [cm] of the mean of the δ^2H - and the δ^{18}O - PSIP of each site belonging to the marl, the sandstone or the shist area. They are further subdivided into groups of the different land use classes which additionally expresses the influence of the land use on the process of transpiration.

3.3.4 Dispersion

Figure 3.20 shows the relation between the hydrological process of dispersion of soil pore water in the vadose zone and the land use at the site. It is visible that there is a strongly significant interrelation which affects the degree of dispersion at the site due to the land use classes. The sites which belong to the grassland do not show that much dispersion compared to the sites which belong to a forest. Here the roots and the connectivity due to the greater number of many fine roots in the forest compared to the grassland may play a role. In the forest there are generally more fine roots which leads to a better connectivity among the soil pores due to the many small channels combined with the many fine roots in the ground. The graphs where the dispersion is plotted versus the environmental characteristics of geology, topographical position and exposition of the site do not show any significance therefore it has to be concluded that the predictive characteristic for the hydrological process of vertical dispersion at a site or even in a functional unit in a catchment is the land use class. The sites in the sandstone area show a significant correlation, a greater canopy leads to a greater dispersion at the site. The soil skeleton does not affect the dispersion either, there is no significant correlation in the graphs which are made

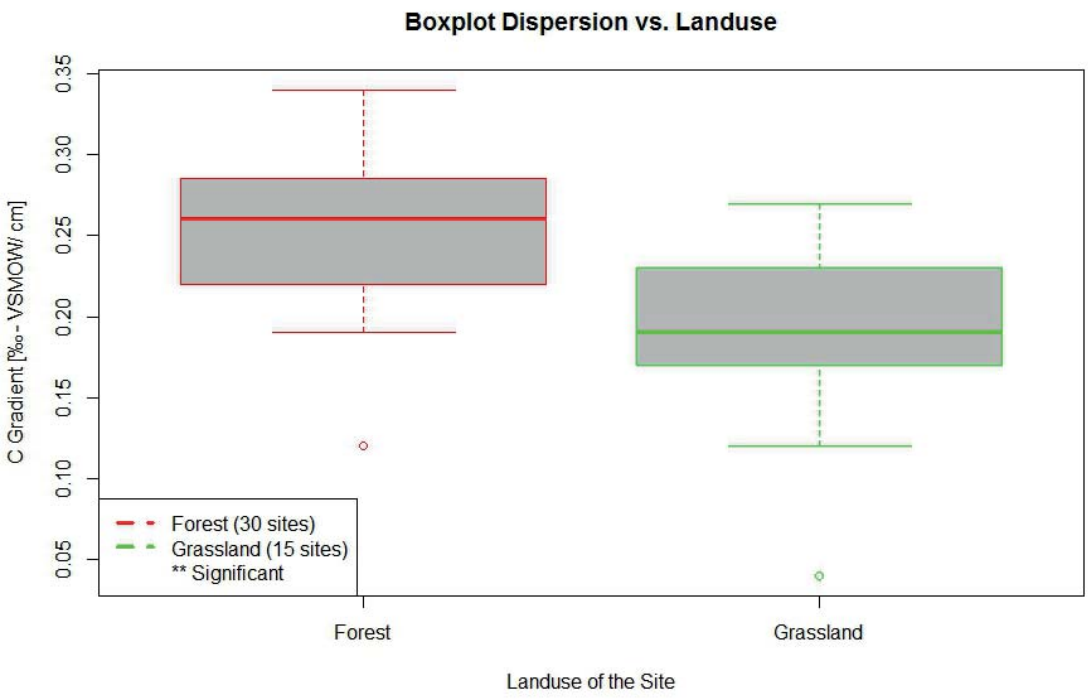

Figure 3.20: The dispersion [[‰]/[cm]] of the soil pore water generated via the concentration gradient (downwards peak extension from peak value to the bottom mean) of the δ^2H - PSIP of each site belonging to either the forest (red box) or the grassland (green box) area. Degree of significance is shown in the legend of the plot.

with GNU R. Interested readers can find these graphs in the appendix.

3.3.5 Mixing

There is no significant relation between the hydrological process of mixing of soil pore water in the unsaturated zone and the predictors of type geology, land use class, topographical position and main exposition of the sites. Even the box-whisker-plots grouped after both the land use classes and topographical position and the land use classes and the type of geology do not show any significance. Obviously the mixing is a process that depends on many factors, therefore it is not possible to statistically describe any interrelation between the environmental or ground characteristics and the hydrological process of mixing within the limits of this master thesis. The only significant correlation appears in Figure 3.21 where the canopy status is plotted

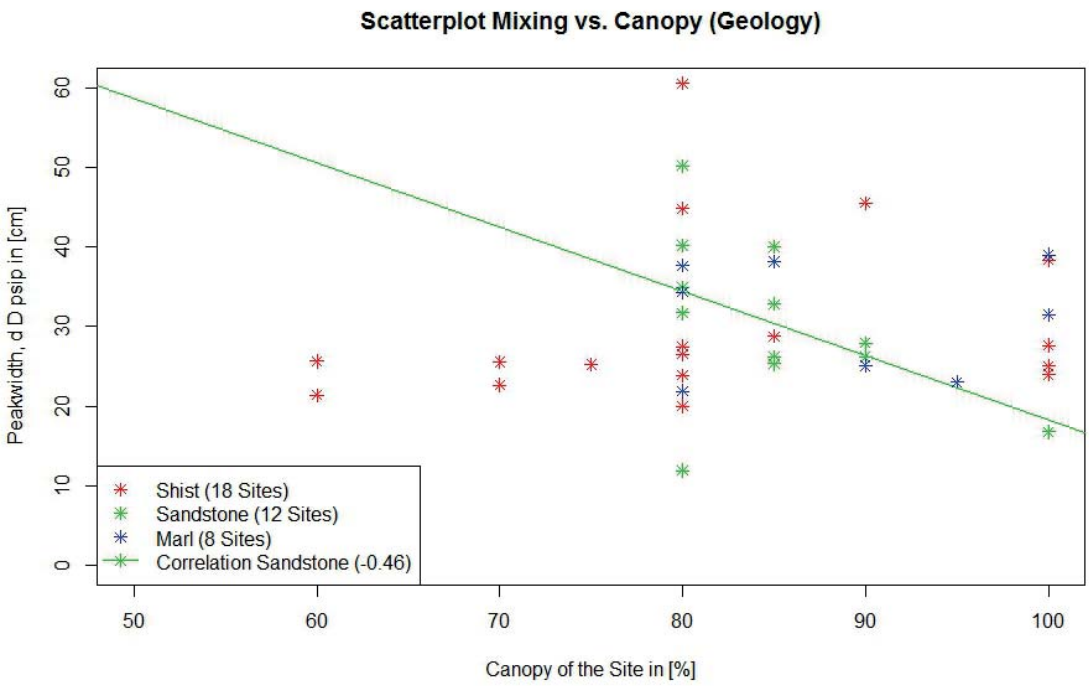

Figure 3.21: The peak width in [cm] of the δ^2H - PSIP of each site is used to describe the process of mixing at each site belonging to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The canopy status in [%] of each site was determined in the field when doing the soil core drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the sandstone area (green line), correlation value is expressed in the legend of the plot.

versus the peak width in [cm] which describes the process of mixing of soil pore water in the unsaturated zone at the sites. The sites which belong to the sandstone area show less mixing when there is more canopy. Therefore the canopy status affects the mixing significantly and should be seen as an important predictor which dominates the process of mixing of soil pore water in the unsaturated zone.

3.3.6 Soil Storage

The soil storage is affected by the topographical position of the site. Figure 3.22 illustrates this relation, one can see that the slope sites tend to have lower water

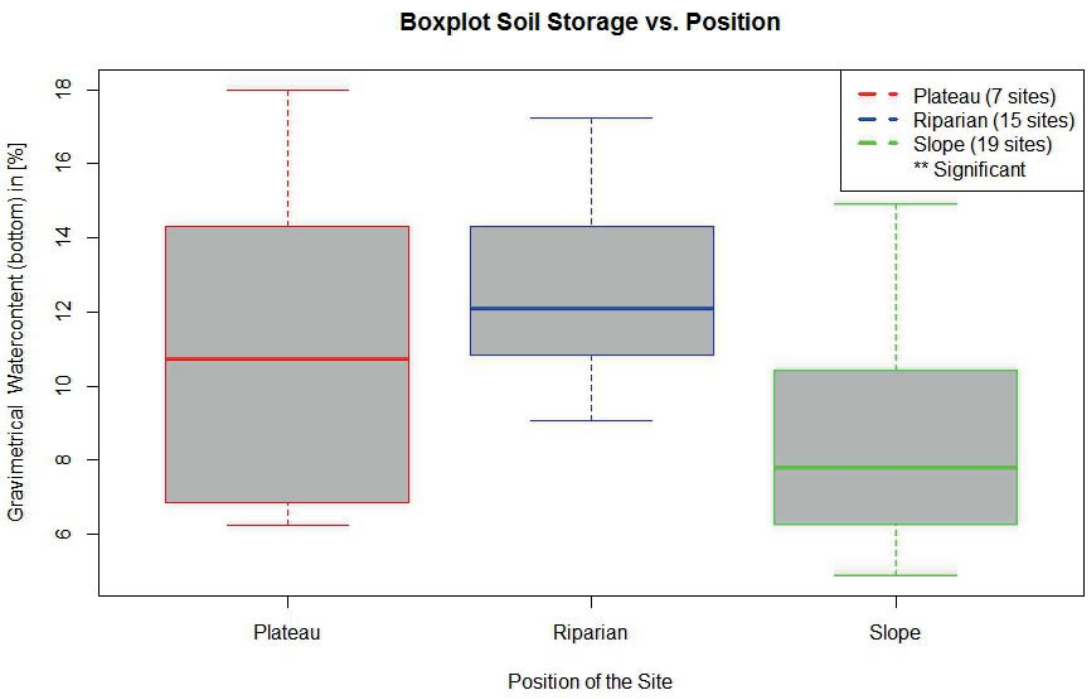

Figure 3.22: The gravimetrical water contents in [%] of the bottom (from -1,2 [m] until the end of the profile) of each depth profile of each site belonging to the plateau (red box), the riparian (blue box) or the slope (green box) area.

contents and the riparian zone holds the highest water contents. The sites which belong to a plateau area show a big range of differences in the soil storage. This relation could be explained by the gravity and the slow movement of the soil pore water downwards the hill slope through the pores, therefore the soil storage is less at the sites which belong to a hill slope. Whereas the sites in the riparian zone hold their soil pore water and exhibit higher water contents.

Figure 3.23 outlines the relation between the soil storage, the topographical position and the land use class of each site. It becomes clear that the sites which belong to a hill slope in a grassland area are not showing the same effect like the sites which belong to a hill slope in a forest. The small number of data dots has to be considered. All sites which belong to a the riparian zone show high soil storage percentages. The dominant environmental predictor is the topographical position of the site with reference to the hydrological process of soil storage in the vadose zone.

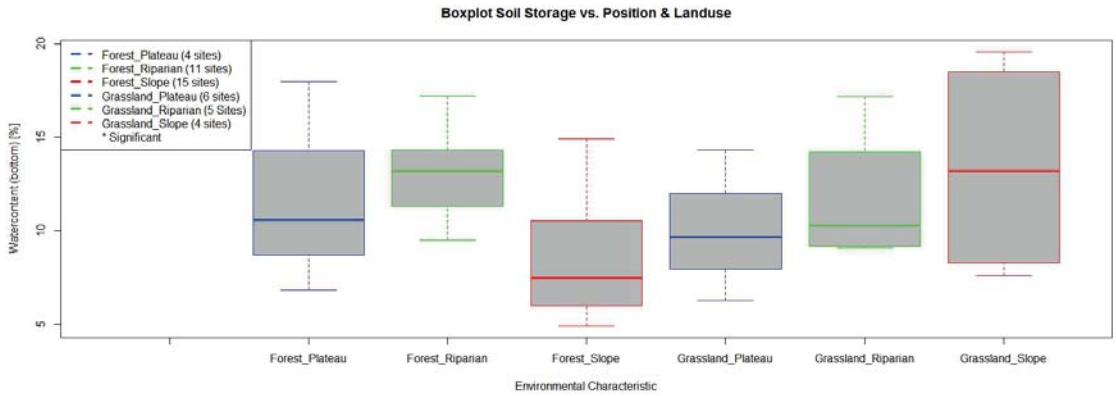

Figure 3.23: The gravimetrical water content in [%] of the bottom (from -1,2 [m] until the end of the profile) of each depth profile of each site belonging to the plateau (red box), the riparian (blue box) or the slope (green box) area they are further subdivided into groups of the different land use classes which additionally expresses the influence of the land use on the process of soil storage.

3.3.7 Recharge

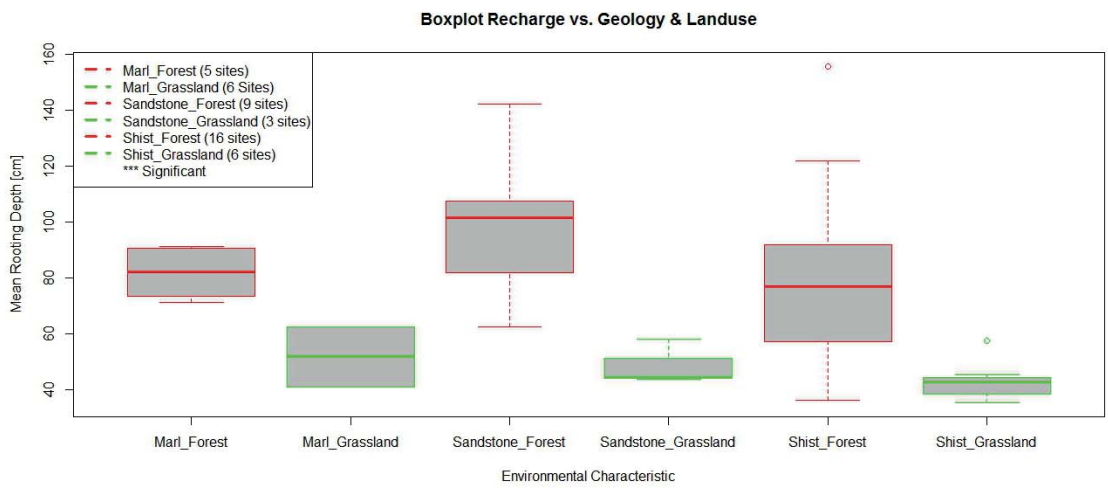

Figure 3.24: Mean rooting depth [cm] of each site belonging to either the riparian, the slope or the plateau area. They are further subdivided into groups of the different land use classes which additionally expresses the influence of the predictors land use and topographical position on the process of recharge of soil pore water into the aquifer.

Figure 3.24 presents the interrelation between the hydrological process of recharge

of soil pore water into the aquifer and the geological media as well as the land use class of each site. It becomes apparent that the sites in the forest all have greater rooting depths and therefore show less recharge compared to the sites which belong to a grassland. Further there is no significant relation between the geology and the process of recharge. The grassland areas tend to have extreme high percentages of canopy, therefore there is a significant correlation of the canopy status and the degree of recharge at a site (see appendix). The deeper the rooting depth the lower the recharge and vice verse. This correlation is not expressed with the data within the marl area, just the data within the shist and the sandstone area shows this correlation.

Chapter 4

Discussion

4.1 Measuring Methods Comparison

There is a small bias of the isotopic signal towards more depleted values when the cryogenic vacuum extraction method is used. This could be due to various reasons. As the soil material is exposed to the atmosphere for the time when the sub samples are prepared in the laboratory, fractionation due to evaporation of light ^{16}O and ^{1}H atoms can occur. Another reason for this small deviance could be that the isotopic signal in the head space of the bag after the direct equilibrium does not include the correct isotopic signal which is contained in the pore water of the soil material. It could be assumed that the very fine pores especially will keep the heavier ^{18}O and ^{2}H atoms and even mainly lighter isotope signals will result in the water vapor which is measured with the Picarro when using the direct equilibrium method.

4.2 Similarity

Until a certain degree the PSIP methodology can be implicated in order to line out various functional units or groups of similar responding sites in the catchments. The biggest problem is the large range of possible differences regarding the shape of the PSIP. We can establish groups of similar environmental characteristics and we then have to deal with PSIP that are quite similar but also with PSIP which

are not similar at all, although these PSIP belong to the same group. The upper, the middle and the lower part can show similarities or dissimilarities, one has to focus on one of these three parts. There are some PSIP which are very similar in the upper and middle part but are not similar in the lower part or vice verse. The degree of similarity is impossible to measure, an attempt of creating graphs with the measurements which are also used to describe and correlate the sites and their hydrolgical processes did not lead to good graphics which offer an visual comparison. The various hydrological processes and their degree of occurrence at a specific site does vary that much that it is not possible to line out significant similarities in the means of this study approach. If we want to make another approach here we have to work with a smaller range of differences regarding the environment of the sites. An increment of the number of sensor cluster sites also could lead to a progress regarding the implication of the PSIP methodology.

4.3 Evaluation of the Measurements

Table 4.1: Overview of results which are shown and explained in chapter 3 some of the graphs which are not showing significant relations are listed in the appendix. The signal code and the values for the correlation is the same like described in chapter 2 (see Table 2.7).

Characteristic/ Process	Infiltration	Evaporation	Transpiration	Mixing	Dispersion	Soil Storage	Recharge
Geology	***	*	***		**		
Land Use	**			**			***
Position						**	*
Exposition							
Skeleton A [%]		0.3;0.13;0.27	0.26				
Skeleton B [%]		-0.14					
Canopy [%]	0.42	-0.21	-1.9	-0.46	0.77		-0.51; -0.39

Table 4.1 summarizes the results which we worked out with the descriptive statistical analysis. The correlations with the non classifiable variables like the soil skeleton of the A and the B horizon as well as the canopy status are expressed with the correlation values, positive values refer to positive correlations which means the higher the variable the greater the occurrence or impact of the specific hydrological process at the site and vice verse. The environmental characteristics like the type of geology, the land use class or the canopy have a bigger influence on the hydrogical response compared to the ground characteristics like the soil skeleton. This table just summarizes the significant interrelation which we carried out with the models. The goodness of the implication and therefore the goodness and representativeness of the results which were worked out are regulated by the goodness of the measurements which are used to establish the graphs. The evaluation of the usage of the certain measurements for the different processes is discussed below.

Basically we have to be aware of the great uncertainty which goes along with the approach and implication of the PSIP. We can measure the isotopic signal of the precipitation water which is regarded as the only input water. The great variability and the large range of possible effects on the input water has to be considered first. Each drop of precipitation water automatically will start to change the composition isotopically from the moment when it reaches the surface and starts to be a part of the large amount of soil pore water if it does not run off at the surface directly. The best way to interpret the isotope signal is to create a good imagination for the flow path of the soil pore water as a group of water drops which arrived at the same time on the surface. In the wintertime when there is a certain snow cover and rain on snow events can occur the arriving water first mixes with melting water in the snow layer and therefore dramatically will have changed its composition isotopically when this water starts to infiltrate into the unsaturated zone. The interaction of the winter precipitation as snow or rain with the preexisting snow cover leads to a great possible variance which literally escapes the measurability of the input isotopic signal. Further the great complexity and interaction between the hydrolgical processes like mixing, evaporation and dispersion in the upper vadose zone leads to a second great intervention of the isotopic signal which originally started to infiltrate

into the ground. After all these great uncertainties regarding the origin of the soil pore water there are several uncertainties which belong to the measuring method and basically the sampling in the field. The air temperature, loss or gain of material during the sampling, the transport, the storage until the measurement is established in the laboratory the on going processes during the field work campaign and many more factors lead to a certain range of possible errors which have to be considered when we are interpreting the results. Another great difficulty lies in the detection of flux rates via the PSIP, as the mixing with older soil pore water and the influence of raising and falling groundwater levels leads to an elution or a loss of the isotopic signal in deeper parts of the PSIP which not allows to detect a recharge rate due to for example the detection of the second PPW which could belong to the winter precipitation of the years 2012/ 2013. We literally deal with a great uncertainty which has to be considered when trying to find suitable measurements which should describe the degree of a certain process at a specific site.

4.3.1 Infiltration

The measurement for the process of infiltration is without any doubt the best most accurate measurement in order to describe the process of the infiltration in the upper part of the soil column as these peak depths refer to values from 20 to 60 [cm.u.g.]. All the sites show this distinctive peak but some sites which belong to ground water influenced areas where the groundwater which is supposed to be isotopically unique throughout the years [O'Driscoll et al., 2005]. The site which are ground- or stream water influenced all show a gleyic B horizon (see Table 2.3) and no peak at all. The shape of the peak differs from site to site, there are vertical or horizontal variations regarding the width and length of the peak. The infiltration is most affected by the type of geology and the type of the land use class, these two predictors have a big influence on the type of soil and therefore on the soil texture, the soil skeleton, the canopy status as well as the topography of the various functional units in the catchment. Whereas the canopy has to be regarded as a predictor which shows a great seasonality and big spatial variability compared to

the other predictors which are taken into account here, the ground characteristics do not change that rapid compared to the environmental characteristics. Another important information which affects interaction between the environment and the hydrological process of infiltration of precipitation water into the unsaturated zone is that vertical percolation is not restricted to low slope angles. Even at a slope angle of about 46 the water can percolate vertically within the soil profile to deeper soil layers [Mueller et al., 2014].

4.3.2 Evaporation

The Deuterium Excess (DExcess) delivers a powerful measurement with reference to the description of the hydrological process of evaporation of soil pore water out of the unsaturated zone and especially out of the upper soil layer. The DExcess values of the PSIP contain information about a certain degree of fractionation which has to be correlated with the process of evaporation of soil pore water. As evaporation mainly is supposed to happen in the upper soil layer the deviance between the mean of the three upper DExcess values and the DExcess values of the rest of the profile should deliver an accurate measurement in order to describe the process of evaporation because there is no other process which influences the DExcess at this position of the PSIP. The mixing and dispersion processes are assumed to have a possible influence on the DExcess values too but do not occur preferentially in the upper soil layer. Descriptive statistical analysis shows that the soil skeleton interacts significantly with the evaporation and has to be seen as most important predictor for that process, if the soil skeleton of the A horizon is big the more evaporation happens at a site. Why do the south facing sites do not show a significant interrelation with the process of evaporation compared to the north facing sites? The lack of importance of the predictor exposition does lead to this result, there is no significant interrelation in the specific graph. This has to have the small number and therefore the small variance of the data belonging to a south- or north facing site. The appendix shows this graph where no significance is expressed.

4.3.3 Transpiration

The transpiration is modeled with the greatest uncertainty regarding the goodness of the measurement in order to describe the process of transpiration. It is assumed that the transpiration does extract light pore water with a small reference and it is also assumed that the transpiration is also happening in the wintertime in a very dimmed way. The problem of the incertitude with reference to the knowledge which soil pore water belongs to which precipitation event forces us to work with the assumption regarding the WPP. In February the evaporation does not have a measurable influence and is negligible, therefore the process of transpiration should show an interaction with the soil pore water. Because of this the deviance of the isotopic signal of the weighted precipitation input data of the month of February and the mean of the isotopic signal of each peak is used as measurement here. This approach contains many error sources and is supported by many assumptions. Therefore this is not an accurate measurement, the results do show some significant interrelations between the geology as predictor and the process of transpiration. However, lack of the knowledge about the interaction between the vegetation and a possible preference of light or heavy soil pore water leads to the limitation of implication of the PSIP methodology in order to describe the process of transpiration. More research belonging to the type of the vegetation is requested in order to improve the implementation of the PSIP methodology in this way.

4.3.4 Mixing

The peak width which is used in order to describe the degree of the process of mixing refers to the vertical extension of the peak in the PSIP. The process of mixing of soil pore water in the unsaturated zone comes along with the gravity and therefore the topography of the catchment, sites without any gradient, sites in the riparian zone and sites which belong to a plateau, should show greater mixing processes than sites which are located at hill slopes. Due to out wash of the isotopic signal because of the mixing process of soil pore water and ground- or stream water the WPP is no longer detectable in the PSIP which leads to a missing measurement for the descriptive

statistic analysis for this specific site, therefore just the canopy shows a significant correlation with the process of mixing (see Figure 3.17). Nevertheless the peak width also is an inaccurate measurement in order to describe the process of mixing because a wide peak can result also due dispersion processes and transpiration processes, this measurement gives a general overview with means of the description of the hydrological process of mixing.

4.3.5 Dispersion

The dispersion of infiltrated precipitation water which is moving slowly through the soil pores due to gravity comes along with the many small preferential pathways this soil pore water can take. The measurement which is used to describe the dispersion is linked with the concentration loss of the WPP in the downwards direction. If there is a very distinctive PEP present in a certain PSIP the dispersion process will lead to a stretching of this signal and vice verse. The problem is that the other processes also affect the shape of the peak and that dispersion is just described in the specific range of the depth profile and not in the upper and lower part of the PSIP. The sites which belong to the forest area show greater dispersion effects than the sites which belong to grassland areas. The results may not be the same if the measurement would have been generated in the upper 25 [cm] of the PSIP. Nevertheless the dispersion is not easy to measure in general [Cheng et al., 2014] and the PSIP do deliver an opportunity which literally has to be evaluated as an acceptable measurement tool for the description of the hydrological process of dispersion of soil pore water in the unsaturated zone at the depths where the specific concentration gradient is determined. It has to be considered that the degree of the dispersion may differ from soil layer to soil layer and therefore we have to be cautious with interpretations which belong to the whole site. But in order to establish a first approach this study shows that it makes sense to implicate the PSIP methodology in that way.

4.3.6 Soil Storage

The process of storage of soil pore water in the unsaturated zone is linked to the topographical position as well as to the parameters which regulate the connectivity along the pores and the volume of the pores itself. Gravity and slow water flux rates are considered to be the most important physical forces which determine the degree of the storage of soil pore water at a site. The water content of the bottom of the PSIP is used as a measurement of the degree of the process of soil storage, this measurement has to be evaluated as very good because there is no other process which affects the moist of the soil material in these positions of the PSIP. Further the interrelation between the topographical position and the soil storage are accurate results because of the logical fluid dynamics in the unsaturated zone due to the gravity. The land use class also affects the process of soil storage, the sites which belong to a forest do show greater soil storage compared to the sites which belong to the grasslands. However this is not true for the sites which belong to a hill slope and a grassland,here a great variance of soil moist values is detected in the bottom of the PSIP.

4.3.7 Recharge

There are several studies which are dealing with the challenging question of how to measure and quantify the recharge into the aquifers of soil pore water from through the unsaturated zone [Nimmo et al., 2006, Cheng et al., 2014, O'Driscoll et al., 2005]. The big difficulty lies in the great complexity of this process due to the great variability of characteristics in the vadose zone [Nimmo et al., 2006]. The best way in order to describe the recharge rate at a specific site would be via a determination of the flux rate in the downer soil column where no more roots appear. This part of the soil column is just effected by the degree of soil storage which happens at the specific site. All the water which will continuously follow the flow path from top to the bottom of the soil column will force the water in the downer area to recharge the aquifer sooner or later. The flux rate is supposed to be spatially and time inconsistent and can not be determined exactly in the limits of this thesis. The

measurement we used for the determination of the degree with which the process of recharge occurs at the specific sites does no deliver any quantifying information on the recharge rate. We just assume that if the rooting depth is deep the less recharge happens because less water generally arrives to the area where the amount of recharge water is stored before literally recharging the aquifer. This is a non quantifying measurement and therefore has nothing to do with the recharge rate. This measurement and the implication of PSIP in order to estimate the degree of recharge at a site can be used as a gross estimation measurement only. The solution lies in the finding of another WPP in the bottom of the PSIP, if we would have found one we would be able to calculate the flux rate via the two WPP. But the isotopic signal is dominated by groundwater in the depth which makes such a detection impossible in our study area. Also the drill depth over 2 [m.u.g] is not easy to achieve with the drill machinery we used.

Chapter 5

Conclusions

The exploitation of soil material through an extraction of 45 soil cores with simple drill machinery and a group of four persons can be done in two weeks of accurate fieldwork. Thus we are able to create (more or less) time independent PSIP of these sites when we assume that the hydrological processes in the unsaturated zone do happen very slowly. Three months of full time laboratory work leads to the creation of 45 PSIP and includes a measuring method comparison in order to validate the measuring methods. Two and a half months of statistical analysis and illustration of everything we made to accomplish this master thesis with great aid of the Software GNU R, Microsoft Excel, Adobe Illustrator CS2 as well as Latex leads to this document. The creation of the PSIP contains a great range of possible error sources from the time the samples are taken in the field until the final measurement of the equilibrated soil pore water vapor in the head space of the bag is measured in the laboratory, all these errors belong to the fractionation and thus to a loss of the original isotopic signal of the soil pore water. Nevertheless we are able to measure certain isotopic compositions of the soil pore water which have to be calibrated with reference to the GMWL after the measurements. The calibrated data is to be used for the generation of the PSIP. As long as one stays with the same work routine in the filed and the same measuring machinery the final measuring error which is finally not exclusionary and determinable will remain the same in all measurements. And thus does not effect the results because mainly the shapes of the PSIP are

used in order to find the process describing variables which are used to establish the descriptive statistics. The hypotheis of this thesis have been: (i) Similarities in the shape of PSIP taken at different sites show that the hydrological processes at these sites are similar. (ii) If the environmental characteristics of a location are similar the local hydrological response shows a similarity too and therefore the shape of the PSIP belonging to these sites also show similarity. (iii) There are specific environmental characteristics which influence the local hydrological processes more than others. Hypothesis (i) and (ii) are not true. The shape of the PSIP is affected by a big range of processes and a comparison of the whole PSIP shape does not refer to similar hydrological responses in the unsaturated zone at various sites which show similar PSIP and vice verse. Just parts of the PSIP have to be considered when trying to find out site similarities, maybe a smaller range of different characteristics paired with more sites will lead to better results regarding this research topic. Hypothesis (iii) is true, the PSIP offer a great opportunity to figure out the dominant environmental or ground characteristics which play the biggest role regarding the various hydrological processes in the vadose zone. Table 4.1 summarises all findings belonging to this hypothesis. However, the goodness of the used variables which are supposed to describe the degree of appearance of a process regulates the meanings of the results. And thus this approach has to be discussed, improved as well as evaluated by more research and further implication in the same way. Nevertheless this implication of the PSIP methodology leads to great insights regarding the very complex interrelations of the hydrological processes in the vadose zone and their affecting environmental or ground site characteristics. Future research has to focus on the development of a quicker way to determine the isotopic composition directly in the field. Further the PSIP analysis has to be implicated within more and more catchments with similar and also new approaches for the statistical analysis referring to the shape of the PSIP in order to be able to work out and understand the behavior of several functional units in the catchments.

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Appendix A

Additional Information

This appendix includes additional documents which help the interested reader to see better for instance how the environments of the sites were analysed during fieldwork or how the soil texture is determined. Further there are more graphs illustrated which include more results which do not show any significance or are not seen to be worth to explain in the text but these graphics still show some important interrelations. All the data and the programming codes are on the CD which comes together with the printed document of the thesis.

Cluster:

Datum	
Bearbeiter	
Wetter	
Ohne Regen seit	
Exposition	
Lage im Relief	
Nutzungsart	
Bedeckungsgrad [%]	
Bodenorganismen	

Wurzeltiefe [cm u. GOK]	
Stauende Bereiche	
Feuchte Bereiche	

Tiefe Borhloch [cm u. GOK]	
Bohrkernlänge [cm]	

Tiefe 1. Bohrung	
Bohrkern 1. Bohrung	
Tiefe 2. Bohrung	
Bohrkern 2. Bohrung	
Tiefe 3. Bohrung	
Bohrkern 3. Bohrung	

Gestörte Probe aus den Horizonten	
Bemerkungen	

Horizont	Tiefe [cm]	Bodenfarbe	Hydromorphie	Wurzeln	Bodenart	Skelettanteil [%]	Sonstiges

Figure A.1: The environmental characteristics are written down on this document during fieldwork.

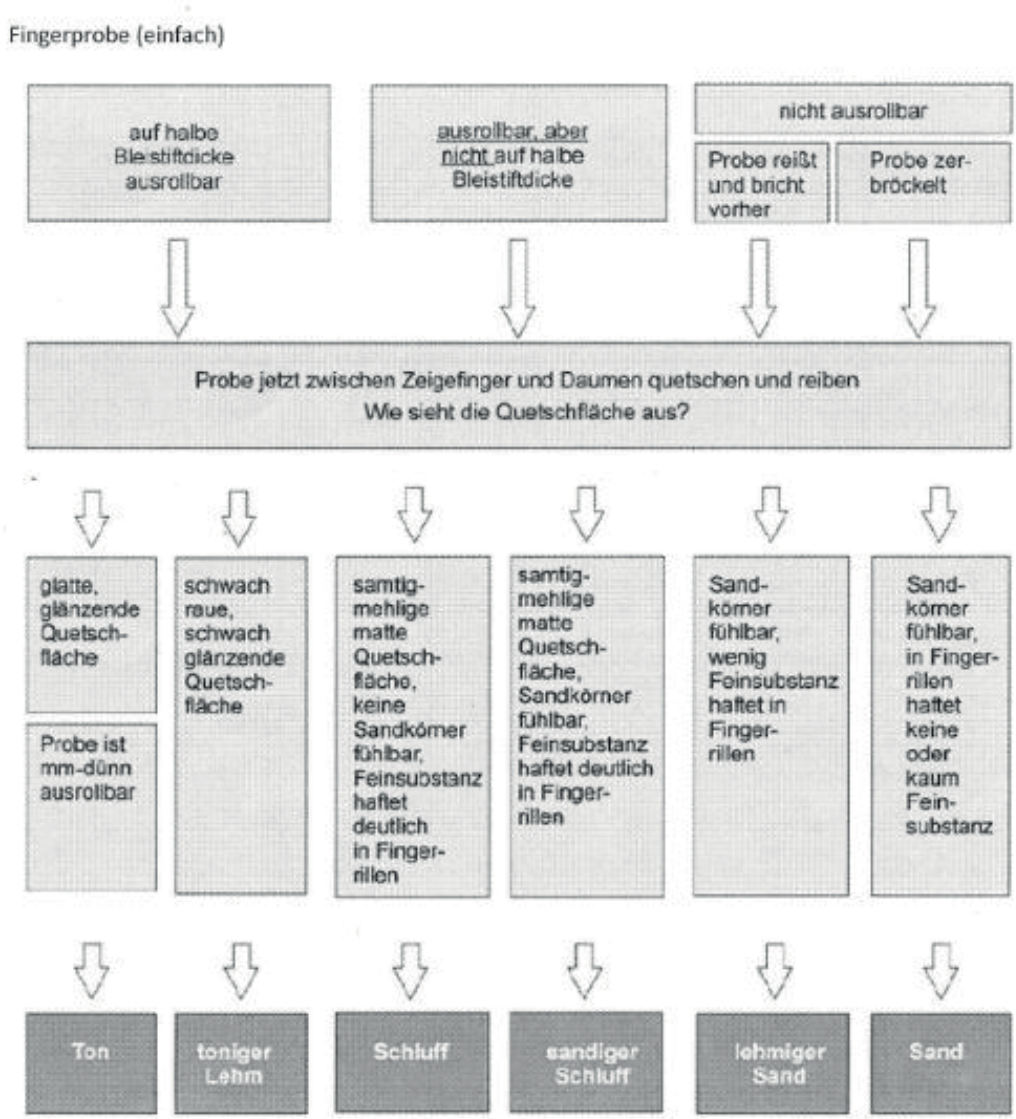

Figure A.2: The determination of the soil texture is done after this approach, it is just an easy way to describe the soil texture.

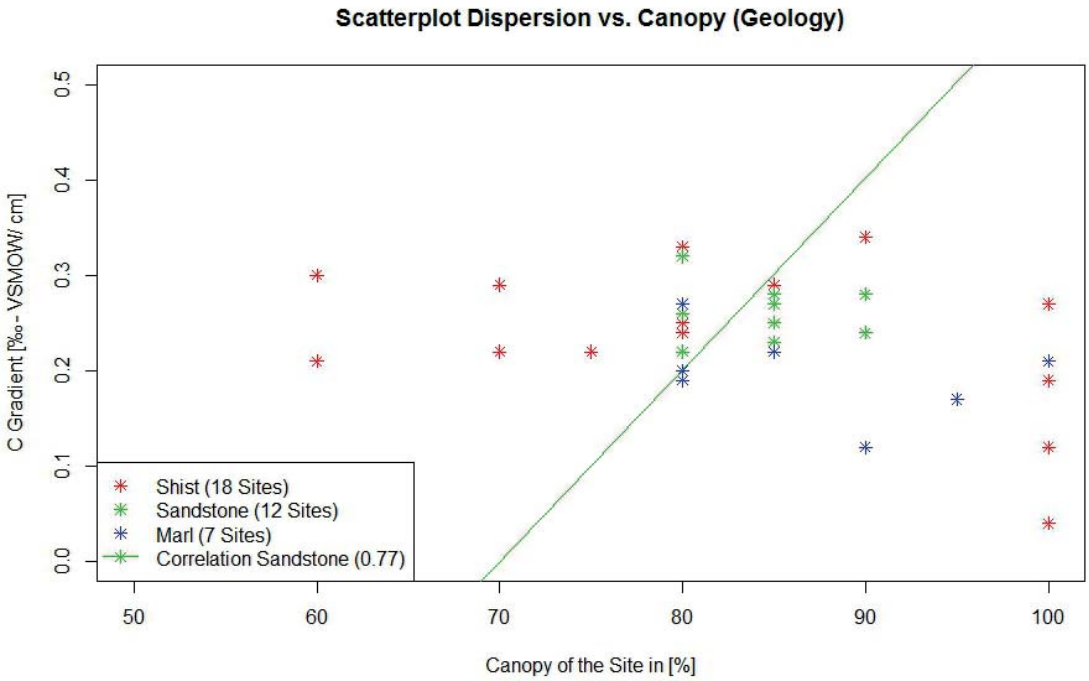

Figure A.3: The dispersion [[‰]/[cm]] of the soil pore water generated via the peak extension of the δ^2H - PSIP of each site belonging to either to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The canopy status [%] of each site was determined in the field when doing the drills in June 2014, a regression line is drawn in order to describe the trend of the correlated data dots of the sandstone area (green line), correlation value is expressed in the legend of the plot.

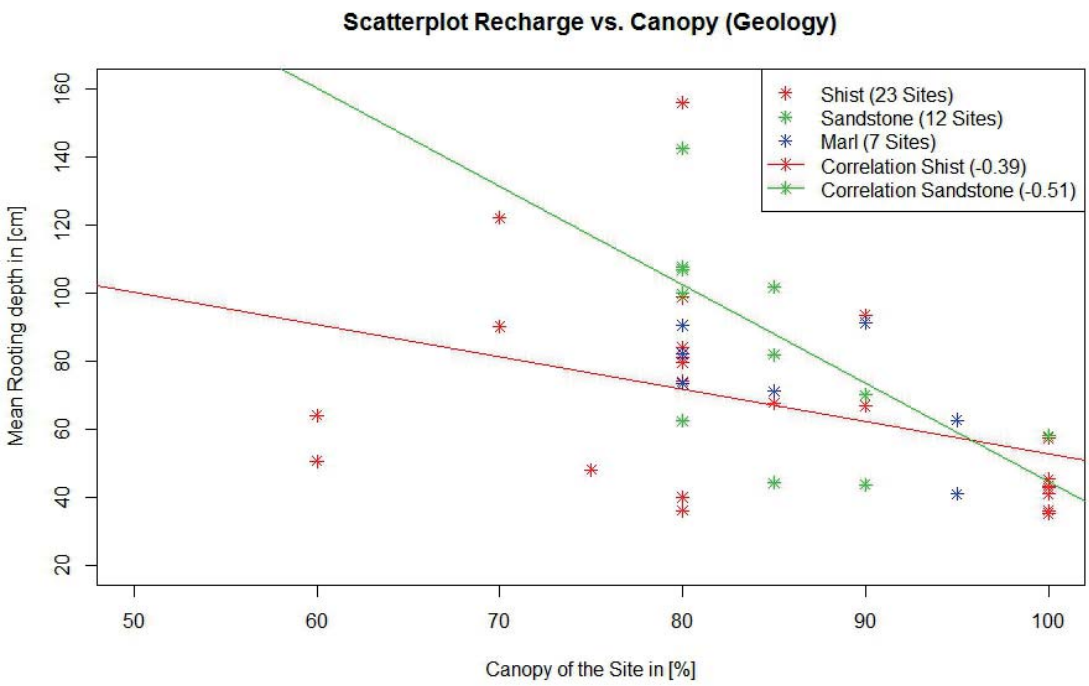

Figure A.4: Mean rooting depth [cm] of each site belonging to either the marl (blue stars), the sandstone (green stars) or the shist (red stars) area. The canopy status in [%] of each site was determined in the field when doing the drills in June 2014, two regression lines are drawn in order to describe the trend of the correlated data dots of the sandstone area (green line) and the shist area (red line), the correlation values are expressed in the legend of the plot.