

Utilizing stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) to study soil-water origin in a sloped vineyard: first results

Kovač, Zoran; Krevh, Vedran; Filipović, Lana; Defterdarović, Jasmina; Buškulić, Patricia; Han, Luka; Filipović, Vilim

Source / Izvornik: **Rudarsko-geološko-naftni zbornik, 2022, 37, 1 - 14**

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

<https://doi.org/10.17794/rgn.2022.3.1>

Permanent link / Trajna poveznica: <https://um.nsk.hr/um:nbn:hr:169:229233>

Rights / Prava: [Attribution 4.0 International](#)/[Imenovanje 4.0 međunarodna](#)

Download date / Datum preuzimanja: **2024-07-30**



Repository / Repozitorij:

[Faculty of Mining, Geology and Petroleum Engineering Repository, University of Zagreb](#)



Utilizing stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) to study soil-water origin in a sloped vineyard: first results

Rudarsko-geološko-naftni zbornik
(The Mining-Geology-Petroleum Engineering Bulletin)
UDC: 556.3
DOI: 10.17794/rgn. 2022.3.1

Original scientific paper



Zoran Kovač¹; Vedran Krevh²; Lana Filipović²; Jasmina Defterdarović²; Patricia Buškulić¹; Luka Han²; Vilim Filipović²

¹ University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, Zagreb

² University of Zagreb, Faculty of Agriculture, Svetošimunska cesta 25, Zagreb

Abstract

The diversity of processes taking place in hillslope agro-ecosystems makes the estimation of vadose zone dynamics rather challenging. This paper presents the first insight into the research of volumetric water content, granulometric composition, meteorological data, precipitation and soil-water isotopic composition conducted within the SUPREHILL project at its vadose zone observatory. The main goals of this research are related to the evaluation of soil-water origin at the hillslope vineyard, but also to the estimation of depths until which precipitation infiltrates and where the occurrence of preferential flow is possible. For that purpose, hydrometeorological data, granulometric composition and stable isotopes of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) from precipitation and sampled soil water have been used. The results indicate the existence of a different isotopic signature in soil water, which suggests different infiltration patterns in the investigated area. Also, the results point out that surface runoff, subsurface runoff, and most of the passive wick lysimeters respond to precipitation, while the response of suction probes located at deeper depth is not that evident. This corresponds to the results related to the variation of water content at different depths. All the results indicate the possible existence of a low permeable layer at an approximate depth of 60 cm. Furthermore, preferential flow, if it exists, can be expected from the shallowest depths of the vineyard to a maximum depth of 80 cm. It is expected that an established long-term monitoring network at the SUPREHILL Observatory will give a more precise definition of soil-water behaviour and the existence of preferential flow.

Keywords:

soil-water behaviour; precipitation infiltration; stable isotopes of water; hillslope vineyard; vadose zone

1. Introduction

Soil vadose zone research is crucial for understanding and modeling of hydrological processes at a larger scale (Spraeuger et al., 2016; Wong et al., 2017). The diversity of processes taking place in hillslope agricultural sites makes the estimation of vadose zone dynamics in such an ecosystem rather challenging due to a variety of processes occurring within (surface runoff, vertical flow, erosion, subsurface preferential flow, nonlinear chemical behaviour, crop uptake, evapotranspiration, etc.). Additional complexity of the hydrology of hillslope agro-ecosystems is caused by the intensity of management, the effects of erosion, tillage, crop, or compaction caused by trafficking (Bosch et al., 2012; Rodrigo-Comino et al., 2019; Tarolli and Straffelini, 2020), among others. Factors as terrain inclination and soil structural development shape soil properties and its horizons, and consequently the distribution of water and solute fluxes at hillslope landscapes (Filipović et al.,

2018; Rieckh et al., 2012). A closer look at these factors can uncover processes that govern water dynamics and redistribution in agro-ecosystems.

Usually, two types of water are distinguished: bulk water and mobile water. Some research showed that bulk water can be affected by the evaporation process, while mobile water is generally related to the infiltration of precipitation (Goldsmith et al., 2012; René Brooks et al., 2010; Sprenger et al., 2017). The precipitation infiltration in soil presents a very complex process which is affected by numerous soil properties, i.e. soil structure, soil texture, soil moisture and degree of heterogeneity. In general, this process can be described as preferential or piston flow, where preferential flow presents channelled water that flows through more permeable pathways, while piston flow is more related to the water from recent precipitation which forces the already present water to flow downward (Gazis and Feng, 2004). Vertical preferential flow describes soil conditions where the vertical movement of water is much higher in a small fraction of the total volume of soil than in the rest, which greatly affects the transport of solutes in agro-ecosys-

Corresponding author: Vedran Krevh

e-mail address: vkrevh@agr.hr

tems (Jarvis, 2007). On the other hand, lateral preferential flow often occurs when percolating water in a soil profile encounters a hydrologically restrictive layer which can deliver a substantial amount of water downslope. This process may be initiated during intensive rainfall events, above the impeding soil layer or a soil profile with contrasting textures or a low-permeable layer at the hillslope (Scherrer et al., 2007), while the development of macropores across the hydraulically restrictive layer of the subsoil during the year adds further complexity (Guo et al., 2014). Local scale studies of soil-water processes have the potential to improve the understanding of agricultural areas that have restrictive subsoil layers and thus to improve the management system (Jung et al., 2014).

Various methods are used and combined for the quantification of soil-water interaction in the vadose zone. However, combining methods is necessary to unlock their full potential. Unsaturated zone investigation commonly employs time-domain reflectometry (TDR) data for diagnostic and monitoring purposes, due to its high accuracy and relatively low implementation costs, while having the capability of carrying out continuous real-time measurements, often in high temporal resolution (Persico et al., 2019). Furthermore, it has been shown that sensor performance can vary at different soil depths and soil water contents (Marković et al., 2015). While sensor data carries valuable information, direct measurements of water fluxes often provide more in-depth results, which cannot be captured with sensors alone. Lysimeters are commonly used for this kind of measurements, where a quantity of drainage volume is measured over time. There are various types of lysimeters depending on the purpose of the research. Passive wick lysimeters maintain tension in soil by using an inert wicking material, which is typically fiberglass, and are considered as a compromise between expensive and demanding equilibrium lysimeters and less accurate pan lysimeters (Gee et al., 2009). Along with lysimeters, instruments with suction cups are often employed for sample collection, due to their advantages such as the installation process or leaving the soil profile negligibly disturbed (Grossman and Udluft, 1991). Mentioned instruments can also be accompanied with surface and subsurface runoff measuring devices (Stewart et al., 2015), especially on hillslopes for a full hydrology component insight.

In numerous studies related to the soil and unsaturated zone, stable isotopes of hydrogen and oxygen ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) have provided very useful information in the evaluation of soil-water dynamics and modeling at different scales (Knighton et al., 2017; Rothfuss and Javaux, 2017; Sprenger et al., 2017, 2018). Also, results of other research showed that macropore flow can have different isotopic signature from the precipitation, i.e. that subsurface flow can be presented by a mixture of event and pre-event water. (Kelln et al., 2007). Further-

more, it has been shown that preferential flow can be identified by high variability of water isotopic composition at different depths, but also in time and space (Peralta-Tapia et al., 2015; Song et al., 2011), but also that mixing between soil matrix and macropore flow is possible (Sprenger et al., 2016) and that water isotopes of mobile and bulk water are likely to be more different the drier the soil becomes (Sprenger et al., 2018). Some research observed that isotopic composition depends on field capacity and soil water content (Berry et al., 2018), while other suggested that second order parameter used in isotope hydrology, i.e. d-excess, can be a better tracer for evaluating mean residence time of soil water and recharge processes (Lee et al., 2007). Although different kind of research has been done, (Newberry et al., 2017) pointed out that are still a lot of things to be explored to explain main differences between isotopic composition between soil bulk and mobile water. In the wider research area, the usage of stable isotopes of oxygen and hydrogen from water were used mostly for the definition of groundwater-surface water interaction (Parlov et al., 2019) and determination of long-term isotope records of precipitation (Krajcar-Bronić et al., 2020). Additionally, stable isotopes of nitrogen and oxygen from nitrate were used to define nitrate origin and main processes which take place in the Zagreb aquifer (Kovač et al., 2018). Although stable isotopes were used in wider research area, it must be emphasized that stable isotopes of water have never been used in the wider area of the City of Zagreb to define water origin in the hillslope vineyard, i.e. the agricultural slope area.

Within this paper, we present the first results from the SUPREHILL Observatory related to the research of volumetric water content, granulometric composition, meteorological variables and stable isotopes of hydrogen and oxygen in precipitation and soil water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) which were used to evaluate origin of soil water origin and precipitation infiltration in the observed period, as well as an assessment of the depths at which the occurrence of preferential flow is possible in the agricultural sloped area. Furthermore, although not related to the objectives of this paper, these data will be used for the definition of initial and boundary conditions which will be used in the modeling of soil water dynamics in future research.

2. Materials and methods

2.1 Investigated area

The investigations were conducted at the SUPREHILL vadose zone observatory (<https://sites.google.com/view/suprehill/>) on an agricultural sloped area, within the experimental field Jazbina (45°51'24"N 16°00'22"E; **Figure 1**). The average annual precipitation of the investigated area (1970-2020) is 856.5 mm, while the average annual air temperature is 11.2°C. The

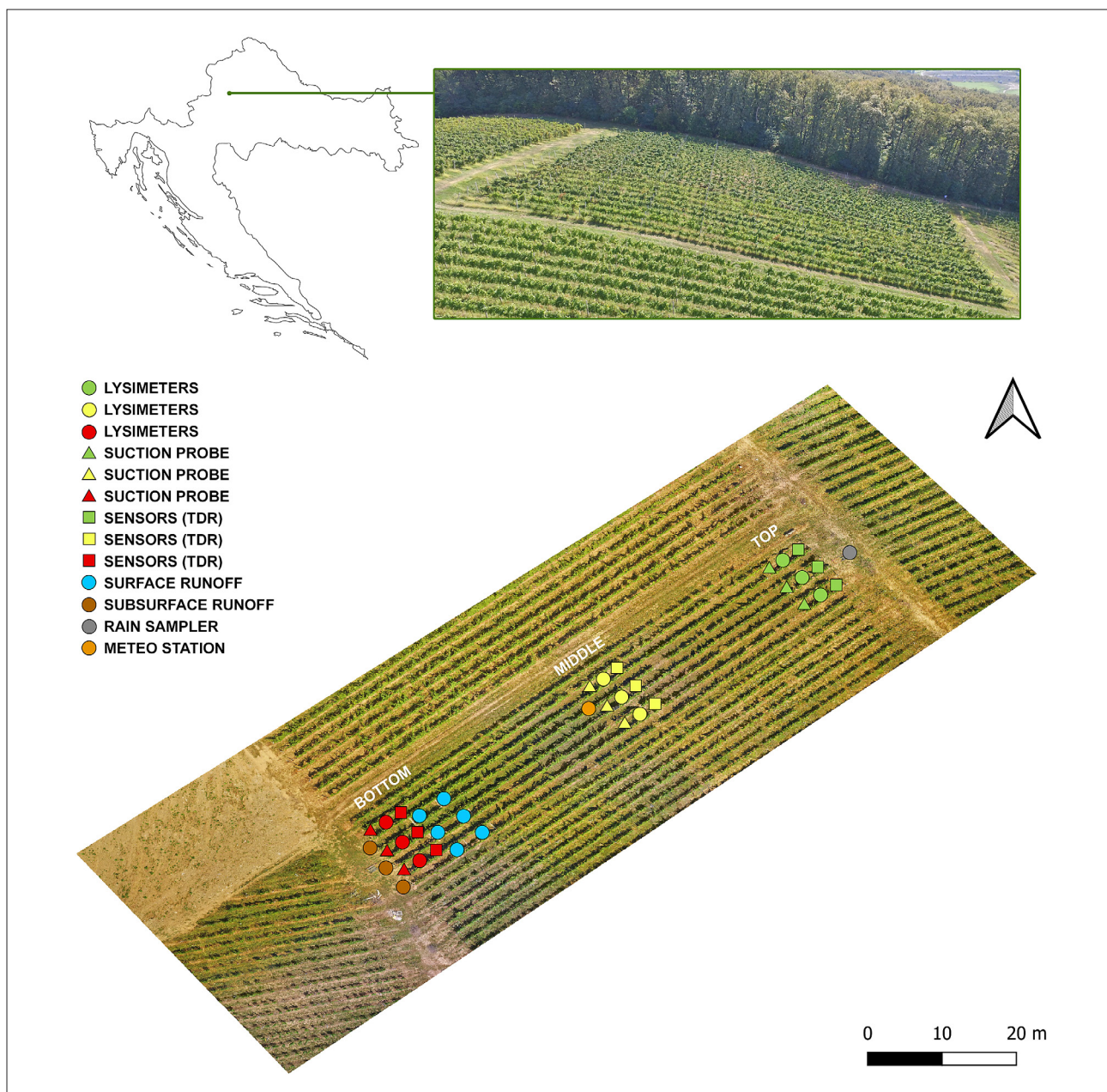


Figure 1: Location of the established the SUPREHILL Observatory (Croatia), aerial photo of the site and scheme of the installed equipment throughout the hillslope

observatory is located on a hillside with southwest exposition, with vineyard rows oriented along the slope. The hillslope is divided into three zones - top, middle and bottom. The sloping at the top is 15%, while the middle and bottom are steeper, with a 25% slope. The 15-year-old vineyard has an in-row distance between the vines of 1 m, and an inter-row grass-covered zone of 2 m.

2.2 Hydrological monitoring

For the measurement of near surface drainage in the vadose zone, passive wick lysimeters were used. They were installed at a 40 cm depth, at the top, middle and bottom of the hillslope, four per row, in three repetitions

(vineyard rows), counting 36 in total. Lysimeter dimensions are 250 x 250 x 40 mm. The surface of the lysimeter is covered with a filter mesh to prevent clogging, while inside the lysimeter, a fiberglass wick is placed. For water sampling in the deeper layers, suction probes (UGT Umwelt-Geräte-Technik, Germany) with a ceramic cup were installed 1 m below ground level at the top, middle and bottom of the hillslope, in three repetitions (vineyard rows). For the purpose of surface water runoff investigation, a self-constructed instrument was installed at the bottom of the hillslope (2 x 2 m) in three repetitions (vineyard rows), in pairs (counting 6 in total). For subsurface runoff collection a self-constructed instrument was installed 60 cm below ground level in

three repetitions (vineyard rows). TDR sensors were (TEROS 10 / TEROS 12, METER, USA) installed at the top, middle and bottom of the hillslope in three repetitions at 20, 40, 60 and 80 cm depth and measured on an hourly basis. For the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of cumulative precipitation samples, a rain collector RS-1 (Palmex Ltd, Croatia) whose design allows evaporation-free rain sampling (Gröning et al., 2012) was installed at the top of the hillslope at 1 m above ground. Meteorological data, measured in a 15-minute interval is acquired from a meteorological station (ATMOS41, METER, USA) installed in the middle position of the hillslope at a 2 m height.

2.3 Methods

Water isotopic composition ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) from precipitation and soil water was determined by laser absorption spectroscopy at the Laboratory for spectroscopy of Faculty of Mining, Geology and Petroleum Engineering (Los Gatos Research laser LWIA-45-EP). All values are expressed in ‰ notation relative to VSMOW (Vienna Standard Mean Ocean Water) with uncertainty of 0.9‰ for $\delta^2\text{H}$ and 0.19‰ for $\delta^{18}\text{O}$. The data were analyzed using the Laboratory Information Management System (LIMS for lasers; (Coplen and Wassenaar, 2015)). Within this paper, the first four sampling campaigns were taken for the evaluation of water isotopic composition (7.12.2020., 18.12.2020., 7.1.2021. and 25.1.2021.). Water isotopic composition was evaluated in three steps. In the first step, basic statistic parameters have been calculated and examined. In the second step, data was compared to the Global Meteoric Water Line (GMWL) and the newest Local Meteoric Water Line (LMWL) for the City of Zagreb (Krajcar-Bronić et al., 2020), while in the third step, isotopic data was evaluated in time.

Disturbed soil samples from the observatory were taken from three soil depths (0 – 30, 30 – 60, 60 – 90 cm) at each position (top, middle, and bottom of the hillslope) in three repetitions (27 samples in total), for granulometric soil composition analysis (HRN ISO 11277:2004). Based on the granulometric soil composition results, soil layers have been classified with the United States Department of Agriculture (USDA) soil classification system (USDA, 1999).

Evapotranspiration is part of the hydrologic cycle which, depending on the geographic location, can contribute to the water budget from a few percent up to the majority of water (Bernier, 2020). It has been shown that evapotranspiration dynamics can affect travel times related to water percolation through an unsaturated zone (Heße et al., 2017; Sprenger et al., 2016). Furthermore, some research showed that in a relatively low energy environment, temporal variability of isotopic enrichment in soil water was driven by changes of soil evaporation over the year (Sprenger et al., 2017). Within this study, Reference evapotranspiration has been calculated based

on the meteorological data via Penman-Monteith (Allen, 2004):

$$ET_o = \frac{0.408\Delta(Rn - G) + \gamma \frac{900}{T + 23} u_2 (e_s - e_a)}{\Delta + \gamma(1 + 0.34u_2)} \quad (1)$$

where ET_o is the reference crop evapotranspiration [mm day^{-1}], Rn is the net radiation at the crop surface [$\text{MJ m}^{-2} \text{day}^{-1}$], G is the soil heat flux density [$\text{MJ m}^{-2} \text{day}^{-1}$], T is the air temperature at 2 m height [$^{\circ}\text{C}$], u_2 is the wind speed at 2 m height [m s^{-1}], e_s the saturation vapour pressure [kPa], e_a is the actual vapour pressure [kPa], $e_s - e_a$ is the saturation vapour pressure deficit [kPa], Δ is the slope vapour pressure curve [$\text{kPa } ^{\circ}\text{C}^{-1}$], and γ is the psychrometric constant [$\text{kPa } ^{\circ}\text{C}^{-1}$].

Statistical data analysis was carried out in SAS (Statistical Analysis Software, SAS Institute Inc., Version 8.3 Update 1, Cary NC USA, 2019-2020). One-Way ANOVA was used for the separate analyses of variance for outflows measured in passive wick lysimeters with the position at the hillslope as an independent variable. A significant difference between the average values was determined with Tukey test (Tukey's Range Honest Significant Difference - HSD Test) at $p < 0.05$. The statistical parameters used were mean, minimum, maximum value, standard deviation, standard error, variance, coefficient of correlation, coefficient of variation (%). Box-plots were produced for the visual statistical representation of d-excess values.

3. Results and discussion

3.1 Hydrometeorological data

Over the investigated period (01.12.2020.-25.01.2021.) passive wick lysimeters captured average cumulative leachate (out of 12 lysimeters per position) of 28.9, 19.8 and 21.9 L, at the top, middle and the bottom of the hillslope, respectively. The highest amount of cumulative volume measured at the top positioned lysimeter is possibly influenced by sloping, as the top position has the mildest slope (15%). Average cumulative values for surface (out of 6 instruments) and subsurface runoff (out of 3 instruments) were 286.2 and 414.2 L, respectively (see Figure 2). Regarding the meteorological data, 150.2 mm of precipitation was measured in the researched period while temperature varied between -5.7 to 14.2°C , with 3.2 as average temperature. Low cumulative reference evapotranspiration is assumed during the period (23.1 mm), with 0.4 mm as a daily average (see Figure 3), which suggests that evapotranspiration has minor to no influence on the soil-water dynamics in the observed period.

A statistically significant difference in the volumes of the passive wick lysimeters in relation to their position on the hillslope was found between the top (4.1 L) and middle (2.89 L), while the volume of the near surface

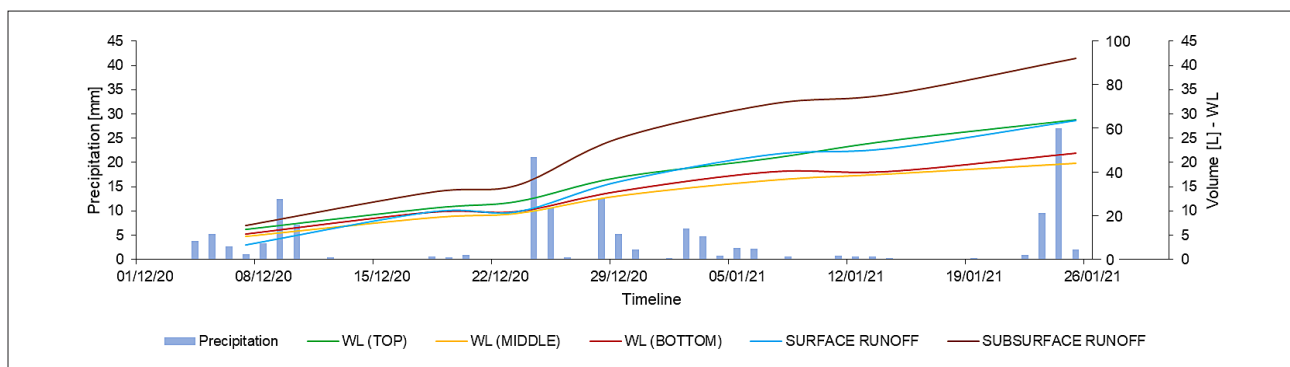


Figure 2: Average measured values of passive wick lysimeters (WL), surface runoff instruments (SR) and subsurface runoff instruments (SS) [L] in regard to the position on the hillslope (top – A, middle – B, bottom – C) for the period 01.12.2020 – 25.01.2021. at the SUPREHILL Observatory

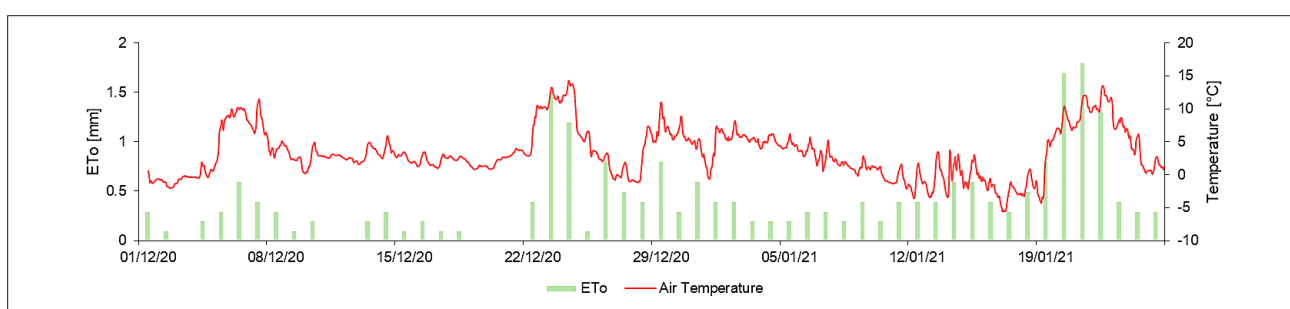


Figure 3: Reference evapotranspiration (ET_0 [mm]) and air temperature [$^{\circ}C$] for the period 01.12.2020 – 25.01.2021. at the SUPREHILL Observatory

drainage water on the bottom (3.29 L) did not significantly differ from the top or middle of the hillslope. The highest measured volume was found at the top of the vineyard, while the lowest value was found at the middle (see **Table 1**).

Table 1: Results of the One-way ANOVA statistical analysis of measured volume in the passive wick lysimeters (WL) in regard to the position on the hillslope (top, middle and bottom) for the period 07.12.2020 – 25.01.2021. at the SUPREHILL Observatory

Position	Mean	SD	SE	V	Max
	[L]				
Top	4.12 a	2.35	0.26	5.52	10.75
Middle	2.89 b	2.29	0.25	5.23	7.4
Bottom	3.29 ab	3.11	0.34	9.96	10

Average values marked with the same letter are not significantly different at $P < 0.05$

3.2 Granulometric soil composition analysis

In **Table 2** the results of the granulometric soil composition analysis are presented. The analysis revealed that the percentage (%) of fine silt fraction (particle size 0.02 – 0.002 mm) and coarse silt (0.063 – 0.02 mm), at the soil layer of 0 – 30 cm is the highest (42.7 and 32.3%, respectively) at the bottom, in respect to all depths and

positions at the hillslope. The mentioned values correspond to silt erosion often occurring at hillslopes (**Am-pontuah et al., 2006**), while there is a decreasing trend in both coarse and fine silt amount in relation to depth, in all positions. Furthermore, there is also a decreasing trend present in clay amount (< 0.002 mm), complementary in relation to slope elevation, while the amount of clay at each position increases in regard to the soil depth. The least amount of clay (18.3%) is found at the bottom of the hillslope at soil layer 0 – 30 cm and the highest (32.3%) at the top in soil layer 60 – 90 cm. Low clay soils are more prone to erosion by water due to their high degree of cohesiveness and instability and mentioned is in line with the findings for silt amount. Highest amount of sand, both coarse (11%) and fine (5.7%) was found at the middle of the hillslope soil layer 60 – 90 cm. Based on USDA soil classification, all soil layers are considered silt loam, with the exception of soil layers 60 – 90 cm at the top and middle of the hillslope, as they are classified as silty clay loam.

3.3 Volumetric water content

The highest average soil water content ($0.41 \text{ cm}^3 \text{ cm}^{-3}$), out of all measured series throughout the investigated period, was found at the bottom of the hillslope at the depth of 40 cm, while the lowest average soil water content ($0.34 \text{ cm}^3 \text{ cm}^{-3}$) was found at the top at the depth of 60 cm (see **Figure 4**). In relation to the depth of installa-

Table 2: Granulometric soil composition analysis results taken at three depths (30, 60 and 90 cm) at the SUPREHILL Observatory with the USDA soil classification

Position	Depth [cm]	Coarse sand	Fine sand	Coarse silt	Fine silt	Clay	Soil classification based on USDA
		2 – 0.2	0.2 – 0.063	0.063 – 0.02	0.02 – 0.002	< 0.002	
[mm]							
Top	0-30	1.7	4.0	31.7	39.3	23.3	silt loam
	30-60	1.3	3.3	30.7	38.3	26.3	silt loam
	60-90	3.7	3.7	25.3	35.0	32.3	silty clay loam
Middle	0-30	2.7	4.0	30.3	39.7	23.3	silt loam
	30-60	3.7	4.7	30.3	37.0	24.3	silt loam
	60-90	11.0	5.7	23.7	32.3	27.3	silty clay loam
Bottom	0-30	3.0	3.7	32.3	42.7	18.3	silt loam
	30-60	3.0	4.0	32.0	40.0	21.0	silt loam
	60-90	2.7	3.7	30.7	37.0	26.0	silt loam

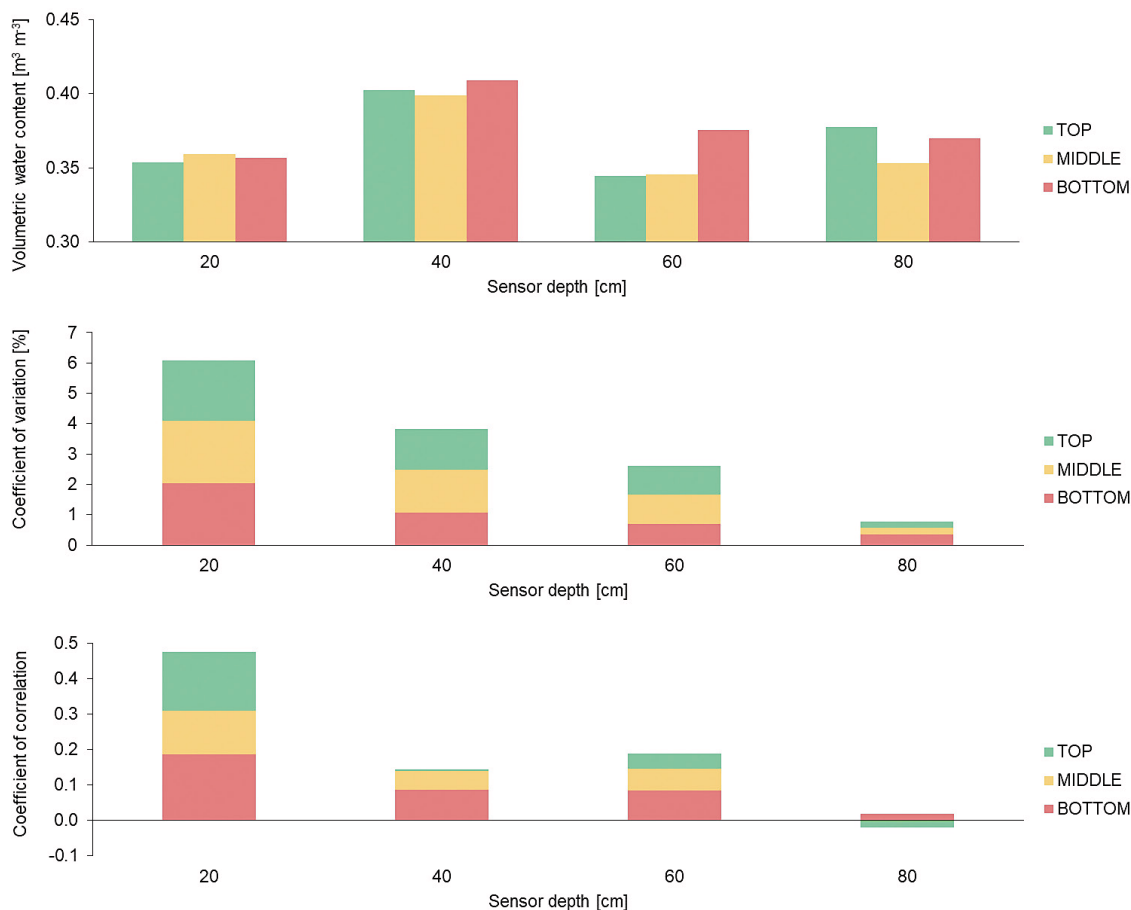


Figure 4: Average volumetric water content (TDR), coefficients of variation and coefficients of correlation data (compared with precipitation) in relation to the position on the hillslope (top, middle, bottom) and installation depth (20, 40, 60 and 80 cm) for the period of 01.12.2020-25.01.2021 at the SUPREHILL Observatory

tion throughout the hillslope, the highest water contents were found as well at the depth of 40 cm ($0.40 \text{ cm}^3 \text{ cm}^{-3}$) on average, while the lowest were found at the depth of 60 cm ($0.36 \text{ cm}^3 \text{ cm}^{-3}$). Considering the fact that soil compression in soils with moderate texture is highly probable, based on the agricultural system, granulomet-

ric analysis and TDR data, there is a reasonable concern of compression occurrence at the site, ultimately leading to a low-permeable soil layer, similar found in (Brouwer and Fitzpatrick, 2002) and possibility of one below 40 cm which would contribute substantially in the sub-surface flow. Furthermore, (Fox and Wilson, 2010)

Table 3: Results of the descriptive statistical analysis with statistical parameters of isotopic water composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and d-excess) measured in passive wick lysimeters in regard to the position on the hillslope (top, middle and bottom) for the period 07.12.2020 – 25.01.2021. at the SUPREHILL Observatory

	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
	$\delta^2\text{H}$ in [‰]			$\delta^{18}\text{O}$ in [‰]			d-excess in [‰]		
MEAN	-51.1	-51.6	-53.2	-8.1	-7.9	-8.2	13.4	12.0	12.3
MED	-51.9	-51.8	-52.3	-8.1	-8.0	-8.1	13.1	11.7	12.3
MIN	-67.0	-68.9	-73.3	-9.8	-10.1	-10.6	11.0	10.3	10.1
MAX	-35.7	-38.6	-39.7	-6.4	-6.4	-6.6	18.5	13.7	14.5
SD	6.5	6.1	7.0	0.8	0.8	0.9	2.0	1.0	0.9
CV (%)	-12.8	-11.9	-13.1	-9.5	-9.5	-10.4	15.2	8.6	7.6

Table 4: Results of the descriptive statistical analysis with statistical parameters of isotopic water composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and d-excess) measured in suction probes in regard to the position on the hillside (top, middle and bottom) for the period 07.12.2020 – 25.01.2021. at the SUPREHILL Observatory

	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
	$\delta^2\text{H}$ in [‰]			$\delta^{18}\text{O}$ in [‰]			d-excess in [‰]		
MEAN	-50.8	-51.4	-49.2	-7.7	-7.6	-7.8	11.0	11.0	11.9
MED	-50.5	-51.4	-49.3	-7.7	-7.6	-7.8	10.8	10.8	11.4
MIN	-52.2	-52.9	-51.8	-7.9	-8.0	-8.0	10.4	9.8	10.6
MAX	-49.6	-50.1	-47.0	-7.5	-7.3	-7.6	12.8	12.6	14.4
SD	0.9	0.9	1.5	0.1	0.2	0.1	0.7	0.9	1.2
CV (%)	-1.8	-1.8	-3.0	-1.9	-2.6	-1.5	6.5	7.8	10.2

Table 5: Results of the descriptive statistical analysis with statistical parameters of isotopic water composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$ and d-excess) measured in surface and subsurface runoff instruments and installed rain sampler for the period 07.12.2020 – 25.01.2021. at the SUPREHILL Observatory

	Surface runoff			Subsurface runoff			Precipitation		
	$\delta^2\text{H}$ in [‰]	$\delta^{18}\text{O}$ in [‰]	d-excess in [‰]	$\delta^2\text{H}$ in [‰]	$\delta^{18}\text{O}$ in [‰]	d-excess in [‰]	$\delta^2\text{H}$ in [‰]	$\delta^{18}\text{O}$ in [‰]	d-excess in [‰]
MEAN	-70.8	-10.4	12.4	-51.3	-7.9	11.7	-88.0	-12.8	14.4
MED	-63.9	-9.8	12.5	-52.5	-8.0	11.7	-87.6	-12.9	14.4
MIN	-113.2	-15.3	8.2	-62.5	-9.1	9.3	-112.8	-15.6	11.6
MAX	-52.0	-8.2	15.6	-41.6	-6.8	13.6	-64.0	-9.9	17.1
SD	17.7	2.0	2.3	5.9	0.7	1.2	23.9	2.7	2.3
CV (%)	-25.0	-19.3	18.5	-11.4	-8.5	10.0	-27.2	-21.4	16.3

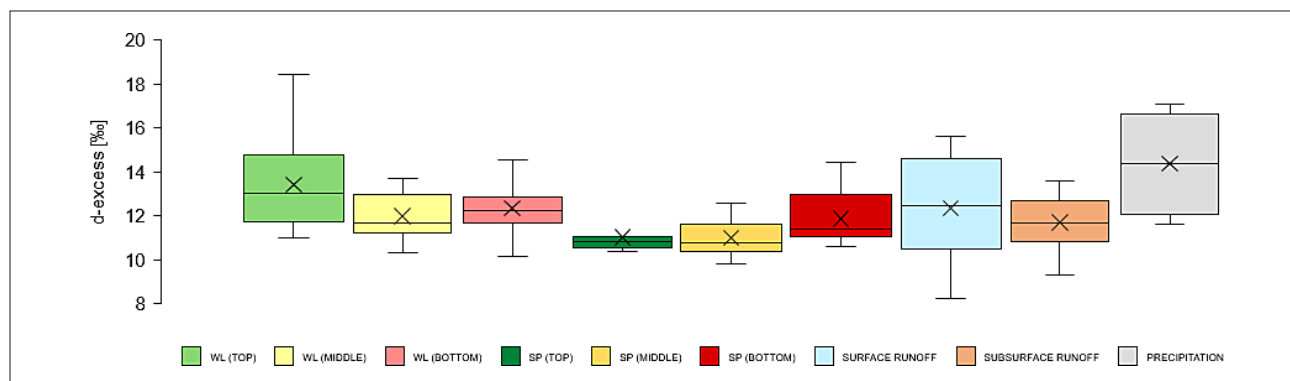


Figure 5: Boxplot of d-excess values [in ‰] for passive wick lysimeters (WL), and suction probes (SP) at the top, middle and bottom of the hillslope, and surface runoff, subsurface runoff and precipitation

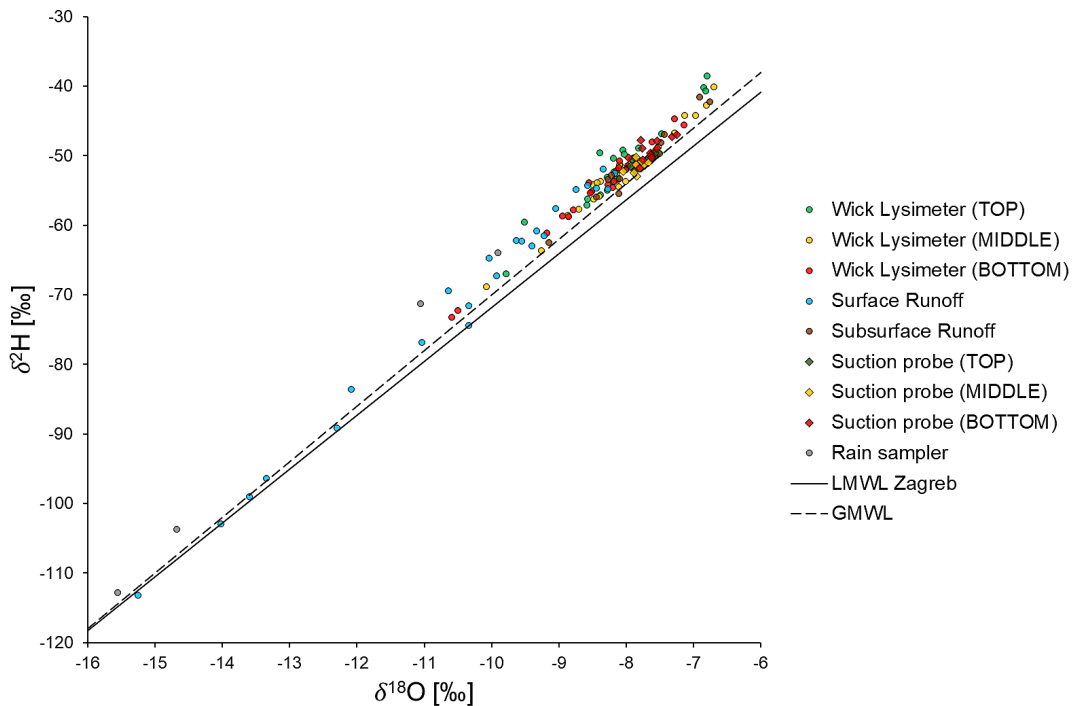


Figure 6: Precipitation and soil water isotopic composition sampled between 01.12.2020.-25.01.2021. at the SUPREHILL Observatory

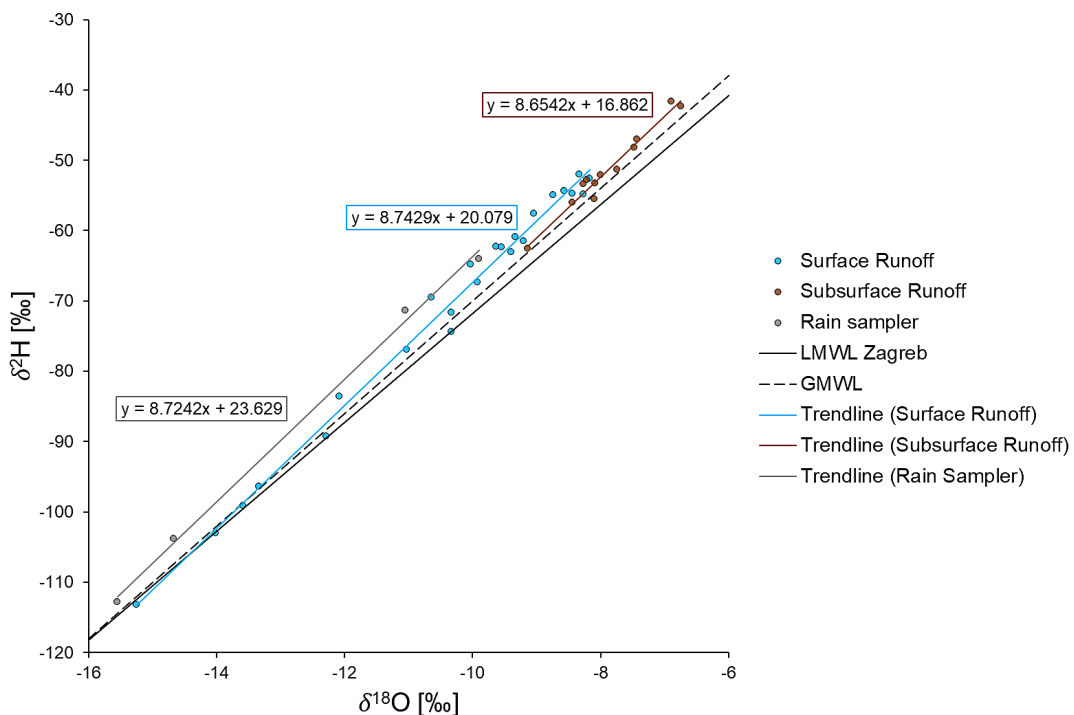


Figure 7: Meteoric water lines of precipitation, surface runoff and subsurface runoff

stated that subsurface flow contributions are typically associated with water-restricting layers, which may involve thin layers with subtle contrasts in hydraulic conductivity.

The generally lower volumetric water content sensors installed at depth 60 and 80 cm at the middle of the

hillslope point to a connection with the highest amounts of sand (11 %) of soil layer 60 – 90 cm as sand has a property of weak soil-water retention (Schelle et al., 2013). The highest average coefficient of variation, calculated based on the sensor data, was found at the middle of the hillslope at depth of 20 cm (2.06), while the

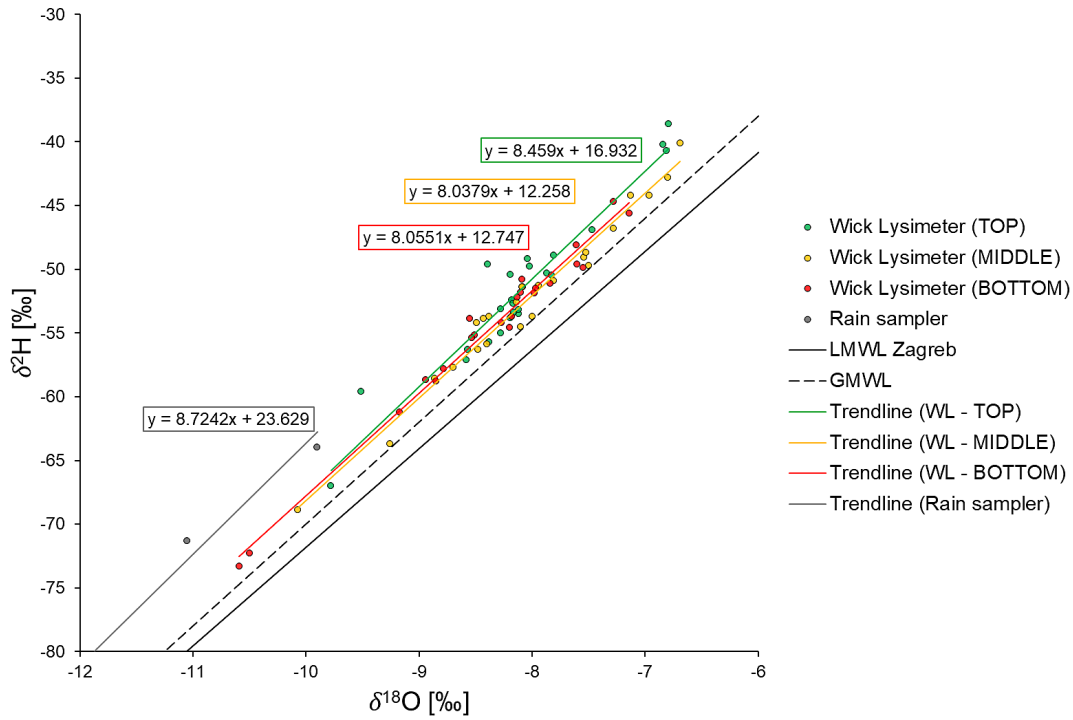


Figure 8: Meteoric water lines of wick lysimeters at the top, middle and the bottom of the hillslope and precipitation

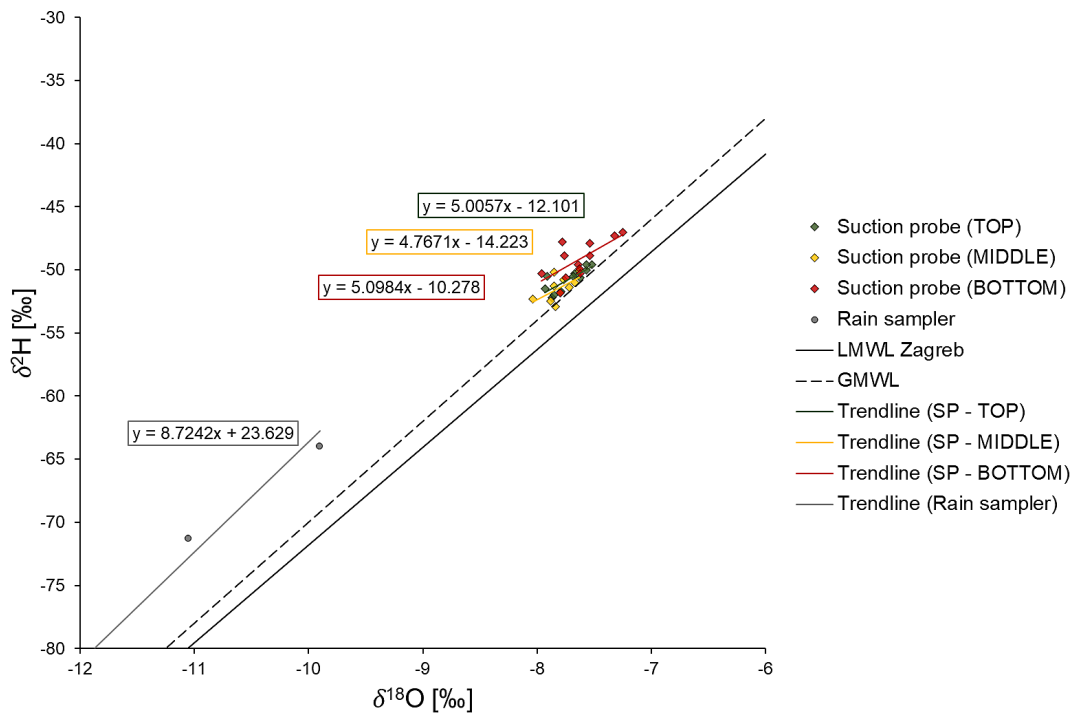


Figure 9: Meteoric water lines of suction probes at the top, middle and the bottom of the hillslope and precipitation

lowest average coefficient of variation was found also at the middle of the hillslope, but at the depth of 80 cm (0.21) (see **Figure 4**). The coefficient of variation decreases according to the depth of the sensor installation. This suggests that the influence of infiltration will be less seen with depth, and probably not seen at a depth of

80 cm. For gaining a better insight into the relationship between the precipitation and soil water content at different depths, the coefficient of correlation was used, as it poses as a common method in such evaluation (**Sehler et al., 2019**). Although in general very low and not significant, the highest average coefficient of correlation,

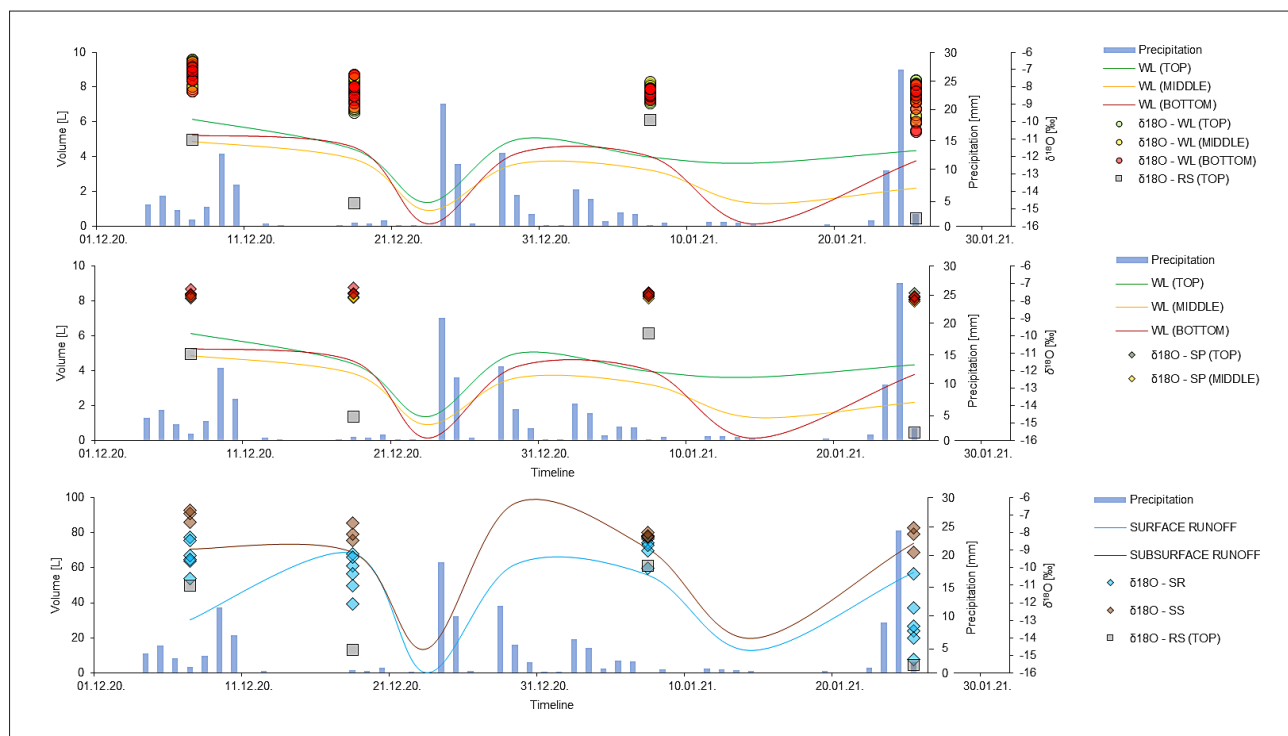


Figure 10: Difference in water isotopic composition ($\delta^{18}\text{O}$) in time (wick lysimeters (WL), suction probes (SP), surface runoff (SR), subsurface runoff (SS) and precipitation (RS) with measured volume in field instruments at the top, middle and bottom of the hillslope and precipitation

calculated based on the sensor and precipitation data, was found at the bottom of the hillslope at a depth of 20 cm (0.19), while the lowest average coefficient of correlation, i.e. no correlation was found at the top, at a depth of 80 cm (-0.02) (see **Figure 4**), suggesting that quicker infiltration rates can be expected in the shallower layer at the bottom of the hillslope during the observed period.

3.4 Results of the Isotope Analysis

If isotopic composition of soil water from wick lysimeters in all locations is explored (see **Table 3**), it is evident that the average and median values are almost the same, especially when observing $\delta^{18}\text{O}$ values. A similar situation can be seen in water from suction probes (see **Table 4**) and subsurface runoff (see **Table 5**). More detailed insight into the statistical parameters shows that after precipitation, surface runoff has the highest standard deviation and coefficient of variation. Furthermore, deviation and variation of water isotopic composition is very similar to those of subsurface runoff, while data from suction probes indicate very small or no change, in general smaller than instrument uncertainty. Although in general, the results of d-excess suggest similar conclusions, it can be seen that data deviation and variation are the biggest at the top of the hillslope when observing water from wick lysimeters, and the smallest when observing data from suction probes. This is also consistent with the box-plot analysis shown in **Figure 5**. Box-plot

analysis of d-excess suggests that the greatest variation in d-excess, except in precipitation, can be seen in surface runoff and wick lysimeters located at the top of the vineyard. Furthermore, if observing suction probes, it can be seen that d-excess values show bigger variation at the bottom of the field. Few reasons can be associated with this issue, from the possible influence of installed equipment for monitoring surface and subsurface runoff due to a smaller percentage of clay observed at the bottom of the hillslope.

It can be clearly seen from **Figure 6** that all data fall slightly above both lines but are closer to GMWL rather than to the newest LMWL Zagreb. Also, the results suggest that not all soil water is related to the precipitation which has fallen in the observed time period around the vineyard except the water related to the surface and subsurface runoff, and probably some wick lysimeters. However, if data from surface and subsurface runoff and the rain sampler are evaluated in more detail, it can be clearly seen that all of them result in very similar regression lines (see **Figure 7**). The same thing is evident when observing water lines generated by data from wick lysimeters (see **Figure 8**) which are very close to those of fallen precipitation and GMWL and LMWL for Zagreb. However, water lines made based on the values from suction probes show different slopes (see **Figure 9**). On the other side, although in part of the analysis, data from wick lysimeters are very similar to those from suction probes. The results show much greater variation in data from wick lysimeters, which is expected due to

the shallower installation depth (40 cm with respect to 100 cm, **Figure 6**, **Tables 3-4**) and is consistent with the interpretation of basic statistical parameters made on water isotopic composition. Furthermore, the results of soil water isotopic composition coincide with the results of volumetric water content, which show great difference in variation of water content till a 60 cm depth with respect to an 80 cm depth. A similar conclusion can be examined when observing the results of correlation analysis between precipitation and water content data. All this suggests that most of the mobile water should be found in the upper soil zone (till a 100 cm depth).

In the third step of data interpretation, the results were evaluated in time (see **Figure 10**). The results confirmed the response of surface and subsurface runoff, but also suggest that some wick lysimeters respond more quickly to precipitation infiltration, especially those on the bottom of the vineyard. The topsoil layer (0 – 30 cm) at the bottom of the hillslope has the least amount of clay, while containing the greatest amount of both sand and silt, resulting from hillslope erosion, which seems to have affected the infiltration rates to a certain degree. This can especially be seen in the data from the last sampling campaign where isotopic composition in water from wick lysimeters, although a lot different from precipitation, was more similar than water related to subsurface runoff. Although this is not explicitly emphasized, in a lot of cases isotopic composition from wick lysimeters follow the pattern of precipitation, i.e. the values observed in wick lysimeters are more negative when precipitation is more negative. The exception is the period before the third sampling campaign where isotopic of all examined water is the most similar to fallen precipitation. However, this is probably related due to the most continuous occurrence of precipitation in that period. Furthermore, in **Figure 10** the results unequivocally show that isotopic composition in suction probes installed at 100 cm depth does not change in time which suggests that precipitation didn't infiltrate till that depth in the observed period. This observation is consistent with all previously presented results which all together indicate that preferential flow can be possible only in the first 80 cm depth at the SUPREHILL Observatory.

4. Conclusions

A different isotopic signature has been observed in various depths and locations in a small area. This suggests that different infiltration patterns, as well as different soil-water dynamics, exist in the investigated hillslope vineyard. The results indicate that surface, subsurface runoff and most of the passive wick lysimeters respond to precipitation in the investigated period, while the response of suction probes located at a 100 cm depth is not that evident. This can be seen through the examination of various parameters, from variation of water content up to water isotopic composition and its change

in time. Passive wick lysimeters respond differently although in average have very similar isotopic composition of water which is probably due to a combination of high soil water content state in the period of observation, different sloping of the observed positions and slight differences in soil textures. Granulometric soil composition analysis corresponds to silt erosion often occurring at hillslopes, with a decreasing trend in silt amount in relation to depth, at all positions. There is also a decreasing trend present in clay content complementary in relation to slope elevation, while the content of clay at each position increases in regard to the soil depth. Soil water content data evaluation showed that in relation to the depth of installation throughout the hillslope, the highest water contents were found as well at a depth of 40 cm on average, while the lowest were found at a depth of 60 cm, which could help in further investigations at the observatory, regarding the possibility of low-permeable layer development, considering the vulnerability of such soils to compaction. The highest average coefficient of correlation, calculated based on the sensor and precipitation data, was found at the bottom of the hillslope, suggesting that quicker infiltration rates can be expected at the shallower layer at the bottom of the hillslope in the observed period, which backed up the analysis of isotopic composition of water from passive wick lysimeters. Isotopic composition of water and the non-existence of change in isotopic composition of soil water from suction probes, as well as evaluation of different statistical parameters related to depths greater than 60 cm, suggest that water from suction probes is slightly older than all other water observed within the first four sampling campaigns. However, values of d-excess observed in water from suction probes suggest that more variation can be expected in the bottom of the hillslope and that water captured in the bottom of the hillslope could be more similar to the precipitation pattern with respect to those located at the mid and top part of the vineyard. All results indicate that the existence of preferential flow can be expected in the shallowest parts of the hillslope vineyard, i.e. till the maximum depth of 80 cm.

Acknowledgement

This research was funded by Croatian Science Foundation, grant number UIP-2019-04-5409, project: "Subsurface preferential transport processes in agricultural hillslope soils – SUPREHILL".

5. References

- Allen, R. (2004): Penman-Monteith equation. In: Hillel, D., Rosenzweig, C., Powlson, D., Scow, K., Singer, M., Sparks, D. (eds.): *Encyclopedia of Soils in the Environment*. - Academic Press, 180-187, 570 p.
- Ampontuah, E. O., Robinson, J. S., and Nortcliff, S. (2006): Assessment of soil particle redistribution on two contrast-

- ing cultivated hillslopes. *Geoderma*, 132, 3–4, 324–343. <https://doi.org/10.1016/j.geoderma.2005.05.014>
- Bernier, T. P. (2020): The use of water vapor isotopes to determine evapotranspiration source contributions in the natural environment. *Water*, 12, 11, 1–18. <https://doi.org/10.3390/w12113203>
- Berry, Z. C., Evaristo, J., Moore, G., Poca, M., Steppe, K., Verrot, L., Asbjornsen, H., Borma, L. S., Bretfeld, M., Hervé-Fernández, P., Seyfried, M., Schwendenmann, L., Sinacore, K., De Wispelaere, L., and McDonnell, J. (2018): The two water worlds hypothesis: Addressing multiple working hypotheses and proposing a way forward. *Ecohydrology*, 11, 3, e1843. <https://doi.org/10.1002/eco.1843>
- Bosch, D. D., Truman, C. C., Potter, T. L., West, L. T., Strickland, T. C., and Hubbard, R. K. (2012): Tillage and slope position impact on field-scale hydrologic processes in the South Atlantic Coastal Plain. *Agricultural Water Management*, 111, 40–52. <https://doi.org/10.1016/j.agwat.2012.05.002>
- Brouwer, J., and Fitzpatrick, R. W. (2002): Restricting layers, flow paths, and correlation between duration of soil saturation and soil morphological features along a hillslope with an altered soil water regime in western Victoria. *Australian Journal of Soil Research*, 40, 6, 927–946. <https://doi.org/10.1071/SR02009>
- Coplen, T. B., and Wassenaar, L. I. (2015): LIMS for Lasers 2015 for achieving long-term accuracy and precision of $\delta^2\text{H}$, $\delta^{17}\text{O}$, and $\delta^{18}\text{O}$ of waters using laser absorption spectrometry. *Rapid Communications in Mass Spectrometry*, 29, 22, 2122–2130. <https://doi.org/10.1002/rcm.7372>
- Filipović, V., Gerke, H. H., Filipović, L., and Sommer, M. (2018): Quantifying Subsurface Lateral Flow along Sloping Horizon Boundaries in Soil Profiles of a Hummocky Ground Moraine. *Vadose Zone Journal*, 17, 1, 170106. <https://doi.org/10.2136/vzj2017.05.0106>
- Fox, G. A., and Wilson, G. V. (2010): The Role of Subsurface Flow in Hillslope and Stream Bank Erosion: A Review. *Soil Science Society of America Journal*, 74, 3, 717–733. <https://doi.org/10.2136/sssaj2009.0319>
- Gazis, C., and Feng, X. (2004): A stable isotope study of soil water: Evidence for mixing and preferential flow paths. *Geoderma*, 119, 1–2, 97–111. [https://doi.org/10.1016/S0016-7061\(03\)00243-X](https://doi.org/10.1016/S0016-7061(03)00243-X)
- Gee, G. W., Newman, B. D., Green, S. R., Meissner, R., Rupp, H., Zhang, Z. F., Keller, J. M., Waugh, W. J., Van Der Velde, M., and Salazar, J. (2009): Passive wick fluxmeters: Design considerations and field applications. *Water Resources Research*, 45, 4, 1–18. <https://doi.org/10.1029/2008WR007088>
- Goldsmith, G. R., Muñoz-Villers, L. E., Holwerda, F., McDonnell, J. J., Asbjornsen, H., and Dawson, T. E. (2012): Stable isotopes reveal linkages among ecohydrological processes in a seasonally dry tropical montane cloud forest. *Ecohydrology*, 5, 6, 779–790. <https://doi.org/10.1002/eco.268>
- Gröning, M., Lutz, H. O., Roller-Lutz, Z., Kralik, M., Gourcy, L., and Pöhlstein, L. (2012): A simple rain collector preventing water re-evaporation dedicated for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis of cumulative precipitation samples. *Journal of Hydrology*, 448–449, 195–200. <https://doi.org/10.1016/j.jhydrol.2012.04.041>
- Grossman, J., and Udluft, P. (1991): The extraction of soil water by the suction-cup method: a review. *Journal of Soil Science*, 42, 1, 83–93. <https://doi.org/10.1111/j.1365-2389.1991.tb00093.x>
- Guo, L., Chen, J., and Henry, L. (2014): Subsurface lateral preferential flow network revealed by time-lapse ground-penetrating radar in a hillslope. *Water Resources Research*, 50, 12, 9127–9147. <https://doi.org/10.1002/2013WR014603>
- Heße, F., Zink, M., Kumar, R., Samaniego, L., and Attinger, S. (2017): Spatially distributed characterization of soil-moisture dynamics using travel-time distributions. *Hydrology and Earth System Sciences*, 21, 1, 549–570. <https://doi.org/10.5194/hess-21-549-2017>
- Jarvis, N. J. (2007): A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. *European Journal of Soil Science*, 58, 3, 523–546. <https://doi.org/10.1111/j.1365-2389.2007.00915.x>
- Jung, H. W., Yun, S. T., Kim, K. H., Oh, S. S., and Kang, K. G. (2014): Role of an impermeable layer in controlling groundwater chemistry in a basaltic aquifer beneath an agricultural field, Jeju Island, South Korea. *Applied Geochemistry*, 45, 82–93. <https://doi.org/10.1016/j.apgeochem.2014.03.008>
- Kelln, C., Barbour, L., and Qualizza, C. (2007): Preferential Flow in a Reclamation Cover: Hydrological and Geochemical Response. *Journal of Geotechnical and Environmental Engineering*, 133, 10, 1277–1289. [https://doi.org/10.1061/\(asce\)1090-0241\(2007\)133:10\(1277\)](https://doi.org/10.1061/(asce)1090-0241(2007)133:10(1277))
- Knighton, J., Saia, S. M., Morris, C. K., Archiblad, J. A., and Walter, M. T. (2017): Ecohydrologic considerations for modeling of stable water isotopes in a small intermittent watershed. *Hydrological Processes*, 31, 13, 2438–2452. <https://doi.org/10.1002/hyp.11194>
- Kovač, Z., Nakić, Z., Barešić, J., and Parlov, J. (2018): Nitrate Origin in the Zagreb Aquifer System. *Geofluids*, 2018, 2789691, 1–15. <https://doi.org/10.1155/2018/2789691>
- Krajcar-Bronić, I., Barešić, J., Borković, D., Sironić, A., Mikić, I. L., and Vreča, P. (2020): Long-Term isotope records of precipitation in Zagreb, Croatia. *Water*, 12, 1, 1–29. <https://doi.org/10.3390/w12010226>
- Lee, K. S., Kim, J. M., Lee, D. R., Kim, Y., and Lee, D. (2007): Analysis of water movement through an unsaturated soil zone in Jeju Island, Korea using stable oxygen and hydrogen isotopes. *Journal of Hydrology*, 345, 3–4, 199–211. <https://doi.org/10.1016/j.jhydrol.2007.08.006>
- Marković, M., Filipović, V., Legović, T., Josipović, M., and Tadić, V. (2015): Evaluation of different soil water potential by field capacity threshold in combination with a triggered irrigation module. *Soil and Water Research*, 10, 3, 164–171. <https://doi.org/10.17221/189/2014-SWR>
- Newberry, S. L., Prechsl, U. E., Pace, M., and Kahmen, A. (2017): Tightly bound soil water introduces isotopic memory effects on mobile and extractable soil water pools. *Isotopes in Environmental and Health Studies*, 53, 4, 368–381. <https://doi.org/10.1080/10256016.2017.1302446>

- Parlov, J., Kovač, Z., Nakić, Z., and Barešić, J. (2019): Using water stable isotopes for identifying groundwater recharge sources of the unconfined alluvial Zagreb aquifer (Croatia). *Water*, 11, 10, 1-15. <https://doi.org/10.3390/w11102177>
- Peralta-Tapia, A., Sponseller, R. A., Tetzlaff, D., Soulsby, C., and Laudon, H. (2015): Connecting precipitation inputs and soil flow pathways to stream water in contrasting boreal catchments. *Hydrological Processes*, 29, 16, 3546–3555. <https://doi.org/10.1002/hyp.10300>
- Persico, R., Cataldo, A., and De Benedetto, E. (2019): Time-domain reflectometry: Current uses and new possibilities. In: Persico, R., Piro, S. and Linford, N. (eds.): *Innovation in Near-Surface Geophysics*. - Elsevier, 59–96, 518 p. <https://doi.org/10.1016/b978-0-12-812429-1.00003-9>
- Renée Brooks, J., Barnard, H. R., Coulombe, R., and McDonnell, J. J. (2010): Ecohydrologic separation of water between trees and streams in a Mediterranean climate. *Nature Geoscience*, 3, 2, 100–104. <https://doi.org/10.1038/ngeo722>
- Rieckh, H., Gerke, H. H., and Sommer, M. (2012): Hydraulic properties of characteristic horizons depending on relief position and structure in a hummocky glacial soil landscape. *Soil and Tillage Research*, 125, 123–131. <https://doi.org/10.1016/j.still.2012.07.004>
- Rodrigo-Comino, J., Senciales, J. M., Sillero-Medina, J. A., Gyasi-Agyei, Y., Ruiz-Sinoga, J. D., and Ries, J. B. (2019): Analysis of Weather-Type-Induced Soil Erosion in Cultivated and Poorly Managed Abandoned Sloping Vineyards in the Axarquía Region (Málaga, Spain). *Air, Soil and Water Research*, 12, 1-12. <https://doi.org/10.1177/1178622119839403>
- Rothfuss, Y., and Javaux, M. (2017): Reviews and syntheses: Isotopic approaches to quantify root water uptake: A review and comparison of methods. *Biogeosciences*, 14, 8, 2199–2224. <https://doi.org/10.5194/bg-14-2199-2017>
- Schelle, H., Heise, L., Jänicke, K., and Durner, W. (2013): Water retention characteristics of soils over the whole moisture range: A comparison of laboratory methods. *European Journal of Soil Science*, 64, 6, 814–821. <https://doi.org/10.1111/ejss.12108>
- Scherrer, S., Naef, F., Fach, A. O., and Cordery, I. (2007): Formation of runoff at the hillslope scale during intense precipitation. *Hydrology and Earth System Sciences*, 11, 2, 907–922. <https://doi.org/10.5194/hess-11-907-2007>
- Sehler, R., Li, J., Reager, J., and Ye, H. (2019): Investigating Relationship Between Soil Moisture and Precipitation Globally Using Remote Sensing Observations. *Journal of Contemporary Water Research & Education*, 168, 1, 106–118. <https://doi.org/10.1111/j.1936-704x.2019.03324.x>
- Song, X., Wang, P., Yu, J., Liu, X., Liu, J., and Yuan, R. (2011): Relationships between precipitation, soil water and groundwater at Chongling catchment with the typical vegetation cover in the Taihang mountainous region, China. *Environmental Earth Sciences*, 62, 4, 787–796. <https://doi.org/10.1007/s12665-010-0566-7>
- Sprenger, M., Leistert, H., Gimbel, K., and Weiler, M. (2016): Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. *Reviews of Geophysics*, 54, 3, 674–704. <https://doi.org/10.1002/2015RG000515>
- Sprenger, M., Tetzlaff, D., Buttle, J., Laudon, H., Leistert, H., Mitchell, C. P. J., Snelgrove, J., Weiler, M., and Soulsby, C. (2018): Measuring and Modeling Stable Isotopes of Mobile and Bulk Soil Water. *Vadose Zone Journal*, 17, 1, 170149. <https://doi.org/10.2136/vzj2017.08.0149>
- Sprenger, M., Tetzlaff, D., and Soulsby, C. (2017): Stable isotopes reveal evaporation dynamics at the soil-plant-atmosphere interface of the critical zone. *Hydrology and Earth System Sciences Discussions*, 21, 7, 3839-3858. <https://doi.org/10.5194/hess-2017-87>
- Stewart, R. D., Liu, Z., Rupp, D. E., Higgins, C. W., and Selker, J. S. (2015): A new instrument to measure plot-scale runoff. *Geoscientific Instrumentation, Methods and Data Systems*, 4, 1, 57–64. <https://doi.org/10.5194/gi-4-57-2015>
- Tarolli, P., and Straffelini, E. (2020): Agriculture in Hilly and Mountainous Landscapes: Threats, Monitoring and Sustainable Management. *Geography and Sustainability*, 1, 1, 70–76. <https://doi.org/10.1016/j.geosus.2020.03.003>
- USDA (1999): *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. Soil Survey Staff, United States Department of Agriculture, Washington, 436 p.
- Wong, T. E., Nusbaumer, J., and Noone, D. C. (2017): Evaluation of modeled land-atmosphere exchanges with a comprehensive water isotope fractionation scheme in version 4 of the Community Land Model. *Journal of Advances in Modeling Earth Systems*, 9, 2, 978-1001. <https://doi.org/10.1002/2016MS000842>

SAŽETAK

Korištenje stabilnih izotopa vode ($\delta^2\text{H}$ i $\delta^{18}\text{O}$) za proučavanje podrijetla vode u tlu padinskoga vinograda: prvi rezultati

Raznolikost procesa koji se odvijaju unutar vadozne zone pri padinskim agroekosustavima čini procjenu dinamike vode izazovnom. Ovaj rad predstavlja prvi uvid u rezultate volumetrijskoga sadržaja vode, granulometrijskoga sastava tla, meteoroloških podataka te izotopni sastav oborina i vode u tlu istraživanih u sklopu projekta SUPREHILL, to jest njegova opservatorija. Glavni ciljevi ovoga rada vezani su za procjenu podrijetla vode u tlu padinskoga vinograda, ali i za procjenu dubine do koje se oborine infiltriraju te gdje je moguća pojava preferencijalnoga toka. Za navedenu svrhu korišteni su hidrometeorološki podatci, granulometrijski sastav tla te stabilni izotopi vodika ($\delta^2\text{H}$) i kisika ($\delta^{18}\text{O}$) iz oborina te iz uzorkovane vode iz tla. Rezultati upućuju na postojanje različitoga izotopnog potpisa u vodi u tlu, što sugerira različite obrasce infiltracije na istraživanome području. Također, rezultati pokazuju da sustavi za površinsko i podzemno otjecanje te većina pasivnih lizimetara reagiraju na oborine, dok odaziv usisnih sondi instaliranih na većim dubinama nije očit. Navedeno odgovara rezultatima koji se odnose na varijaciju sadržaja vode u tlu na različitim dubinama. Svi rezultati upućuju na mogućnost postojanja slabije propusnoga sloja na približno 60 cm dubine. Nadalje, preferencijalni tok vode, ako postoji, prema ovim saznanjima može se očekivati do dubine od 80 cm. Očekuje se da će dugoročno praćenje podataka putem uspostavljene senzorske mreže u SUPREHILL opservatoriju preciznije definirati ponašanje vode u tlu i postojanje preferencijalnoga toka vode.

Ključne riječi:

kretanje vode u tlu, infiltracija oborina, stabilni izotopi vode, obronačni vinograd, vadozna zona

Author's contribution

Zoran Kovač (Assistant Professor) collaborated in the initiation of the idea, developed a methodological approach, performed the laboratory analyses, provided literature review and data interpretation. **Vedran Krevh** (Research assistant) provided field work, sampling, data analysis, interpretation and presentation of the results. **Lana Filipović** (Assistant Professor) collaborated in the initiation of the idea, provided field work and provided interpretation. **Jasmina Defterdarović** (Research Assistant) provided field work, sampling and literature review. **Patricia Buškulić** (Research Assistant) performed the laboratory analyses and interpretation of the results. **Luka Han** (Research Assistant) provided literature review and assisted in the presentation of the results. **Vilim Filipović** (Assistant Professor) collaborated in the initiation of the idea, provided field work, supervised the research and provided interpretation.