Technical note: A new laboratory approach to extract soil water for stable isotope analysis from large soil samples~~Simple, exact and reliable way to extract soil water for stable isotope analysis~~

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Abstract. A correct soil water extraction represents an initial step in stable water isotope analysis.~~Water stable isotope analysis in ecohydrological studies often requires soil water extraction. Here~~To this aim, we present a new soil water extraction method based on the principle of complete evaporation and condensation of the soil water in a closed circuit. ~~We have developed an apparatus that~~The proposed device has four extraction slots and can be used ~~multiple~~ up to two times a day. ~~Thanks~~ Owing to its simple design, there is no need for any chemicals, gases, high pressure or high-temperature regimes. ~~A set of system functionality~~The experimental tests ~~confirmed~~ proved that the extraction itself~~ method has high accuracy and high precision and~~ does not cause any major isotope fractionation effects leading to erroneous results. ~~When extracting~~Extraction of pure water samples ~~, the~~ shifts the isotope composition by~~accuracy is~~ 0.04 ± 0.06 ‰ and 0.06 ± 0.35 ‰ for δ^{18}O and δ^{2}H, respectively.~~,~~ ~~with a precision of ± 0.06 ‰ and ± 0.35 ‰ respectively.~~ Soil water extraction tests were conducted with ~~three~~ five distinct soil types (loamy sand, sandy loam, ~~and~~ sandy clay, silt loam, and clay) using ~~50~~40-~~80~~ 150 grams of pre-oven-dried soil, which was subsequently ~~and~~ rehydrated to~~water content of~~ 10 and 20 % water content. The ~~accuracy for the extraction~~shift in the isotopic composition of ~~oven-dried and rehydrated soils~~these tests ranged between -0.04 and 0.~~03~~ 07 ‰ for δ^{18}O and 0.~~06~~ 4 and ~~0.68~~1.3 ‰ for δ^{2}H with ~~precision~~ the standard deviation of ± (0.~~06~~ 08 ~~to~~ – 0.~~13~~ 25) ‰ and ± (0.34 ~~to~~ – 0.58) ‰ for δ^{18}O and δ^{2}H, respectively~~ in individual tests~~. The~~se~~ results exhibit high accuracy which makes this method suitable for high-precision studies where unambiguous determination of the water origin is required.~~are more accurate than results achieved by cryogenic vacuum extraction, which is the most widely used extraction method for soils. So far, our method was only tested for soil water extractions.~~

1 Introduction

Measurements of soil water isotopic composition (^{2}H and ^{18}O) ~~are useful tool to describe~~provide a description of soil water movement and mixing processes in the vadose zone (Stumpp et al., 2018). In some cases, different trends in soil water samples characterisation without an application of exact isotopic composition method (~~or just proof that two soil water samples are different without knowing the absolutely exact isotopic composition (~~tracer experiments to prove interconnection) ~~may be~~give a sufficient information about samples dissimilarity. However, f~~F~~or ~~inter-laboratory comparison,~~ characterizing the transport processes and residence time, accurate ~~proof~~ evaluation of sample origin, ~~or~~ soil water dynamics modelling or inter-laboratory comparison, the exact values of the isotopic composition ~~is~~ are ~~required~~indispensable. ~~For all these purposes~~This justifies an emphasis paid to correct~~,~~ soil water extraction~~ is necessary~~. Unlike liquid water samples of precipitation, snow cover, stream or groundwater, where the isotopic compositions are~~is~~ easily accessible, the extraction of matrix-~~bound soil water~~ or tightly~~-~~-bound soil water is challenging ~~when it comes to exact values of~~from the viewpoint of exact determination of isotopic composition. It has been shown that the storage and sample preparation for extraction, soil texture, soil water content as well as organic matter and carbonate content ~~have a major impact on~~strongly influence the final results (West et al., 2006; Wassenaar et al., 2008; Koeniger et al., 2011; Meißner et al., 2014; Hendry et al., 2015; Orlowski et al., 2016a; Newberry et al., 2017). ~~Also~~Parallelly, the specifics of extraction methods, e.g., the different pore spaces that may or may not be extracted via the different approaches (Orlowski et al., 2019; Kübert et al., 2020) and the modifications of the procedures themselves (Orlowski et., 2018) can affect the isotope results.

There are ~~many~~ several classes of different extraction methods, some of them were compared in ~~to choose from and several studies that compare them (~~Zhu et al.~~,~~ (2014); Sprenger et al.~~,~~ (2015); and Orlowski et al.~~,~~ (2016b, 2018). ~~For a~~In brief ~~overview~~, there are the methods using

~~-~~a) various chemical compounds or elements like toluene for azeotropic distillation (Revesz and~~and~~ Woods, 1990; Thorburn et al., 1993), dichloromethane for accelerated solvent extraction techniques (Zhu et al., 2014), zinc or uranium for microdistillation (Kendall and~~and~~ Coplen, 1985; Brumsack et al., 1992);

~~;~~ b) microwave water extraction (Munksgard et al., 2014);

~~;~~ c) force in terms of mechanical squeezing (Wershaw et al., 1966; White et al., 1985; Böttcher et al., 1997) or centrifugation (Mubarak and Olsen, 1976; Batley and Giles, 1979; Barrow and Whelan, 1980; Peters and Yakir, 2008);

~~;~~ d) equilibration methods such as in situ equilibration (Garvelmann et al., 2012; Rothfuss et al., 2013, 2015; Volkmann and Weiler, 2014; Gaj et al., 2016), CO_2- and H_2-equilibration (Jusserand, 1980; Scrimgeour, 1995; Hsieh et al., 1998; McConville et al., 1999; Koehler et al., 2000; Kelln et al., 2001) and the direct liquid-vapour equilibrium laser spectroscopy (DVE-LS) method (Wassenaar et al., 2008; Hendry et al., 2015);

e) cryogenic vacuum extraction (CVE) (Dalton, 1988; West et al., 2006; Koeniger et al., 2011; Goebel and Lascano, 2012; Orlowski et al., 2013, 2016; Gaj et al., 2017), modified CVE – He-purging method (Ignatev et al., 2013) and automatic cryogenic vacuum distillation (ACVD) system LI-2100 (Lica United Technology Limited Inc.).

~~-~~In addition, many laboratories use various modifications of these methods (Walker et al., 1994; Munksgaard et al., 2014; Orlowski et al., 2018). ~~For a~~A more detailed description of the above-stated methods is presented in ~~, we refer to~~ Sprenger et al. (2015) and Ceperley et al. (2024).

At present, the DVE-LS and CVE are t~~T~~he most commonly used methods for soil water extraction~~ today are DVE-LS and CVE~~. Both methods provide very accurate results, but only under ~~certain~~ specific conditions. For the DVE-LS method, the different equilibration~~ium~~ times, low water content as well as the selection of bags play a crucial role (Hendry et al., 2015; Gra~~h~~lher et al., 2016). I~~Also, i~~t has been also shown~~,~~ that soil samples with a high content of fine particles, thus high soil tension, can cause isotope fractionation in closed systems (Gaj and McDonell, 2019). For the CVE method, the major challenge is the treatment of soils containing clay minerals. Such soils require application of higher temperatures (up to 300 °C).~~Soils containing clay minerals are also a major limitation of CVE. It has been shown that higher temperature is needed for such soils (up to 300 °C).~~ However, this results in~~This can affect the results by~~ releasing water by oxidation of organics and dihydroxylation of hydroxide-containing minerals such as goethite (Gaj et al., 2017), and in such a way in affecting the experimental results. Moreover, the soil sample size acceptable for this method is rather low, usually between 10 to 20 grams, allowing for the extraction of only grams of the soil water. Another disadvantage of the CVE method consists in in~~that obtained results are not in~~comparable outputs among~~between~~ different laboratories due to the CVE setup ~~apparatus~~ modifications and different workflows (Orlowski et al., 2018). Laboratories‘ differences in their setups are: the extraction containers (form, size, volume, and material), the heating module and its ~~application~~ working temperature (heating tapes or lamps, water baths or hot plates), the type of fittings and connections (glass, stainless steel), and the vacuum-producing units. In addition, different temperatures, pressures, extraction times and sample sizes are ~~used~~ applied by different laboratories. However, if ~~the~~ a certain setup of all these parameters for the given situation is chosen, very accurate results can be achieved for certain soil types and water contents. Nevertheless, each of these two methods exhibits apparent inconvenience:

- in the case of the DVE-LS method, significant time consumption (a requirement of the permanent presence of an operator);
- in the case of the CVE method an application of technically complicated methods (work with liquid nitrogen, low pressures and high temperatures in an open laboratory apparatus).

In this study, we present a new extraction method – Circulating Air Soil Water Extraction (CASWE). It is a~~n undemanding and~~ relatively simple inexpensive method ~~that can~~ handling~~e~~ soil samples of different sizes, moisture contents and textures. It is based on the simple principle of complete evaporation and condensation in a closed circuit and does not require an application of~~working with~~ hazardous substances (acids, toluene, liquid nitrogen), high temperatures and~~or~~ pressures. ~~-~~In the following~~,~~ we (1) introduce a ~~the~~ new extraction principle, (2) present the results of soil extraction efficiency testing, and (3) compare the results with other state-of-the-art approaches. The advantage of the ~~this~~ proposed method over the others is its ~~excellent~~ accuracy, even with clay samples, ~~which are~~ known ~~to~~ for causing~~e~~ inaccurate results for other extraction methods (Ceperley et al., 2024). The biggest advantages of this extraction method are

a) high accuracy of the results;

b) simple design and low cost of the apparatus setup;
c) low operating costs;
d) time reduction in operating the device;
e) ability to process large soil samples and thus obtain large and representative quantities of soil water.

~~However, this accuracy is at the expense of lower throughput. Therefore, rather than for large-scale studies, this method is suitable for studies where quality is more important than quantity.~~

2 Methodology

2.1 Principle of extraction

The ~~Circulating air extraction method (CAEM~~CASWE method~~)~~ is based on the principle of complete evaporation and subsequent condensation of soil water in a closed circuit~~,~~ using~~with~~ air as the circulating medium. The soil sample is heated ~~to 105 °C~~ inside the evaporation chamber to 105 °C, and the evaporated soil water is carried by air circulation to a cooling unit, w~~. T~~here~~,~~ the ~~air moisture~~water vapour ~~is~~ condenses,~~d~~ and finally, the liquid water is collected. Dried cool air is then circulated back into the evaporation chamber. The process continues until ~~there is~~ no ~~visible~~ air moisture condensation is visible.

The extraction temperature was chosen based on the standard Czech methodology for soil drying (ISO 11 465, 1998), which is consistent with standard methodologies used in the UK (BSI 1377: 105 ± 5 °C) and US (ASTM D2216: 110 ± 5 °C). Values exceeding 100 °C have to be chosen as pore water remains in the soil when temperatures below 100 °C are used (O’Kelly 2004, 2005). The water vapour is then condensed by tap water at a temperature of 8 °C. Usage of tap water for cooling is motivated by the following reasons

a) its availability;
b) temperature of cooling water is close to the ambient air dew temperature (preventing an appearance of ambient air condensation on the cooling loops and hence, possible sample contamination);
c) prevention from frost formation inside the apparatus, which otherwise increases the risk of blocking the inlet pipes, damaging the glass parts, and causing the difficulty of extracted sample handling (prior to the sample handling, frost on the cooler and collecting vessel walls has to be melted);
d) with respect to the vapour pressure at the extraction temperature (105 °C: 121 kPa), there is no apparent difference in the extraction rates or residual soil moisture at the equilibrium with the cooling circuit operated at 8 °C (1 kPa) or -10 °C (0.3 kPa).

2.2 Description of the apparatus

The newly designed apparatus (Fig. 1a) is composed ~~consists~~ of three main system units – ~~the~~ heating ~~system~~, ~~the~~ cooling ~~system~~ and ~~the~~ air circulation ~~system~~ (Fig. 2). The apparatus ~~consists of~~has four separate circuits ~~allowing~~ for simultaneous water extraction ~~of water~~ from four different soil samples.

The heating system comprises a standard kitchen oven (model VT 332 CX; MORA MORAVIA s. r. o., Czechia) housing four evaporation chambers – stainless steel boxes equipped with ~~an~~ airtight insulation. Each box has two openings, one for a dry air inlet and ~~second~~ the other for a moist air outlet. The soil sample inside the box is placed on a stainless-steel wire-mesh bed ~~allowing for~~providing good contact between the sample and air, which enhances~~ing~~ the water evaporation rate (Fig. 1b). The dry air is led to the evaporation chamber through a silicone rubber tube coiled inside the oven; its length (~ 2 m) is sufficient to preheat the air close to the oven temperature (Fig. 1c). The hot and moist air from the evaporation chamber is led through the insulated silicone tube to the cooling system; the length of the outlet tubes is as short as possible to minimize the heat losses and prevent undesired water condensation. To monitor the extraction process, a temperature sensor is installed inside each box close to the air outlet.

The cooling system consists of three glass components – spiral cooler, custom-made connecting part and jacketed collecting vessel (Fig. 3). ~~Both, the spiral cooler and collecting vessel are cooled using a tap water (~ 8 °C);~~ T~~t~~wo separate cooling water circuits are used for the spiral coolers and for the collecting vessels (Fig. 2).

The cooled and dried air from the cooling system is fed back to the evaporation chamber by means of the air circulation system comprising two regulated high-speed fans per circuit ensuring the air flow rate of ~ 10 L/min. The temperature sensors and fan speed ~~for~~ in each circuit are monitored by the control unit running on the Arduino platform. The apparatus is complemented by an air diaphragm pump that can be connected to any circuit to flush the circuit with fresh dry air to remove possible residual moisture in the apparatus prior to extraction and thus achieve more accurate results. The tests presented in this work were carried out without the use of this pump. However, for the extraction of soil water with significantly different isotopic compositions, the execution of an initial purge between extractions would be appropriate.

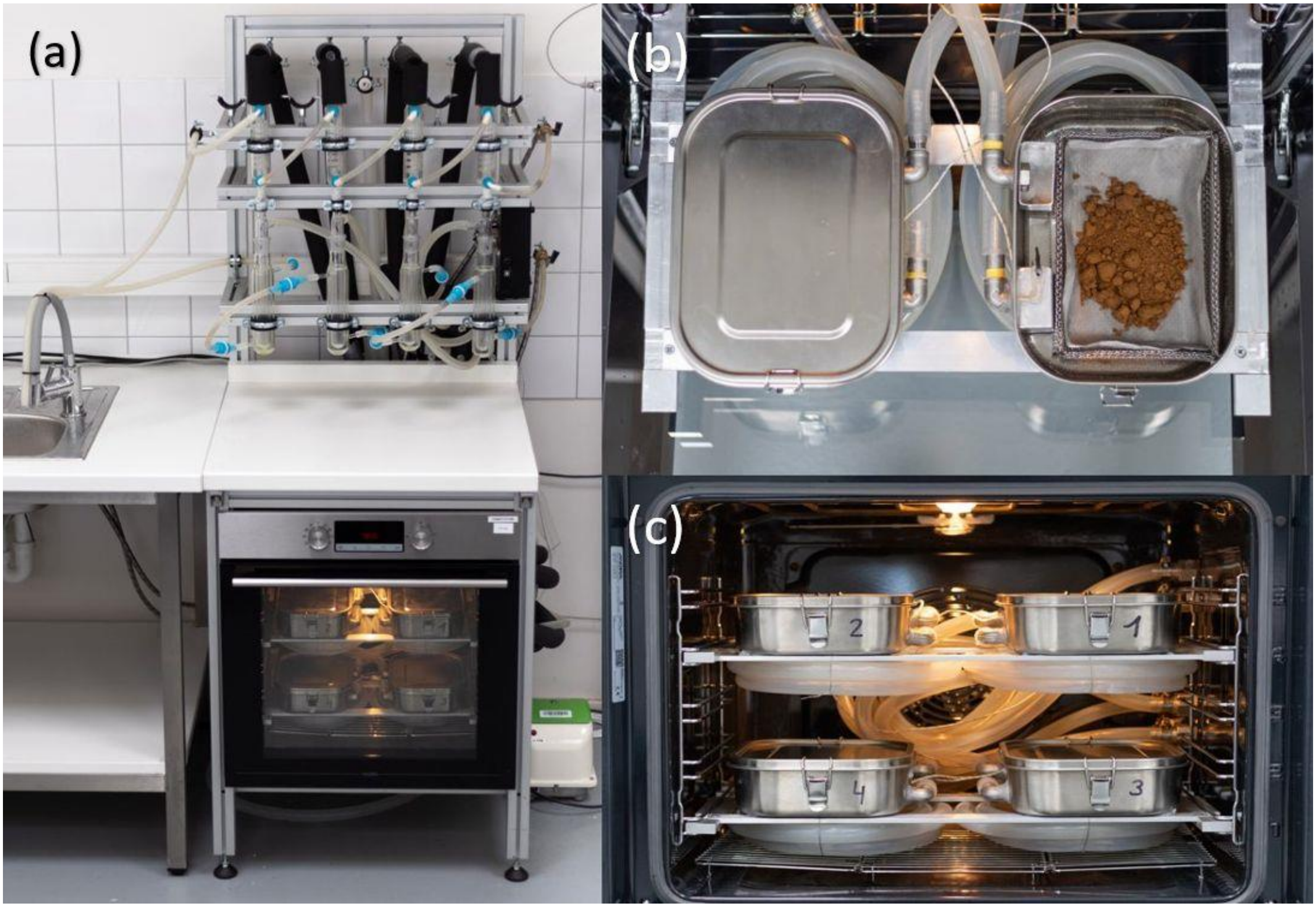


Figure 1: a) Photo of the ~~newly designed~~proposed CASWE apparatus ~~(a)~~; b) detail of the ~~inside of the~~ heating chamber with wire-mesh bed and aluminium fabric bedding ~~(b)~~; c) internal arrangement of heating chambers and coiled supply hoses ~~(c)~~.

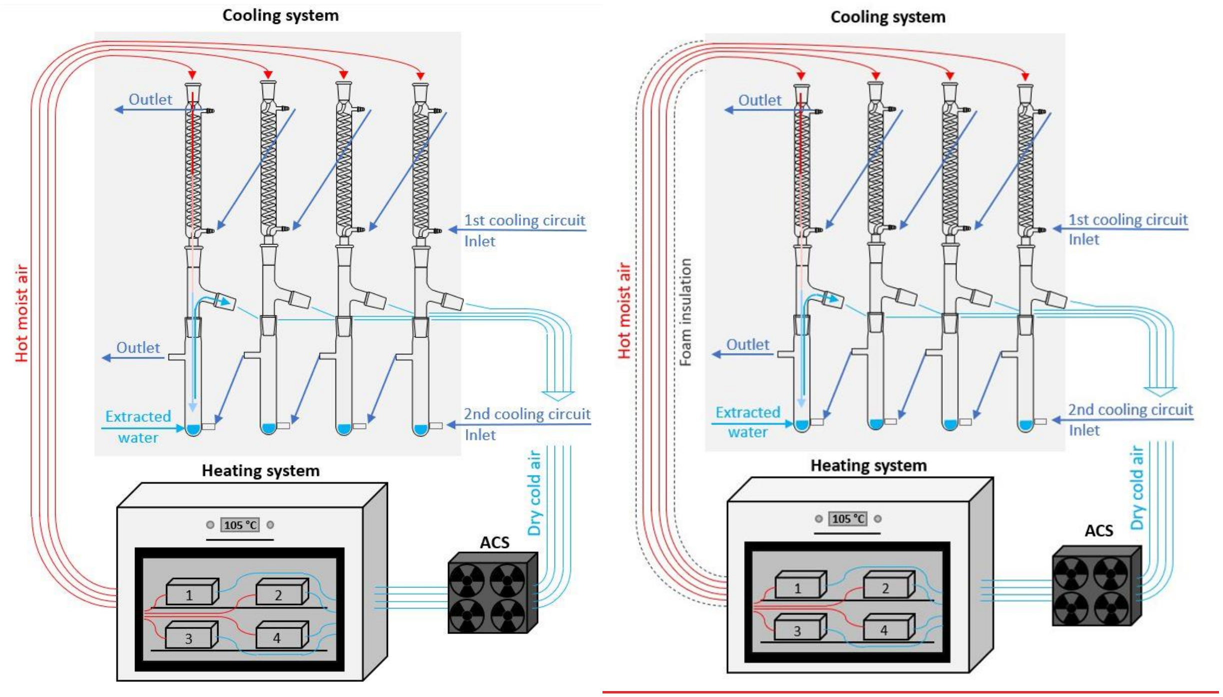


Figure 2: A ~~S~~simplified diagram of ~~of the~~ three main components of the CASWE apparatus (heating ~~system~~, cooling ~~system~~ and air circulation systems (ACS)). The apparatus consists of four separate drying circuits and two cooling circuits.

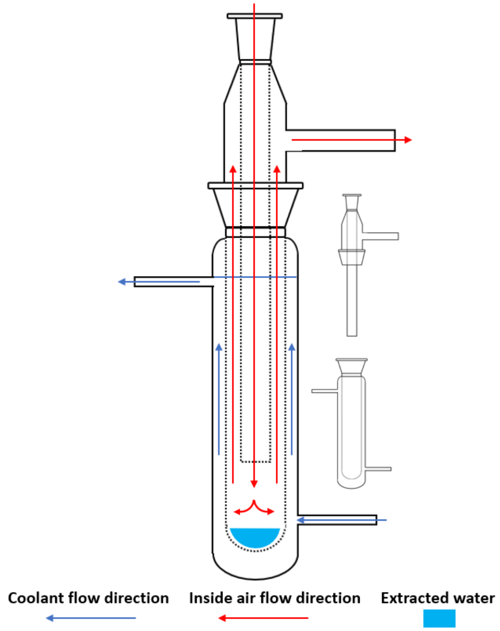


Figure 3: Lower part of the cooling system – custom-made connecting part and jacketed collecting vessel. The arrows indicate the ~~the~~ flow direction ~~of flow~~ within the assembly. Thumbnails show individual parts before assembly.

2.3 Extraction procedure

Soil samples are inserted ~~into the evaporation chambers~~ on the wire bed of the evaporation chambers. A ~~standard temperature for drying soil samples of~~target temperature of 105 °C ~~(Suchara, 2007)~~ is reached approximately within 15 minutes ~~after the start-up~~. ~~From that time,~~This initiates the first intensive part of the drying process, during which both cooling circuits operate and most of the water is extracted~~, is in process~~. The upper cooling circuit (Fig.2) is disconnected once the spiral cooler starts to dry out. The extraction continues with the bottom cooling circuit only. During this time, residual moisture in the apparatus is collected in the cooled collection vessel.

The extraction is complete ~~Once~~when there are no visible signs of condensation elsewhere than in the collection vessel~~moisture on the walls of the cooling apparatus, the extraction is complete~~. To check the completeness of the extraction, the recovery ratio was calculated for each extraction, by comparing the weights of added and extracted waters. For complete checking of the functionality of the apparatus, some soil samples were weighed after pre-oven-drying and after extraction. Depending on the sample type, water content, and size, the extraction time intervals~~s~~ ranged from 3 to ~~5~~ 6 hours per sample. ~~Please note that not all water from the circuit is collected as some of it remains in the form of residual air humidity; based on the circuit volume (~ 5 L) and cooling water temperature (~ 8 °C), the residual water content of ~ 50 mg is estimated.~~ Between each extraction, the circuit is disassembled to retrieve the extracted water from the collection vessel and exchange soil samples. Thorough mixing of the sample before pouring from the collection vessel and catching all droplets from the walls to ensure the homogeneity of the sample is needed. The collection vessel must then be dried ~~between individual extractions~~ to avoid contamination ~~with water from previous~~during further extraction~~s~~.

2.4 Functional tests

In total, ~~four~~six functional tests were performed~~ with twelve repetitions for each~~. All the tests aimed ~~to~~ at recovering the same amount of water that was used ~~for the test~~ with no~~out~~ ~~any~~ changes in its isotopic composition. The f~~The f~~irst test served ~~to~~ for a verification of~~y~~ the principle of~~ the~~ extraction and ~~the~~ for checking waterproofing and airtightness of the apparatus. The ~~second, third and fourth~~remaining five tests verified the accuracy of the extraction with soil samples via spike experiments ~~(Orlowski et al., 2018)~~. In these experiments, disturbed soil samples were pre-oven-dried (105 °C for 24 h), spiked in the evaporation chamber with a specific amount of labelled water, mixed and then left to equilibrate for two hours. ~~In total,~~F~~ three~~ive sets of spike experiments with different soil textures were performed ~~because it is well-known, that~~as soil texture plays a crucial role during soil water extraction (Orlowski et al., 2016a). In each spike experiment, identical samples were rewetted repeatedly (with the exception of artificially prepared sandy clay, described below) to reveal any shift in the isotopic composition of the extracted water and thus to eliminate any possible influence of the residual water from the sample due to incomplete drying prior to extraction. This follows a procedure described in Gaj et al. (2017).

Six consequent tests (Tab. 1) were carried out in the following way:

F~~or the f~~irst test:~~,~~ W~~only w~~ater of known isotopic composition and quantity (15 ~~ml~~mL) was ~~inserted ~~poured into the heating chambers.

~~-~~S~~For the s~~econd test:~~,~~ D~~d~~isturbed soil samples (~~80 ~~65 g each) of loamy sand texture were ~~first oven-dried at 105 °C for 24 hours and then ~~spiked with 15 ~~ml ~~mL of water of known isotopic composition. The soil samples were reused and re-hydrated ~~in total 4 ~~3 times~~ in this experiment~~.

~~-~~T~~In the t~~hird test:~~,~~ T~~t~~he procedure was the same, as in the second test, ~~with the ~~using~~e~~ ~~of ~~sandy loam soil samples.~~ (Tab. 1).~~

~~For the f~~Fourth test:~~,~~ ~~50 ~~40 g ~~of ~~samples were prepared in the laboratory by mixing sand (60 %) with clay (40 %) and spiking with 10 mL ~~in proportions of 60 % sand and 40 % clay. They were oven-dried at 105 °C for 24 hours and then spiked with 10 ml of water ~~of known isotopic composition. A ~~smaller ~~lower sample size and water amount~~ of water ~~were used to reduce the corresponding extraction time. In this case, a new sample was prepared for each extraction run ~~as ~~due to concerns of possible sealing of the sample after extraction, which would make it difficult to re-hydrate~~the clay samples could not be re-hydrated after extraction~~.

Fifth and sixth tests were used to verify the functionality of the method with a lower water content (10 %). To the fifth test, disturbed soil samples (150 g each) of silt loam texture were spiked with 15 mL of water of known isotopic composition. Since we did not observe any significant sealing in the previous test the soil samples were reused and re-hydrated 2 times. The same procedure was used for the sixth test, only with a different soil texture (clay) where the samples were reused and re-hydrated 3 times.

Table 1: ~~Parameters ~~Sample properties~~of samples used~~ to verify the apparatus functionality~~ of the apparatus~~.

Test	Sample (g)	Water (mL)	Soil (g)	W (%)	θ (%)	Soil texture	% sand	% silt	% clay
1st	15	15	-	-	-	-	-	-	-
2nd	80	15	65	23	18.75	Loamy sand	85.5	5.5	9
3rd	80	15	65	23	18.75	Sandy loam	56.5	34.8	8.7
4th	50	10	40	25	20	Sandy clay	60	-	40
5th	165	15	150	10	9	Silt loam	16	60	24
6th	165	15	150	10	9	Clay	28	28	44

W is gravimetric water content and θ is volumetric water content.

For each test there was used ~~L~~labelled water ~~with a~~ slightly ~~different~~ differing in stable isotope composition ~~was used for each test~~ (Tab. 2), which~~. Isotopic signatures~~ ~~were~~ was analysed at the Institute of Hydrodynamics (Czech Academy of Sciences) ~~on~~ with the~~a~~ L2140-i isotope analyser (Picarro Inc., US). Standard mode (precision of ± 0.03 ‰ and ± 0.15 ‰ for δ^{18}O and δ^{2}H, respectively) was used with 6 injections per sample with the first 3 injections discarded. The isotope ratios are reported in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) (~~(~~δ^{2}H or δ^{18}O = ($R_{sample}/R_{standard}-1$) × 1000 ‰~~)~~, where R_{sample} is the isotope ratio of the sample and $R_{standard}$ is the known reference value (i.e., VSMOW) (Craig, 1961)). The target accuracy of the method is given by the limit of ± 0.2 ‰ for δ^{18}O and ± 2 ‰ for δ^{2}H, which is considered reasonable for hydrologic studies (Wassenaar et al., 2012; Orlowski et al., 2016b). The terms 'shift' and 'bias' were used for an evaluation of the results, where 'shift' means a difference from the labelled water and 'bias' indicates the standard deviation of the data. Please note that these terms are often replaced by the terms accuracy (shift) and precision (bias) in some studies (Revesz and Woods, 1990; Koeniger et al., 2011; Ignatev et al., 2013; Zhue et al., 2014; Sprenger et al., 2015; Gaj et al., 2017).

3 Results

3.1 Waterproof and airtightness test

To test the extraction method and the water- and air-tightness of the apparatus (1st test), 15 ~~ml~~ mL of water of known isotopic composition was used. Extraction of this water amount ~~of water~~ took on average 5 hours. The resulting ~~sample quantity~~recovery ratio after the extraction process averaged~~averaged~~ 99.7 % of the volume of the used labelled water. The ~~missing~~ remaining water fractions were given by the sum of ~~grams of water were mainly due to~~ the residual thin layer of moisture left on the walls inside the collection vessel during the transfer of the samples into the vials, residual moisture inside the apparatus and possible diffusion through the silicon tubing~~the residual thin moisture film that remained on the walls inside the collection vessel~~. The stable isotope composition~~signature~~ of labelled water used for this test was -9.61 ± 0.01 ‰ for δ^{18}O and -66.34 ± 0.05 ‰ for δ^{2}H ~~with a d-excess of 10.5 ‰~~ (N=~~3~~4) (Tab. 2, Fig. 4). The ~~resulting~~ total average of the mean stable isotope composition of extracted water (N=~~12~~13) was ~~depleted~~ shifted by -0.04 ‰ (bias ± 0.06 ‰) and 0.06 ‰ (bias ± 0.35 ‰) for δ^{18}O and δ^{2}H, respectively~~± 0.06 ‰ in δ^{18}O and enriched by 0.06 ± 0.35 ‰ in δ^{2}H which is within measurement inaccuracy of the isotope analyser~~.~~ The d-excess increased to 10.9 ‰ (Fig. 4).~~

3.2 Spike experiments

The other ~~three~~ five tests – spike experiments ~~—~~ ~~to~~ verif~~y~~ying the functionality of the extraction took on average 3 hours for the ~~second (~~loamy sand~~)~~, 4 hours for the ~~third (~~sandy loam~~) tests, and~~ 5 hours for the ~~fourth test (~~sandy clay and silt loam,~~)~~ and 6 hours for the clay samples.~~-~~ The resulting recovery rate after the extraction process attained on average~~d~~ 99.3~~2~~ % of the used labelled water volume ~~of the used labelled water~~ (Tab. 2). ~~-~~The remaining water fractions were given, analogously as before, by the sum of the residual thin layer of moisture left on the walls inside the collection vessel during the transfer of the samples into the vials, residual moisture inside the apparatus and possible diffusion through the silicon tubing. ~~The missing fractions of grams of water were mainly due to the residual thin moisture film that remained on the walls inside the collection vessel.~~ The sixth test represented the only exception (clay soil from the Halaba area, Central Ethiopia), where the recovery rate often exceeded 100 %. Since a similar phenomenon was not observed with the other samples and the apparatus was tested for possible leakage (which was not found), we hypothesize that this error is due to the extreme chemical composition of the selected samples (potential release of crystalline water from the soil itself) or insufficient pre-oven-drying (despite applied 72 hours).

~~For~~ In the second test (loamy sand)~~second test~~, the stable isotope ~~signature~~ composition of labelled water was -9.22 ± 0.01 ‰ for δ^{18}O and -64.56 ± 0.04 ‰ for δ^{2}H ~~with d-excess of 9.2 ‰~~ (N=3) ~~(Tab. 2)~~. The average obtained isotopic ~~signature~~ composition was depleted by 0.03 ± 0.08 ‰ in δ^{18}O and enriched by 0.4 ± 0.34 ‰ in δ^{2}H (N=~~12~~11) (Tab. 2, Fig. 4). As in the first test, the δ^{18}O values were slightly depleted but almost matched the labelled water. However, the δ^{2}H values were relatively enriched ~~and thus the d-excess increased to 9.8 ‰~~ (Fig. 4; Tab. A2).

~~For~~ In the third test (sandy loam), the stable isotope composition~~signature~~ of labelled water was -9.37 ± 0.01 ‰ for δ^{18}O and -64.70 ± 0.05 ‰ for δ^{2}H ~~with d-excess of 10.3 ‰~~ (N=3). The mean isotope composition of extracted water was enriched for both isotopes but with no statistical significance for δ^{18}O (Tab. A2). ~~For~~ The average shift and bias attained~~δ^{18}O by~~ 0.03 ± 0.13 ‰ for δ^{18}O and ~~for δ^{2}H by~~ 0.51 ± 0.5 ‰ for δ^{2}H ~~and the d-excess increased to 10.5 ‰~~ (N=~~12~~15). Compared to the second test~~s~~, the variance of the values ~~has~~ increased.

~~For~~ In the fourth test (sandy clay), the stable isotope composition~~signature~~ of labelled water was -9.54 ± 0.01 ‰ for δ^{18}O and -75.92 ± 0.05 ‰ for δ^{2}H ~~with d-excess of 0.4 ‰~~ (N=3). The mean isotope composition of extracted water was enriched for both isotopes but with no statistical significance for δ^{18}O.~~The mean isotope composition of extracted water was enriched in both isotopes.~~ The values of~~For~~ δ^{18}O increased by 0.03 ± 0.11 ‰ and of ~~for~~ δ^{2}H by 0.68 ± 0.58 ‰ ~~. The d-excess increased to 0.9 ‰~~ (N=~~12~~11).

In the fifth test (silt loam), the stable isotope composition of labelled water attained -9.35 ± 0.02 ‰ for δ^{18}O and -66.06 ± 0.05 ‰ for δ^{2}H (N=3). The mean isotope composition of extracted water was enriched for both isotopes but with no statistical significance for δ^{18}O. The values of δ^{18}O increased by 0.07 ± 0.11 ‰ and of δ^{2}H by 1.31 ± 0.55 ‰ (N=8).

In the sixth test (clay), the same labelled water was used as in the fifth test. The mean isotope composition of extracted water was enriched for both isotopes but with no statistical significance for δ^{18}O. The values were shifted by 0.01 ± 0.25 ‰ for δ^{18}O and 0.96 ± 0.39 ‰ for δ^{2}H (N=12).

The Kolmogorov-Smirnov test at 5% significance level was performed for all sets of the results to determine the normality of the data. The measured data for all six tests exhibited a normal distribution. Furthermore, one sample t-test was performed at 5% significance level to determine whether the extracted values were significantly different from the standard used in the given test. For the first set of the results (extraction test with water only), the average of the data is not statistically different from the standard used. In the remaining extraction tests, using soil, the mean is always statistically identical to the standard used only in the case of $\delta^{18}O$. In the case of $\delta^{2}H$ values, the null hypothesis was always rejected. Furthermore, the data variance of $\delta^{2}H$ is increasing with a higher amount of fine particles in the soil (silt, clay). The statistical test results are summarized in Table A2.

Since the normality test, which is a prerequisite for the t-test, may not be valid on such small data sets, we also performed the Bootstrap analysis which does not require this assumption. This analysis calculates the 95% confidence interval in which the true value is located (Fig. A3). The results of this analysis were consistent with the results of the t-test.

Table 2: Summary of the individual test results.

Test	Type	N	$\delta^{18}O$ (‰)	SD (‰)	$\delta^{2}H$ (‰)	SD (‰)	Sample type	Extraction time (h)	Recovery rate (%)
1st	L	4	-9.61	± 0.01	-66.34	± 0.05	Water	5	99.7
	E	13	-9.65	± 0.06	-66.28	± 0.35			
2nd	L	3	-9.22	± 0.01	-64.56	± 0.04	Loamy sand	3	99.5
	E	11	-9.25	± 0.08	-64.16	± 0.34			
3rd	L	3	-9.37	± 0.01	-64.70	± 0.05	Sandy loam	4	99.2
	E	15	-9.34	± 0.13	-64.19	± 0.50			
4th	L	3	-9.54	± 0.01	-75.92	± 0.05	Sandy clay	5	99.3
	E	11	-9.51	± 0.11	-75.24	± 0.58			
5th	L	3	-9.35	± 0.02	-66.06	± 0.05	Silt loam	6	99.1
	E	8	-9.27	± 0.11	-64.75	± 0.55			
6th	L	3	-9.35	± 0.02	-66.06	± 0.05	Clay	6	99.9
	E	12	-9.34	± 0.25	-65.11	± 0.39			

L and E indicate the labelled and extracted water used in the test, respectively. N stands for the number of samples. The isotope ratios ($\delta^{18}O$, $\delta^{2}H$) and their standard deviations (SD) are reported in per mil (‰) relative to Vienna Standard Mean Ocean Water (VSMOW). The extraction times quoted are average times valid for the disturbed soil samples and may vary with other samples depending on the sample size, texture and water content. The recovery ratio was calculated as the weight of extracted water divided by the weight of the added labelled water and multiplied by 100.

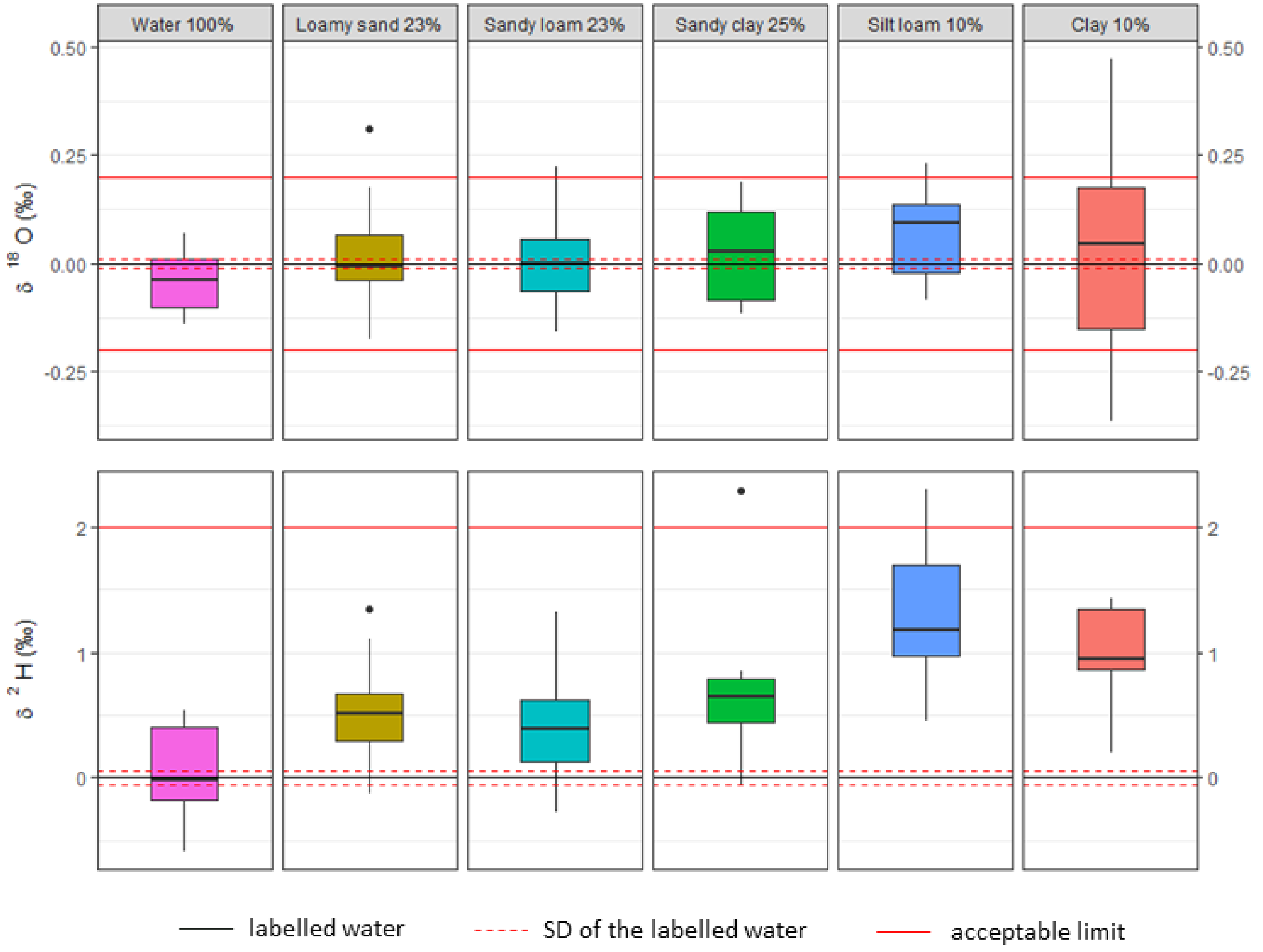
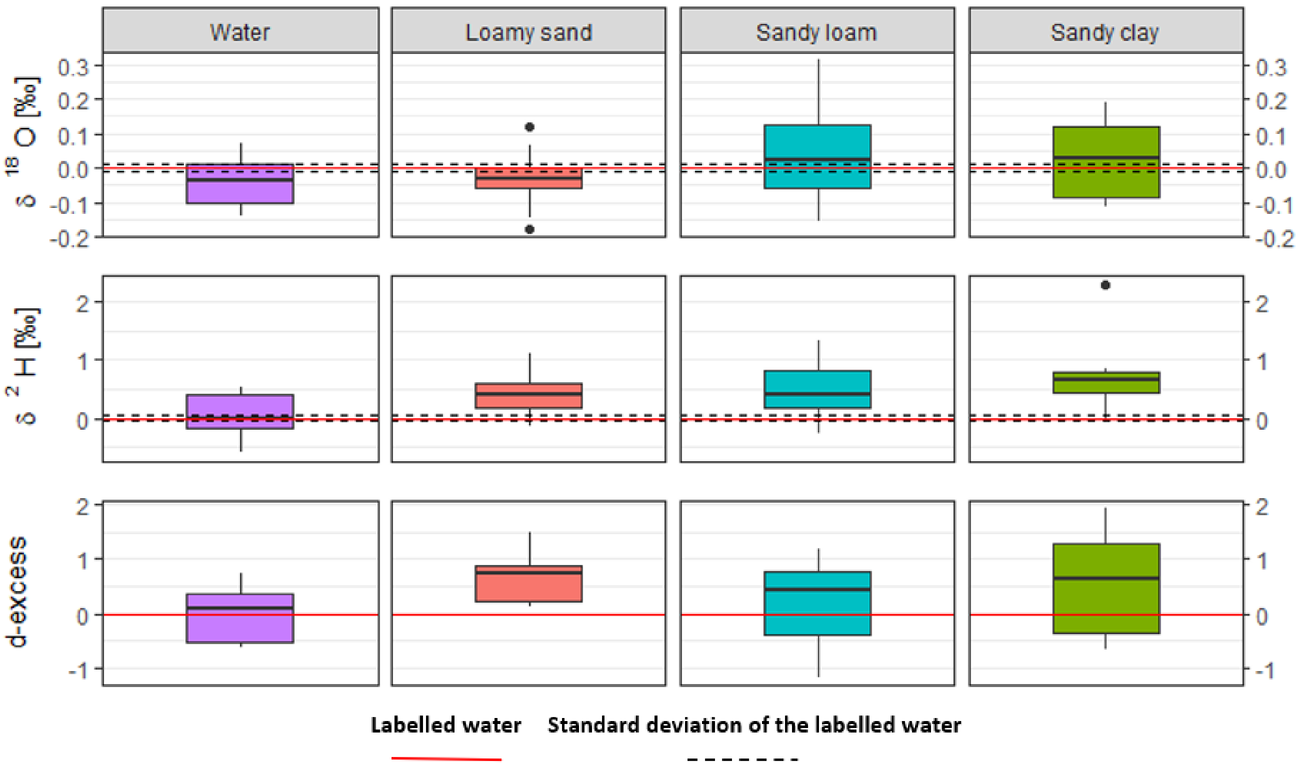


Figure 4: Relative deviation of the isotopic ratio of extracted water compared to the labelled water and its standard deviation. For better clarity, all results are recalculated as if the used labelled water had a VSMOW composition. The acceptable limits are represented by the error of ± 0.2 ‰ for δ^{18}O and ± 2 ‰ for δ^{2}H, which is considered reasonable for hydrologic studies (Wassenaar et al., 2012; Orlowski et al., 2016b).



~~**Figure 4: Relative deviation of the isotopic ratio of extracted water compared to the labelled water (red line) and its standard deviation (black dashed line). For better clarity, all results are recalculated as if the used labelled water had a VSMOW composition.**~~

4 Discussion

4.1 Residual moisture in the apparatus

The apparatus is designed to handle an entire standard soil core (100 cm^3). The sample size is limited only by the ~~size~~ volume of the heating chamber (roughly 400 cm^3 of usable space) and the size of the collection vessel (~ 25 ~~ml~~mL). An advantage of extracting a bigger soil sample over the smaller ones (e.g. < 10 g)~~,~~ is a much better ~~that it~~ representation of the sample properties.~~s a larger area in the soil in comparison to smaller subsamples (e.g.< 10g), which might not be as representative. For this reason~~However, because of this the extraction time and total throughput are lower compared to other methods (e.g. CVE, DVE-LS). The larger amount of obtained extracted water with ~~our~~the proposed extraction apparatus ~~might overprint~~lower a potential inaccuracy ~~due to~~accompanied by lower sampling amounts in other extraction methods. Additionally, it offers the advantage ~~of~~ to run~~ning~~ the same extracted water sample using both~~on~~ ~~an~~the Isotope Ratio Mass Spectrometry (IRMS) and the~~or~~ Isotope Ratio Infrared Spectroscopy (IRIS) machines. ~~We are aware that even~~However, ~~with this apparatus~~ not all water ends up in the collection vessel~~,~~. Based on the estimated gas volume of 4 L, the ideal gas law and equilibrium conditions at 8 °C, the amount of water left in the circuit is approximately 50 mg~~ but a negligible fraction of molecules (approx. 50 mg) remain somewhere inside the circuit~~. Furthermore, humidity gains and losses can occur during the extraction procedure because of the silicon hoses' permeability. The estimates of humidity losses for the extraction time not exceeding 24 h are less than 0.5 % of the total sample mass, regardless of the extracted water amount. The estimates are based on the water-silicone solubility and permeability (Barrie and Machin, 1969), supposing 50 % relative humidity in the room outside the extractor, and 8 °C cooling water. Under these conditions the absolute air humidity inside the extractor is higher (during the proceeding extraction) or equal to the ambient air humidity, allowing for minor sample losses (< 0.5 %) via vapour permeation when the extraction proceeds, and no losses once the sample is almost or completely dry. The hoses can also absorb water vapour from the air. The water absorbed in the silicone hoses is released back into the circuit when heated (by calculation estimated to approximately 50 μg). Although silicone hoses may not seem ideal for this purpose, the choice of construction materials was a compromise between handling and operating the extractor and material resistance/neutrality with respect to the extracted water. Despite the potential sample gains/losses~~However~~, these~~is~~ amounts are still~~is~~ marginal compared to the amount of extracted water~~ extracted~~, so it does not ~~have ~~exhibit a major effect on the results (as demonstrated).

Most of these~~these potential~~ error sources can be suppressed by using larger sample sizes. F~~However, f~~or even more accurate results, it might help to choose a different construction material (PTFE, stainless steel), to seal entirely ~~completely seal ~~the apparatus during idle time, pre-drying the empty apparatus or purging the apparatus with dry air, or nitrogen (as inert gas~~es~~). However, the extraction procedure would be more complicated and the nuances that this would resolve are negligible in comparison to other factors (e.~~-~~g. the amount of clay in the sample, the accuracy of measurements of the stable isotope composition itself) which will affect the final composition~~ much ~~more significantly.

Thorough mixing of the sample before pouring from the collection vessel and catching all droplets from the walls to ensure the homogeneity of the sample is necessary. Because of that, the water adheres to the walls of the collecting vessel, whereby the residual amount always remains there while pouring the sample into the vials. This adhered water contributes significantly to the incomplete recovery rate and often covers the majority of this error. Since the sample was mixed (homogenized) during the collection of all residual droplets on the walls of the collection vessel, we assume that the residual film in the glass will not affect the isotopic composition of the sample but only the recovery ratio.

With respect to the Rayleigh distillation principle (Dansgaard, 1964; Araguás-Araguás et al., 1995), the observed shift of extracted soil water towards enriched values of the heavier isotopes also points to imperfect collection of extracted water. The slight enrichment indicates incomplete water condensation and the presence of lighter isotopes (as quantified above) inside the apparatus as also evidenced by the high but incomplete recovery rate. Complete evaporation of the soil water is confirmed by comparison of soil sample weights (weight after extraction for selected samples was equal or slightly lower to the sample weight after pre-oven-drying).

As discussed earlier, two following factors can notably influence the composition of the collected water, thus the reliability of the proposed method: insufficient tightness of the whole circuit (joints, etc.) and permeability of the pipes made of silicon. The absence of the former factor is checked by the recovery rate close to 100 %. The latter factor – possible sample contamination with ambient moisture comprising substantially lighter isotopic composition (~ -13 ‰ and -125 ‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively) – is almost completely suppressed, as the experimental results exhibit only negligible change in the labelled water isotopic composition. Moreover, the observed shift in the water composition (enrichment by heavier isotopes) indicates marginal sample fractionation instead of its contamination by ambient moisture.

~~The missing fractions of grams in the recovery rate are not due to residual moisture in the apparatus, which will contribute only a very small fraction to this error. The incomplete recovery rate is mainly due to the water adhering to the walls of the collecting vessel, whereby the residual amount always remains there while pouring the sample into the vials. Thorough mixing of the sample before pouring and catching all droplets from the walls will ensure homogeneity of the sample. Thus, the residual film in the glass will not affect the isotopic composition of the sample after that.~~

4.2 Extraction time

For many methods, extraction time often plays a significant role in the resulting isotopic composition of the sample (Revesz and~~&~~ Woods, 1990; West et al., 2006; Zhu et al., 2014; Hendry et al., 2015; Orlowski et al., 2018; Orlowski and~~&~~ Bauer, 2020). In ~~our~~ this case, ~~we did not observe~~no ~~any~~ significant differences were observed between ending the extraction at the time when the circuit is visibly dry ~~or~~and prolonging the extraction by an hour or more, because the same dry, cold air is still flowing when the extraction is completed. Once the extraction is complete, the apparatus reaches an equilibrium state at which the amount and composition of the water sample ~~does not change~~are fixed. ~~Our~~ The proposed method is ~~among~~ one of the slower ones ~~when~~ compared to other extraction methods. The extraction time using the CVE method varies from 15 minutes (Orlowski et al., 2018) to 6 hours (Mora and Jahren, 2003). However, it should be added that for the CVE method, sample sizes of 10-20 g are used and only a few mL of water are extracted (Tab. 3), whereas in the presented method extraction of the sample size attained up to 150 g and extracted liquid water amounts up to 15 mL. T~~T~~he extraction time ~~-~~is therefore longer and varies between 3 to ~~5~~ 6 hours depending on the soil texture~~;~~ (the larger ~~surface area and~~ porosity of the sample reduces the extraction time significantly), water content and sample size. The presence of pores in the soil and thus larger surface area for evaporation is also the reason, why the extraction time of some soil samples was shorter than the extraction of water alone (1st test). The soils are dried on a manufactured bed to allow air to reach the soil sample from all sides. Contrarily, the water sample was placed in a small stainless steel bowl enabling air-water interaction only on the surface (upper side). By making this surface larger for the soil, the extraction is faster. Also, the soil itself exhibits a higher thermal conductivity than air.

In the case of low soil moisture, a larger soil sample should be used (to extract at least 7-10 mL of water) resulting in a longer extraction time. The extraction times quoted above are average times valid for the samples used in this study and may vary with other samples (especially undisturbed samples, or samples with different water content).

In large-scale studies, higher sample throughput is an important factor. For these purposes, apparatuses with higher throughput that can handle 30 or more samples in an 8-hour working day are used (Goebel and~~&~~ Lascano, 2012; Orlowski et al., 2013; Yang et al, 2023). ~~Our~~ The proposed apparatus has currently ~~has~~ only four circuits, ~~so~~ hence four soil samples can be processed ~~at the same time~~simultaneously. Depending on the soil type and water content a maximum of two runs per day can be processed. T~~Rather than for large-scale studies and obtaining trends instead of exact values, t~~he apparatus is suitable for smaller~~studies where high~~ high-precision studies where ~~is needed to~~ unambiguous~~ly~~ determination of the water origin is required~~separate the different water pools (McDonell, 2014)~~. Reduction of~~ing~~ the sample size ~~would~~ could increase the throughput ~~by reducing the~~resulting in a reduction of the extraction time, but it could ~~affect the accuracy~~be projected in higher inaccuracy of the results. To apply this method in large-scale studies, it would be necessary to ~~either~~ use more ~~of these~~ apparatuses, change the heating source and use a larger oven to ~~fit~~ accommodate more heating chambers or increase the air circulation speed in the apparatus.

4.3 Comparison of soil water extraction approaches

In order to compare ~~our~~ the proposed method of soil water extraction with other approaches, we gathered ~~precision and accuracy~~the results~~ values~~ presented in other ~~scientific papers~~references. The results proved~~showed~~ (Tab. 3 and Fig. 5) that the presented method is able to fit safely within an acceptable range of accuracy (± 0.2 ‰ for δ^{18}O and ± 2 for δ^{2}H ‰ (Wassenaar et al., 2012)) which is for other methods rather problematic, even if different soil types are used.~~has high accuracy and high precision compared to others.~~ For example, ~~W~~with a ~~clay~~ clay-rich soil sample, ~~we achieve better results than~~the DVE-LS method (Wassenaar et al., 2008) achieves low standard deviations (± 0.02 ‰ and ± 0.5 ‰ for δ^{18}O and δ^{2}H, respectively) but the shift in the data is at (+ 2 ‰ for δ^{2}H) or beyond (+ 1 ‰ for δ^{18}O) the limit of acceptability. McConville et al. (1999) obtained very accurate results with the direct equilibrium method (0.1 ± 0.12 ‰ for δ^{18}O), but only a sandy soil was studied.~~, which has a high precision (± 0.02 ‰ and ± 0.5 ‰ for δ^{18}O and δ^{2}H, respectively) but low accuracy (+ 1 ‰ and + 2 ‰ for δ^{18}O and δ^{2}H, respectively).~~ A ~~direct~~ comparison with the most commonly used method, CVE, is difficult, given due to the huge ~~range~~ dispersion of values presented by different laboratories (Orlowski et al., 2016b, 2018). In this study, we used the reported values of Yang et al. (2023), Newberry et al. (2017) and Koeniger et al. (2011) as a reference. The reported shifts in the data~~accuracy~~ ~~was~~ were between -0.16 to -0.59 ‰ and -2.6 to 2 ‰ for δ^{18}O and δ^{2}H, respectively and the ~~precision~~ deviation was in the range of~~between~~ ± 0.14 to 0.4 ‰ and ± 1.3 to 3 ‰ for δ^{18}O and δ^{2}H, respectively, where the most problematic samples exhibited~~, with the~~ high content of ~~worst accuracy for~~ clay~~ey soils~~ particles. Based on our tests carried out so far, it seems that in some cases the obtained shifts are up to one order of magnitude lower than the shifts in the above studies. ~~Compared to all these cases, our method performed better by more than one order.~~ Th~~es~~e reported values are depleted in both isotopes which ~~is the opposite of most of~~contradicts the values reported in ~~our~~this study (where especially the δ^{2}H values are rather enriched).~~-~~ Orlowski et al. (2016b) showed, that in the case of extraction from sandy samples, the extracted water by the CVE method is almost identical to the applied label water. However, as the proportion of clay particles in the sample increases, the accuracy significantly decreases ~~greatly~~ and the difference ~~to~~ with the labelled water for clay samples is more than 1.5 ‰ and 12 ‰ for δ^{18}O and δ^{2}H, respectively. ~~In our case~~In this study, with an increasing amount of clay in the sample only a gradual shift in isotopic composition is visible~~ only a gradual decrease in accuracy is visible with increasing amount of clay in the sample~~. For both isotopes, there is a higher enrichment of heavy isotopes in the sample and the dispersion of the values increases. Only the δ^{2}H is statistically different from the labelled water used (Tab. A2, Fig. A3).~~However, the~~

~~results of all tests are safely below the limits of ± 0.2 ‰ for δ^{18}O and ± 2 ‰ for δ^{2}H, which is considered reasonable for hydrologic studies (Wassenaar et al., 2012).~~

Many laboratories ~~also~~ have considerable problems with the extraction of water ~~alone~~ itself (Orlowski et al., 2018). The ~~best~~ best-reported ~~accuracy and precision~~results of extracted water in the interlaboratory study by Orlowski et al. (2018) were 0.1 ± 0.1 ‰ for δ^{18}O and -0.8 ± 0.4‰ for δ^{2}H, which was again almost an order of magnitude ~~worse than in our case~~different from the results presented in this study. ~~But o~~Only 2 of ~~the~~ 16 laboratories in the ~~CVD~~ CVE interlaboratory comparison study ~~(Orlowski et al., 2018)~~ ~~were able to obtain such results~~presented comparable results~~, with the others being much worse~~. This ~~proves~~ indicates that the problem with accuracy is not caused by the method itself (CVE can give very accurate results), but it is connected with the possibility of how to arrange ~~depends on~~ the settings of the apparatus. Minor ~~Also, slight~~ differences may occur due to the measurement of the isotopic composition itself, depending on the instrument and method used (Penna et al., 2010, 2012).

The~~ only~~ method ~~that produced comparable~~providing comparable results ~~to our~~ with this study is a modification of the CVE method presented by Ignatev et al. (2013), ~~which~~ using~~ed~~ He as carrier gas instead of water vapour diffusion only. In both cases, ~~M~~mass transfer coupled with gas flow (air in the presented study and He in Ignatev‘s case) ~~has~~ was shown~~proven~~ to be ~~a~~ more efficient compared~~ective process compared~~ to diffusive mass transfer (Ishimaru et al., 1992) and ~~because of that~~hence, ~~much~~ more accurate results can be achieved. The ~~Accuracy and precision of this method were~~reported values by Ignatev et al. (2013) are 0.03 ± 0.08 ‰ and 0.7 ± 0.7 ‰ for δ^{18}O and δ^{2}H, respectively. In comparison with ~~our~~ the proposed method, there is a higher shift for δ^{18}O values~~results~~ ~~were better for the He-purging method~~but a lower shift in ~~and~~ δ^{2}H values in the He-purging method.~~on the contrary for our method.~~ However, it should be noted that these differences of hundredths (δ^{18}O) to units of tenths (δ^{2}H) are mostly within the measurement inaccuracy of an isotope analyser.

-Another step, in our opinion, possibly affecting the CVE results (that is not present in the proposed procedure) is the actual vacuum formation in the CVE apparatus. Although in the prevailing majority, the soil sample is inserted into the apparatus frozen, there is no guarantee that evaporation or sublimation does not occur at very low pressures.~~Compared to other methods (extraction with accelerated solvent, centrifugation, and azeotropic distillation), the accuracy difference in our case is within an order of magnitude higher (Zhu et al., 2014; Leaney et al., 1993; Revesz & Woods, 1990).~~

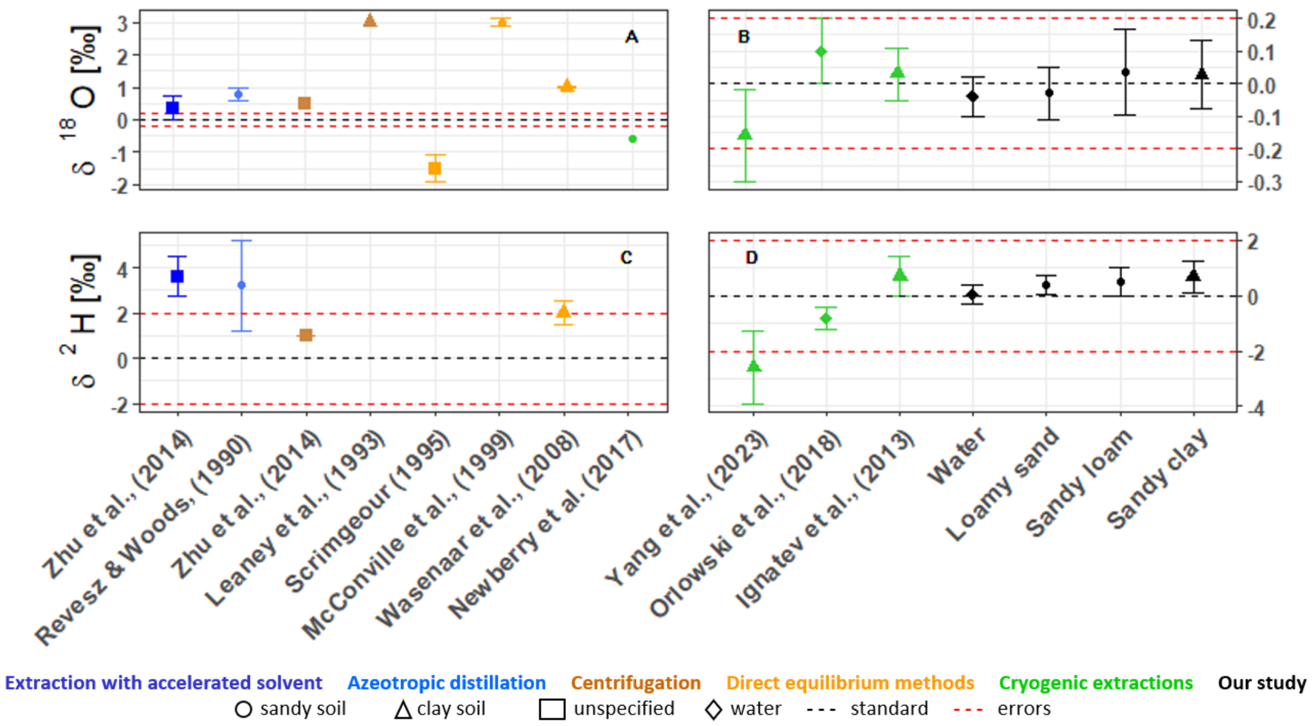
As in the cases of other studies, the reported results in this study were obtained with experimental and partly manipulated test samples. Results may therefore vary when using any other unknown field samples (e.g. with different amounts of organic matter, different texture, etc.).

Table 3: Comparison of the ~~accuracy and precision~~reported results of selected soil water extraction methods in different studies.

Method	Study	Sample type	Average δ^{18}O shift ± SD (‰)	Average δ^{2}H shift ± SD (‰)	N	T (min)	Spiked water (mL)

Extraction with accelerated solvent	Zhu et al. (2014)	unknown soil	0.36 ± 0.37	3.6 ± 0.89	1*	30	1
Azeotropic distillation	Revesz & Woods (1990)	Sandy soil	0.35–0.77 ± 0.2	2–3.2 ± 2	1*	25	3
Ultrasonic centrifugation	Zhue et al. (2014)	unknown soil	0.49 ± –	1 ± –	10	40	1
Centrifugation	Leaney et al. (1993)	Clayey soil	0–3 ± –	–	-	-	-
Direct equilibrium	Scrimgeour (1995)	unknown soil	-1.5– -0.11 ± 0.4	– ± 2	1	16	-
Direct equilibrium	McC~~c~~onville et al. (1999)	Sandy soil	~~3~~ 0.1 ± 0.12	–	1	15	-
Direct equilibrium	Wassenaar et al. (2008)	Clay-rich soil	1 ± 0.02	2 ± 0.5	1	5	-
ACVD	Yang et al. (2023)	Clay loam	-0.16 ± 0.14	-2.6 ± 1.3	14	240	1.2
CVE	Koeniger et al. (2011)	Sandy soil	– ± 0.4	– ± 3	12	15	0.5
CVE	Newberry et al. (2017)	Sandy soil	-0.59 ± –	–	6	90	3
CVE	Orlowski et al. (2018)	Water	0.1 ± 0.1	-0.8 ± 0.4	24	90	2
He-purging	Ignatev et al. (2013)	Clay & silt	0.03 ± 0.08	0.7 ± 0.7	12	180	1.5
~~CAEM~~CASWE (~~our study~~proposed method)	1st test	Water	-0.04 ± 0.06	0.06 ± 0.35	4	300	15
	2nd test	Loamy sand	-0.03 ± 0.08	0.40 ± 0.34	4	180	15
	3rd test	Sandy loam	0.03 ± 0.13	0.51 ± 0.50	4	240	15
	4th test	Sandy clay	0.03 ± 0.11	0.68 ± 0.58	4	300	10
	5th test	Silt loam	0.07 ± 0.11	1.31 ± 0.55	4	360	15
	6th test	Clay	0.01 ± 0.25	0.96 ± 0.39	4	360	15

The values represent the average shift from the labelled water used ± the standard deviation. ACVD stands for automatic cryogenic vacuum distillation, CVE stands for cryogenic vacuum extraction and ~~CAEM~~ CASWE stands for Circulating air soil water extraction method. The CVE results from the study by Orlowski et al. (2018) show only the best results achieved in the comparison of CVEs made in that study. Average δ^{18}O and δ^{2}H shifts represent the deviation from the mean of used *labelled waters ~~(accuracy)~~. SD stands for standard deviation (bias) ~~(precision)~~. T is the extraction time for N samples, that can be processed simultaneously. The number of samples marked with * may vary depending on the size of the apparatus. The last column gives the amount of labelled water used.*



δ ¹⁸O [‰]
δ ²H [‰]
A
B
C
D
3
2
1
0
-1
-2
0.2
0.1
0.0
-0.1
-0.2
-0.3
4
2
0
-2
2
0
-2
-4
Zhu et al., (2014)
Revesz & Woods, (1990)
Zhu et al., (2014)
Leaney et al., (1993)
Scrimgeour (1995)
McConville et al., (1999)
Wasenaar et al., (2008)
Newberry et al. (2017)
Yang et al., (2023)
Orlowski et al., (2018)
Ignatev et al., (2013)
Water
Loamy sand
Sandy loam
Sandy clay
Extraction with accelerated solvent
Azeotropic distillation
Centrifugation
Direct equilibrium methods
Cryogenic extractions
Our study
○ sandy soil
△ clay soil
☐ unspecified
◇ water
- - - standard
- - - errors

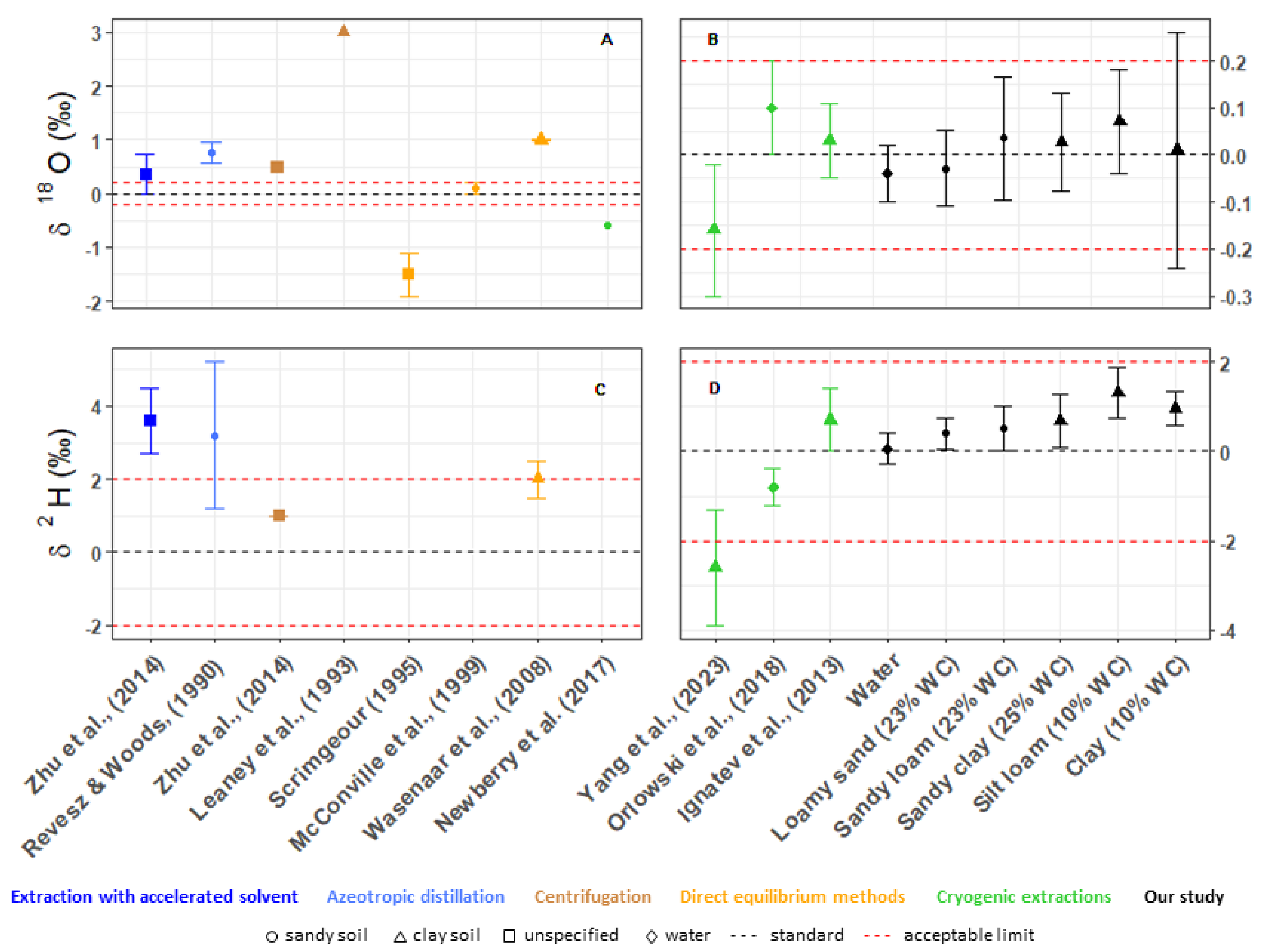


Figure 5: A g~~G~~raphical comparison of ~~our~~ the presented results with other methods (A, B for δ^{18}O; C, D for δ^{2}H). Different markings indicate different sample types. ~~Dashed black line represent the standards used in those tests.~~ The acceptable limits are represented by the error of ± 0.2 ‰ for δ^{18}O and ± 2 ‰ for δ^{2}H, which is considered reasonable for hydrologic studies (Wassenaar et al., 2012; Orlowski et al., 2016b).~~Dashed red lines represent errors of ± 0.2 ‰ for δ^{18}O and ± 2 ‰ for δ^{2}H, which is considered reasonable for hydrologic studies (Wassenaar et al. 2012).~~ The right side of the oxygen graph (B) with more accurate methods has a zoomed y-axis.

5 Conclusions

~~In this study, we presented a~~A new method for soil water extraction – Circulating A~~a~~ir Soil Water E~~e~~xtraction ~~method~~ (~~CAEM~~CASWE) – is presented and the new apparatus developed for this purpose. The method~~that~~ works on the principle of complete evaporation and condensation in a closed circuit~~ and the apparatus developed for this purpose~~. T~~We successfully extracted t~~he soil ~~soil~~ water was successfully extracted from dried and rehydrated soil samples of different textures (~~soil types:~~ loamy sand, sandy loam, ~~and~~ sandy clay, silt loam, and clay). Depending on the soil texture, the~~ with~~ ~~an accuracy~~average shift from the labelled water used ranged between -0.04 and 0.~~03~~ 07 ‰ for δ^{18}O and 0.~~06~~ 4 and ~~0.68~~ 1.3 ‰ for δ^{2}H ~~and~~ with ~~a precision~~the bias ranging ~~of~~from ± 0.~~06~~ 08 to 0.25~~13~~ ‰ and ± 0.34 to 0.58 ‰ for δ^{18}O and δ^{2}H, respectively~~ in individual tests depending on the soil texture~~. The differences between extracted and used labelled water were often within measurement ~~inaccuracy~~ error of the used isotope analyser. From the test we executed so far, we obtained the results with lower shift than the results reported by other soil water extraction/equilibration methods such as the CVE and DVE-LS methods and up to an order of magnitude lower shift than other methods (extraction with accelerated solvent, centrifugation, azeotropic distillation). ~~It provides a better accuracy of results than most other soil water extraction/equilibration methods such as CVE and DVE-LS and up to an order of magnitude better results than other methods (extraction with accelerated solvent, centrifugation, azeotropic distillation).~~ The developed apparatus for this method has a ~~medium~~ low throughput with a maximum of eight samples a day. ~~, high accuracy and high precision.~~ The method has proven its versability in ~~to~~ handling~~e~~ various soil types with different soil textures. The results exhibit high accuracy which makes this method suitable for high-precision studies where unambiguous determination of the water origin is required~~and is suitable for experiments and studies where high precision is required to distinguish individual water pools and where mere trend detection is not sufficient~~.

Appendix

Appendix A

This appendix contains two additional tables and one figure. Table A1 shows all measured data from all functional tests. Table A2 presents the statistical results (test of variance, Kolmogorov-Smirnov test and t-test). Figure A3 depicts the results of the Bootstrap analysis.

Table A1: Summary of the measured data

Sample No.	1st test (water)		
	Extracted water		Labelled water
	δ^{18}O	δ^{2}H	δ^{18}O
1	-9.74	-66.10	-9.60
2	-9.68	-66.49	-9.60
3	-9.65	-66.93	-9.62
4	-9.73	-66.71	-9.61
5	-9.59	-66.36	
6	-9.60	-66.52	
7	-9.71	-66.41	
8	-9.57	-65.83	
9	-9.59	-65.92	
10	-9.54	-65.94	
11	-9.71	-66.04	
12	-9.64	-65.81	
13	-9.64	-66.09	
14			
15			
Average	-9.65	-66.28	-9.605
Standard deviation	0.06	0.35	0.01

	2nd test (loamy sand)				3rd test (sandy loam)				4th test (sandy clay)				5th test (silt loam)
	Extracted water		Labelled water		Extracted water		Labelled water		Extracted water		Labelled water		Extracted water
δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
-66.25	-9.30	-64.26	-9.23	-64.62	-9.06	-63.36	-9.36	-64.66	-9.64	-75.42	-9.53	-75.85	-9.43
-66.38	-9.36	-64.25	-9.22	-64.52	-9.20	-63.74	-9.37	-64.67	-9.64	-75.98	-9.53	-75.95	-9.25
-66.33	-9.26	-64.16	-9.21	-64.54	-9.15	-63.53	-9.38	-64.77	-9.49	-73.63	-9.53	-75.96	-9.12
-66.39	-9.40	-64.68			-9.44	-64.44			-9.65	-75.55			-9.13
	-9.22	-64.47			-9.35	-64.08			-9.45	-75.27			-9.24
	-9.26	-64.62			-9.47	-64.29			-9.39	-75.28			-9.25
	-9.23	-63.89			-9.34	-63.38			-9.62	-75.20			-9.36
	-9.15	-63.92			-9.28	-64.31			-9.52	-75.89			-9.41
	-9.1	-63.46			-9.43	-64.70			-9.39	-75.31			
	-9.22	-64.04			-9.21	-64.01			-9.35	-75.07			
	-9.25	-64.04			-9.5	-64.97			-9.51	-75.07			
					-9.37	-64.58							
					-9.53	-64.97							
					-9.31	-64.12							
					-9.41	-64.32							
-66.337	-9.25	-64.16	-9.22	-64.56	-9.34	-61.19	-9.37	-64.70	-9.51	-75.24	-9.54	-75.92	-9.27
0.05	0.08	0.34	0.01	0.04	0.13	0.5	0.01	0.05	0.11	0.58	0.01	0.05	0.11

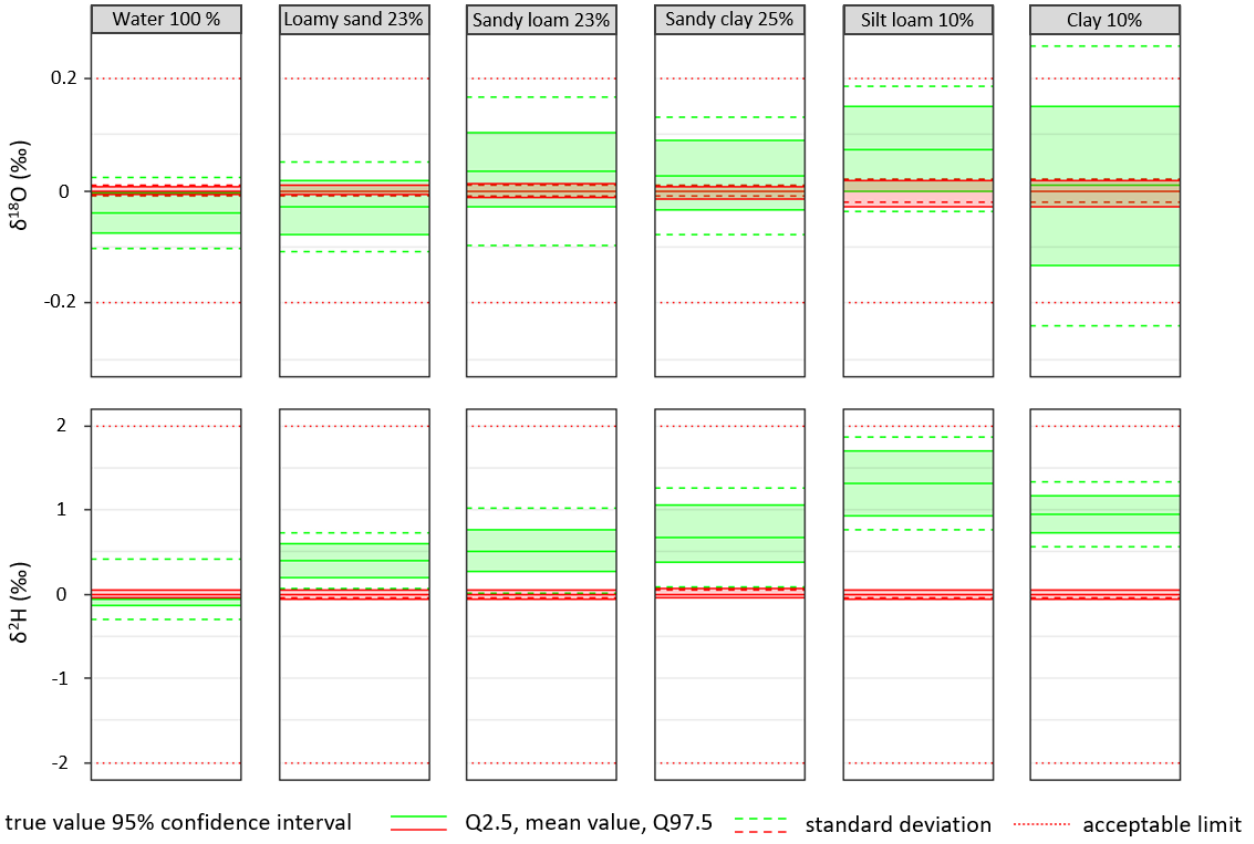
			6th test (clay)			
	Labelled water		Extracted water		Labelled water	
δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H
-64.22	-9.34	-66.12	-9.17	-65.28	-9.34	-66.12
-63.77	-9.33	-66.02	-9.11	-65.18	-9.33	-66.02
-64.41	-9.38	-66.05	-8.88	-65.16	-9.38	-66.05
-64.78			-9.31	-65.86		
-64.98			-9.30	-64.64		
-65.17			-9.70	-65.76		
-65.06			-9.43	-64.72		
-65.62			-9.17	-64.65		
			-9.71	-65.11		
			-9.37	-65.12		
			-9.70	-65.09		
			-9.23	-64.70		
-64.75	-9.35	-66.06	-9.34	-65.11	-9.35	-66.06
0.55	0.02	0.05	0.25	0.39	0.02	0.05

Table A2: Statistical test results

Test		Variance	KS p-values	H_0	t-test p-values	H_0
1st	$\delta^{18}O$	0.004	0.870	TRUE	0.052	TRUE
	δ^2H	0.134	0.837	TRUE	0.553	TRUE
2nd	$\delta^{18}O$	0.007	0.766	TRUE	0.284	TRUE
	δ^2H	0.126	0.976	TRUE	0.004	FALSE
3rd	$\delta^{18}O$	0.018	0.985	TRUE	0.337	TRUE
	δ^2H	0.270	0.983	TRUE	0.002	FALSE
4th	$\delta^{18}O$	0.012	0.786	TRUE	0.440	TRUE
	δ^2H	0.375	0.228	TRUE	0.004	FALSE
5th	$\delta^{18}O$	0.014	0.933	TRUE	0.121	TRUE
	δ^2H	0.349	0.978	TRUE	4×10^{-4}	FALSE
6th	$\delta^{18}O$	0.068	0.850	TRUE	0.909	TRUE
	δ^2H	0.162	0.761	TRUE	4×10^{-6}	FALSE

KS H_0: The Data set has a normal distribution. T-test H_0: The sample mean is equal to the reference value. TRUE means accepting the null hypothesis, and FALSE means rejecting it. The values were rounded to three valid decimal figures respecting the uncertainty of the experimental errors.

Figure A3: The results of Bootstrap analysis



Green colour represents the extracted values and red colour represents the standards used in these tests.

Appendix B

Table B1: List of used components

Component	Type	Supplier	Reference	Quantity	Price [€]
Oven	VT 332 CX	MORA MORAVIA, s.r.o	https://www.alza.cz/mora-vt-332-cx-d6977919.htm?o=1	1	219
Stainless steel bowl	1400 mL	GoEco	https://www.dedra.cz/sk/da30751-dozivotni-celonerezova-doza	4	96
Spiral cooler	Dimroth 14/23	VERKON, s.r.o.	https://www.verkon.cz/chladic-spiralovy-dle-dimrotha/?keyword=dimrotha	4	549
Customized glass	Figure 3	Institute of Chemical Technology in Prague		8	239
Fan	PF40281B1-000U-A99	SUNON	https://www.gme.cz/v/1500620/sunon-pf40281b1-000u-a99-dc-ventilator	8	132
Control unit + accessories	Arduino	Arduino	https://store.arduino.cc/?gad_source=1&gclid=CjwKCAjwkJm0BhBxEiwAwT1AXIKf44cTbvuNm3HGYdzOgppb_OPpGEhaKcywffRo7OP_m2G709MI9RoCE-EQAvD_BwE	-	80
Aluminium profile	40x40 - 104040	ALUTEC KK, s.r.o.	https://katalog.aluteckk.cz/produkt/profil-40x40-104040/	13 m	449
Silicon tube	R973851; R098081	P-LAB	https://www.p-lab.cz/hadicka-silikonova-silnostenna?search=hadice	25 m	510
Glass elbow	14/23	VERKON, s.r.o.	https://www.verkon.cz/koleno-s-nz/?keyword=koleno	4	45
Temperature sensors	(TP-01) K	HOTAIR	https://www.hotair.cz/detail/merici-pristroje/teplomery-a-sondy/termoclankova-sonda-typu-k-tp-01-s-kevlarovou-izolaci-295cm.html	4	40
Technical stainless steel fabric	2/0.56/1000 mm	Euro Sitex, s. r. o.	https://eshop.eurositex.cz/produkt/281/technicka-tkanina-nerezova-2-0-56-1000-mm/	1	52
	0.05/0.035/1000 mm	Euro Sitex, s. r. o.	https://eshop.eurositex.cz/produkt/257/technicka-tkanina-nerezova-0-05-0-035-1000-mm/	1	73
Hose couplings	R034351	P-LAB	https://www.p-lab.cz/spojka-hadicova-system-keck?v=R035451_V_7406	15	96
	R034351			10	84
3D printing material	PETG	Prusa Research a. s.	https://www.prusa3d.com/cs/produkt/prusament-petg-jet-black-2kg/	4 kg	95

Rubber hose insulation	KAIFLEX EF	HORNBACH BAUMARKT CS, s r. o.	https://www.hornbach.cz/p/potrubni-izolace-kaiflex-ef-tube-ef-o-22-mm-sirka-vrstvy-13-mm-delka-1-m/5852909/	8	12
Other components	Fittings; hose holders, reducers; bolts and nuts	-	-	-	239
				Total:	3,010

Author contribution

Concept – JH, OG; Methodology – JK, JH, OG; Software – JH, OG; Investigation – JK; Validation – JK, KF, VS, MS, LV; Visualization – JK; Writing – original draft preparation – JK, KF; Writing – review & editing – JK, JH, OG, KF, VS, MS, NO, LV; Supervision – LV.

~~JH, OG created the concept; JK, JH and OG set the methodology; JH, OG wrote the software; JK carried the investigation; JK, KF, VS, MS and LV performed the validation; JK created visualizations; JK and KF wrote the manuscript draft; all authors reviewed and edited the manuscript; LV was supervising the work.~~

Competing interests

~~At least one~~One of the ~~(~~co-~~)~~authors (NO) is a member of the E~~e~~ditorial B~~b~~oard of the journal Hydrology and Earth System Sciences.

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