HESS Technical Note:

Simple, exact and reliable way to extract soil water for stable isotope analysis

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AUTHORS' RESPONSE

REVIEWER 2

RC:

The paper aimed to introduce a novel extraction device (Circulating air extraction method, CAEM) capable of accurately obtaining soil water and analyzing isotopic compositions. This could significantly contribute to research on soil hydrology employing isotope techniques, given the existing techniques' weaknesses in precision. Nonetheless, I harbor two main concerns regarding this newly developed apparatus:

First, the principle of CAEM aligns with the widely-used CVE system, which separates pore water through evaporation and condensation. Its main contribution is enhancing the capability to transport water vapor using dry air. Based on current experimental data, the accuracy of soil water isotopic analysis seems to have been improved. However, the reasoning behind the increased precision is not adequately explained. Why, given the same principle applied, do the two systems (CAEM and CVE) provide vastly differing accuracies in determining soil water isotopes? These questions are not adequately addressed in the paper.

AR:

We would like to thank the reviewer for his/her time and effort to provide a valuable feedback, we appreciate it a lot. Now to the first comment. The difference is briefly described in the text in the section 4.3 Comparison of soil water extraction approaches. Here we point out probably the most accurate modification of CVE by Ignatev et al. (2013). This method, like our method, uses carrier gas (in the case of Ignatev it is He, in our case it is air), which increases the extraction efficiency. As shown by Ishimaru et al. (1992) mass transfer coupled with gas flow has proven to be a more effective process compared to diffusive mass transfer, which is used alone in most of the CVE approaches. Another step that, in our opinion, could afect the CVE results and is not present in our procedure is the actual vacuum formation in the CVE apparatus. Although the soil sample is in the vast majority inserted into the apparatus frozen, there is no guarantee that evaporation or sublimation does not occur at very low pressures. We will try to discuss the advantages in more detail in the revised text version.

RC:

Second, soil water isotope analysis, especially for soil with high clay content and low water content, remains a critical challenge. The present study just tested CAEM's isotopic accuracy on high water content soils (>18.75%), but this alone does not warrant a definitive claim about its superiority in overall

reliability and precision. Without adequate validation in low water content soils, any claims about its better performance would be baseless and illogical.

AR:

Yes, this is absolutely true. We chose the analysed samples due to their high occurence in the Central Europe where all our experimental sites are located. This was the reason, why we preffered these types of soil. However, in order to support our claims concerning efficiency of the proposed method, consequent experiments were carried out with silt loam and clay soils (with 10 % gravimetric water content). The obtained results are within the limits of acceptability (0.2 ‰ for $\delta^{18}O$ and 2 ‰ for δ^2H) and support efficiency of the method and apparatus also in this range of soil texture, water content and extreme chemical composition (in case of the Ethiopian soil sample). The results will be included in the revised manuscript.

Added soils:

	Origin	Clay (%)	Silt (%)	Sand (%)	Soil (g)	Water (ml)	W (%)	θ (%)
Silt loam	Czechia	24	60	16	150	15	10	9
Clay	Ethiopia	44	28	28	150	15	10	9

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

Results with added tests:
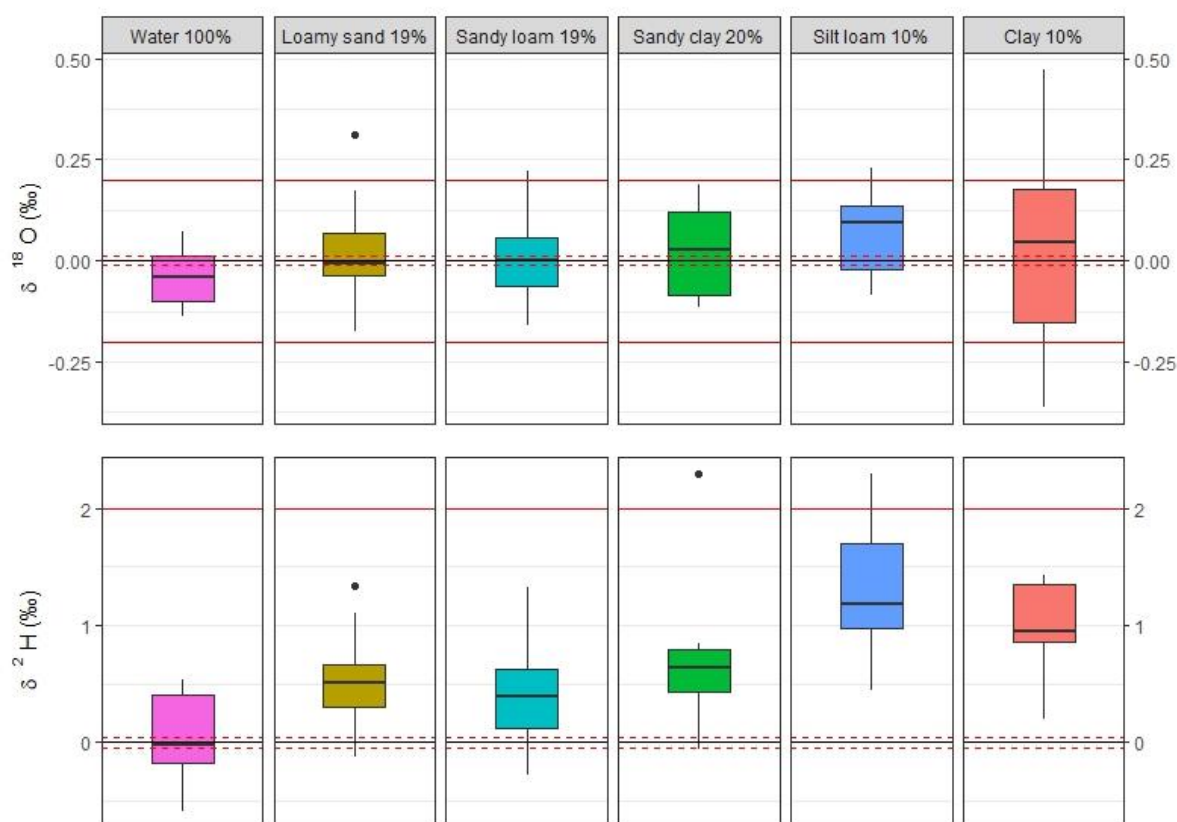
RC:

Line 99: Why choose tap water at 8 °C for cooling? At this temperature, water vapor in the pipes does not fully condense, meaning some evaporated soil water remains uncollected. It might potentially affect the accuracy of isotopic analysis.

AR:

Using the tap water for cooling is motivated by its availability, cooling temperature close to the ambient air dew temperature (preventing the ambient air condensation on the cooling loops and possible sample contamination), and prevention of formation of frosting inside the apparatus, which in our experience could increase the risk of blocking the inlet pipes, damaging the glass parts and increase the difficulty of extracted sample handling (frost on the cooler and collecting vessel walls would have to be melted first, prior the sample handling). On top of that, with respect to the vapor pressure at the extraction temperature (105 °C: 121 kPa), there is no such a difference in the extraction rates between using the cooling circuit operated at 8 °C (1 kPa) and the one operating at, for example, -10 °C (0.3 kPa).

RC:

Line 110: Figure 2 presents the cooling systems. The cooling pipes are connected in series with four distinct evaporation circuits. This configuration would provide better cooling for the first circuit and somewhat less effectiveness for the last one. As a result, the time required for completion of water extraction might vary among the four circuits. Is that a problem in your experiment?

AR:

Thank you for this logical question. The differences in the temperature of the cooling water in cooler 1 and 4 are negligible since the water is flowing through the cooling system permanently. We did not observe any differences between circuits in terms of recovery ratio, stable isotopic composition of the samples or extraction time due to this. During the actual use with real samples the time required for extraction will of course vary within a circuit, but this will be mainly due to the different soil properties, amounts of water extracted in each circuit and also slightly different lenghts of individual circuits.

RC:

Section 2.3 : Separation pore water from soil by evaporation and recondensation involves the error of evaporation fractionation. The first thing to ensure is that the soil pore water could be completely evaporated and all water vapor would be condensed and collected. Therefore, the extraction efficiency or collection efficiency are important quantitative indicators to evaluate whether this set of procedures is qualified. Please add how to measure or calculate the extraction efficiency.

AR:

For this purpose, we randomly performed a test with some samples where we compared the weight of the dry sample from the extractor which was always lighter or at most the same as the dry weight of the

sample from a conventional Memmert dryer, where the sample was also dried at 105 °C for 24 h. This procedure is copied from CVD extraction efficiency determinations and is therefore not unique to our method. However, these tests were not performed with every sample. The control of collection efficiency was carried out for each sample by weighing the water used before and after extraction. From these numbers, the recovery rate reported in the text was calculated. We will make this more clear in the revised manuscript version.

RC:

Line139： Why repeated drying and wetting 4 times?

AR:

Identical samples were rewetted to see any shift in the isotopic composition of the extracted water. This shift could be due to residual water from the sample due to incomplete drying prior to extraction (Gaj et al. (2017)). With repeated extractions we should see how the memory effect of this residual water diminishes. However, we did not see any such shift in the isotopic composition, from which we concluded that we had prepared the samples correctly for the extraction itself.

In the tests with artificial soil, a different soil sample was used for each extraction run because we were concerned that we would not be able to re-saturate the dried sample. Please note, that this did not prove to be the case. The statement on lines 143-144: „In this case, a new sample was prepared for each extraction run as the clay samples could not be re-hydrated after extraction." is incorrect since it was only our assumption and will be corrected in the final text. At the end of the extraction, we did not observe any significant compaction or sealing of the sample. That is why we used the same samples repeatedly also for the clay soil sample extraction test.

RC:

Section 2.4： How is the soil-water mixture evenly mixed in the spiking test? If water does not uniformly moisten the soil particles, the actual soil water content will be higher than the design value.

AR:

The samples were moistened in the evaporation chamber and left to rest for a period of time (2 h) to absorb the added water. For better moisture distribution, it is advisable to use a spray instead of pouring water into the sample or injections directly into the soil. But from a pedological point of view, even the soil itself is not homogeneous and there are drier and wetter places in the soil profile, and the resulting soil moisture is only the average of the soil volume examined (so a more realistic representation of field conditions). The bigger the sample, the bigger the differences. It would be possible to play with the homogenization of the soil sample, however, the process itself would most likely lead to a change in the isotopic composition of the water used even before the actual extraction takes place. We will describe the procedure in more detail in the revised manuscript version.

RC:

Line 159: Why does it take 5 hours to extract pure water? but soil takes three hours?

AR:

The reasons are three-fold. First 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). Second, the difference is also in the size of the active surface from where the water can evaporate. By making this surface larger for the soil, the extraction is faster. Finally, the soil itself has also a higher thermal conductivity than air. We will make this clearer in the revised manuscript version.

RC:

Line 170 : How to determine whether the lost water is left in the pipe wall?

AR:

The lost water (incomplete recovery rate) has two main reasons. First, a small amount of water always remains in the apparatus. The water is not left at the pipe wall, it remains as a vapor in the pipes, because it is at equilibrium with the collected water cooled to 8 °C. There is no liquid water left in the circuit, except for the collecting vessel. Based on the estimated gas volume of 4L, the ideal-gas law and equilibrium conditions at 8 °C, the amount of water left in the circuit is approximately 50 mg.

The second reason is diffusion through silicone tubes. The engineering estimates of humidity gains and losses during the extraction procedure are less than 0.5 % of the total sample mass, regardless of the amount of water extracted and the extraction time not exceeding 24 h. The estimates are based on the water-silicone solubility and permeability (Barrie & Machin (1969)), 50 % relative humidity in the room outside the extractor, and 8 °C cooling water. At 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 vapor permeation when the extraction proceeds, and no losses once the sample is almost or completely dry.

Assumptions for the calculation:

-        Constant air properties in the hose and room throughout the extraction (temperature humidity) - we have controlled conditions in the laboratory

-        Validity of the ideal gas equation of state

-        Hose temperature is the same as the gas temperature in the hose (insulation + oven heating)

RC:

Section 3.2 : What role does the d-excess value play in your analysis?

AR:

Thank you for this point. In the study of Sprenger et al. (2015), the d-excess was used to correlate with the soil water content for the CVE method where there was a weak correlation of 0.4. But since we used different labelled water for each test, we can not try to do the same correlation. For that reason, we will delete the d-exces values from the manuscript.

RC:

Section 4.1：A comparison of the amount of water collected with the amount added should be given in order to show the air tightness.

AR:

Thank you for this comment. We will add the % values from section 3.1 and 3.2 to that section.

RC:

The amount of residual water and its effect on isotope measurements are discussed here, but these statements are mainly based on qualitative descriptions, lacking quantitative evidence. Rayleigh model is proposed to quantify the effect of residual water on the isotope of extracted water. In addition, there is not even one paper cited in this section.

AR:

We will add a citation regarding the Rayleigh model in the results section to the added statistical values that for hydrogen show the enrichment of the sample in heavier isotopes. This indicates that the residual moisture will be mainly composed of lighter isotopes, which coreesponds to our results.

RC:

Line 237-238：How could CAEM distinguish between pools of water in soil? Its working principle is the same as CVE, but CVE is difficult to achieve such a purpose.

Thank you for pointing out this confusing phrase. The method we have developed cannot extract only certain pools of water. It extracts all the water in the sample. The idea was that if we are going to be involved in studies where it is the isotopic composition itself that is important (for example, if we separate mobile and immobile water by other experiments), we will need to use extraction methods with high precision to describe the origin of that water. The phrase will be edited to avoid confusion.

RC:

Line263：Change CVD to CVE.

AR:

Thank you for this point. It will be corrected in the revised manuscript.

We would like to thank our reviewer for his/her helpful review, which – we hope – will help us to improve our final work. Thank you really very much.

References:

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Ignatev, A., Velivetckaia, T., Sugimoto, A., Ueta, A.: A soil water distillation technique using He-purging for stable isotope analysis, J. Hydrol., 498, 265–273, https://doi.org/10.1016/j.jhydrol.2013.06.032, 2013

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Statistical results:

Statistical test results

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

Kolmogorov-Smirnov H_0: Data set has normal distribution.
t-test H_0: The sample mean is equal to the reference value.
TRUE means accepting the null hypothesis, FALSE means rejecting it.

The values were rounded to three valid decimal figures respecting uncertainty of the experimental errors.