

Review of Revision Technical note: A fast and objective autosampler for direct vapor equilibration isotope measurements.

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Overall

This paper introduces "VapAuSa," (not sure how this is pronounced) a new automated vapor-equilibration autosampler system designed for implementing the direct vapor equilibration method for H and O isotope measurements of soil porewater (or any medium with water in it). It advances isotope analyses of porewater by improving sample throughput, reducing manual labor, and improving the reliability and reproducibility of stable isotope analysis, particularly for soil porewater samples. Previously, the approach was manual, laborious, involved many steps, and was unique to operational procedures of each laboratory, which often led to systematic difference between laboratories. The benefits of automation are a significant increase in sample throughput, a 90 % reduction of labor, and generally standardizing the measurement process, thereby reducing potential for human error, and minimizing potential evaporitic isotopic changes in stored samples due to faster processing times. This is an invaluable advance for porewater isotopic measurements, and hopefully can achieve a wider adoption by some form of commercialization.

Recommendation: Accept, with major revisions. Some key critical information is missing that must be added (see Major comments).

Writing Style

Regarding scientific writing style, there is widespread inconsistency in the manuscript in grammatical tense, causing confusion. The paper needs to be edited to correct this. It seems a minor thing, but it will improve how the paper reads. Here is the rule to follow: YOUR work and findings must be stated in the past tense (did, determined, tested, had, were), but all published citation findings and well-known knowledge are given in present tense (is, are). An example of this inconsistency referring to the same published work (present tense) is in Lines 19 "they are applied..." and Line 21 "they ~~were~~ ARE also used to estimate.". Many other instances.

Major Comments

Hardware – how are samples thermally controlled? You need to add a descriptive paragraph about this because it a critical aspect to back determine the porewater delta values. Are sample boxes held in an insulated box, T-controlled room? How is T controlled and to what precision. Etc. What is recommended for users?

Sample bags – give a description (Part No., volume etc.) in the Methods and a clear summary of the procedure how samples are added and sealed – this is missing (but briefly referred to later). At least one detailed paragraph regarding this aspect of the operation is needed. This must be linked to software timing (a small bag will deflate quicky etc.). Note too the gas sampling flow rate from a Picarro (CRDS) much slower than an LGR (ICOS) that is mentioned as compatible with the system.

Minor Comments

Title: The word “objective” is not appropriate, and you are missing the main object of the assays (porewater). Suggest changing to “An autosampler for rapid and reproducible direct-vapor-equilibration stable isotope measurements ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of porewater”

Line 3. “...bonded to substances like...”. Bonded is a poor work choice here (suggests a chemical structure). Suggest changing to “... water in or adsorbed to...”

Line 6. “... may undergo evaporative isotopic changes... “

Line 7. “lack objectivity” – again poor work choice. Suggest “...manual measurements require many laborious procedural steps that can easily compromise reproducibility.”

Line 7 – delete “currently”

Line 10 - “...connect to a laser isotope analyzer... automated measurements.”

Line 11 “... performance criteria can be specified... facilitating reproducible analyses”

Line 27 (and other locations) – I realize this can “theoretically” be used for plant water, however, its well known that plant water has a lot of VOCs that wreak havoc with laser analyses through spectral interference. In the experience of this reviewer, DVE does not work well on plant water and even on plant water extracts, unless there is cryogenic purification. Because plants are not the focus of this work, I strongly suggest leaving out any references to plant water unless you can prove with data that it works.

Lines 39-42 – Somewhere in this section you need to emphasize that thermal stability is absolutely critical (and tolerance) because you are using the highly temperature dependent isotope fractionation between measured vapor and the liquid to back calculate the porewater isotopic composition. Also give the equilibrium equation used, e.g. Majoube and others ...

Line 55 alters through? evaporation and diffusion...

Global: never use the term isotopic “signature” – use “values” instead.

Line 56 replace “objectivity” with “automation” (everywhere in the paper).

Line 57 – stray ? in Ceperley reference

Line 59 delete “autonomous” use “automated”

Software – are there any failure monitoring features – leak, pumped the bag too long etc.?

Line 123 – how much soil place in the 500 mL bags? Is this ratio important?

Line 125 – samples were stored at $20\text{ C} \pm 1\text{ C}$ – were samples measured in the same room, and was this potential error in T factored into the reported analytical uncertainty?

Line 163 - should be superscript on delta values

Line 169 – “pinched” – do you mean “punctured” ? - unclear.

Line 175-176 - ??? means differences were $-XX \text{ e-}15$???

Line 221 – you need to explain the reasons for drift (only evaporation?) and how it can be combated.

4.3 Objectivity (not a good word) -> Improving Replication?

Line 248 - replace personal with manual

Line 251 – avoid speculating about plant water as noted.