

## ***Interactive comment on “System for $\delta^{13}\text{C}\text{-CO}_2$ and $x\text{CO}_2$ analysis of discrete gas samples by cavity ring-down spectroscopy” by Dane Dickinson et al.***

**Dane Dickinson et al.**

dane.dickinson@ugent.be

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### **Authors' reply to Anonymous Referee #1 interactive comment (RC1):**

Thank you for reviewing our manuscript. We appreciate both the encouraging comments and criticisms.

In terms of line-by-line edits, thank you for spotting the typos and areas of confusion. All of the points will be accommodated without difficulty in revision of the paper.

The more significant issues that were mentioned:

1. Confusion over the operation of the data-processing software script
2. Clarifying the application to soil headspace samples

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3. Ambiguity over the achieved precision of the method

Regarding point 1: Our software script operates in real-time – processing data, monitoring the measurement process, and prompting the user to introduce syringe samples at the correct time. We will re-write part of the methods section and emphasise the utility of the script. We also intend to produce a short demonstration video to accompany the paper, which should provide the audience with a clear understanding of the measurement procedure and software.

For point 2: We will improve the discussion to explicitly mention application to headspace samples and likely performance in such cases.

For point 3: There has been a misunderstanding of method performance / precision. This was not helped by the unintended omission of the caption to Supplementary Figure S1. We will revise our discussion and other relevant sections to clarify our findings and reduce the risk of confusion in the final paper. For completeness, here below we answer specific issues that were queried on this point:

- Measurement precision is independent of reference gas composition. There is no effect on precision (or accuracy) by measuring a sequence of samples with  $\text{CO}_2$  conc. very variable and different to the reference gas compared to a sequence of uniform samples similar to the reference gas. We meant to report that the method works best in terms of sample throughput rate when  $\text{CO}_2$  concentration of the sample is similar to the reference gas, not that measurement precision was improved.
- For headspace samples much higher in  $\text{CO}_2$  conc. than the reference gas, the only real challenge is a potential slow-down in the sample throughput rate due to increased inter-sample waiting time for memory effects dissipate (NB: this is

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a separate issue post-correction of memory effects in actual sample measurements). Our software script monitors the CRDS data-stream, in real-time, and ensures that memory effects from the previous sample are gone before prompting the operator to introduce the next sample. The bigger the difference in CO<sub>2</sub> composition between the reference and the sample, the longer the waiting time between samples (thus reducing sample turnover rate). For instance, if the reference gas is 500 ppm CO<sub>2</sub> and samples ranged 400-600 ppm (all natural <sup>13</sup>C abundances), measuring 12 samples h<sup>-1</sup> is realistic. However, if the difference in CO<sub>2</sub> conc. between samples and the reference were larger, e.g. if the reference is 500 ppm and samples 2000-3000 ppm, then throughput would reduce to around 8 samples h<sup>-1</sup>. With a sample CO<sub>2</sub> conc. >6000 ppm, the memory effect after each sample takes perhaps 15 minutes to clear, and so throughput would be <5 samples h<sup>-1</sup>. The situation is similar for samples highly enriched in <sup>13</sup>C. An additional (but separate) issue in such examples is that because the normal operating range of G2131-i/G2201-i is 380-2000 ppm and natural abundance <sup>13</sup>C, actual CRDS accuracy may become a question at very high concentrations or <sup>13</sup>C-enrichments (although we found that up to ca. 5000 ppm and +2000 ‰ vs. VPDB, CRDS accuracy is still very good).

- In terms of precision, the repeatability for CO<sub>2</sub> concentration measurements is ca. 0.05 % of the measured value, irrespective of the actual concentration (e.g. it's 0.2 ppm for 400 ppm samples, 1 ppm at 2000 ppm). An exception is at low concentrations (e.g. CO<sub>2</sub> <100 ppm) when CRDS resolution holds constant in absolute terms at around 0.02-0.05 ppm instead of a relative 0.05 %. Precision in δ<sup>13</sup>C is difficult to communicate because δ<sup>13</sup>C is a relative measure itself and describing the precision of a relative measure becomes confusing and misleading when a large range of values is covered, as in our precision tests. The most important point to understand is that, all else being equal, higher CO<sub>2</sub> conc. improves precision in isotope ratio measurement. For samples with natural <sup>13</sup>C

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abundance and atmospheric CO<sub>2</sub> conc., we found that precision in δ<sup>13</sup>C is ca. 0.15 ‰ (inter-sample SD). The reported 0.33 ‰ is the SD of 200 samples over a 9-month period. However, that is not a good indication of the repeatability from successive samples during 1 day in the lab. The gap between 0.15 ‰ and 0.33 ‰ shows the additional presence of small random instrument/methodological drift (inaccuracy) over the course of 9-months of operation. The report of 0.35 ‰ is the mean intra-sample SD of the 200 samples, and this value does indeed match our observations from the systematic precision testing. For the case of soil headspace samples (with natural abundance <sup>13</sup>C-CO<sub>2</sub>), if multiple samples are taken at a time, then precision of ca. 0.15 ‰ can be expected (inter-sample SD). However if only one headspace sample is taken at each time-point, the only precision value available is the intra-sample SD of that single sample, which will be ca. 0.3 ‰. At higher CO<sub>2</sub> concentrations, both these precisions may improve slightly.

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