Readme and additional discussion: Emanuelsson et al. 2015 AMT

Data and Matlab code for key stability test figures (Emanuelsson et al. (2015), Figures 4 and 5), Allan deviation plots, are presented here. This document also contains some additional discussion about the Emanuelsson et al. (2015) paper.

Files:

Allan_deviation_wvia_DE_github_2018.m

ImportLGRall.m

ImportLGRall2014.m

allan.m (File Exchange file)

https://se.mathworks.com/matlabcentral/fileexchange/13246-allan

Excel file

allan_a_b.csv (get assigned start and stop # for LGR data files)

LGR raw data files are available for download here:

https://figshare.com/articles/_/6895010

https://figshare.com/s/bfc2a74ac5af2577b82e

https://figshare.com/s/349a79c1c8ba9d36bab8

Introduction

You can use the data and analyzes code provided on the github (https://github.com/demanuelsson) to check my results or adapt the code for your own project. If you find the code helpful and decide to use it for your project please recognize this by using the following citation.

Emanuelsson, B. D., W. T. Baisden, N. A. N. Bertler, E. D. Keller, and V. Gkinis (2015), High-resolution continuous-flow analysis setup for water isotopic measurement from ice cores using laser spectroscopy, Atmos. Meas. Tech., 8(7), 2869–2883, doi:10.5194/amt-8-2869-2015.

Paper abstract. Here we present an experimental setup for water stable isotope (δ18O and δD) continuous-flow measurements and provide metrics defining the performance of the setup during a major ice core measurement campaign (Roosevelt Island Climate Evolution; RICE). We also use the metrics to compare alternate systems. Our setup is the first continuous flow laser spectroscopy system that is using off-axis integrated cavity output spectroscopy (OA-ICOS; analyzer manufactured by Los Gatos Research, LGR) in combination with an evaporation unit to continuously analyze water samples from an ice core. A Water Vapor Isotope Standard Source (WVISS) calibration unit, manufactured by LGR, was modified to (1) enable measurements on several water standards, (2) increase the temporal resolution by reducing the response time and (3) reduce the influence from memory effects. While this setup was designed for the

continuous-flow analysis (CFA) of ice cores, it can also continuously analyze other liquid or vapor sources. The custom setups provide a shorter response time (~54 and 18 s for 2013 and 2014 setup, respectively) compared to the original WVISS unit (~62 s), which is an improvement in measurement resolution. Another improvement compared to the original WVISS is that the custom setups have a reduced memory effect. Stability tests comparing the custom and WVISS setups were performed and Allan deviations (σAllan) were calculated to determine precision at different averaging times. For the custom 2013 setup the precision after integration times of 10^3 s is 0.060 and 0.070‰ for $\delta^{18}O$ and δD, respectively. The corresponding σAllan values for the custom 2014 setup are 0.030, 0.060 and 0.043‰ for $\delta^{18}O$, δD and $\delta^{17}O$, respectively. For the WVISS setup the precision is 0.035, 0.070 and 0.042 ‰ after 10^3 s for $\delta^{18}O$, δD and $\delta^{17}O$, respectively. Both the custom setups and WVISS setup are influenced by instrumental drift with $\delta^{18}O$ being more drift sensitive than δD. The σAllan values for $\delta^{18}O$ are 0.30 and 0.18‰ for the custom 2013 and WVISS setup, respectively, after averaging times of 10^4 s (2.78 h). Using response time tests and stability tests, we show that the custom setups are more responsive (shorter response time), whereas the University of Copenhagen (UC) setup is more stable. More broadly, comparisons of different setups address the challenge of integrating vaporizer/spectrometer isotope measurement systems into a CFA campaign with many other analytical instruments.

Results

Figures 1a and 1b reproduce figures 4 and 5 in Emanuelsson et al. (2015). Figures 1c and 1d is the same as Figure 1a and 1b, but also show additional 2013 setup stability tests (thick dark red lines). And figures 1e and 1f show additional 2014 setup stability tests (thick dark blue lines). The additional 2013 tests all fall close to the previously published tests (Figures 1a and 1b). The additional 2014 does not all fall close to the previously published runs and the 2014 tests vary more between tests compared to the 2013 tests.

Discussion

As the additional 2013 setup test fall close to the previously published results, the paper provide a good estimate of the stability of the 2013 setup. In contrast, the 2014 setup tests show a wider spread than the two test published in Emanuelsson et al. (2015) and the tests originally displayed in the Emanuelsson et al. (2015) paper shall be viewed as a depiction of the system when its performance is optimal. The focus the Emanuelsson et al. (2015) paper is on the 2013 setup. The tests described in Emanuelsson et al. (2015) were done prior to the 2014 RICE CFA ice-core processing. Preliminary results from the 2014 setup were however included.

Figure 1 shows that the 2014 setup has great potential, indicated by the presence of a number of long stable runs. When the article was written we believed that this stability would be achievable during the 2014 processing. However, with ideal conditions being hard to achieve, the Allan tests for the 2014 setup are not likely to be representative for the actual operational conditions during the 2014 ice-core processing. Thus, the Emanuelsson et al. (2015) paper mainly describes the 2013 setup, which were used for the majority of the processing of the RICE core (down to 500 m). A follow-up study, Keller et al. (2018), estimates the uncertainty of the isotope CFA measurements during the 2014 ice-core processing.

Figure 1 indicate that the 2013 setup is associated with reduced uncertainty compared to the WVISS setup for shorter integration times. However, the 2013 setup is associated with more long-term drift compared to the WVISS. The Copenhagen Picarro system outperforms the other setups. During ideal conditions the 2014 setup reaches similar level of stability for δD. Further system development would be needed, however, to ensure that the 2014 setup is consistently stable, that is, that there is less variability between the stability tests.

Interestingly, four consecutive runs (12 June–15 June 2014, not included in the 2015 paper) show no signs of long-term δD drift, i.e. the Allan plot does not slope upwards for longer integration times ($>10^3$ s). And these runs resemble the stable Copenhagen system for δD. (If you run the code you can confirm this by comment out all the additional runs except these).

Additional discussion. Note, that the calibration scheme used in the Emanuelsson et al. (2015) is unconventional and has been criticized. The middle standard RICE and ITASE, the most depleted standard, is used for the two-point calibration. The relatively enriched standard, WS1, is used as the check standard. Conventionally you would choose your standards so that the standards used for the two-point calibration envelops the sample data, that is, in our case, ITASE and WS1. The rationale for this choice was that using the RICE-ITASE scheme the calibrated CFA data agreed better with discrete measurements of the ice core data. The discrete ice-core isotope data was measured on the same or a similar LGR (DLT-100) analyzer. But, importantly, in the GNS NIC lab, which utilize other internal standards that envelop the isotope sample data. Therefore, in my mind, one cannot argue the data was “pushed” in a certain direction (towards lower values). I regret that the calibration scheme wasn’t described in a clearer way in the paper. As it was written it is hard for the reviewer to catch that the scheme is unconventional and they thus don’t get a chance to raise any potential questions. Discrete measurements could also have analyzed on IRMS instrument, to investigate this potential problem further. Note that the Allan and response time tests presented in the paper are utilizing raw (uncalibrated) data.

We got help from the Boulder Colorado ice-core team when we started to set up our CFA isotope system. This should have been acknowledge in the paper. We use the same type of multi-port valve, tubing and fittings as they did. However, we never claimed to have invented the use of the nebulizer in ice-core science (Jones et al. 2017). The nebulizer, among several other key components used in our system, was, in fact, part of the LGR WVISS evaporator package. One of the points of the paper was that we used the WVISS framework and just put in our own efficient evaporator unit, which was relatively simple to construct. Note, however, that the 2014 evaporator is more intricate piece of engineering (HAL archive ref).

Minor comments (highlighted by one of my PhD thesis examiners, Nerilie Abram, and corrected in the thesis version of the article (Emanuelsson 2016)):

Third paragraph in the “Introduction of the sample into the carrier gas” section. It should say plumbing here, not pluming.

At the end of the first paragraph of the “2.2.1 WVISS system section” and in the second to last paragraph in the “Introduction of the sample into the carrier gas” section it should say pump P3 (Not P2; Figure 2, Emanuelsson et al. 2015). That is, it should be: “Additional flow resistance introduced by the multi-port valve necessitated the use of a peristaltic pump (P3; MP2, Elemental Scientific) to…” and “P3 provides a constant water flow rate of 50 to 150 µL min-1 to the nebulizer…”.

References

Emanuelsson BD, Baisden WT, Bertler NAN, et al (2015) High-resolution continuous-flow analysis setup for water isotopic measurement from ice cores using laser spectroscopy. Atmos Meas Tech 8:2869–2883. doi: 10.5194/amt-8-2869-2015

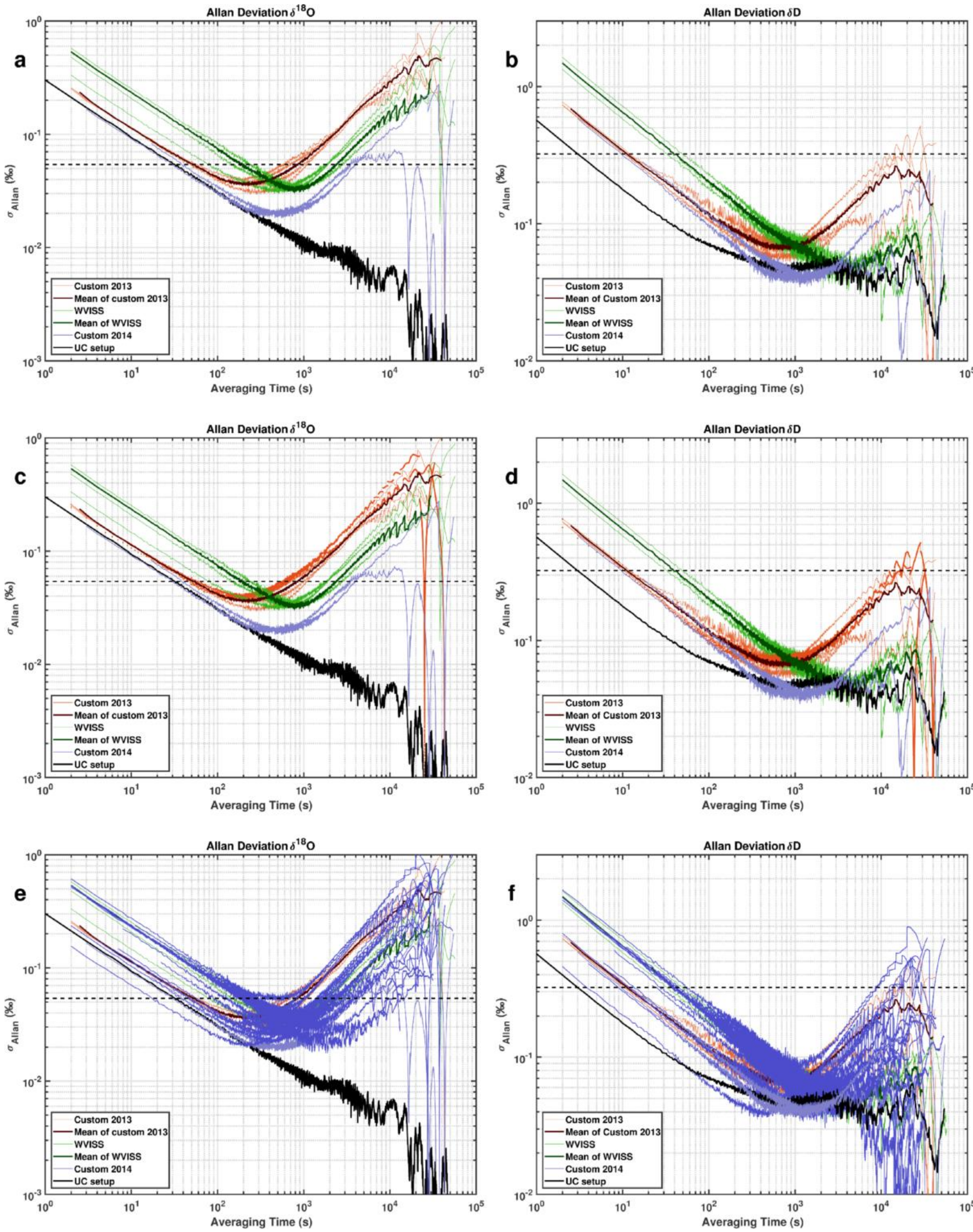
Emanuelsson D (2016) High-Resolution Water Stable Isotope Ice-Core Record: Roosevelt Island, Antarctica: a thesis submitted to the Victoria University of Wellington in fulfilment of the requirements for the degree of Doctor of Philosophy (Geology) / by B. Daniel Emanuelsson. Thesis (Ph.D.)--Victoria University of Wellington, 2016.

Jones TR, White JWC, Steig EJ, et al (2017) Improved methodologies for continuous-flow analysis of stable water isotopes in ice cores. Atmos Meas Tech 10:617–632. doi: 10.5194/amt-10-617-2017

Keller ED, Baisden WT, Bertler NAN, et al (2018) Calculating uncertainty for the RICE ice core continuous flow analysis water isotope record. Atmos Meas Tech Discuss 2018:1–20. doi: 10.5194/amt-2017-387

Daniel Emanuelsson. Continuous vapor mode LGR manual Measuring water stable isotopes (δD, δ 18 O, δ17O) using laser spectroscopy. [Research Report] GNS Science. 2017. 〈hal-01847099〉

Figures


a
Allan Deviation δ18O
σ Allan (‰)
Averaging Time (s)
Custom 2013
Mean of custom 2013
WVISS
Mean of WVISS
Custom 2014
UC setup
b
Allan Deviation δD
σ Allan (‰)
Averaging Time (s)
Custom 2013
Mean of Custom 2013
WVISS
Mean of WVISS
Custom 2014
UC setup
c
Allan Deviation δ18O
σ Allan (‰)
Averaging Time (s)
Custom 2013
Mean of custom 2013
WVISS
Mean of WVISS
Custom 2014
UC setup
d
Allan Deviation δD
σ Allan (‰)
Averaging Time (s)
Custom 2013
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WVISS
Mean of WVISS
Custom 2014
UC setup
e
Allan Deviation δ18O
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Averaging Time (s)
Custom 2013
Mean of custom 2013
WVISS
Mean of WVISS
Custom 2014
UC setup
f
Allan Deviation δD
σ Allan (‰)
Averaging Time (s)
Custom 2013
Mean of Custom 2013
WVISS
Mean of WVISS
Custom 2014
UC setup

Figure 1. Allan deviation stability plots for δ18O (left column) and δD (right column). Red lines depicts the 2013 setup, blue lines the 2014 setup and green lines the WVISS setup. (a, b) As in Emanuelsson et al. (2015), (c, d) as in (a, b) but also showing additional 2013 setup tests (dark thick red lines), (c, d) as in (a, b) but also showing additional 2014 setup tests (dark blue lines).