

Interactive comment on “Improving measurements of SF₆ for the study of atmospheric transport and emissions” by B. D. Hall et al.

Anonymous Referee #2

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The paper describes in the first part a significantly improved gas chromatographic measurement system for N₂O and SF₆, and then presents a history of atmospheric SF₆ growth rate based on a dataset compiled from archived high pressure cylinders, continuous measurements and flask samples from twelve locations around the globe. The paper is well written and concise. The technical modifications described could be relatively easily tested or implemented in other laboratories, thus the paper can in principle contribute to improving the SF₆ measurement precision worldwide. The growth rate computed from monthly averages shows interesting intra-annual features that could not be observed from previous annual mean-based estimates.

General comments

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The first part of the paper consists in a description of a new GC –ECD setup that significantly improves the SF₆ measurement. Two important modification sets have been made: (1) the mass flow controllers (MFCs) were replaced by electronic pressure controllers (EPCs); (2) a Molsieve 5A column was added, the initial Porapak-Q columns were shortened and all the column temperatures were modified. I have two comments here:

1. A 3-column ECD setup that is conceptually similar (although implemented into a different GC) has been already described in detail in Moore et al., 2003. The authors should state clearly which is the significant advance or novelty that the present paper brings compared to Moore et al.
2. It is repeatedly declared or suggested through the paper that the new setup with three columns is the reason for the improved precision. However, other significant changes were made at the same time. Moreover, Fig. 4 strongly suggests that the most significant improvement for the lab GC occurred after the introduction of EPCs at the end of 2005, before the change to the 3-column setup. For the in-situ GC, the two changes (3-column and EPCs) were made at the same time, thus the improvement cannot be clearly attributed. Thus based on the evolution of the lab GC, I would rather assume that the improvement was due to the use of EPCs. The precision of the new 3-column system should be compared to the most recent one just before the change (i.e. after the EPC introduction), not only to the old setups.

Specific comments

- typo: page 4134 line 5: “Geller at al”
- page 4136 lines 17-23: does the SF₆ signal to noise ration decrease with increasing CO₂? If yes, could the SF₆ measurement precision be even better at a lower level of CO₂ doping?
- page 4141 lines 14-16: I think the calibration procedure should be explained in more

C1686

detail. The non-linearity cannot be estimated with only two calibration gases, but that's how I understand the text now.

- Fig. 4. What are the grey triangles and the black circles?
- Fig. 10. I suggest moving the model-SF6 red line to the upper plot.

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