Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2017-442-RC2, 2018

Atmospheric Measurement Techniques Discussions

Interactive comment on "Field measurements of methylglyoxal using Proton Transfer Reaction-Time of Flight Mass Spectrometry and comparison to the DNPH/HPLC-UV method" *by* Vincent Michoud et al.

Anonymous Referee #1

Received and published: 13 June 2018

Michoud et al. present a series of measurements and acquisition parameters for the use of measuring methylglyoxal (MGLY) in field measurements with Time-of-Flight Proton Transfer Mass Spectrometry (ToF-PTR-MS). They extensively discuss mass spectrometric interferences and work toward accounting for these interferences to provide a highly sensitive (LOD = 22pptv) technique for the detection of MGLY.

I recommend publication with minor revisions as noted below.

General Comments:

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Discussion paper

The authors present a framework for utilizing ToF-PTR-MS to measure methylglyoxal in the ambient atmosphere. The sampling set up and methodology for the PTR-MS are well developed. What is generally unclear is why the DNPH cartridge sampling method used to compare didn't have a better developed sampling system that would minimize and account for loss mechanisms in the inlet and other bias. If it is known in the literature that MGLY is considered "sticky" for inlets, then steps should be taken to mitigate or quantify the issue, rather than have to use inferences from the field campaign to explain differences later. It would have been a logical next step to apply the calibration procedure used post field campaign with the PTR-MS with the DNPH set up as well to understand and quantify the loss processes of the MGLY in the DNPH set up such as the sampling line and the KI ozone scrubber. As the paper stands the authors have done a good job of sorting out what they can based on the ambient data and the post campaign calibrations with regard to the interference of water clusters and other factors on the MGLY measurements.

In the review of other techniques used to measure MGLY (pages 3-4), the authors rightly point out many of the advantages and disadvantages of other analytical techniques including derivatization and measurement with either GC or HPLC, highly reflective cavity instruments (CE-DOAS and IBBCEAS), and Laser-Induced Phosphorescence. The authors point out the fragile equipment and the need for highly skilled operators as a draw back for these techniques, implying that PTR-MS does not have these as an issue. It could definitely be argued that PTR-MS which comes with a much larger price tag and can certainly be described as temperamental (as any field instrument involving a mass spec and ionization source could be described) certainly need the attention of highly skilled operators and a knowledgeable analyst doing the data work up. The PTR-MS definitely beats out the other techniques in terms of the possible low detection limits, as even in isoprene rich environments such as the LA basin (Washenfelder et al., 2011), while glyoxal is reported by multiple instruments, MGLY is not.

Specific comments:

Page 5 line 21: Methyl glyoxal should also be considered as a 1st generation oxidation product of isoprene oxidation. This was shown mechanistically by Paulot et al. (2009), inferred by Galloway et al. (2011) and measured by Thalman (2013) as a 1.8(0.4)%.

Page 9 line 10: The authors state that the calibration range was higher than the actual ambient range, why not just dilute further to reach the ambient range? Page 10 Line 9: Use “concurrent” rather than “concomitant” which implies that the accompanying of the two measurements was ‘naturally occurring’.

Page 11 line 2: As Reviewer 1 has pointed out, an R2 of 0.48 for two techniques measuring the same compound is much worse than expected, though Thalman et al. (2015) reported R2 values for MGLY in mixed compound experiments in the range of 0.65 between the CE-DOAS and SPME techniques.

Page 14 line 34: It is generally considered that methylglyoxal has a much shorter atmospheric lifetime than glyoxal (which is one of the reasons that it is much harder to measure in ambient air), where MGLY has both a larger rate constant for reaction with OH and a 5x larger quantum yield from photolysis (Plum et al., 1983).

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Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-442, 2018.