

1 We thank Anonymous Referee 2 for their careful reading of our manuscript and appreciate their thoughtful  
2 feedback. We have edited the manuscript to incorporate their critiques, which we feel has improved the overall  
3 quality of this work.

4  
5 Below, Referee comments are presented in bold, and our responses are written in regular type. Line numbers in  
6 responses refer to the “track changes” version of the manuscript, which will be uploaded separately. For explicit  
7 clarity in text changes, added text will be in blue font, while deleted and/or moved text in ~~red-strikethrough~~ for  
8 clarity. Changes to figures will only be outlined in the responses to the Referee.

## 10 Anonymous Referee 2

11 **Halfacre et al. report the construction and evaluation of a spectrometer for quantification of HCl in the**  
12 **atmosphere. The instrument is thoroughly described and was evaluated in the field as part of the**  
13 **Integrated Research Observation System for Clean Air" (OSCA) campaign in Manchester. The**  
14 **instrument's figures of merit are an improvement over existing technology (Table 1). The paper should be**  
15 **published once my comments below have been addressed.**

16 **Title: Please remove the term "Novelty" from the title. Novelty is implied when publishing. Further,**  
17 **TILDAS using astigmatic Herriott cells has been around for at least a quarter century. The main novelty**  
18 **of this work is the extension of known technology (QCL-TILDAS) to a new molecule (HCl).**

19 The title has been modified to “Using Tunable Infrared Laser Direct Absorption Spectroscopy for ambient  
20 hydrogen chloride detection: HCl-TILDAS”.

21 **line 21/301 - "high accuracy". It would help to be more quantitative here and nuanced in the discussion of**  
22 **accuracy. The authors report that the instrument measured 3.6% lower than a commercial HCl cylinder,**  
23 **certified to contain a known concentration within  $\pm 5\%$ . The certification applies to what the**  
24 **manufacturer added to the cylinder; what comes out can be an entirely different matter (subject to**  
25 **regulator passivation etc.). As such, a comparison to a single cylinder does not suffice to validate a new**  
26 **instrument's accuracy in my opinion.**

27 **In this context, are the absorption line strengths well known (and can be used to justify accuracy)?**

28 The line positions for HCl are extremely well known,  $\pm 0.0002 \text{ cm}^{-1}$ , with absorption cross-section line  
29 intensities uncertainties ranging between 1-2%:

30 Li, G., et al., Reference spectroscopic data for hydrogen halides, Part II: The line lists. Journal of Quantitative  
31 Spectroscopy and Radiative Transfer, 2013. 130: p. 284-295.

32 We have added this information and citation within Sect. 2.2.1 (lines 155-157). Further, the cylinder was not  
33 used as a calibration or correction tool, for the exact reasons the reviewer mentions, but instead as a validation

34 of our method. As such, the slope / intercept reported via Fig 4 were not used to adjust any data (now clarified in  
35 Fig. 4 caption and lines 333-336). However, the combination of the well-known line-strengths and consistency  
36 of cylinder measurements are suitable for justifying the accuracy of this instrument.

37 **There is also a zero offset to be considered when discussing accuracy since the instrument reports**  
38 **negative mixing ratios (e.g., Figure 9) which are inaccurate by default. Consider stating a slope**  
39 **uncertainty and a zero offset uncertainty.**

40 The slope/uncertainty reported in Fig 4 were not used in correcting any data (now clarified in Fig. 4 caption, and  
41 lines 333-336). Concentrations were determined using the well-known absorption cross section line strengths,  
42 as above.

43 The negative mixing ratios shown in Fig. 9 are real measurements and would be expected for an instrument with  
44 a non-zero precision error measuring a concentration at or below its limit of detection. Higher time averaging of  
45 the data to reduce the random precision error results in HCl values within the stated uncertainty of zero for all  
46 time periods where negative mixing ratios are shown.

47 **Have the authors considered calibrating or comparing against a wet chemistry technique?**

48 We attempted to confirm our permeation device concentrations as measured on TILDAS via wet chemistry.  
49 Furlani et al (2021) describe a validation technique in which the permeation source is flowed into a basic  
50 solution over 24 hours, and then Cl<sup>-</sup> concentrations are confirmed via ion chromatography.

51 Furlani, T. C., Veres, P. R., Dawe, K. E. R., Neuman, J. A., Brown, S. S., VandenBoer, T. C., and Young, C. J.:  
52 Validation of a new cavity ring-down spectrometer for measuring tropospheric gaseous hydrogen chloride,  
53 Atmospheric Meas. Tech., 14, 5859–5871, <https://doi.org/10.5194/amt-14-5859-2021>, 2021.

54 However, our attempts to use this method with our standardized HCl cylinder produced inconsistent results,  
55 significantly underestimating the cylinder mixing ratio by at least a factor of 2. A variety of flow durations and  
56 conditions were attempted, but these experiments were ultimately abandoned since reproducibility could not be  
57 achieved.

58 **line 114 - replace detection with quantification**

59 The word “detection” has been replaced with “quantification”.

60 **line 128 - I was wondering about the safety of perfluorobutanesulfonic acid, which is partially discussed**  
61 **on lines 186-188. Consider adding a comment regarding safe handling of this compound.**

62 We have now stated that PFBS is handled in a laboratory chemical fume hood, and that the bubbler that houses  
63 the chemical is installed within a sealed container that would contain any potential, albeit unlikely, spillage.  
64 This can now be found on lines 195-210.

65 **lines 147 - 154. Please state the line strengths (or cross-sections) used and how those were determined**  
66 **(Hitran?)**

67 Line strengths for all species are based upon the HITRAN 2016 database:

68 Gordon, I. E., et al.: The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf.*,  
69 203, 3–69, <https://doi.org/10.1016/j.jqsrt.2017.06.038>, 2017.

70 The HCl linestrength is  $4.198 \times 10^{-19}$  cm/molecule. This information has been included in Section 2.2.1 (lines  
71 150-165.

72 **line 153 "well-resolved" - please state the FWHM of these lines and add a graph showing the spectrum**  
73 **you are discussing here (at high and low concentration), so the readers can see for themselves.**

74 The FWHM is 0.010 cm<sup>-1</sup>, which is primarily pressure- and doppler-broadened. The inherent laser linewidth is  
75 <0.001 cm<sup>-1</sup>. This information has been added lines 150-165. Additionally, the requested HITRAN spectrum  
76 has been added as Fig. A1.

77 **line 501-514. Please try to be more quantitative in this paragraph - for example, rather than saying**  
78 **'greatly improve' or 'higher flow inlets' or 'reduce sample air residence time', state by how much or the**  
79 **actual value.**

80 This section has been amended to include pertinent quantitative details (lines 555-570).

81 **Figure 6 - replace sec with s**

82 This has been corrected.

83 **Figure 8 - what caused the second hump at 14:10? Please add an explanation to the caption.**

84 It was not determined what caused the 2<sup>nd</sup> hump. These experiments occurred in an air-conditioned laboratory,  
85 so it is possible it is related to an ambient temperature effect on the instrument inlet or HNO<sub>3</sub> permeation device.  
86 However, this experiment was repeated several times, and we have replaced this figure with an alternate  
87 experiment where a 2<sup>nd</sup> hump is not present.

88 **Figure 9 panels (a) and (c) - both the HCl and NO<sub>2</sub> data exhibit spikes and negative concentrations, even**  
89 **when averaged. Please add some discussion to the text as to the meaning of this, potential causes, and**  
90 **remedies. Consider adding a horizontal line to show limits of detection or quantification.**

91 Negative concentrations for the reported HCl data may be caused by blank measurements being recorded as  
92 larger than ambient measurements. Cylinder HCl addition experiments during the day between 19-21 July may  
93 have influenced the blanks if not enough time for signal recovery was allowed. This has been clarified in the  
94 caption of Fig. 9. We have additionally added a 1Hz, 3 sigma LOD line to Fig. 9.

95 Despite calibrations and nearly complete convertor efficiency testing, the NO<sub>z</sub> measurement is highly uncertain,  
96 as its calculation relies on individual measurements of NO<sub>y</sub>, NO, and NO<sub>2</sub>; because it is an additive  
97 measurement, the uncertainties are also additive. This has been explored in more detail by San Martini et al.  
98 (2006):

99 San Martini, F. M., Dunlea, E. J., Grutter, M., Onasch, T. B., Jayne, J. T., Canagaratna, M. R., Worsnop, D. R.,  
100 Kolb, C. E., Shorter, J. H., Herndon, S. C., Zahniser, M. S., Ortega, J. M., McRae, G. J., Molina, L. T., and Molina,  
101 M. J.: Implementation of a Markov Chain Monte Carlo method to inorganic aerosol modeling of observations  
102 from the MCMA-2003 campaign – Part I: Model description and application to the La Merced site, Atmospheric  
103 Chem. Phys., 6, 4867–4888, <https://doi.org/10.5194/acp-6-4867-2006>, 2006.

104 We now emphasize the high uncertainty in this NO<sub>z</sub> measurement and that it is used for comparative, not  
105 quantitative, purposes (lines 517-519).

106 **Figure 10 panel (a) - change units to pptv to avoid the x10<sup>3</sup>**

107 This figure has been revised to avoid the x10<sup>3</sup>