

# ***Interactive comment on “Atmospheric gaseous hydrochloric and hydrobromic acid in urban Beijing, China: detection, source identification and potential atmospheric impacts” by Xiaolong Fan et al.***

## **Anonymous Referee #2**

Received and published: 23 January 2021

Fan et al present measurements of HCl and HBr in Beijing during winter. This is a unique dataset for which publication is worthwhile. My comments below mainly focus on clarifications and reporting uncertainties.

Measurement uncertainties need to be reported and shown throughout (including in main text and in figures), with the proper significant figures reported reflecting this uncertainty. In particular, often HBr values are presented quantitatively and with more certainty (over-reported in terms of significant figures) than is appropriate when the methods (Line 259) state that HBr concentrations should be treated as semi-quantitative (fix

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word in text); for example, HBr is reported with 2 significant figures even at the single ppt level on Line 52 in the abstract, giving the impression of much greater certainty in this number. When error is reported, it should be with 1 significant figure (unlike on Line 286, where it should also be clarified that this is the standard deviation, I believe?). In addition, for improved comparisons to other work and other atmospheric species, it would be helpful for HCl and Br to be reported as mole ratios, in addition to the units of molec cm<sup>-3</sup> (also please add “molec” before cm<sup>-3</sup> throughout for clarity); this can be done in parentheses following the current units of molec cm<sup>-3</sup>, for example. Also, I did not see background/blank measurements discussed, and measurement limits of detection need to be reported.

Please clarify the discussion on Lines 287-291 about the correlations between HCl and HBr with temperature and UVB, as the discussion is limited and it is difficult to discern these points from the figures provided. Also, the authors state that “HCl and HBr concentrations being to increase together with the rising of temperature and UVB during April 2019”, but the corresponding Figure 3 only shows data until April 2. Further, in the data shown, the concentration appears to decrease in late March even with higher temperature, showing the opposite of what is discussed in the text.

Throughout the manuscript (including the SI), please clarify whether the particulate chloride discussed is from the ACSM (non-refractory PM1 chloride) or MARGA (total PM2.5 chloride). This differentiation in which particulate chloride is shown may impact the interpretation of the results. It would seem most appropriate to use the MARGA data, but the methods section seems to imply that ACSM data is presented, although this is not clear. Regardless of which data are presented, justification and a quantitative comparison of the ACSM and MARGA chloride data need to be included in the SI. Also, please clarify the text on Lines 276-277, as it suggests as written that the ACSM measured PM2.5 chloride, which is not the case for the standard instrument.

Figure S9 shows the temporal variations in HCl compared to particulate chloride, and this is a key contribution to this work. Therefore, I highly suggest moving this figure to

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the main text, with the following suggested modifications. Please state in the caption whether ACSM or MARGA Cl<sup>-</sup> is presented in the figure. In part b, plot both HCl and Cl<sup>-</sup> as mole ratios for improved comparison and evaluation of the assertion of gas-particle partitioning dominating the diel profile. Then use these mole-based values for a more quantitative discussion on page 7.

It is stated on Lines 294-295 that HCl and HBr began to increase after sunrise, but the diel plots of Figure 4 do not include radiation for evaluation of this statement. Further, while Figure 3 shows these data as a stacked plot, it is too zoomed out to be able to allow evaluation of this statement. I suggest adding radiation to Figure 4.

HBr, similar to HCl, is also formed from the reaction of bromine atoms with hydrocarbons, which would be expected to occur during daylight, when temperature is also higher. It is not clear how the authors are differentiating this process from gas-particle partitioning. Please clarify.

The 24 h air mass trajectory analysis for HBr is not consistent with the typical atmospheric lifetime of 2.5 h reported on Line 129. What is the estimated atmospheric lifetime of HBr under the conditions of this study? Please make sure that the length of the air mass trajectory analysis is appropriate considering the lifetime.

Additional Comments: Line 56 & elsewhere: Please change “gas-aerosol partitioning” to “gas-particle partitioning”.

Introduction, Paragraph 1: The authors are encouraged to also include mercury in the motivation to study atmospheric bromine chemistry.

Lines 142-144: Additional inland measurements of chlorine chemistry include Mielke et al. 2016 (Can. J. Chem.) and McNamara et al. 2020 (ACS Central Sci.).

Lines 164-165: Please clarify this sentence as it not clear what species are included here, and the manuscript title mentions the stratosphere.

Lines 178-181 and 312: Note that McNamara et al. 2020 (ACS Central Sci.) also

reported inland HCl measurements.

Line 223: Do the authors mean 5 s averaging here, as TOFs operate with much higher time resolution than 5 s.

Line 302: Please add explanation of Figure 4d to this paragraph to improve the clarity of the discussion here.

Figure 4: Please consider showing Parts a and b on linear scales in ppt. Part d needs more explanation in the caption. Is this a mass or mole ratio? Also, I did not see measurements of NO<sub>2</sub> in the methods section, so are both NO<sub>2</sub> and OH calculated values here? Please clarify here in the caption, on Line 374, and SI Line 275 how NO<sub>2</sub> was obtained.

Lines 364-366: Please clarify where these measurements were made, as this context is needed for understanding the relevance of the statement.

Lines 366-368: Please clarify these sentences. What is meant by extractable gaseous organic bromine? What is the statement “high concentration and reactivity of both organic/inorganic Br” referring to here (as only HBr is presented in this work and organic Br is generally not very reactive)?

Lines 375-378: Note that McNamara et al 2020 (ACS Central Sci) also reported similar Cl atom production rates from OH + HCl for the inland urban environment.

Lines 382-383: Please provide references for this statement of previous work and also compare the Cl atom production rates from HCl in this work to ClNO<sub>2</sub> and Cl<sub>2</sub> photolysis in the previous studies.

Line 387: This statement about the ubiquity of bromine chemistry in the polluted urban environment is speculative and not supported by the paper cited.

Lines 499-503: This reference is listed twice.

Figure 1: The font on these maps is not readable as currently presented.

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Figure 2: Consider showing HCl on the left axis and HBr on the right axis, both on linear scales. Incorporate measurement uncertainty.

Figure 7: Please clarify in the caption that all of the 'data' shown are calculations, not measurements, as implied by the text in the caption.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-1235>, 2020.

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