Reviewer(s)' Comments to Author:

Reviewer: 1

Comments:

General Comment

Gaseous hydrochloric and hydrobromic acid play important roles in tropospheric physicochemical processes, however, the atmospheric gaseous HCl and HBr in urban environments, are much less studied. This manuscript focused on the concurrent measurement of gaseous HCl and HBr by a CI-APi-LTOF mass spectrometer in urban Beijing, China, which is rarely reported before. Strong gaseous HCl and HBr were observed in Beijing where marine sources only have limited influence. Anthropogenic emissions seem to be a more important factor. This study estimates the production of atomic Cl and Br by the reactions of HCl and HBr with OH, which further contribute to atmospheric oxidation capacity. It provides a new insight of halogen chemistry in Chinese megacities and fits the scope and the interest of the journal of ACP. It is well organized and professionally written. Therefore, I recommend this manuscript for publication after minor revisions.

Reply: We are very grateful to the positive comments and helpful suggestions from Reviewer #1, and have carefully revised our manuscript accordingly. A point-to-point response to reviewers' comments, which are repeated in italic, is given below.

Comments:

1. Line 5: In the authors list, it seems to be press error that some affiliations are marked with superscript and the rest ones are with subscript.

Reply: Thanks for pointing it out. We have corrected this typo in our revised manuscript.

2. Line 115: Besides HNO_3, some other strong acids such as gaseous H_2SO_4 can also displace HX from sea-salt particles (Thornton et al., 2010). The authors should also add that information.

Reply: We have added this information to our revised manuscript.

Revised text in the main text (line 112-115):

"It is known that sea-salt particle is a major source of atomic halogens in the marine environment. The chloride (Cl^-) and bromide (Br^-) in the sea-salt particles can be displaced by strong acids (i.e., nitric acid (HNO_3) and sulfuric acid (H_2SO_4)) to release gas-phase hydrogen halides HX (reaction (R1); X = Cl or Br) into the atmosphere (Gard et al., 1998;Thornton et al., 2010)."

3. Line 174 delete the words of "atmospheric Br".

Reply: We have removed the words "atmospheric Br".

Revised text in main text (line 173-176):

"Yet, since the phasing out of leaded gasoline, the long-term atmospheric Br exhibited a continuous decreasing trend for 2 to 3 decades in Germany (Lammel et al., 2002), and a similar situation is expected in Beijing as the usage of leaded gasoline was banned from the years around the 2000s in China (Cai et al., 2017)."

4. Line 178 "Crisp et al. (Crisp et al., 2014) summarized that…" should be revise to "Crisp et al. summarized that…".

Reply: We have revised accordingly.

Revised text in the main text (line 179-184):

"Some limited studies focused on the atmospheric HCl, for example, Crisp et al. (2014) summarized that the concentration of HCl is typically less than 1 ppb over the continental regions and McNamara et al. (2020) measured the concentration of HCl is around 100 ppt from inland sources, while an airborne measurement showed HCl concentrations of around 100 ppt was typically observed over the land area of northeast United States, except near power plant plumes with concentrations over 1 ppb (Crisp et al., 2014;McNamara et al. 2020;Haskins et al., 2018)."

5. To better present the results, I recommend the authors to improve the quality of the figures. Take Figure 6 for example, to better present the comparison, panel C can be divided into two sub-panels. The sizes of the panels of Figure 4, Figure S9 and S10 should be the same.

Reply: Thank you for your advice. These figures have already been improved accordingly. Figure S9 has been moved to the revised main text as Figure 5. The original Figure 6 and Figure S10 were changed to Figure 7 in the revised main text and Figure S9 in revised SI, respectively. To make it easier to view, these revised figures were attached below.

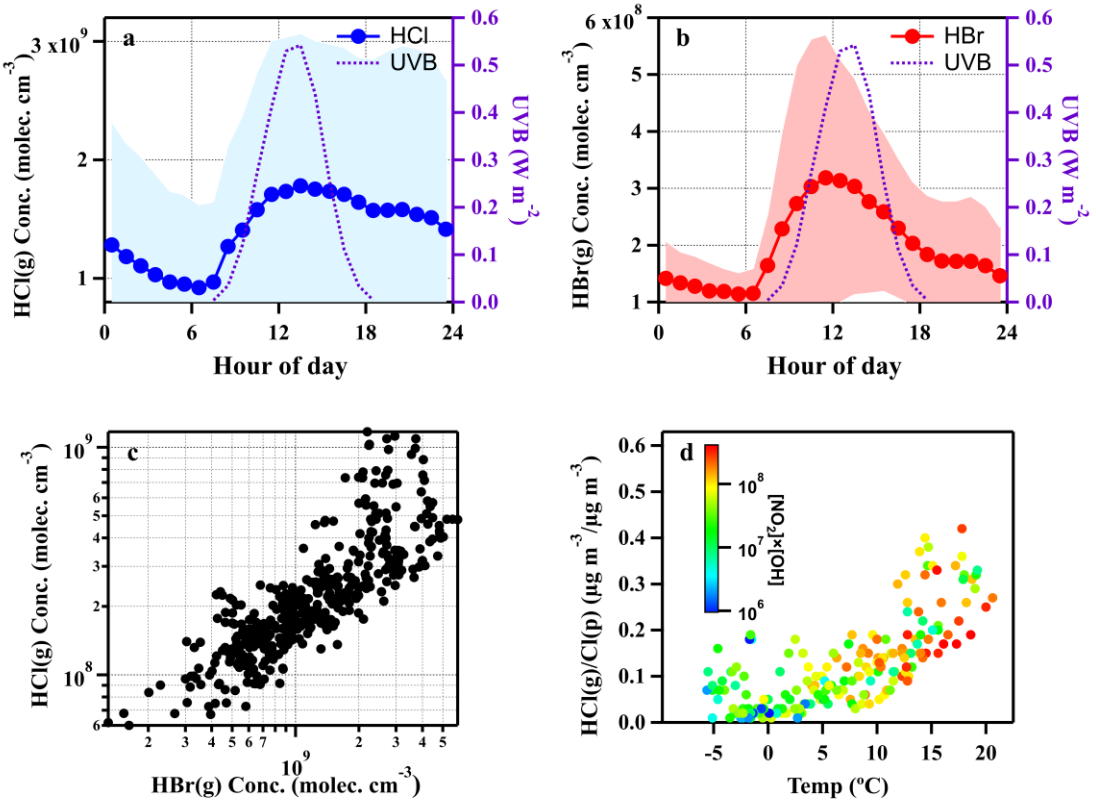

Figure R1 (Figure 4 in the revised main text). Diurnal variations of UVB intensities, HCl and HBr concentrations (averaged values ± one standard deviation) (**a** and **b**) and the correlation between HCl and HBr (**c**). In panel c, the data points are hourly averaged ones during daytime (8:00-17:00). Temperature dependence of gas to particle partitioning ratios of mass concentration of chloride, colour-coded by $[NO_2]$*[OH] which was indicated as the abundance of HNO_3 (**d**). All snowy and rainy days during the sampling period were excluded.

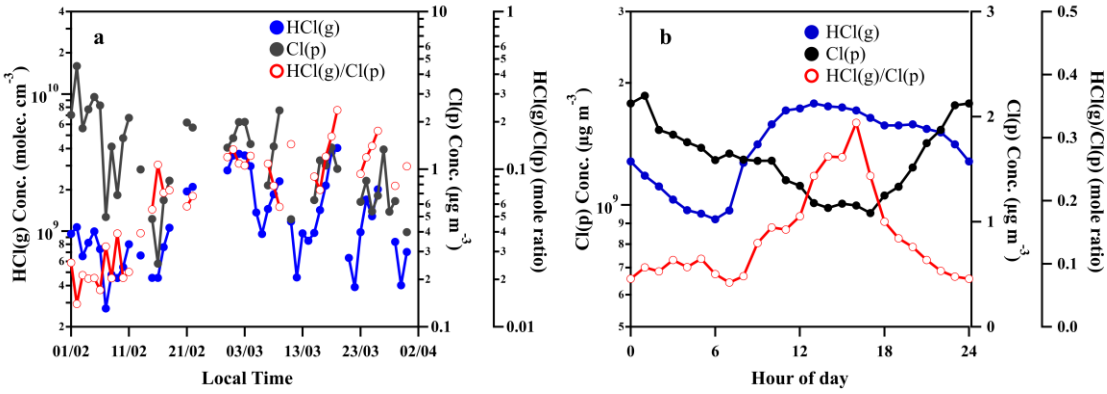

Figure R2 (Figure 5 in the revised main text). Time profile of daily averaged concentration of particulate chloride (Cl(p)) measured by ACSM, gaseous HCl (HCl(g)) measured by CI-APi-LTOF and the mole ratio of HCl(g)/Cl(p) (**a**) and diurnal variation of HCl(g), Cl (p) and HCl(g)/Cl(p) (**b**).

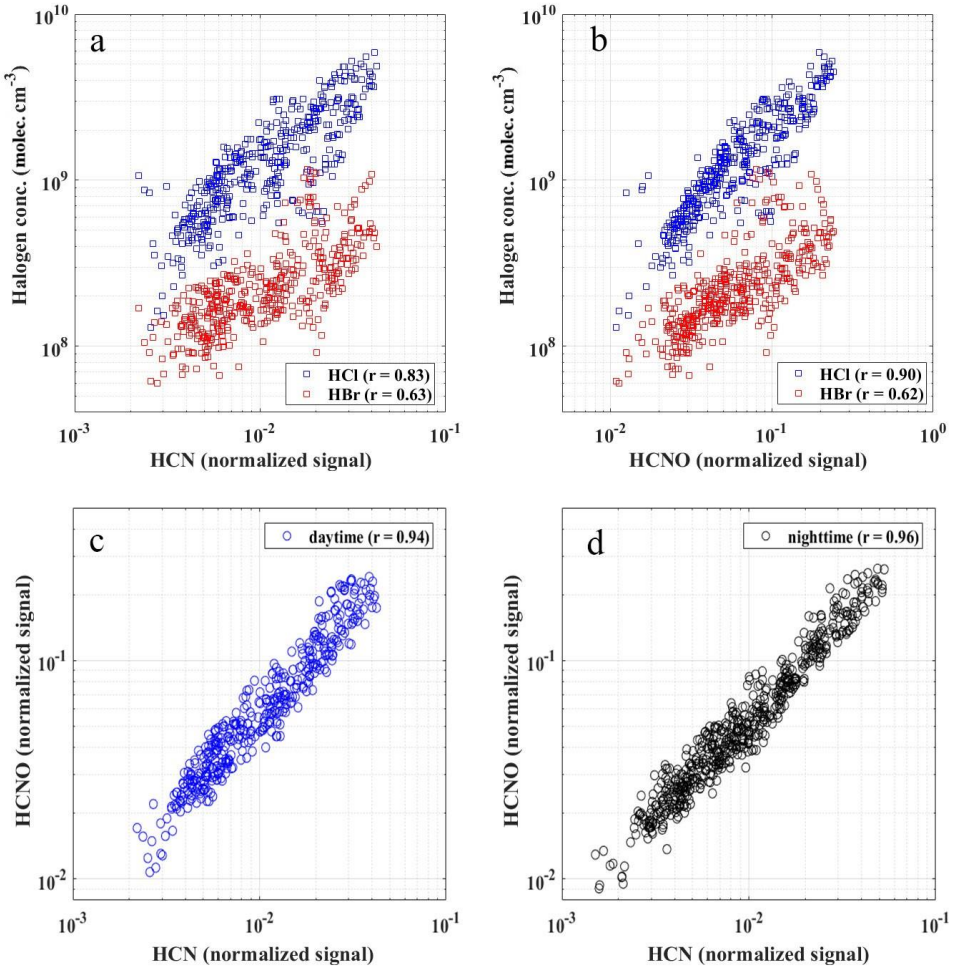

Figure R3 (Figure 7 in the revised main text). The relationship of HCl and HBr concentrations with HCN (**a**) and HCNO (**b**) during the daytime (08:00-17:00) and the correlations between HCN and HCNO during both daytime (08:00-17:00) (**c**) and nighttime (18:00-07:00 the next day) (**d**). The data points are hourly averaged ones.

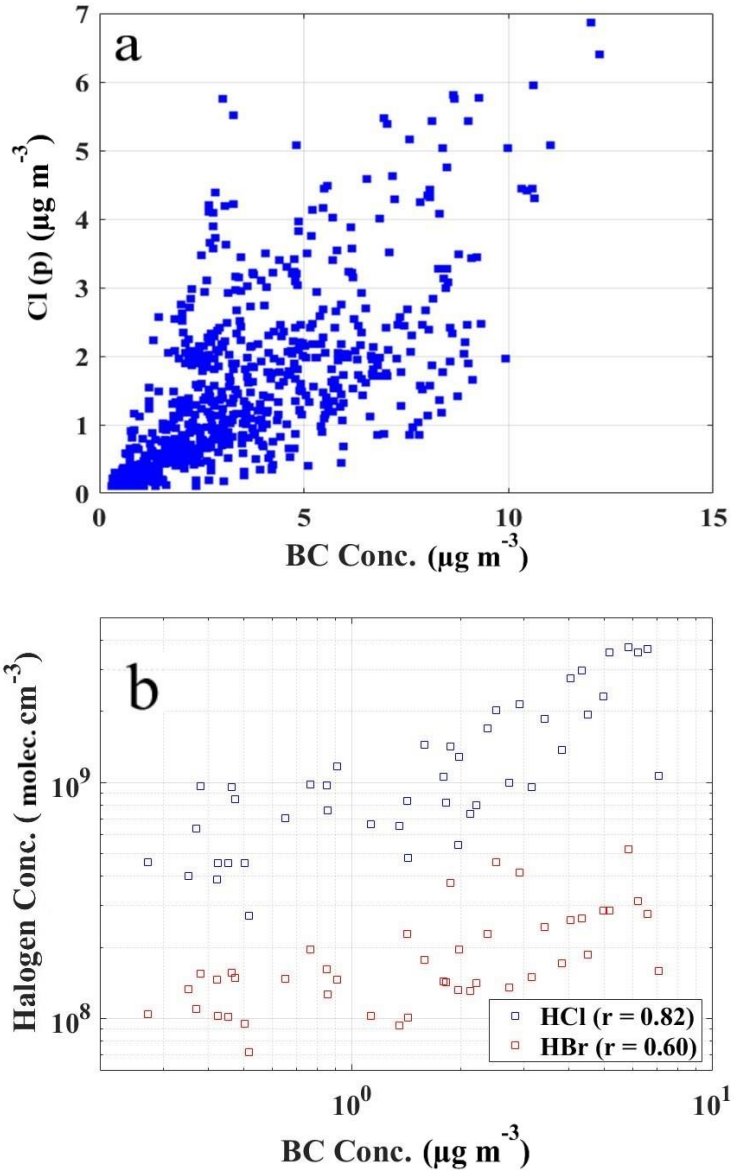

Figure R4 (Figure S10 in the revised SI). The correlation (r = 0.67) between hourly mean mass concentrations of particulate Cl (Cl(p)) and black carbon (BC) (**a**); correlations between daily mean concentrations of HCl (r = 0.82), HBr (r = 0.60) and BC during observation periods from 1 February to 31 March, 2019 (**b**).

6. In the manuscript, to compare the concentrations of HCl and HBr between Beijing, China in this study and other locations from previous ones (Lee et al., 2018; Simpson et al., 2015), it is better to also include the unit of mixing ratios (i.e., ppt) beside number concentrations (# cm^{-3}) in the measurement.

Reply: We have included the mixing ratios as ppt to the text.

Revised text in the main text (line 52-54):

"We observed significant HCl and HBr concentrations ranged from a minimum value at 1×10^8

molecules cm^{-3} (4 ppt) and 4×10^{7} molecules cm^{-3} (1 ppt) up to 6×10^{9} molecules cm^{-3} (222 ppt) and 1×10^{9} molecules cm^{-3} (37 ppt), respectively."

Revised text in the main text (line 302-304):

"The mean concentrations of HCl and HBr are 1×10^{9} molecules cm^{-3} (37 ppt) and 2×10^{8} molecules cm^{-3} (7 ppt), respectively. The maximum concentrations reach up to 6×10^{9} molecules cm^{-3} (222 ppt) for HCl, and 1×10^{9} molecules cm^{-3} (37 ppt) for HBr during the daytime."

7. How do HCl and HBr behave on clean days and polluted days? are their concentrations higher during polluted days?

Reply: HCl and HBr have different behaviors between clean days and polluted days during our observation period. HCl and HBr are more abundant on haze days (daily mean $PM_{2.5} \geq 75$ ug/m^3) than that on clean days (daily mean $PM_{2.5} < 75$ ug/m^3). The detail has been added in "3.3 halogen-atom productions." Please also refer to the reply below for Comment 8.

8. The title of "3.3 halogens atom production" should be "3.3 halogens' atom productions" or "3.3 halogen-atom productions". Besides, this part is interesting and important. Can the authors expend this part a bit to better elucidate the potential applications of the results from the measurement?

Reply: The title "3.3 halogens atom production." has been changed to "3.3 halogen-atom productions.".

Also, this section has been expanded accordingly (Line 414-419):

"The average HCl and HBr concentrations were observed to be higher during the polluted days (daily mean $PM_{2.5} \geq 75$ μg/m^3), which is about 2-3 times higher than the clean days (daily mean $PM_{2.5} < 75$ μg/m^3), as shown in Figure 8b. Consequently, the radical production rate also showed a difference between clean and polluted days (Figure 8d). The daily mean value of P_{Cl}. (up to 8×10^{3} molecules cm^{-3} s^{-1}) and P_{Br}. (2×10^{4} molecules cm^{-3} s^{-1}) in polluted days were both higher than that of clean days by up to 2 times. This hints that the roles of HCl and HBr may be more significant in polluted environments."

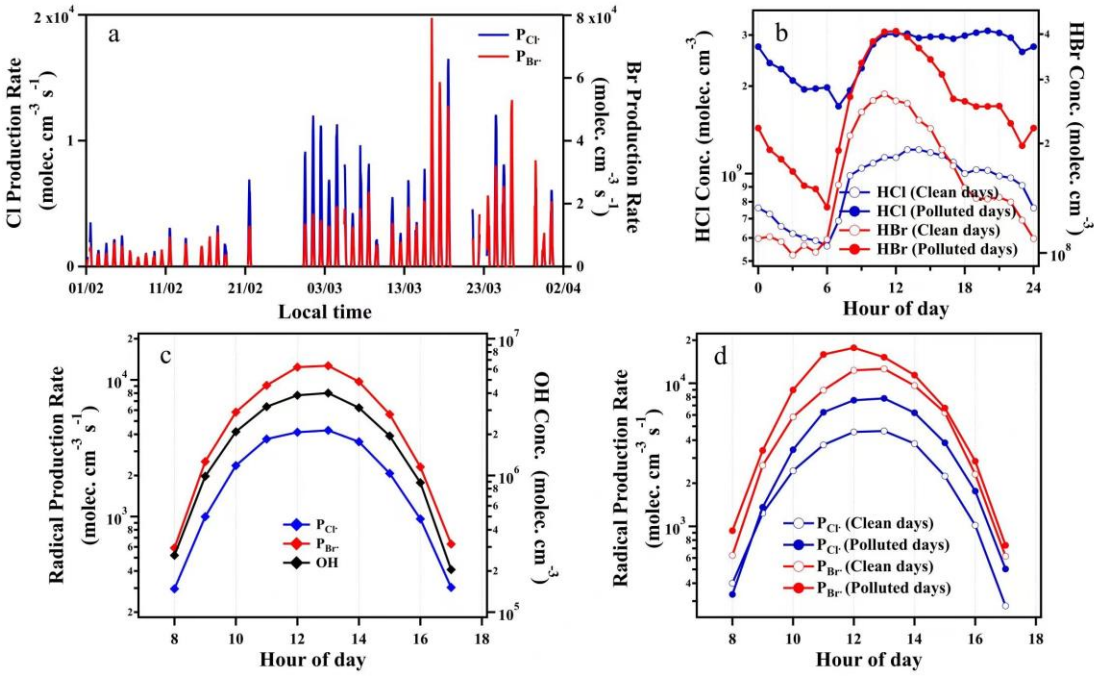

Figure R5 (Figure 8 in the revised main text). Time series of calculated production rates of Cl and Br radicals during the observation period (**a**); diurnal variations of HCl and HBr concentrations in clean and polluted days (**b**); diurnal variations of production rates of Cl and Br radicals, together with calculated OH radical concentrations (**c**) and production rates of Cl and Br radicals in clean and polluted days (**d**). The clean and polluted days were classified as daily $PM_{2.5} < 75$ μg/m^3 and $PM_{2.5} \geq 75$ μg/m^3, respectively. The data points are in the hourly-average interval and measured during observation periods from 1 February to 31 March 2019.

9. In SI, a good correlation was observed between measured J_{NO2} and modelled J_{NO2} (Figure S11). Please add the brief description of the model that used.

Reply: In this study, unfortunately, direct measurement of J_{NO2} is not available during our observation periods. The photolysis rate constants of NO_2 (J_{NO2}) were calculated according to the solar zenith angle and the location using a box model (FACSIMILE 4) (Liu et al., 2020). Then, the output (modelled J_{NO2}) was compared to the measured J_{NO2} (by using NO_2 photolysis sensor (J_{NO2}, Metcon)) for the period when J_{NO2} measurements were available, as shown in Figure S10, to ensure that the modelled J_{NO2} is relevant. We have added the brief description of the model into the SI Section S8 "The calculations of OH concentration and production rate of atomic Cl and Br".

Revised text in SI (line 365-368):

"Photolysis rate constants of NO_2 (J_{NO2}) were calculated according to the solar zenith angle and the location using a box model (FACSIMILE 4) (Liu et al., 2020). Using another dataset collected from 21 May to 10 June 2019, a good correlation (r=0.97) between calculated and measured J_{NO2} confirmed the validation of our calculated J_{NO2} (Figure S11a)."

References:

Liu, Y., Zhang, Y., Lian, C., Yan, C., Feng, Z., Zheng, F., Fan, X., Chen, Y., Wang, W., Chu, B., Wang, Y., Cai, J., Du, W., Daellenbach, K. R., Kangasluoma, J., Bianchi, F., Kujansuu, J., Petäjä, T., Wang, X., Hu, B., Wang, Y., Ge, M., He, H., and Kulmala, M.: The promotion effect of nitrous acid on aerosol formation in wintertime in Beijing: the possible contribution of traffic-related emissions, Atmos. Chem. Phys., 20, 13023-13040, 10.5194/acp-20-13023-2020, 2020.