

Review report on

Iodine oxoacids and their roles in sub-3 nanometer particle growth in polluted urban environments

By Zhang, Y., Li, D., He, X.-C., Nie, W., Deng, C., Cai, R., Liu, Y., Guo, Y., Liu, C., Li, Y., Chen, L., Li, Y., Hua, C., Liu, T., Wang, Z., Wang, L., Petäjä, T., Bianchi, F., Qi, X., Chi, X., Paasonen, P., Liu, Y., Yan, C., Jiang, J., Ding, A., and Kulmala, M.

The manuscript of Zhang et al. provides significant measurements of HIO_x and their findings show the relation between new particle formation (NPF) and iodine oxoacids, in two polluted urban areas in China. Based on back trajectory analysis, it was found that iodine species mainly originate from marine and terrestrial sources instead of local human activity. Moreover, they calculated the contribution of HIO_3 and H_2SO_4 to growth rate and survival probability, when an NPF event occurred at both examined sites. Their findings indicate that during a NPF day HIO_3 promotes the survival of particles with diameters below 3 nm, while no impact is observed for particles between 3 and 7 nm. This study shines light into the crucial role of HIO_3 to NPF events under polluted conditions, using experimental measurements.

The manuscript is well written and interesting, with an added value of the presented results being from an area of the globe with significant population growth. However, there are several details missing and more thorough discussion should be made in specific sections. Other than that the paper can be recommended for publication after addressing the issues listed below.

- 1) L155-156: The authors consider that an undefined event is regarded as non-NPF event. Please comment. Also, do the authors believe that no freshly nucleated particles at the size below 3 nm is observed?
- 2) L302: Authors mention that the H_2SO_4 is lower in cold seasons. Could you elaborate on this?
- 3) L305: Please make a discussion about the calibration issues on HIO_x measurements. What is the kind of calibration and the frequency?
- 4) L311: "The results indicate that the H_2SO_4 concentrations are generally higher than that of iodine oxoacids at both sites." -> Overall?? Because the time period of the measurements was different at both examined sites. What is the percentage difference among the H_2SO_4 iodine oxoacids concentrations at both sites? Why H_2SO_4 is constantly higher from iodine oxoacids. Please comment.
- 5) L155-156: The authors support that H_2SO_4 is the main contributor to NPF, however in Figure 1 increased H_2SO_4 concentrations are related to low NPF frequency. Please provide an explanation of why this feature does not occur here.

- 6) L356-357: "H₂SO₄ concentrations are higher in the spring and autumn, lower in the summer, and lowest in the winter." -> Please add an explanation regarding this seasonal diversity.
- 7) L400: "The authors found that ambient level of O₃ was not the limiting factor for HIO₃ formation." -> How the authors came to this conclusion? Could you elaborate on this? A reference is needed here.
- 8) L401: "...indicating that O₃ may influence terrestrial HIO₃ formation." -> It would be useful to provide a scatter plot for O₃ vs. HIO₃ to advocate this conclusion.
- 9) L403: "This mechanism mainly explains..." -> In which exactly process the authors refer to? Please explain.
- 10) L406: "Another possibility is that air temperature may strongly perturb the formation of HIO₃ ..." -> A reference is needed here. This means that the augmentation of temperature involves increased HIO₃ concentrations? I would be careful of using the verb "perturb" here.
- 11) L428-429: "...land indicates that the continental outflows may also play a significant role in transporting HIO₃ precursors." -> The authors consider that air masses coming from South have continental properties. However, in Figure S4a the southern cluster can travel over the sea, showing marine properties. Please comment on this?
- 12) L434: "...impact from residential coal burning and fossil fuel combustion power plant in Beijing is the largest." -> Are there any BC measurements in AHL/ BUCT station? A figure for BC vs. HIO₃ would be useful to advocates the author's conclusion.
- 13) L559: "Only events with clear growth..." -> This assumption means NPF events of class I. However, the classification of NPF episodes is not easily identifiable from the text. A classification could be added to the main text (2.2.1) and in the respective Table.
- 14) L567: "...environments with higher CoagS, such as Beijing, a fixed GR enhancement can lead to larger SP..." -> What does fixed GR enhancement mean? Please clarify.
- 15) L568-569: "Results in both Fig. 7 and Fig. S5 show that the median contribution of HIO₃ to the GR of particles in the 1.5-3 nm size range is 7.4% using the MOD method..." -> This contribution is referring to all NPF episodes in Beijing?
- 16) L569-571: "...whereas the contribution is only around 3% and 2% using the APT-x and APT-y methods, respectively. This is resulted from the difference in the measured GR calculated using either the APT or the MOD methods." -> Measured or calculated GR?? Therefore, this variation derives from the different estimated GR. What is the amount of uncertainty?

Technical corrections:

L24: "New particle formation processes contribute" -> New particle formation contributes

L25: "... ultrafine particles (UFP), and have great..." -> ultrafine particles (UFP; $d \leq 100$ nm)

L27: "...proved to dominate NPF events at some sites." -> proved to dominate NPF.

L28: "... we conducted a long-term comprehensive observation of gaseous..." -> ... long-term measurements of gaseous ...

L30: "... concentration in urban..." -> ... concentration in both urban....

L31: "HIO₃ concentration is..." -> HIO₃ is

L32-33: "...and is lowest in winter..." -> ... and is lowest in winter by xxx% and xxx%, respectively. HIO₃ exhibits more prominent variation than H₂SO₄ in both urban sites.

L34: "...temperature, radiation and ozone..." -> ...temperature, solar radiation and ozone...

L40: "...suggesting HIOx are non-negligible contributor to UFPs in polluted urban areas." -> ...suggesting that HIOx are significant contributor to UFPs in polluted urban areas.

L46-49: "Primary aerosol emissions include natural sources including the emission of sea spray, release of soil mineral dust, emission of biomass burning smoke, and the injection of volcanic debris (Claudio Tomasi, 2017) and anthropogenic emissions such as fuel combustion, industrial processes and transportation (Claudio Tomasi, 2017)." -> Primary aerosol emissions stem from natural sources, including sea spray, soil mineral dust, biomass burning, and volcanic debris (Claudio Tomasi, 2017), and anthropogenic sources such as fuel combustion, industrial processes and transportation (Claudio Tomasi, 2017).

L53: "...form new particles under atmospheric conditions..." -> ... form new particles under appropriate atmospheric conditions...

L57: "...influence cloud formation and have climatic effects (Kerminen et al., 2005)." -> Use a more recent reference, e.g. Kalkavouras et al. (2019); Jiang et al. (2021)

L59: "...These small particles (< 50 nm) can penetrate..." -> You mean UFP, thus use ≤ 100 nm instead of 50 nm in the parenthesis.

L60: "...understanding NPF processes is..." -> delete the word "processes"

L61: "...terms of predicting climate change..." -> Use evaluating instead of predicting

L70: "...vapours depending on the particle sizes. In urban Beijing,..." -> ...vapours depending on the particle size. In Beijing...

L76-77: Use capital letter for O' Dowd.

L85: "...that HIO₃ (with HIO₂)..." -> Please clarify the content in the parenthesis. Its vague

L98: "...in urban Beijing from 2019 to 2021,..." -> ...in urban Beijing from January 2019 to October 2021, ...

L107-108: "The measurement in urban Beijing was conducted from January 2019 to October 2021. The site locates on the fifth floor..." -> Measurements in urban Beijing were conducted from January 2019 to October 2021, on the fifth floor...

L107-115: It would be useful to provide a figure with the exact location of both stations in main text or in the SM.

L122 and L124: Be sure about the unit of measurement

L125: "...from January 2020 to February 2020." -> or ...from March 2020 to February 2020. ?

L135-142: Long sentence, please rephrase

L168: "...correction factor for mass flux as a function..." -> ... correction factor for mass flux (Fuchs and Sutugin, 1970) as a function...

L174: "To quantify if notable growth is to occur, especially at sizes below a few nanometers, it is..." -> What do you mean a few nanometers? Please explain.

L225: "The counterbalance of CoagS and GR considerably affects the survival of small clusters." -> Please add a reference here.

L269: Put the sentence in line 269, after the equation (11).

L286: "Based on current knowledge about HIO₃ formation pathways,..." -> Please add a reference here.

L315: "...from none to more than three quarters of the days..." -> Why present it as $\frac{3}{4}$ and not e.g. 75% ?

L347: "To better understand the roles of the studied acids in new particle formation and growth, we further..." -> To better understand the roles of the studied acids in NPF, we further....

L358: "The HIO₃ concentrations measured at the two sites are significantly lower than that at pristine coastal..." -> How low? Please add a percentage to express the variation of HIO₃.

L363: "... concentrations in Beijing and Nanjing are comparable to that in Helsinki, Finland." -> A reference is needed here.

L387-388: "The distinct diurnal variation in HIO_x concentration with around one order of magnitude implies fast in-situ chemistry." -> This clear diurnal variation is observed during summer? It's vague. Please clarify.

L390: "This phenomenon is pronounced during summer daytime when daily maximum of H₂SO₄ appears around 2 hours earlier than that of HIO₃" -> This behavior was also apparent in autumn. It would be nice to refer this with some comments.

L393: "...cycle of H₂SO₄ follow that of radiation in spring, summer and winter." -> But not for fall?
From Fig. 2 it is clear that the daily pattern of H₂SO₄ follows that of solar radiation.

L429-430: "...and terrestrial precursors (Li et al., 2014; Wang et al., 2017) may..." -> Terrestrial precursors such as?

L472: "...terrestrial biomes (Sive et al., 2007), and minor wetlands (Dimmer et al., 2001), biomass burning..." -> ...terrestrial biomes (Sive et al., 2007), minor wetlands (Dimmer et al., 2001), and biomass burning...

L525-526: "When P is below 50 in clean environment or 100 in polluted urban cities, the SP of the sub-3 nm particles is agreed with the atmospheric observations." -> A reference is needed here.

L526: "As shown in Fig. S6, the..." -> The Fig. S6 in which station is referred to? The right y axis expresses the P? It is not clear.

L535-537: "Under the typical CoagS (around 0.0025 s⁻¹) at both sites, the SP could be enhanced by more than two orders of magnitude when GR is varied from 1 to 10 nm h⁻¹." -> It would be useful to provide a new figure, showing this CoagS value, because it's difficult for a reader to find/ see the value of 0.0025 s⁻¹.

L537-538: "Increased GR caused by additional condensing vapours enables faster growth, which in turn facilitates the survival of sub-10 nm particles from coagulation scavenging." -> Please add a reference here.

L540: "A limited variation of GR was suggested to cause considerable variation of SP (Cai et al., 2021a)." -> Repetition. The same sentence is written in the beginning of paragraph (line: 531-532).

L562-563: "The results in Table S2-S4 show that the contributions of HIO₃ to GR on May 25 and 26 were lower than 5%, whereas the contribution was more than 10% on May 29" -> In Table S4 the contribution of HIO₃ to GR for <3 nm particles is 9.4% (i.e. below 10%) on May 29. Furthermore, in this paragraph (L: 555-574) the authors analyze the MOD method. Why they add Tables S2 and S3?

L598-599: "At the SORPES station from June to November 2019, HIO₃ contributes 6.1% (median) and 6.7% (mean) to sub-3 nm particles growth compared to H₂SO₄." -> You mean that HIO₃ exhibits higher contributions compared to H₂SO₄ ?

Fig. S9: In the caption SORPES instead of SOREPS.

References

Kalkavouras, P., Bougiatioti, A., Kalivitis, N., Stavroulas, I., Tombrou, M., Nenes, A., and Mihalopoulos, N.: Regional new particle formation as modulators of cloud condensation nuclei

and cloud droplet number in the eastern Mediterranean, *Atmos. Chem. Phys.*, 19, 6185–6203, <https://doi.org/10.5194/acp-19-6185-2019>, 2019

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Fuchs and Sutugin, *Highly dispersed aerosol*, Ann Arbour Science Publishers, Ann Arbour, London, 1970, <https://doi.org/10.1016/B978-0-08-016674-2.50006-6>, 1970.