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Climate of the Past Discussions

Interactive comment on "Holocene atmospheric iodine evolution over the North Atlantic" *by* Juan Pablo Corella et al.

Anonymous Referee #1

Received and published: 29 July 2019

Review of Corella et al. (https://doi.org/10.5194/cp-2019-71)

General comments Corella et al. present a relatively high-resolution ice core record of atmospheric iodine variability during the Holocene from the Renland Ice Core, Greenland. Iodine concentrations are extremely low in ice cores (<0.1 ng g-1), and require meticulous sample preparation and ultra-trace analytical protocols. This study presents a very nice lab intercalibration experiment between two ice core labs - Curtin University, Australia and IDPA-CNR, Italy, which I commend. Over the Holocene, the authors suggest the large variability in iodine concentrations and iodine fluxes, measured in the ice core, reflect changes in marine primary production over the North Atlantic. They derive a conceptual model to explain the three-step changes in iodine levels over the last 11 ka, i.e., Holocene Thermal Maximum, Neoglacial Period, and Late Holocene.

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This iodine record will be of interest to a number of communities including atmospheric chemists, palaeoclimatologists and marine biogeochemists. However, the authors have not addressed post-depositional processes that are known to modify the original iodine deposition to snow. These photochemical processes need to be quantified before ice core records of iodine can be interpreted at the Renland site. After addressing the issue of post-depositional processes, I am happy to recommend this manuscript for publication in Climate of the Past.

Specific comments Post-depositional processes, such as UV-photolysis, can cause reactive halogen species in the snowpack to be lost to the overlying atmosphere (e.g. Frieß et al., 2010;Gálvez et al., 2016;Simpson et al., 2005), i.e., the snowpack can release gas-phase iodine. Firstly, this local iodine source needs to be added in the "origins and cycling of iodine" section in the introduction. Secondly, the manuscript is lacking discussion on photochemical post-depositional processes related to iodine loss from the snowpack. Such processes need to be quantified, especially at individual ice core sites due to their relationship with snow accumulation, before archived concentrations of iodine can be interpreted. Do you have any surface snow and atmospheric iodine measurements from Renland you could use? At the very least, you could make some assumptions that post-depositional processes are negligible at relatively high accumulation sites, such as Renland, but this would need to be backed up by evidence from the literature.

The authors have produced a nice schematic diagram (Figure 3) showing the three phases of iodine evolution over the Holocene. The figure is only mentioned once in text and I recommend a fuller explanation of the figure throughout the discussion.

The study uses a combination of ice core and modelling evidence. The manuscript is rather ice core heavy and I recommend extending the modelling results and discussion sections especially for ice core readers who are not experts in atmospheric chemistry.

Lastly, I suggest restructuring the manuscript to combine the results and discussion

into one section, and making the final conclusions separate. That would leave the reader with the key take home messages of the study.

Technical corrections L17 Insert “the” between “large influence on. . .oxidising capacity” L21 Spell out “ReCAP” acronym L21 Which region does your atmospheric iodine represent? L23 Delete “-“ between “before. . .present” L23 Replace “ocean” with “marine” L24 “Biological iodine explosion” is this term reported previously or are you suggesting it? Needs a little further explanation. L24 What is the “iodine trend” doing during the early Holocene? L29 This sentence is out of place. The paragraph is about the impact of halogen chemistry on the oxidising capacity of the atmosphere and thus your topic sentence should reflect this. L30 Remind the reader what time period the Holocene encompasses. L32 Please add reference. L45 Throughout the manuscript, you refer to ozone as “ozone”, “tropospheric ozone”, “atmospheric ozone”, “surface ozone”. Please be consistent with your terminology. L51 Here you need a greater explanation of the recycling processes of iodine in surface snow. L58 Capital “Ice”. L60 You states there are only two iodine records from ice cores. However, later in the paragraph you mention other records. Please add references for all iodine ice core records (e.g. Spolaor et al., 2013;Cuevas et al., 2018;Legrand et al., 2018). L66 What does the Talos Dome iodine record reflect? L72 Add the reference for the “recent study” upfront. L86 Add “the” between “plateau and. . .Scoresby” L91 Please add reference for ReCAP age model. L101 Were samples transported frozen? L102 Replace “of” with “at” L102 “Curtin University of Technology” is now “Curtin University”. Please replace here and throughout the manuscript. See https://www.curtin.edu.au/ L105 Change “CUT” to “CU” here and throughout. L105 Please add reference to the Curtin University ICP-MS method or if these are the first measurements for iodine reported from that lab then please add methods and a table in the supplement with the operating parameters (e.g. torch, spray chamber, nebuliser). L106 You define the Italian ICP-MS as “IDPA-CNR” please make sure you are consistent with your terminology throughout the manuscript. L107 Reference is repeated twice. Please delete one. L107 Add resolution for sodium measurements. L109 Spell out ultrapure water “UPW” acronym.

L109 What are these instrumental errors? Are they related to reproducibility or accuracy? Please add accuracy and precision for iodine and sodium measurements. What certified reference material did you use? L110-111 Use consistent terminology for Italian and Australian ICP-MS. L113 Yes there is a strong correlation between the two labs but it is non-linear at low concentrations. Include a note on the large area at low iodine concentrations. L116 Add "our" between" model and. . .sampling". L116 Add "mass" between "depositional. . .fluxes". L118 Please add reference for accumulation rates. L119 Please add the different climatic phases in the introduction. L121 Calcium is not mentioned previously. Either include Ca methods or remove entirely. L124 MBL spell out acronym. L128 First mention of photolytic processes. Need to include iodine snow photochemistry in the introduction. L132 HTM spell out acronym. L132 Delete "rs" in ""ky-1". L135 Replace "results" with "ice core and modelling results" and add a fuller explanation of the modelling results here. Could you add a figure or table summarising the results? L137-138 Symbol μ. L139 What causes re-mobilisation? L140 Please add reference of iodine concentration and accumulation rate studies. You haven't quantified how the accumulation rate impacts iodine loss at the Reland site so please include some evidence to justify the your assumption that post-depositional processes are negligible. L154 Symbol μ. L147 What are the biomarkers? L166 "The increase in nutrient supply from terrestrial sediment delivery". L172 Replace "The" with "An". L174 Can you provide a reference "biological iodine explosion". L184 ssa acronym. L185 Please mention calcium dust proxy and add reference. L185-186 Is this result from your model? L193 Replace "on" with "of". L186 Period. L194 Replace "value" with "level". L195 Add location of Kara and Laptev Seas to Fig. 1. L200 What measure of sea ice referring to? Sea ice extent or concentration or thickness? Here and throughout manuscript please specify. L204 How much thicker does the sea ice need to be? Can you give estimates of thickness and light penetration depth? L204 Add sea ice as a source of iodine in the introduction. L211 Should the fluxes and concentrations be reported as 2 significant figures? L222 Can you quantify the frequency? L223 What is the second part? L247 What are the associated radiative impacts? Fig-

ure 1 Mention the references in the caption to help the reader. Figure S1 What does the 1:1 line indicate? Be consistent with the naming of the Australian and Italian iodine measurements.

References Cuevas, C. A., Maffezzoli, N., Corella, J. P., Spolaor, A., Vallelonga, P., Kjær, H. A., Simonsen, M., Winstrup, M., Vinther, B., and Horvat, C.: Rapid increase in atmospheric iodine levels in the North Atlantic since the mid-20th century, Nature communications, 9, 1452, 2018. Frieß, U., Deutschmann, T., Gilfedder, B., Weller, R., and Platt, U.: Iodine monoxide in the Antarctic snowpack, Atmospheric Chemistry and Physics, 10, 2439-2456, 2010. Gálvez, Ó., Baeza-Romero, M. T., Sanz, M., and Saiz-Lopez, A.: Photolysis of frozen iodate salts as a source of active iodine in the polar environment, 2016. Legrand, M., McConnell, J. R., Preunkert, S., Arienzo, M., Chellman, N., Gleason, K., Sherwen, T., Evans, M. J., and Carpenter, L. J.: Alpine ice evidence of a three-fold increase in atmospheric iodine deposition since 1950 in Europe due to increasing oceanic emissions, Proceedings of the National Academy of Sciences, 115, 12136-12141, 2018. Simpson, W. R., AlvarezâĂŘAviles, L., Douglas, T. A., Sturm, M., and Domine, F.: Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine airâĂŘsnow chemistry during springtime, Geophysical research letters, 32, 2005. Spolaor, A., Vallelonga, P., Plane, J., Kehrwald, N., Gabrieli, J., Varin, C., Turetta, C., Cozzi, G., Kumar, R., and Boutron, C.: Halogen species record Antarctic sea ice extent over glacial–interglacial periods, Atmospheric Chemistry and Physics, 13, 6623-6635, 2013.

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