

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

**Juan Pablo Corella et al.**

pcorella@iqfr.csic.es

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Referee #1: 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,

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and Late Holocene. 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*.

Response: We appreciate the positive feedback from reviewer 1. We have addressed below all the comments and suggestions made by reviewer that have certainly improved the quality of the manuscript. In particular, we have added a new section in the revised manuscript in which we address all the possible post-depositional processes occurring at the Renland site.

Specific comments Referee #1: Post-depositional processes, such as UV-photolysis, can cause re-active 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.

Response: We do not have atmospheric iodine measurements at the coring site but iodine recycling in surface snow and ice in the Arctic have been fully discussed in recent field experiments in Svalbard where similar photochemical processes on snow and ice

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can be found (Spolaor et al., 2019). According to this study (and previous laboratory (Galvez et al., 2016; Kim et al., 2016) and field studies (Frieb et al., 2000; Simpson et al., 2005; Spolaor et al., 2014) iodine concentrations from in polar regions may suffer from significant photolytical post-depositional processes that affect the iodine concentration in ice at daily to seasonal scales. Nevertheless, significant changes in the net iodine depositional fluxes due to loss of iodine from snow at centennial to millennial time scales in coastal Greenland ice cores are not expected. We have now added a section in the revised manuscript where all the possible post-depositional processes affecting iodine re-emission from surface snow at daily to millennial time-scales are fully addressed.

Referee #1: 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.

Response: We have added more explanation in the revised version of the manuscript regarding the conceptual model shown in Fig. 3

Referee #1: 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.

Response: We have extended the 2.3 section (Atmospheric Chemistry modelling) including more detail about the models run and the purpose of the experiments. Besides, we have also extended the result section of the manuscript with more information about the model results.

Referee #1: 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.

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Response: We have restructured the manuscript combining results and discussion and adding a conclusion section as recommended by reviewer.

Technical corrections Referee #1:L17 Insert “the” between “large influence on...oxidising capacity”

Response: Done

Referee #1:L21 Spell out “ReCAP” acronym

Response: Done

Referee #1:L21 Which region does your atmospheric iodine represent?

Response: The North Atlantic, we have added this information to the abstract in the new version of the manuscript

Referee #1:L23 Delete “-“ between “before...present”

Response: Done

Referee #1:L23 Replace “ocean” with “marine”

Response: Done

Referee #1:L24 “Biological iodine explosion” is this term reported previously or are you suggesting it? Needs a little further explanation.

Response: We are suggesting this term. We have elaborated on that concept in the discussion in the new version of the manuscript

Referee #1:L24 What is the “iodine trend” doing during the early Holocene?

Response: We have rephrased it with “the high and stable iodine levels”

Referee #1: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.

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[Discussion paper](#)



Response:The sentence has been deleted in the new version of the manuscript

Referee #1:L30 Remind the reader what time period the Holocene encompasses.

Response:Done

Referee #1:L32 Please add reference.

Response:Done

Referee #1:L45 Throughout the manuscript, you refer to ozone as “ozone”, “tropospheric ozone”, “atmospheric ozone”, “surface ozone”. Please be consistent with your terminology.

Response:We have now referred as tropospheric throughout the manuscript

Referee #1:L51 Here you need a greater explanation of the recycling processes of iodine in surface snow.

Response:We have added a complete section regarding post-depositional processes in ice and snow in the new version of the manuscript

Referee #1:L58 Capital “Ice”.

Response:Done

Referee #1: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).

Response:We have rephrased it adding all the iodine records available up to date in polar regions

Referee #1:L66 What does the Talos Dome iodine record reflect?

Response:Talos dome iodine record highlighted that sea-ice dynamics, algal productivity and dust controlled iodine variability at millennial time-scales variability in the

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Antarctic region (Spolaor et al., 2013). We have added this information in the new version of the manuscript.

Referee #1:L72 Add the reference for the “recent study” upfront.

Response:Done

Referee #1:L86 Add “the” between “plateau and...Scoresby”

Response:Done

Referee #1:L91 Please add reference for Re-CAP age model.

Response:We have added the reference of the ReCAP age-depth model (Simonsen et al., in press)

Referee #1:L101 Were samples transported frozen?

Response:The samples were melted for sampling and frozen immediately after sampling. They were then kept frozen and away from light sources until they were analysed.

Referee #1:L102 Replace “of” with “at”

Response:Done

Referee #1:L102 “Curtin University of Technology” is now “Curtin University”. Please replace here and throughout the manuscript. See <https://www.curtin.edu.au/>

Response:Done

Referee #1:L105 Change “CUT” to “CU” here and throughout.

Response:Done

Referee #1: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).

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Response: The details on the Curtin University ICP-MS method is fully described in Maffezzoli et al., 2018, we have added that reference in the new version of the manuscript.

Referee #1:L106 You define the Italian ICP-MS as “IDPA-CNR” please make sure you are consistent with your terminology throughout the manuscript.

Response: Done

Referee #1:L107 Reference is repeated twice. Please delete one.

Response: Done

Referee #1:L107 Add resolution for sodium measurements.

Response: This information has been added in the section 2.2 of the revised manuscript

Referee #1:L109 Spell out ultrapure water “UPW” acronym.

Response: Done

Referee #1: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?

Response: The error bars on each data point reflect the standard deviation (1sigma) of the set of 5 mass scans performed by the ICP-MS for each sample detection. Therefore, they reflect the single-measurement precision. As Standard Reference Material we used one of the standards (NIST traceable commercial standards: High-Purity Standards, (Charleston, USA)) used during the calibrations as Quality Controlled Standards (QCs, as described in Maffezzoli et al., 2018, Appendix A1), continuously monitored during the analyses, for a total of  $n=82$  detections. The spread (relative standard deviation) of the  $n=82$  QCs concentrations (precision) was: 16% (iodine); 4% (sodium). The accuracy (as the ratio between the measured QCs concentration and the nominal QCs concentration) was on average  $95\pm 29\%$  (iodine);  $98\pm 7\%$  (sodium), See plots

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from supplementary figure A

Referee #1:L110-111 Use consistent terminology for Italian and Australian ICP-MS.

Response:Done

Referee #1: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.

Response:We agree with reviewer on the non-linear relation at low concentrations and we have added a note in the text regarding this. Nevertheless, the HTM iodine concentrations would still be significantly higher than the Neoglacial and the late Holocene iodine values, even accounting for the concentration non-linearity.

Referee #1:L116 Add “our” between” model and...sampling”.

Response:Done

Referee #1:L116 Add “mass” between “depositional...fluxes”.

Response:Done

Referee #1:L118 Please add reference for accumulation rates.

Response:Done

Referee #1:L119 Please add the different climatic phases in the introduction.

Response:Done

Referee #1:L121 Calcium is not mentioned previously. Either include Ca methods or remove entirely.

Response:We have added Ca methods in the new version of the manuscript

Referee #1:L124MBL spell out acronym.

[Printer-friendly version](#)

[Discussion paper](#)





Response:Done

Referee #1:L128 First mention of photolytic processes. Need to include iodine snow photochemistry in the introduction.

Response:In line 128 (within the Atmospheric Chemistry modelling section) we are referring to the photochemistry in the gas phase, not to the photochemistry in the snow-pack. In this work, we are using THAMO to estimate the amounts of inorganic and organic iodine emissions that would reproduce the tropospheric iodine levels recorded in the ice core. Therefore, we are referring to the photolysis of the different species emitted to the troposphere, and more specifically to the photolysis of the different reactive iodine precursors (inorganic: HOI, I<sub>2</sub> and organic: CH<sub>3</sub>I, CH<sub>2</sub>I<sub>2</sub>, CH<sub>2</sub>IBr and CH<sub>2</sub>ICl). Nevertheless, we have included a note in the supplementary information concerning the post-depositional processes.

Referee #1:L132 HTM spell out acronym.

Response:We have spelled out the acronym in the introduction in the new version of the manuscript

Referee #1:L132Delete “rs” in “ky-1”.

Response:Done

Referee #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?

Response:We have modified this heading as “Results and Discussion” in the new version of the manuscript. We have added Table 1 into the main text and we have added a new figure in the supplementary material summarizing the THAMO modelling main results

Referee #1:L137-138 Symbol $\mu$ .

[Printer-friendly version](#)

[Discussion paper](#)



Response:Corrected

Referee #1:L139 What causes re-mobilisation?

Response:There are several wide range of factors that may contribute to iodine re-mobilization from surface snow and ice (e.g. photo-activation of reactive iodine, ice/firn characteristics, effect of snowfall rates, changes in meteorological conditions, etc) summarized in the literature (Frieb et al., 2000; Spolaor, et al 2014; Galvez et al., 2016; Kim et al., 2016; Legrand et al., 2018, Cuevas et al., 2018; Spolaor et al., 2019). The different mechanisms controlling iodine re-mobilization have been fully explained in a full section in the revised version of the manuscript.

Referee #1: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 that your assumption that post-depositional processes are negligible.

Response:We have added key references to the different accumulation rate studies in Greenland (e.g. Maselli et al., 2017, Rhodes et al., 2017). As discussed above, we have added a new section in the revised version of the manuscript regarding post-depositional effects on ReCAP site.

Referee #1:L154 Symbol $\mu$ .

Response:Corrected

Referee #1:L147 What are the biomarkers?

Response:Biomarkers are summarized in Table S2 and Fig. 1 and explained below in the text.

Referee #1:L166 "The increase in nutrient supply from terrestrial sediment delivery".

Response:This has been corrected in the new version of the manuscript.

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Referee #1:L172 Replace “The”with “An”.

Response:Done

Referee #1:L174 Can you provide a reference “biological iodine explosion”.

Response:“Biological Iodine Explosion” is a term suggested in this study for the first time.

Referee #1:L184 ssa acronym.

Response:ssa acronym has been previously spelled out in line 57 of the former version of the manuscript.

Referee #1:L185 Please mention calcium dust proxy and add reference.

Response:We have mention calcium as a dust proxy in Greenland and provided key references (i.e. (Schüpbach et al., 2018))

Referee #1:L185-186 Is this result from your model?

Response:Yes, we have specified it in the text now

Referee #1:L193 Replace “on” with “of”.

Response:We have not modified it since we consider “ on” is more appropriate in this case

Referee #1:L186 Period.

Response:Ok, we have rephrased it accordingly

Referee #1:L194 Replace“value” with “level”.

Response:Done

Referee #1:L195 Add location of Kara and Laptev Seas to Fig. 1.

Response:Their location cannot be shown in Fig. 1 since they are located in the

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[Discussion paper](#)



Russian Arctic. We have explained its location in the text in the new version of the manuscript

Referee #1:L200 What measure of sea ice referring to? Sea ice extent or concentration or thickness? Here and throughout manuscript please specify.

Response:Sea ice extent and thickness we have clarified this throughout the manuscript

Referee #1:L204 How much thicker does the sea ice need to be? Can you give estimates of thickness and light penetration depth?

Response:In Antarctica, the light transmitted through sea-ice (with an average depth of  $\sim 50$  cm) has significant transmission down to  $\sim 1$  m (King et al., 2005). This contrast with the sea-ice thickness in the Arctic ( $\sim 3$  m), where iodine emissions are not significant (Saiz-Lopez et al., 2015). Therefore, a sea-ice thickness of  $\sim 3$  m would lead to negligible emissions of iodine from sea ice. We have now mention this in the manuscript.

Referee #1:L204 Add sea ice as a source of iodine in the introduction.

Response:Sea-ice as a source of iodine is new mentioned in the introduction in the new version of the manuscript explaining the biogenic production of HOI and I<sup>-</sup> from algae underneath the sea ice and its subsequent diffusion through brine channels to the atmosphere.

Referee #1:L211 Should the fluxes and concentrations be reported as 2 significant figures?

Response:Iodine concentration and fluxes curves are shown in Fig. 2 and in Figs. S2 and S3 for further details. Both fluxes and concentrations are shown in the same figures to allow intercomparison between them.

Referee #1:L222 Can you quantify the frequency? L223 What is the second part?

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[Discussion paper](#)



Response: We have rephrased the sentence as follows in order to make it more readable “The iodine time series in this part of the record reveals a higher variability mainly due to a reduced ice compression towards the surface and thus an increased temporal resolution of the samples”

Referee #1: L247 What are the associated radiative impacts?

Response: In this line we are referring to the impacts on the radiative balance of the atmosphere and therefore on climate. These impacts are on tropospheric ozone (Hossaini et al., 2015; Saiz-Lopez et al., 2012; Sherwen et al., 2017) and particle formation (Allan et al., 2015; Roscoe et al., 2015; Sipilä et al., 2016), as already commented at the end of the first paragraph of the Introduction section. We have now included these impacts in the discussion and provided the related references.

Referee #1: Figure 1 Mention the references in the caption to help the reader.

Response: Done

Referee #1: Figure S1 What does the 1:1 line indicate? Be consistent with the naming of the Australian and Italian iodine measurements.

Response: The 1:1 line indicates the  $x=y$  relation (it is not a fit). We have modified the naming according to reviewer suggestion

References Allan, J. D., Williams, P. I., Najera, J., Whitehead, J. D., Flynn, M. J., Taylor, J. W., Liu, D., Darbyshire, E., Carpenter, L. J., Chance, R., Andrews, S. J., Hackenberg, S. C., and McFiggans, G.: Iodine observed in new particle formation events in the Arctic atmosphere during ACCACIA, *Atmos. Chem. Phys.*, 15, 5599-5609, 2015

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,

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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. Hossaini, R., Chipperfield, M., Montzka, S., Rap, A., Dhomse, S. and Feng, W., Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, *Nature Geoscience*, 8(3), 186, 2015.

Kim, K., Yabushita, A., Okumura, M., Saiz-Lopez, A., Cuevas, C. A., Blaszczyk-Boxe, C. S., Min, D., W. Yoon, H.-I. and Choi, W., Production of molecular iodine and triiodide in the frozen solution of iodide: implication for polar atmosphere, *Environmental science & technology*, 50(3), 1280-1287, 2016.

King, M. D., France, J. L., Fisher, F. N., & Beine, H. J.. Measurement and modelling of UV radiation penetration and photolysis rates of nitrate and hydrogen peroxide in Antarctic sea ice: An estimate of the production rate of hydroxyl radicals in first-year sea ice. *Journal of photochemistry and photobiology A: Chemistry*, 176(1-3), 39-49. 2005

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. Maffezzoli, N., Vallelonga, P., Edwards, R., Saiz-Lopez, A., Turetta, C., Kjær, H. A., Barbante, C., Vinther, B. and Spolaor, A., 120,000 year record of sea ice in the North Atlantic, *Climate of the Past Discussions*, <https://doi.org/10.5194/cp-2018-80>, 2018.

Maselli, Olivia J., Chellman, Nathan J., Grieman, Mackenzie, Layman, Lawrence, McConnell, Joseph R., Pasteris, Daniel, Rhodes, Rachael H., Saltzman, Eric and Sigl, Michael. Sea ice and pollution-modulated changes in Greenland ice core methane sulfonate and bromine. *Climate of the Past*, 13 (1). pp. 39-59. 2017

Rhodes, R. H., Yang, X., Wolff, E. W., McConnell, J. R., & Frey, M. M. Sea ice as a

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source of sea salt aerosol to Greenland ice cores: a model-based study. *Atmospheric Chemistry and Physics*, 17(15), 9417-9433. 2017 Roscoe, H. K., Jones, A. E., Brough, N., Weller, R., Saiz-ÅrÅopez, A., Mahajan, A. S., Schoenhardt, A., Burrows, J. P., and Fleming, Z. L., Particles and iodine compounds in coastal Antarctica, *Journal of Geophysical Research: Atmospheres*, 120(14), 7144-7156, 2015 Saiz-Lopez, A., Plane, J. M., Baker, A. R., Carpenter, L. J., von Glasow, R., GõlÅmez MartiÅn, J. C., McFiggans, G. and Saunders, R. W., Atmospheric chemistry of iodine, *Chemical reviews*, 112(3), 1773-1804, 2012.

Saiz-Lopez, A., Blaszczak-Boxe, C.S. and Carpenter, L., A mechanism for biologically induced iodine emissions from sea ice, *Atmospheric Chemistry and Physics*, 15(17), 9731-9746, 2015. Schüpbach, S., Fischer, H., Bigler, M., Erhardt, T., Gfeller, G., Leuenberger, D. et al. Greenland records of aerosol source and atmospheric lifetime changes from the Eemian to the Holocene. *Nature communications*, 9(1), 1476. 2018

Sherwen, T., Evans, M. J., Carpenter, L. J., Schmidt, J. A., and Mickley, L. J., Halogen chemistry reduces tropospheric O<sub>3</sub> radiative forcing, *Atmos. Chem. Phys.*, 17, 1557-1569, 2017. Sipilä, M., Sarnela, N., Jokinen, T., Henschel, H., Junninen, H., Kontkanen, J., Richters, S., Kangasluoma, J., Franchin, A. and Peräkylä, O., Molecular-scale evidence of aerosol particle formation via sequential addition of HIO<sub>3</sub>, *Nature*, 537(7621), 532, 2016 Spolaor, A., Vallelonga, P., Plane, J., Kehrwald, N., Gabrieli, J., Varin, C., Turetta, C., Cozzi, G., Kumar, R., and Boutron, C.: Halogenspecies record Antarctic sea ice extent over glacial–interglacial periods, *Atmospheric Chemistry and Physics*, 13, 6623-6635, 2013. Simonsen, M.F., Baccolo, G., Blunier, T., Borunda, A., Delmonte, B., Frei, R., Goldstein, S., Grinsted, A., Kjær, H.A., Sowers, T., Svensson, A., Vinther, B., Vladimirova, D., Winckler, G., Winstrup, M. and Vallelonga, P. East Greenland ice core dust record reveals timing of Greenland ice sheet advance and retreat. *Nature Communications*, 2019, in press.

Spolaor, A., Barbaro, E., Cappelletti, D., Turetta, C., Mazzola, M., Giardi, F., Björkman, M.P., Lucchetta, F., Dallo, F., Pfaffhuber, K.A., Angot, H., Dommergue, A., Maturilli, M.,

Saiz-Lopez, A., Barbante, C. and Cairns, W.R.L. Diurnal cycle of iodine and mercury concentrations in Svalbard surface snow. *Atmos. Chem. Phys. Discuss.* 2019, 1-25. 2019

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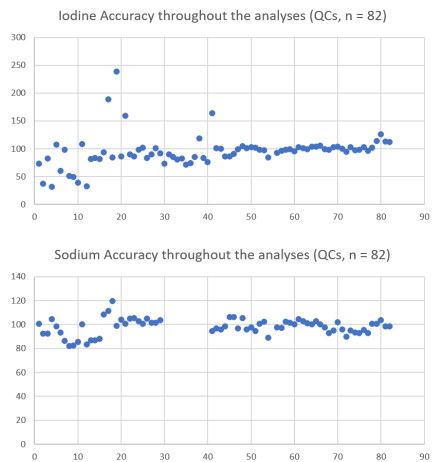
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**Fig. 1.** Supplementary figure A: Iodine and sodium accuracy in the measured samples