Reply to Referee #1

We thank the reviewer for your careful review, constructive comments, and corrections suggested for the manuscript. All changes are highlighted in the track-changes manuscript. A detailed description of our revisions is presented below.

This latter point is well made, however, as it advocates for a rethinking of the representation of iodine fluxes from the ocean it demands a rather high level of scrutiny. The critical illustration is Fig. 3, in which three box-model cases: 1) only O_3-dependent iodine fluxes, 2) roughly half dependent half independent fluxes, 3) fully independent fluxes are compared with observations of O_3 and IO. While the overall correlation is negative, The Case-1 envelop guides the eye to see that the low O_3 observations appear to cluster as two populations which are displaced along the overall negative correlation but individually have positive correlation. All box model cases show consistent behavior for O_3 above ~13 ppbv, roughly parallel to the overall correlation, only those with an O_3-independent iodine source can reproduce the lowest O_3 mixing ratios. However, without offering specific evidence of the O_3-independent source other explanations bear consideration. I have the following suggestions for the authors to consider:

1. Is there any specific evidence to support an O_3-independent source of iodine?
    1. What measurements of organic iodine fluxes and concentrations are available in the study area, what are the modeled organic fluxes from e.g. Ordóñez et al., (2012)?
    2. For the photooxidation of I^- (Watanabe et al., 2019) is there a difference in solar illumination or some other photo-activity proxy between the different observations?

As the referee has pointed out, positive correlation with two populations can be recognized in low O_3 and high IO condition in Case 1 in Figure 3. One suitable explanation of the two populations can be done by flux change from wind speed or SST. However, no clear relation was found between IO and wind speed or IO and SST in the two populations (Figure A). Because the HOI flux could be higher in lower wind conditions (MacDonald et al., 2014), the flux change that occurs as a result of wind speed might partly explain the two populations. Actually, high IO concentration was sometimes observed at low wind speed (on Nov. 27, for example; Figure A), but low IO concentration was also observed at low wind speed. Thus, no clear correlation between the two was found in the whole IO-O_3 plot.

Another suitable explanation can be Case 2 in Figure 3, in which most of observation points are covered. In this case, the weakened flux is accounted for (as described in the original manuscript, the weakened flux might be explained by dissolved organic carbon (Shaw and Carpenter, 2013) or the presence of a sea-surface microlayer (Tinel et al., 2020) impeding

iodine vaporization). In this case, the added "O_3-independent" flux (~4.8×10^7 molecules cm^{-2} s^{-1}) is not explainable solely by flux from photolysis of iodocarbons (approximately 10^7 molecules cm^{-2} s^{-1}) generally assumed in the 3D models (Saiz-Lopez et al., 2014; Sekiya et al., 2020; Sherwen et al., 2016). While indirectly considering the global total fluxes of CH_2IX (X = I, Br, Cl) as described by Ordóñez et al. (2012) in these model simulations, the "Chl-a-based" parameterization reduced the fluxes to too-low levels over this oceanic region. Actually, as previously described in the text, the iodocarbon flux originally reported from a cruise (TransBrom) in the closest oceanic region was even higher, ~6.81×10^7 molecules cm^{-2} s^{-1} assuming immediate photolysis from CH_2IX (X = I, Br, Cl). Although we have not measured iodocarbons during the studied cruises, we believe that the past results provide good support. We might not need a brand new flux mechanism but rather a good parameterization of the traditional organoiodine fluxes (including their photolysis) over the region. More measurements and parameterizations must be made available for future studies. We added related descriptions to the revised manuscript (P7, L194−196, track-changes manuscript).

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2. Since the points not captured by Case 1 are plausibly only vertically displaced from it, what is the effect of varying the initial O_3 mixing ratio? This could be caused by some upwind loss process or else reflect variable entrainment (Kanaya et al., 2019).

Figure B is a scatter plot of O_3 and IO for the O_3-dependent case, but the initial O_3 mixing ratio reduce to 16 ppbv. The covering area is almost equal to that in Figure 3 (18 ppbv); the shift is not purely downward but toward the lower-left corner because the lower initial O_3 concentrations assumed here resulted in overall lower flux of inorganic iodine. Therefore, the observed behavior does not appear to be simply explained by the varied initial O_3 mixing ratio.

3. The subcases already illustrate the effect of varying the magnitude of the iodine flux, and by extension sea-surface I^-, but what about the speciation of the iodine flux (i.e. I_2 vs HOI), would changing this change the correlation? There is likely a pH dependence to speciation of the O_3-dependent fluxes (e.g. Macdonald et al., (2014); Moreno and Baeza-Romero, (2019)). In addition, since the photooxidation pathway emits I_2 (and not HOI) this could offer insight into that hypothesis also.

We made a sensitivity model run with all the flux as I_2. However, the changes were only 1% for IO levels and 2% for O_3 levels, respectively, with Figure 3. The negative correlation between the two was the same.

4. It seems that the authors have not included heterogeneous reactions which recent studies have suggested have been previously underestimated (Tham et al., 2021), could these impact the trend?

The heterogeneous processes on sea-salt aerosol of Tham et al. (2021) were incorporated into our 3-D model (Sekiya et al., 2020). Sensitivity tests of the heterogeneous uptake coefficient on sea-salt aerosol were done. HOI and other gases were sensitive to the uptake coefficient, but IO was not sensitive to the uptake coefficient. Further research on this point is needed.

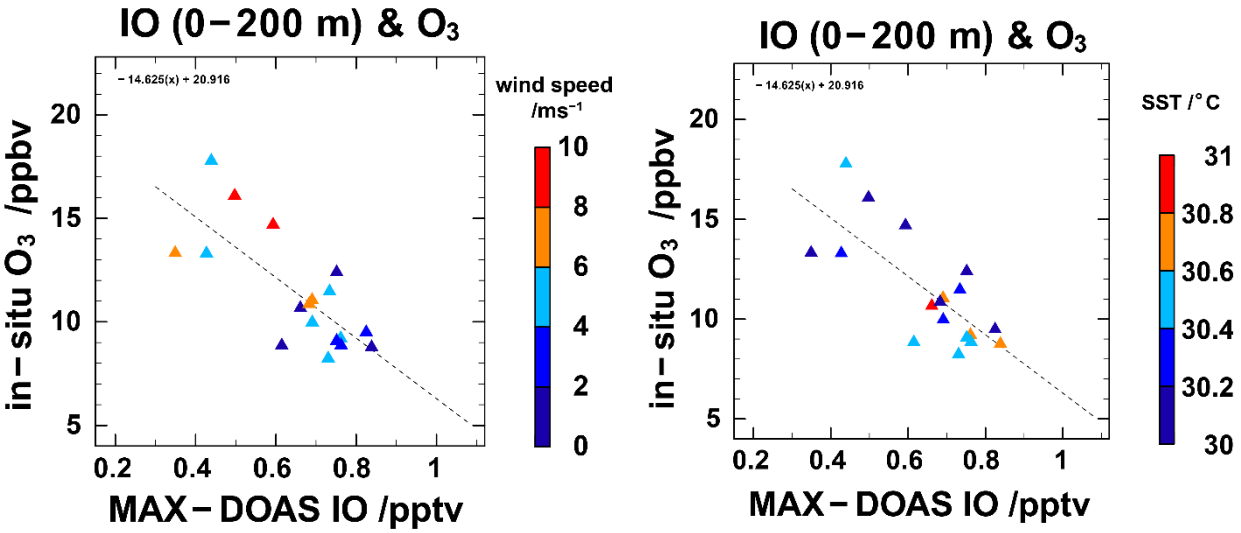

Figure A: IO mixing ratio observed by MAX–DOAS (pptv) versus *in situ* ozone mixing ratio (ppbv). Colors indicate wind speed (left) and SST (right).

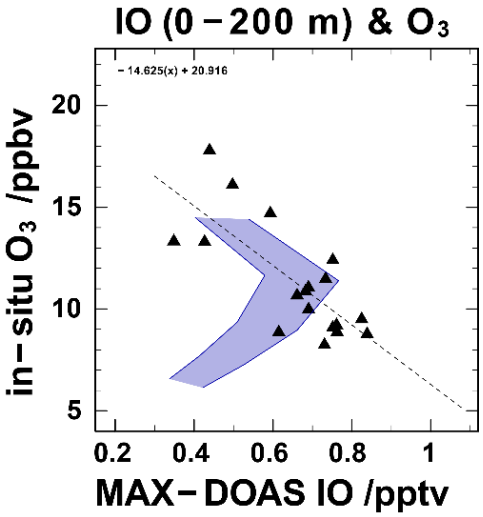

Figure B: IO mixing ratio observed by MAX–DOAS (pptv) versus *in situ* ozone mixing ratio (ppbv). Results of box-model simulations with "O_3-dependent" emission fluxes of iodine compounds are superimposed as blue same as Figure 3, but initial O_3 mixing ratio reduce to 16 ppbv.

Furthermore, it would be helpful if the authors could be more specific in where they expect the posited O_3-independent source to be relevant. Is this a feature of the WPWP or relevant across latitudes? Is it possible that there is a less direct influence O_3 might play? In particular, studies of ice cores and tree rings (Cuevas et al., 2018; Legrand et al., 2018; Zhao et al., 2019) indicate a roughly threefold increase in iodine since c. 1950 at least ~50% attributed to anthropogenic O_3. If half of the inorganic flux were O_3-independent as suggested by Case 2, then either some other cause should be searched for, or the change in O_3-dependent fluxes to produce the observed change is even more dramatic than previously thought.

Thank you very much for pointing out this important aspect. We added related descriptions to the revised manuscript (P7, L225−229, track-changes manuscript).

Results of recent studies indicate a roughly threefold increase in iodine since the 1950s, with at least 50% attributed to anthropogenic O_3 (Cuevas et al., 2018; Legrand et al., 2018; Zhao et al., 2019). If half of the inorganic flux were O_3-independent, as suggested by Case 2, then either some other cause should be sought, or the change in O_3-dependent fluxes to produce the observed change is even more dramatic than previously thought.

Line 160-161: Chlorophyll alone is not enough to exclude an organic iodine source on two counts. Firstly, organic iodine fluxes are not necessarily biotic in origin but might have an abiotic source. Secondly, the mesotrophic conditions characterized by MODIS correspond to those conditions observed to have the largest fluxes of organic iodine in some previous studies e.g. Jones et al., (2010).

We included corresponding descriptions to the revised manuscript (P6, L172, track-changes manuscript).

In addition, the chlorophyll content, based on satellite MODIS measurements (NASA Level-3 ver. 2018) in the source region, was also low (Figure 5), implying that any organic source of iodine can be expected to be negligible (although we also must consider abiotic organic source as well as mesotrophic conditions (Jones et al., 2010)).

In addition, the chlorophyll content, based on satellite MODIS measurements (NASA Level-3 ver. 2018) in the source region, was also low (Figure 5), implying that organic sources of iodine would be weak. However, importance of abiotic sources and mesotrophic conditions (Jones et al., 2010) needs to be paid attention. Later we will come back to this point.

Line 167: The authors state that there are insufficient data to document diurnal IO variations accurately, however, Fig. 2 indicates good temporal coverage was achieved for some days and it seems evident that there is wealth of IO data more generally. Is there some particular set of data which are missing or something else limiting the retrieval of diurnal variation?

We added a figure of diurnal variation (Figure S4). Although no clear diurnal variation was observed, clear day-to-day variation was observed as shown in Figure 7.

The authors describe an "iodine fountain" in the WPWP which does appear to exist in Fig. 4, however, as the authors acknowledge Fig. 6 shows no clear correlation between SST and IO. The evidence for attributing the fluxes to SST seems at best mixed. For both the WPWP and the Maritime Continent it is clear that there is a lot of variability. Examining the temperature contours it doesn't seem clear that SST would better explain the pattern than latitude. What distinguishes the "fountain" from being a tropical feature of unknown cause from specifically tying it to SST? Relatedly, the authors have described a number of differences between the western Pacific and Atlantic, e.g. higher SST, lower O_3. Related to the point above about latitudes, the authors seem to suggest that the "iodine fountain" is a particularity of the WPWP and perhaps maritime continent but not of the Atlantic. But a clearer message on this point would be helpful.

Here we described an "iodine fountain" as a large-scale feature of the WPWP from the global point of view. In detail, as the reviewer pointed out, the one-to-one correlation is not present between SST and IO; however, high IO content was almost always observed at high SST (over approx. 30°C), although the IO content was not always high over high SST area. The causes of the fine-scale features would be studied in the future. To demonstrate this relation, we added Figure S5 in the Supplemental materials. It is noteworthy that Prados-Roman et al. (2015) reported that the highest IO was observed in the western Pacific (in their Figure 4) (in the open ocean).

Line 34: "006C" here is presumably "I"

Corrected.

Line 39: More recent papers on the O_3-dependent iodine source which should be mentioned for offering further consideration of physical and chemical drivers include Inamdar et al., (2020) and Carpenter et al., (2021).

We added a corresponding description to the revised manuscript.

Line 71: Inamdar et al., (2020) or else Mahajan et al., (2019) which includes the underlying measurements bear mentioning as more recent measurements of IO on the open ocean.

We added a citation of Inamdar et al. (2020) to the revised manuscript.

Line 88: Is this exposure time the same for all ELs or is this for a specific EL? If the latter the angle should be specified.

The exposure time was fixed for all ELs.

Line 96-101: The version of MMF described in Friedrich et al., (2019) uses Tikhonov regularization rather than optimal estimation for the aerosol retrieval. Was a more recent version used? Could the author provide the version numbers for MMF and VLIDORT?

The version of MMF used in this study is the same as used in Frieß et al. (2019) and Tirpitz et al. (2021) but with adjusted a priori and variance-covariance matrix settings to fit for IO retrieval. It uses VLIDORT v.2.7. We added a corresponding description to the revised manuscript (P4, L99−103, track-changes manuscript).

The version of MMF used in this study is the same as used in Frieß et al. (2019) and Tirpitz et al. (2021) but with adjusted a priori and variance-covariance matrix settings to fit for IO retrieval. MMF applies the optimal estimation method and uses a two-step approach in which the aerosol profile is first retrieved from O_4 DSCDs. Then, the IO profile is retrieved from the IO DSCDs using the earlier retrieved aerosol profile in the forward model. We used VLIDORT (v.2.7) (Spurr, 2006) as the forward model in a pseudo-spherical multiple-scattering setting.

Line 103-104: These a priori values are presumably the column integrals, this is should be more explicit by e.g. specifying the IO VCD

We specified the description.

Line 104: While Sa is well understood by an expert audience to be the a priori covariance this should be defined for a non-expert audience.

Corresponding text was added to the revised manuscript (P4, L108, track-changes manuscript).

*The a priori covariance matrix **S**a for both aerosol and IO retrieval was constructed using the square of 100% of the a priori profile on the diagonal and a correlation length of 200 m.*

Line 123: “they” here is presumably the fluxes, this is not clear.

This point was changed in the revised manuscript.

Line 32: Another recent paper with field evidence for iodine-derived aerosol particles is He et al., (2021)

We added a citation to and a reference of He et al. 2021.

Line 125: Hayase et al., (2010) and Hayase et al., (2012) predate Shaw and Carpenter, (2013) and show similar effects.

We added citations of these reports to the revised manuscript.

Line 141: Some more information on the O_3 data filtering would be useful, e.g. is the hourly average a running average or discrete average? What is the typical magnitude or relative magnitude of σ?

The hourly average is a "discrete" average. The typical magnitude of 1σ over the remote ocean was approximately 0.1−0.5 ppbv. We added a corresponding description to the revised manuscript (P5, L148, track-changes manuscript).

The typical magnitude of 1σ over the remote ocean was approximately 0.1–0.5 ppbv.

References

Frieß, U., Beirle, S., Bonilla, L. A., Bosch, T., Friedrich, M. M., Hendrick, F., Piters, A., Richter, A., van Roozendael, M., Rozanov, V. V., Spinei, E., Tirpitz, J. L., Vlemmix, T., Wagner, T., and Wang, Y.: Intercomparison of MAX-DOAS vertical profile retrieval algorithms: studies using synthetic data, Atmos Meas Tech, 12, 2155-2181, 10.5194/amt-12-2155-2019, 2019.

Großmann, K., Frieß, U., Peters, E., Wittrock, F., Lampel, J., Yilmaz, S., Tschritter, J., Sommariva, R., von Glasow, R., Quack, B., Krüger, K., Pfeilsticker, K., and Platt, U.: Iodine monoxide in the Western Pacific marine boundary layer, Atmos Chem Phys, 13, 3363-3378, 10.5194/acp-13-3363-2013, 2013.

Hayase, S., Yabushita, A., Kawasaki, M., Enami, S., Hoffmann, M. R., and Colussi, A. J.: Heterogeneous Reaction of Gaseous Ozone with Aqueous Iodide in the Presence of Aqueous Organic Species, J Phys Chem A, 114, 6016-6021, 10.1021/jp101985f, 2010.

Hayase, S., Yabushita, A., and Kawasaki, M.: Iodine Emission in the Presence of Humic Substances at the Water's Surface, J Phys Chem A, 116, 5779-5783, 10.1021/jp2048234, 2012.

He, X. C., Tham, Y. J., Dada, L., Wang, M. Y., Finkenzeller, H., Stolzenburg, D., Iyer, S., Simon, M., Kurten, A., Shen, J. L., Rorup, B., Rissanen, M., Schobesberger, S., Baalbaki, R., Wang, D. S., Koenig, T. K., Jokinen, T., Sarnela, N., Beck, L. J., Almeida, J., Amanatidis, S., Amorim, A., Ataei, F., Baccarini, A., Bertozzi, B., Bianchi, F., Brilke, S., Caudillo, L., Chen, D. X., Chiu, R., Chu, B. W., Dias, A., Ding, A. J., Dommen, J., Duplissy, J., El Haddad, I., Carracedo, L. G., Granzin, M., Hansel, A., Heinritzi, M., Hofbauer, V., Junninen, H., Kangasluoma, J., Kemppainen, D., Kim, C.,

Kong, W. M., Krechmer, J. E., Kvashin, A., Laitinen, T., Lamkaddam, H., Lee, C. P., Lehtipalo, K., Leiminger, M., Li, Z. J., Makhmutov, V., Manninen, H. E., Marie, G., Marten, R., Mathot, S., Mauldin, R. L., Mentler, B., Mohler, O., Muller, T., Nie, W., Onnela, A., Petaja, T., Pfeifer, J., Philippov, M., Ranjithkumar, A., Saiz-Lopez, A., Salma, I., Scholz, W., Schuchmann, S., Schulze, B., Steiner, G., Stozhkov, Y., Tauber, C., Tome, A., Thakur, R. C., Vaisanen, O., Vazquez-Pufleau, M., Wagner, A. C., Wang, Y. H., Weber, S. K., Winkler, P. M., Wu, Y. S., Xiao, M., Yan, C., Ye, Q., Ylisirnio, A., Zauner-Wieczorek, M., Zha, Q. Z., Zhou, P. T., Flagan, R. C., Curtius, J., Baltensperger, U., Kulmala, M., Kerminen, V. M., Kurten, T., Donahue, N. M., Volkamer, R., Kirkby, J., Worsnop, D. R., and Sipila, M.: Role of iodine oxoacids in atmospheric aerosol nucleation, Science, 371, 589, 10.1126/science.abe0298, 2021.

Inamdar, S., Tinel, L., Chance, R., Carpenter, L. J., Sabu, P., Chacko, R., Tripathy, S. C., Kerkar, A. U., Sinha, A. K., Bhaskar, P. V., Sarkar, A., Roy, R., Sherwen, T., Cuevas, C., Saiz-Lopez, A., Ram, K., and Mahajan, A. S.: Estimation of reactive inorganic iodine fluxes in the Indian and Southern Ocean marine boundary layer, Atmos Chem Phys, 20, 12093-12114, 10.5194/acp-20-12093-2020, 2020.

Jones, C. E., Hornsby, K. E., Sommariva, R., Dunk, R. M., Von Glasow, R., McFiggans, G., and Carpenter, L. J.: Quantifying the contribution of marine organic gases to atmospheric iodine, Geophys Res Lett, 37, 10.1029/2010gl043990, 2010.

MacDonald, S. M., Martin, J. C. G., Chance, R., Warriner, S., Saiz-Lopez, A., Carpenter, L. J., and Plane, J. M. C.: A laboratory characterisation of inorganic iodine emissions from the sea surface: dependence on oceanic variables and parameterisation for global modelling, Atmos Chem Phys, 14, 5841-5852, 10.5194/acp-14-5841-2014, 2014.

Ordóñez, C., Lamarque, J. F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Santos, G. S., Brasseur, G., and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos Chem Phys, 12, 1423-1447, 10.5194/acp-12-1423-2012, 2012.

Prados-Roman, C., Cuevas, C. A., Hay, T., Fernandez, R. P., Mahajan, A. S., Royer, S. J., Gali, M., Simo, R., Dachs, J., Großmann, K., Kinnison, D. E., Lamarque, J. F., and Saiz-Lopez, A.: Iodine oxide in the global marine boundary layer, Atmos Chem Phys, 15, 583-593, 10.5194/acp-15-583-2015, 2015.

Saiz-Lopez, A., Fernandez, R. P., Ordonez, C., Kinnison, D. E., Martin, J. C. G., Lamarque, J. F., and Tilmes, S.: Iodine chemistry in the troposphere and its effect on ozone, Atmos Chem Phys, 14, 13119-13143, 10.5194/acp-14-13119-2014, 2014.

Shaw, M. D. and Carpenter, L. J.: Modification of Ozone Deposition and I_2 Emissions at the Air-Aqueous Interface by Dissolved Organic Carbon of Marine Origin, Environ Sci Technol, 47, 10947-10954, 10.1021/es4011459, 2013.

Sekiya, T., Kanaya, Y., Sudo, K., Taketani, F., Iwamoto, Y., Aita, M. N., Yamamoto, A., and Kawamoto, K.: Global Bromine- and Iodine-Mediated Tropospheric Ozone Loss Estimated Using the CHASER Chemical Transport Model, Sola, 16, 220-227, 10.2151/sola.2020-037, 2020.

Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., Jacob, D. J., Dix, B., Koenig, T. K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A. S., and Ordonez, C.: Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem, Atmos Chem Phys, 16, 12239-12271, 10.5194/acp-16-12239-2016, 2016.

Tham, Y. J., He, X. C., Li, Q. Y., Cuevas, C. A., Shen, J. L., Kalliokoski, J., Yan, C., Iyer, S., Lehmusjarvi, T., Jang, S. H., Thakur, R. C., Beck, L., Kemppainen, D., Olin, M., Sarnela, N., Mikkila, J., Hakala, J., Marbouti, M., Yao, L., Li, H. Y., Huang, W., Wang, Y. H., Wimmer, D., Zha, Q. Z., Virkanen, J., Spain, T. G., O'Doherty, S., Jokinen, T., Bianchi, F., Petaja, T., Worsnop, D. R., Mauldin, R. L., Ovadnevaite, J., Ceburnis, D., Maier, N. M., Kulmala, M., O'Dowd, C., Dal Maso, M., Saiz-Lopez, A., and Sipila, M.: Direct field evidence of autocatalytic iodine release from atmospheric aerosol, P Natl Acad Sci USA, 118, 10.1073/pnas.2009951118, 2021.

Tinel, L., Adams, T. J., Hollis, L. D. J., Bridger, A. J. M., Chance, R. J., Ward, M. W., Ball, S. M., and Carpenter, L. J.: Influence of the Sea Surface Microlayer on Oceanic Iodine Emissions, Environ Sci Technol, 54, 13228-13237, 10.1021/acs.est.0c02736, 2020.

Tirpitz, J. L., Frieß, U., Hendrick, F., Alberti, C., Allaart, M., Apituley, A., Bais, A., Beirle, S., Berkhout, S., Bognar, K., Bosch, T., Bruchkouski, I., Cede, A., Chan, K. L., den Hoed, M., Donner, S., Drosoglou, T., Fayt, C., Friedrich, M. M., Frumau, A., Gast, L., Gielen, C., Gomez-Martin, L., Hao, N., Hensen, A., Henzing, B., Hermans, C., Jin, J. L., Kreher, K., Kuhn, J., Lampel, J., Li, A., Liu, C., Liu, H. R., Ma, J. Z., Merlaud, A., Peters, E., Pinardi, G., Piters, A., Platt, U., Puentedura, O., Richter, A., Schmitt, S., Spinei, E., Zweers, D. S., Strong, K., Swart, D., Tack, F., Tiefengraber, M., van der Hoff, R., van Roozendael, M., Vlemmix, T., Vonk, J., Wagner, T., Wang, Y., Wang, Z. R., Wenig, M., Wiegner, M., Wittrock, F., Xie, P. H., Xing, C. Z., Xu, J., Yela, M., Zhang, C. X., and Zhao, X. Y.: Intercomparison of MAX-DOAS vertical profile retrieval algorithms: studies on field data from the CINDI-2 campaign, Atmos Meas Tech, 14, 1-35, 10.5194/amt-14-1-2021, 2021.