

Interactive comment on “Contribution of liquid, NAT and ice particles to chlorine activation and ozone depletion during Antarctic winter and spring” by O. Kirner et al.

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This study deals with the question what are the relative contributions of the different types of stratospheric clouds to the activation of chlorine. This is still an open question and part of a recent, at times controversial debate (e.g. Drdla and Müller, 2012, *Ann. Geophys.* and the preceding discussion in *Atmos. Chem. Phys. Discuss.*, 10, 28687, 2010, or Solomon et al., *PNAS*, 111, 17, 6220, 2014). The study adds evidence to this ongoing discussion and as such, is worth publishing.

The scientific methods are sound, the used model is state-of-the-art and the

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manuscript is short and concise. In general, it is easy to understand and well structured.

My main comment is that you really need to compare your model results to observations (see “Major comments” for a detailed explanation). Another issue is, that while I am a supporter of short and concise manuscripts, a little bit more of detail wouldn't hurt in some places. Sometimes, information that is necessary to understand what you have done is missing. Some more discussion would also help to assess your results in comparison to other results. I will try to give specific advice for these issues in the specific comments below.

The manuscript has some deficiencies in terms of the correct use of the English language. Some parts (especially towards the end of the manuscript and in the abstract and introduction) could be improved in grammar, wording and style. I will try to give specific advice in the technical corrections, but I would recommend that a native speaker proof-reads the manuscript before publication (since I am no native speaker, my corrections may be wrong).

Major comments

- Your results are of less value than they could be if you don't compare the results of your EMAC model runs to observations. If the model runs compare well to observations, it would strengthen your conclusions, and if there are discrepancies, the discrepancies (and their potential impact on your conclusions) need to be discussed.

Since this is a nudged version of EMAC, it is similar to a CTM and should be treated as such, which includes a validation of the simulated mixing ratios of the key species by observational data.

You are free to choose the observational data that is most appropriate for you (or to cite a reference if these model runs are validated somewhere else). Just as

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a suggestion, I would recommend MLS satellite data for comparison: They are available for the complete time period that is covered by your model runs (and in polar night), many of the key species (ozone, HCl, HNO₃, ClO) are included in the data set and data are freely available.

- You do not provide all necessary information on the model setup that is needed to reproduce your model runs and to interpret the results, even supposed the reader has consulted Kirner et al. (2011). Several pieces of information are missing, e.g. which of the both NAT schemes of the submodel PSC you use, parameters for the calculation of surface area densities are missing etc. See the “specific comments” for details. It may also be helpful to repeat some additional basic information from Kirner et al. in the manuscript, so that the average reader does not have to look it up there. E.g. which types of clouds are allowed to exist at the same time, do NAT clouds form from ice clouds or not etc.

Specific comments

- Abstract: I think it would make sense to mention that you are using a nudged version of the model. You basically use a CTM here and you can expect the temperature and wind fields to follow the actual meteorological evolution of the winters, which is not the case with a CCM. This is important information and would help the reader to know what to expect in the following. That is, I think it will attract more readers if people know that this is not taking place in a “model world” with temperature biases etc., but is based on “real” conditions, or more precisely based on an “ECMWF world”.
- Page 14834, line 7: Can you shortly explain what the difference between the sensitivity runs is? It would help to have this information in the abstract.
- Page 14835, lines 10–11: In addition to the reference to Kirner et al. (2011), I suggest to put a reference to your Section 3 here.

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- Page 14835, line 16: While it is true that assuming only liquid binary particles leads only to a moderate reduction, this is a hypothetical case (we know that ternary liquids exist in reality most of the time). I am not sure, but maybe it is better to skip that.
- Page 14836, line 10: What is the approximate vertical resolution in the stratosphere? Please add to the text.
- Page 14836, line 18 to page 14837, line 6: Please only cite the submodels which are relevant for the results in the stratosphere. Citing tropospheric submodels is not only confusing, it also makes the impression that you are collecting citations for your colleagues here ;-). This is a nudged version of the model, where the tropospheric submodels will play a very minor role for the results.
- Page 14837, lines 7–8: What are the rate coefficients that are not taken from Sander et al. (2011)? Are they important for this study? If the answer is yes (and if it requires not too much additional discussion), it could make sense to cite the references here.
- Page 14837, lines 18–24: I suggest to shortly mention the alternative parameterizations (Abbatt and Molina for NAT, Shi et al. for liquids) and to give reasons for your choices.
- Page 14838, line 1: What is the value of 50 % based on? Measurements? Give a reference or explanation.
- Page 14838, line 3–4: It is nice to know that there are two parameterizations for NAT particles, but unfortunately you don't tell us which one is used here :-)
- Section 3 (comment 1): Given that you use the thermodynamic NAT parameterization: NAT seems only to be allowed to form from ice clouds (if I understand Kirner et al., 2011, correctly). That could limit the occurrence of NAT clouds. Since

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NAT clouds have been observed under conditions where the formation from ice clouds can be excluded (e.g. Voigt et al., 2005, Pitts et al., 2011), this assumption should be discussed.

- Section 3 (comment 2): Some of the necessary information about number densities and particle radius that is required to calculate surface area densities seems to miss here (even if referring to Kirner et al., 2011). If you use the thermodynamic NAT scheme, provide the free parameters r_{\min} and N_{\max} . By the way, maybe I am wrong, but is there a typo in Eq. 17 in Kirner et al.? The way it is written, N_{\max} is a *minimum* and not a maximum number density. Please clarify. If you use the kinetic NAT scheme, it would not hurt to shortly describe how it works and what are the parameters (initial radius, initial number density). Please also provide the necessary parameters for ice. It would also not hurt to shortly repeat how the surface area density for liquids is calculated.
- Section 3 (comment 3): Maybe I missed that when reading Kirner et al. (2011), but what happens if STS and NAT clouds exist at the same time? How do they compete for the available HNO₃? Please discuss.
- Section 3 (comment 4): It seems that there are several sedimentation schemes implemented according to Kirner et al. (2011). Please indicate which scheme is used.
- Section 3 (comment 5): Same for the other parameters from Table 4 of Kirner et al., which cannot be deduced from the existing information in the manuscript.
- Page 14838, line 17: Of course, it makes discussion easier to only switch off the heterogeneous chemistry (e.g. only one Fig. 2 needed), but not to change the formation of the clouds. But this also has a disadvantage: If you would switch off the NAT clouds completely, the HNO₃ condensed in the NAT clouds would be available for STS clouds, i.e. you would expect that the surface area density

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of STS clouds increases. In practice, the effect may be small, since NAT clouds play a small role relative to STS clouds in your model setup. But the more “realistic” assumption would be to switch off the clouds completely (i.e. we know that once we have NAT clouds, there will be reactions on them (provided we don’t believe in the Abbatt and Molina rates). What we don’t know exactly from measurements are the relative surface area densities of STS clouds and NAT clouds). I don’t want you to change the model runs here (I know they are expensive), but I suggest to discuss this.

- Page 14839, line 1: May make sense to give this information earlier (i.e. in Section 2). How well does the nudging work (temperature bias to ECMWF)?
- Page 14839, line 6: Do you only use tropospheric boundary conditions and wait some years until a realistic distribution in the stratosphere is reached? Or do you initialize the stratospheric fields of O₃, N₂O, CH₄, HCl etc. with some data to reduce the spin-up period of the model? What is the maximum Cly and Bry that is observed in the model runs (i.e. do you consider short-lived bromine species)?
- Page 14839, line 15 and Fig. 1 (bottom row): This is a good place to compare your model results to observations. I suggest to show maps of HNO₃ from satellite data similar to the bottom row in Fig. 1. Put another way: You say that PSCs are simulated very reasonably in line 14. But how do you know that if you don’t compare to observations?
- Page 14839, line 19: Please briefly compare to observed number densities from other studies and discuss (e.g. Northway et al., 2002, Voigt et al., 2005, Pitts et al. 2011). Please change the unit to cm⁻³, since this is common usage. It seems to me that the simulated number densities are at the very low end of observations, which helps to explain the low influence of your modelled NAT clouds on chlorine activation. I suggest to write something along these lines in the manuscript.

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- Page 14839, line 25: It is probably no good idea to use a dot between the chemical species. To my knowledge, that implies that exactly one molecule H₂SO₄ is bound to one molecule H₂O etc. Use a slash or hyphen.
- Page 14839, line 26 to page 14840, line 1: Probably a good idea to take an average over the 5 years here, since interannual variability will not be too large and the manuscript gets clearer. Can you show to me that this approach is justified (e.g. by attaching some figures for the single years and the different quantities to your reply)?
- Figure 2 (caption and text page 14840, line 1): Add a remark to the text and figure caption that the plots are scaled very differently.
- Fig. 2: There is a strange artifact here: In the plots for the number density and surface area densities, the values seem to be cut at exactly 200 hPa. Please explain.
- Page 14839, line 27 to page 14840, line 1: Why do you not use equivalent latitude or PV here for latitude? As can be seen in Fig. 1, you are in danger of averaging over areas which are not in the polar vortex.
- Page 14840, line 1–3 and Fig. 2 (caption): Can you put the information that the figure is valid for all runs in the figure caption, too?
- Page 14840, line 4–5: “lower temperatures”. Lower than what? Probably you mean “low” here. But since this is very unspecific, you can skip that.
- Page 14840, line 6 and line 9, Fig. 2: Please change the unit to cm⁻³.
- Page 14840, line 10: At first, it may look like a contradiction that the ice surface area density is high and still not relevant for activation. I suggest to add a note that by the time that the ice clouds form, all chlorine is already activated and

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additional activation by ice clouds does not matter anymore (maybe in Section 6).

- Fig. 3 (add additional figure following Fig. 3): This is a good place to compare your results to observations again. Since you don't have ClO_x from observations, I suggest to compare ClO from satellite and model in a map similar to Figure 1 in an additional figure (to get the diurnal cycle right).
- Fig. 3: Only a minor remark: In the upper right panel, the difference between the “NoHet” and “Liquid” runs is shown. Why is there a difference between these runs *outside* of the area where polar stratospheric clouds form? It is difficult to see how large the difference is from the contour plot and there may be some numerical reasons (diffusion?), but it catches your attention that e.g. in the troposphere, ClO_x seems not be zero in at least one of the runs.
- Fig. 3: The different scales are really confusing. Even the upper two plots don't have the same scale. Add a remark to the text and figure caption that the plots are scaled very differently. And I would suggest to use the same scaling for the upper two plots (yes, I know, some values are cut this way, but it causes more confusion the way it is in the moment, because it is easy to miss the fact that they are scaled differently).
- Fig. 4 (add additional figure following Fig. 4): And again, good place to compare to observations. Following Fig. 4, I suggest to show exactly the same plot as in the upper left corner, just with satellite data for ozone. You would make me perfectly happy if you could add a new figure showing HCl both from satellite and your model as an example for a reservoir gas and discuss the figure.
- Fig. 1, Fig. 5: Just for consistency, you could omit the black lines between the areas of different color in the contour plots. There are no lines in Figs. 2–4.

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- Page 14843, line 1–3: I would express it a little bit more carefully. You don't really definitely confirm a major contribution of liquid particles, since these are still model runs, and the occurrence of liquid and solid clouds is not sufficiently constrained by measurements. I would write something like "suggest" or if you want to put more emphasis on it "strongly suggest".

Technical corrections

I am happy that you implemented most of the technical corrections I suggested in the pre-review, but you did not get the grammar and wording right in some cases.

- Page 14840, line 19: It has to be "subtracting" (verb) and not "subtraction" (noun), see pre-review. Same in line 21 and 23.
- Page 14841, line 14–15: Sounds a little bit better now, but I suggested to start the sentence with "The contribution is. . .". Normally, it is a good idea to start sentences with the subject, followed by verb and object. You often tend to start with the object or dependent clauses, which is difficult to understand and read.
- Page 14841, line 17: Not quite my suggestion from the pre-review. A suggestion for the complete sentence, in (hopefully) correct English: "The NAT particles show only a relevant contribution to chlorine activation in mid-May in the region between 20 hPa and 50 hPa, with contributions of up to 10 %." However, I am not sure where to place "only".

Additional technical corrections. Some parts at the end of the manuscript and in the abstract and introduction can be improved in grammar, wording and style. I will give suggestions below.

- Page 14834, 7–10: Suggestion: "The results of these simulations show that the significance of heterogeneous reactions on NAT and ice particles for chlorine activation and ozone depletion in Antarctic winter and spring is small in comparison
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to the significance of reactions on liquid particles." (i.e. replace "subordinate" by "small", change order, "regarding" was not correct)

- Page 14834, 12–15: Suggestion: "Liquid particles alone are sufficient to activate almost all of the available chlorine, with the exception of the upper PSC regions between 10 and 30 hPa, where temporarily ice particles show a relevant contribution. Shortly after the first PSC occurrence, NAT particles contribute a small part to the chlorine activation." (i.e. change the order of the clauses, omit "the" before "ice particles", shorten "have a relevant contribution to the chlorine activation", change "have" to "show", split into two sentences, "during" following "with the exception of" makes no sense logically)
- Page 14834, line 16: I would suggest to move "In the model simulations" to the very end of the sentence.
- Page 14834, line 17: I would suggest: "Heterogeneous chemistry on ice particles causes only up to 5 DU of additional ozone depletion in the column. . ." (and so on)
- Page 14834, line 25: I would suggest to write "...is essential for the correct simulation of chlorine activation. . ."
- Page 14834, line 26 to Page 14835, line 5: This is a very long sentence. In addition, it is not a correct English sentence ("which cause . . . for the denitrification"). I would suggest to split the sentence into two parts, e.g. "The liquid (cold binary aerosols and STS particles) and solid particles (NAT and ice particles) allow heterogeneous reactions to proceed, which cause the activation of chlorine reservoirs and the production of chlorine radicals leading to ozone destruction. In addition, it causes stratospheric denitrification, resulting in a delay in the deactivation of active chlorine in polar spring. . ." ("activation to chlorine radicals" sounds odd, omit "this" preceding "active chlorine")

- Page 14835, line 6: Delete “To consider. . .” and start with “A new algorithm. . .”
- Page 14835, line 25: Insert comma following “However”
- Page 14835, line 27: Insert comma following “Therefore”
- Page 14836, line 5: I would write “. . . and to determine the corresponding ozone depletion. . .”.
- Page 14836, line 9: “atmospheric” in correspondence to “tropospheric”?
- Page 14836, line 11: Sounds odd. Suggestion: “to link source codes from different institutions”
- Page 14836, line 15–16: Spell out “approx.”
- Page 14837, line 14: Do you mean “surface areas” here?
- Page 14837, line 15: Since you introduced the abbreviations NAT and STS in the introduction, you may want to shorten the sentence here.
- Page 14837, line 23: Add “. . . for ice particles are taken from. . .”
- Page 14838, line 3: You can omit “Besides. . .” and start with “There are. . .” without losing information.
- Page 14838, line 9: Insert comma following “In both cases”
- Page 14838, line 17: Insert comma following “In the three sensitivity simulations”
- Page 14839, line 1: Skip “in all four EMAC simulations” or move to the end of the sentence. You could also move the clause “to simulate. . .” to the end of the sentence.

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- Page 14839, line 7: Split into two sentences: “Boundary conditions for ozone depleting substances are from. . .”
- Page 14839, line 7: Delete hyphen following “NAT”
- Page 14839, line 15: Insert comma following “For example”
- Page 14839, line 17: Insert comma following “NAT formation”
- Page 14839, line 19: Delete “up”
- Page 14839, line 19: Split sentence: “Simultaneously, . . .”
- Page 14839, line 20: Replace hyphen by space in “NAT-PSC”
- Page 14839, line 20: Starting with “In HNO₃” sounds odd. Delete and end the sentence with “. . . in the HNO₃ fields of the model.” or similar.
- Page 14839, line 24: Suggestion: “In addition to NAT particles, ice particles and. . .”
- Page 14840, line 1: “The illustrated results”. Better: “The results shown in Fig. 2”
- Page 14840, line 3: “In average. . .” sounds very odd. Suggestion: “NAT is visible from mid-May until October in the averaged fields of the EMAC simulations.”
- Page 14840, line 5: Simplify a little bit: “. . . increase of the number density to values of more than 200 m⁻³. . .”
- Page 14840, line 6: Suggestion: “. . . differences in the timing of the first NAT appearances. . .”
- Page 14840, line 10–11: I would suggest “surface area densities”

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- Page 14840, line 16: Suggestion: “The contribution of heterogeneous reactions on liquid, NAT and ice particles to chlorine activation and the corresponding ozone depletion in polar spring is determined by comparing the standard and sensitivity simulations.” (start sentence with “The contribution...” and shift the clause “by...” to the end. Replace “reactivity of” by “reactions on”, avoid “possible” (you are really doing it, and you repeat “possible” in the next sentence))
- Page 14840, line 18: Suggestion: “The impact of the liquid particles is assessed by...” (and see far above for “subtraction”)
- Page 14840, line 24: I would first introduce the figures (i.e. sentence Page 14841, line 1) and then talk about the averaging.
- Page 14840, line 26: It doesn’t get quite clear here that you show several zonal means as a function of latitude.
- Page 14841, line 1: Suggestion: “In Fig. 3, the evolution of ClO_x in the standard simulation and the sensitivity simulations is illustrated. The standard run is shown in the top left, the liquid run is shown in...”. A little bit more organized this way.
- Page 14841, line 4, line 6–7: Replace “due to” by “by”
- Page 14841, line 5: Insert “of” following “contributions”
- Page 14841, line 8: Sounds odd. Suggestion: “Ice particles only show a relevant contribution in the upper PSC region...”
- Page 14841, line 8: Replace “extra” by “additional” and write “A maximum of about...”.
- Page 14841, line 13: Suggestion: “Liquid particles contribute more than 90 % to chlorine activation for most of the time.” For the rest of the paragraph, see also above (pre-review comments).

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- Page 14841, line 20: Simply “The evolution of ozone is shown in Fig. 4”?
- Page 14841, line 21: Insert comma following “October”
- Page 14841, line 22: Sounds a little bit odd. Suggestion: “The largest contribution to the ozone depletion comes from chlorine activated on liquid particles with values of more than 2500 ppv.”
- Page 14841, line 24: Suggestion: “In contrast, the contribution that can be attributed to additional chemistry on ice particles reaches values of only 170 ppbv in the upper PSC region.”
- Page 14842, line 1: This sentence sounds very odd. Suggestion: “Figure 5 shows the total effect that heterogeneous chemistry on different PSC particles has on the time development of the ozone column.”
- Page 14842, line 3–5: Split into two sentences: “The ozone column shows a decrease of more than 130 DU in early October in high southern latitudes. Liquid particles are mainly responsible for this decrease.”
- Page 14842, line 5–7: Rearrange: “The contribution... is at least 95 % during September...”
- Page 14842, line 8: Replace comma by period and start new sentence.
- Page 14842, line 10: Insert comma following “hand”
- Page 14842, line 17–21: Sounds odd. See my comment on the similar sentence in the abstract on page 14834, line 12–15 for a suggestion how to improve this sentence.
- Page 14842, line 22–23: See my comment above for page 14834, line 16.

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- Page 14842, line 23–26: See my comment above for page 14834, line 17.
- Page 14843, line 1–9: The whole paragraph needs to be improved in grammar, wording and style. I have difficulties to understand what you want to tell me with the first sentence and I would formulate it a bit more carefully (see specific comments). You could start the following outlook with something like “Open questions that remain are. . .”. “Hence, regarding the ozone development. . .” sounds very odd. Remove “on the one hand . . . on the other hand”. That implies a contradiction, which I cannot see.
- Is it correct that there are no acknowledgements?
- Caption Figure 1: Replace “times” by “dates”.
- Caption Figure 2: Replace “surface densities” by “surface area densities”
- Caption Figure 3 and 4: replace “in 80° to 90°” by “averaged over 80° to 90°”
- Caption Figure 4 and 5: Replace “diffent” by “different”
- All figures: It is still very difficult to read the labels and numbers. Maybe this gets better in the final ACP manuscript, but in the moment, I am not able to read most of the numbers in the printed version.

References

- Abbatt and Molina, *J. Phys. Chem.*, 96, 7674–7679, 1992
- Northway et al., *J. Geophys. Res.*, 107, doi:10.1029/2001JD001079, 2002
- Pitts et al., *Atmos. Chem. Phys.*, 11, 2161–2177, 2011
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- Voigt et al., *Atmos. Chem. Phys.*, 5, 1371–1380, 2005

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