

Interactive comment on “The role of chlorine in tropospheric chemistry” by Xuan Wang et al.

Anonymous Referee #1

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This paper presents results describing the application of the GEOS-CHEM model to understanding the role of chlorine chemistry in the troposphere. The paper makes some new contributions and improves upon previous GEOS-CHEM modeling of halogen chemistry, but has so many major flaws and omissions that will require considerable modification. Since these changes may impact some of the findings, it is hard to know how to assess its publishability at this point. I have the following general and specific comments and questions.

General Comments:

There are number of errors and omissions in the reference list: papers that are noted in the text, but not in list, listed with errors, or just the wrong paper. Here is a list roughly in order of appearance: Liu et al., 2001 – which one, there are two in the reference list? Jaegle et al., 2012 – do you mean Jaegle 2011 here? Wesely 1989 is not in the

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list. Wang 1998 is not in the list. Jaegle et al., 2010 – do you mean Jaegle 2011 here? Martin et al., 2002 – do you mean 2003? Abbatt and Wachewsky, 1998 is not in the list Bey et al., 2001 is not in the list. Pszeny et al., 1991 – do you mean 1993 here? Roberts et al., 2008 is not in the list. Allen et al., 2007 is not in the list unless you mean Allan et al. 2011 Wang et al., 1994 is not in the list. Roberts et al. 2009 is not the correct reference, it should be this Roberts et al., 2009 (Roberts et al., 2009) Mielke et al., 2013 is not on the list.

Chloride Sources: The paper ignores soil and wind-blown dust sources of particle chloride. Those were described by Sarwar et al., 2012 (Sarwar et al., 2012) (which by the way is not referenced in this paper) as the major sources of chloride in the Eastern U.S. and therefore will drive the chlorine budget in the middle of continents. This paper needs to give serious consideration to this source, and can use the IMPROVE network chloride data as a means to assess this continental source.

Comparisons:

The selection of data sets for comparison was certainly not thorough, and obvious opportunities for comparison were apparently not considered.

The paper seems to lean heavily on the Graedel and Keene work from 1995, but I believe further work has been done since then. There are comparisons that could be made that would greatly add to the model analysis and there are a number of data sets that were not included in the comparisons that were done.

Particle chloride can be compared to IMPROVE data (see for example Sarwar et al., 2012) to see how the model does. This is a long-term data set of considerable geographic extent.

There are observations of HCl displacement by HNO₃ in the LA Basin that need to be considered for comparison (Gard et al., 1998).

There are a number of HCl data sets that were not compared with. Here is at least a

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partial list: Kim et al., INTEX-B (Kim et al., 2008), which includes one of the co-authors. CalNex ground site data for both particle chloride and gas phase HCl can be found at: <https://www.esrl.noaa.gov/csd/projects/calnex/>.

There are a considerable number of ClNO₂ data sets that were not compared with: Osthoff et al., 2009 – this covers essentially urban/industrial Houston and the near coastal environment. Sommariva et al., 2018 (Sommariva et al., 2018) covers several sites in England, including coastal sites. Le Breton et al., 2018 (Le Breton et al., 2018) Priestley et al., 2018. (Priestley et al., 2018) Tham et al., 2016 (Tham et al., 2013) Wang, Z. et al., (Wang et al., 2017b) Wang X., et al., 2017 (Wang et al., 2017a) Riedel et al., 2013 (Riedel et al., 2013) Mielke et al., 2015 (Mielke et al., 2015) Bannan et al., 2017 (Bannan et al., 2017) Young et al., 2012 (Young et al., 2012)(data set can be found at <https://www.esrl.noaa.gov/csd/projects/calnex/>) Zhou, et al., 2018 (Zhou, 2018)

It's true that there is only one lab study of the ClNO₂ + Cl⁻ Chemistry (Roberts et al., 2008), but the authors seem to have missed a key point of that paper: that reaction seems to only occur at pH=2 and below. Unless I missed something, this paper seems to allow this reaction after the alkalinity of the aerosol is neutralized. This may account for why the Cl₂ is so high compared to the WINTER observations.

Specific Comments:

Page 10, Line 10, and Table 5. There are several data sets for which the model is a factor of 10 low, so it is hard to say the model performed “credibly”. Also, most if not all of these data sets are available, so could be compared more in depth, not just maxima.

Page 11, lines 2&3. I believe the aircraft did missed approaches over airfields that could be used to do near-surface comparisons.

Page 14, Line 22. Should be ‘troposphere’.

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