

We thank the reviewers for their time and comments. We have made efforts to improve the manuscript accordingly, please find response for corresponding points below.

Reviewer #1

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 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 Wachowsky, 1998 is not in the list Bey et al., 2001 is not in the list. Pszenny 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.

We have corrected the reference 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.

We now include model comparison to the IMPROVE data (Figure 5) and find that the marine source in the model can largely explain the observed chloride concentrations inland. We now cite Sarwar et al. (2012) for the fugitive dust source and point out that it would be small globally on page 5, line 14-17. We have added “global” to the title to emphasize that our focus is on the global scale.

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.

To respond to the reviewer, we have added comparison to the IMPROVE data with a new Figure (Figure 5).

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

Observations in the LA Basin are not particularly relevant to us because of our coarse grid resolution (4°x5°).

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

We do not include the INTEX-B measurements because Kim et al. (2008) was never published (it has remained in ACPD).

We included CalNex ship data (Crisp et al., 2014) data in Figure 4. These data are better suited for evaluating the model at the relevant resolution than the CalNex ground site.

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)

To respond to the reviewer, we have added comparisons with Osthoff et al. (2008), Sommariva et al. (2018), Priestley et al. (2018), Mielke et al. (2015), Bannan et al. (2017), Jeong et al. (2018), Kim et al. (2014), and Tham et al. (2014) in Table 5. The comparison with Riedel et al. (2013)

was already included. Young et al. (2012) report the same dataset as Mielke et al. (2013) which is already included in the paper. Beyond that, Table 5 is already very long and as we now point out in the paper there is large representation error in trying to evaluate our global model with nighttime urban data (page 10, line 14-18). We also emphasize the global emphasis of our model evaluation at the beginning of Section 4.

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 too high compared to the WINTER observations.

The reviewer did miss something. Table 2 gives $\gamma = 0$ for this reaction when $\text{pH} > 2$. But in any case, the aerosol pH reported by Guo et al. (2016) is smaller than 2 during the WINTER campaign and the same holds in GEOS-Chem. We have added more discussion in Section 4.2, page 12, line 9-15.

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.

We now point out that there is large representation error in comparing our coarse-resolution model with nighttime urban data on page 10, line 14-18. More relevant is our detailed comparison to the ClNO₂ WINTER data in Section 4.2.

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

We deleted the sentence about lack of surface layer observations. These missed-approach data are not of much value to us considering the coarse resolution of the model.

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

Corrected (typo).

Reviewer #2

This paper by Wang et al. presents an extensive modelling study of chlorine chemistry using GEOS-Chem. The updates to the GEOS-Chem chemical mechanism are much needed. I think the paper is suitable for ACP, after the authors have addressed the following points.

MAJOR COMMENTS

As a general comment, I think it would be useful to have a more detailed discussion of the difference in the results between the version of GEOS-Chem with the previous mechanism and this new version. As it stands, the reader is mostly referred to previous papers. Figure 9 provides some of this information but it is presented as a sensitivity study, so it is not really a comparison of the old and new mechanisms.

We have added a supplementary figure S1 and a paragraph to Section 5.3 (page 15, line 25-34) comparing our simulation and GEOS-Chem standard version 11-02d.

Another general point is that the choice of datasets to compare with the model seems somewhat arbitrary. I understand it is not possible to use all the available datasets, but you have to explain why you selected certain datasets and not others for this work.

We now emphasize the global emphasis of our model evaluation at the beginning of Section 4 (and have added “global” in the title). We have added comparisons to the IMPROVE Cl⁻ data in new Figure 5 and to additional ClNO₂ datasets in Table 5.

On page 8: you say that the BrCl concentration in this work is lower than in previous modelling studies and you attribute this to a change in the chemical mechanism. Please add a note here that this point is further explained in section 5.2. Also note that BrCl measurements are discussed in the papers by Lawler et al. (see below). You may want to add that to the discussion in section 4.1.

We have added a note in Section 3 (page 8, line 26) that we would further discuss the lower BrCl in Section 5.2. We have also added the BrCl measurement in Lawler et al. (2009) to the discussion in Section 4.1, page 10, line 3-8.

On page 10 there is a brief discussion about the results by Lawler et al. (2010). First of all, it is either the 2009 or 2011 paper, please check which one you are referring to or add both. Both papers (2009 and 2011) reported high concentrations of HOCl and Cl₂ when air was coming from continental Europe, not from Northern Africa as stated here. Please correct your statements. Those papers propose that high HOCl and Cl₂ may be caused by aerosol acidification during long range transport and/or slower conversion of HOCl to Cl₂ in the aqueous phase. These points are also investigated in Sommariva and von Glasow (2012),

which you may want to take into consideration. Is the high HOCl and Cl₂ still unexplained in GEOS-Chem if you take into account the findings of these papers?

We thank the reviewer for raising this point. We have revised this part on page 10, line 3-13, including:

- 1) We were referring to Lawler et al. (2011). We now also add the data in Lawler et al. (2009) to the discussion.
- 2) We have corrected the statement for the sources of high HOCl/Cl₂ concentrations.
- 3) We have cited Sommariva and von Glasow (2012) and added it to the discussion. As Sommariva and von Glasow (2012) pointed out, a lower aerosol pH and/or slower rate for HOCl + Cl⁻ may explain the high HOCl but would decrease Cl₂.

On page 11: note that the results by Roberts et al. (2008) indicate that the reaction of ClNO₂ + Cl⁻ -> Cl₂ is relevant only on very acidic aerosol. It may be that aerosol pH during the WINTER campaign was not low enough, which may explain why removing the reaction improves the agreement with the model. Can you please comment? Also, I think the reference is wrong in the bibliography.

We do consider this pH dependence and it is already listed in Table 2 ($\gamma = 0$ when pH > 2 for R7). In addition, the aerosol pH reported by Guo et al. (2016) are mostly smaller than 2 during WINTER campaign. We have added more discussion for this reaction in Section 4.2, page 12, line 9-15, and corrected the reference.

MINOR COMMENTS

Page 3: the title of 2.1 should be "GEOS"

Changed (typo).

Page 7, line 30: add space in "HCl+OH"

Added.

Page 12: is the lower Cl* in this work driven by lower BrCl, as mentioned on page 8?

The lower Cl* is driven by both the lower rate of Cl_y generation from acid displacement (as discussed in Section 3) and lower BrCl.

Table 5: there are more observations of CINO₂ available than those listed, especially in Europe and Asia. Either expand the table or explain why those were chosen. Also, it is not obvious in which order they are listed (year, season, region, concentration?).

We have added more datasets in our comparison of CINO₂ in Table 5. We also add a statement at the beginning of Section 4 to emphasize that we only include data those not heavily affected by local anthropogenic sources. The order is based on latitude (from north to south), this is now explained in the Table footnotes.

Please tidy the references list, there are many mistakes.

The references list has been corrected.

Short Comments by McDuffie

1. The authors state on page 5, line 10 that anthropogenic sources of HCl were not included in their base case GEOS-Chem simulation. Although minor in a global sense, it is worth noting that Lee et al. (2018) reported observations of direct halogen (i.e. HCl, as well as Cl₂, ClNO₂, Br₂, BrNO₂, and BrCl) emissions from power plants sampled during the WINTER aircraft campaign. This is also important to note in Section 4.2 where model results are directly compared to WINTER chlorine observations.

We now include the power plant source of HCl following Lee et al. (2018) in a sensitivity simulation. This is discussed in Section 4.2, page 11, line 10-15.

2. Page 11, line 3, the authors state that WINTER aircraft observations did not extend to the surface layer. As also noted by one Reviewer, there were a series of missed approaches at airfields that could provide further vertical information.

We deleted the sentence about lack of surface layer observations. These missed-approach data are not of much value to us considering the coarse resolution of the model.

3. On page 10, Table 5 is referred to as a list of ‘available’ field observations of ClNO₂. The GEOS-Chem simulations are then compared to these observations in Table 5 to evaluate the model performance. As noted by both Reviewers, however, there are many additional measurements of ClNO₂ that were not included in Table 5. Measurements in addition to those provided by the Reviewers are from: (Edwards et al., 2013; Jeong et al., 2018; Kim et al., 2014; Liu et al., 2017; Osthoff et al., 2008; Phillips et al., 2016; Reyes-Villegas et al., 2018; Tham et al., 2018; Tham et al., 2014; Wang et al., 2018; Wang et al., 2016; Wang et al., 2014; Wild et al., 2016; Yun et al., 2018).

Thank you for pointing out these measurement data. We have added the comparisons with Osthoff et al. (2008), Sommariva et al. (2018), Priestley et al. (2018), Mielke et al. (2015), Bannan et al. (2017), Jeong et al. (2018), Kim et al. (2014), and Tham et al. (2014) in Table 5. Phillips et al. (2016) used the exactly same dataset as Phillips et al. (2012), which was already included in the paper. Wang et al. (2016) was also already included in the paper. Yun et al. (2018) used the exactly same dataset as Wang et al. (2016). There is no measurement of ClNO₂ concentration presented in Wang et al. (2014).

As pointed out in response to Reviewer 1 and in the revised text on page 10, line 14-18, comparison to nighttime urban ClNO₂ data is of limited interest for model evaluation because of the resolution mismatch. We also emphasize the global emphasis of our model evaluation at the beginning of Section 4.

4. The authors include the HOBr + Cl⁻ → BrCl reaction in their mechanism following Abbatt and Waschewsky (1998) and Fickert et al. (1999). They state in the discussion section on page 7 that the Cl source from this reaction is much higher than past simulations. Later in section 5.2, they also include discussion of previous work by Chen et al. (2017) who included a second HOBr + Cl⁻ → Br₂ pathway that is dependent on the molar ratio of [Br⁻]/[Cl⁻], following Fickert et al. (1999). It is unclear in section 5.2 whether this additional pathway was included in the base case simulation here. If not, the authors should clearly state why it was excluded since the Fickert et al. (1999) laboratory work showed 90% Br₂ formation from this reaction at ratios of [Br⁻]/[Cl⁻] typically found in ambient sea water. If included, this reaction would help reduce this Cl production pathway relative to previous simulations.

We have clarified on page 14, line 8 that we include this mechanism in our model simulation. We have also mentioned this mechanism follows Fickert et al. (1999) and would be further described in section 5.2 in the footnote of Table 2.

5. The authors have also included the direct reaction of ClNO₂ with Cl⁻ to form Cl₂ (there is also mention of ClNO₂+Br⁻ on page 14, which should be added to Table 2. This reaction is thought to occur via heterogeneous uptake of gas-phase ClNO₂ and further reaction with aqueous Cl⁻ (or Br⁻). As noted by one Reviewer, however, it has been shown by Roberts et al. (2008) that this reaction only occurs at pH < 2 and should be limited here to only highly acidic aerosol. That said, the aerosol during WINTER were highly acidic (pH = -3 to 2) (Guo et al., 2016), which should activate this pathway. Even on these highly acidic aerosol, however, a recent study of WINTER ClNO₂ yields by McDuffie et al. (2018a) reported that there was a negative correlation between particle acidity and CIMS observations of Cl₂, which is opposite the trend expected from this reaction. In addition, there was no clear evidence in that study that gas-phase ClNO₂ was being lost to heterogeneous processes (reaction with Cl or Br⁻). Since there is limited field data to support the presence of direct ClNO₂ reactions in ambient aerosol, particularly during WINTER, the authors should consider eliminating direct ClNO₂ reactions or provide further evidence to support their inclusion in this work.

Thank you for raising these points. We have added ClNO₂ + Br⁻ as R8 in Table 2.

We do consider the pH dependence of ClNO₂ + Cl⁻ and it is already listed in Table 2 ($\gamma = 0$ when pH > 2 for R7). We also add more discussion in this section on page 12, line 9-15 citing McDuffie et al. (2018).

6. The heterogeneous yield of ClNO₂ is only mentioned in reaction R3 in Table 2, where it is defined using a laboratory-based parameterization from Bertram and Thornton (2009). This parameterization is used to predict both N₂O₅ uptake coefficient and ClNO₂ yield. It is concerning that there is no discussion in this manuscript of the large uncertainties associated with these processes or parameterizations. First, this particular parameterization for N₂O₅ uptake does not consistently reproduce field-derived observations (e.g., Bertram et al., 2009;

McDuffie et al., 2018b; Wagner et al., 2013) and has been adjusted in recent GEOS-Chem simulations (Jaeglé et al., 2018; Shah et al., 2018) to better match nitrate observations during WINTER. While N₂O₅ is not the topic of this manuscript, this process directly impacts the net production of ClNO₂, thus impacting the chlorine chemical mechanism and budget. The authors should therefore consider updating the N₂O₅ uptake parameterization in their simulations or discuss this as a source of uncertainty in their results. Second, this particular parameterization has over-predicted the ClNO₂ production yield in every study that has compared its predictions to field-derived results (McDuffie et al., 2018a; Riedel et al., 2013; Ryder et al., 2015; Tham et al., 2018; Thornton et al., 2010; Wagner et al., 2013; Wang, Z. et al., 2017; Wang, X. et al., 2017). In addition, McDuffie et al. (2018a) recently found that the median WINTER ClNO₂ production yield was over-predicted by at least 74% by the Bertram and Thornton (2009) parameterization. Since there are no field studies that support this parameterization as written in R3, the authors should adjust this reaction accordingly and discuss its uncertainties.

Jaeglé et al. (2018) and Shah et al. (2018) actually used the Bertram and Thornton (2009) scheme with no adjustment. Both papers updated the N₂O₅ uptake from old GEOS-Chem versions to the exactly same scheme as in our paper and found better match to the nitrate observations during WINTER. A major reason for the difference with McDuffie et al. is likely that GEOS-Chem treats reactive uptake by aerosols assuming an external mixture.

We have added more discussion for the N₂O₅ uptake parametrization and give our tentative explanation for the difference with McDuffie et al. on page 11 line 29 – page 12 line 4.

The role of chlorine in global tropospheric chemistry

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Abstract. We present a comprehensive simulation of tropospheric chlorine within the GEOS-Chem global 3-D model of oxidant-aerosol-halogen atmospheric chemistry. The simulation includes explicit accounting of chloride mobilization from sea-salt aerosol by acid displacement of HCl and by other heterogeneous processes. Additional small sources of tropospheric chlorine (combustion, organochlorines, transport from stratosphere) are also included. Reactive gas-phase chlorine Cl*, including Cl, ClO, Cl₂, BrCl, ICl, HOCl, ClNO₃, ClNO₂, and minor species, is produced by the HCl + OH reaction and by heterogeneous conversion of sea-salt aerosol chloride to BrCl, ClNO₂, Cl₂, and ICl. The model simulates successfully the observed mixing ratios of HCl in marine air (highest at northern mid-latitudes) and the associated HNO₃ decrease from acid displacement. It captures the high ClNO₂ mixing ratios observed in continental surface air at night, and attributes the chlorine to HCl volatilized from sea salt aerosol and transported inland following uptake by fine aerosol. The model simulates successfully the vertical profiles of HCl measured from aircraft, where enhancements in the continental boundary layer can again be largely explained by transport inland of the marine source. It does not reproduce the boundary layer Cl₂ mixing ratios measured in the WINTER aircraft campaign (1-5 ppt in the daytime, low at night); the model is too high at night, which could be due to uncertainty in the rate of the ClNO₂ + Cl⁻ reaction, but we have no explanation for the high observed Cl₂ in daytime. The global mean tropospheric concentration of Cl atoms in the model is 620 cm⁻³ and contributes 1.0% of the global oxidation of methane, 20% of ethane, 14% of propane, and 4% of methanol. Chlorine chemistry increases global mean tropospheric BrO by 85%, mainly through the HOBr + Cl⁻ reaction, and decreases global burdens of tropospheric ozone by 7% and OH by 3% through the associated bromine radical chemistry. ClNO₂ chemistry drives increases in ozone of up to 8 ppb over polluted continents in winter.

1 **1 Introduction**

2 Mobilization of chloride (Cl^-) from sea salt aerosol (SSA) is a large source of chlorine gases to the troposphere
3 (Graedel and Keene, 1995; Finlayson-Pitts, 2003). These gases may generate chlorine radicals with a broad range of
4 implications for tropospheric chemistry including the budgets of ozone, OH (the main tropospheric oxidant), volatile
5 organic compounds (VOCs), nitrogen oxides, other halogens, and mercury (Saiz-Lopez and von Glasow, 2012;
6 Simpson et al., 2015). Only a few global models have attempted to examine the implications of tropospheric chlorine
7 chemistry on a global scale (Singh and Kasting, 1988; Long et al., 2014; Hossaini et al., 2016) and then only with a
8 limited representation of processes. Here we present a more comprehensive analysis of this chemistry within the
9 framework of the GEOS-Chem chemical transport model (CTM).

10 Saiz-Lopez and von Glasow (2012) and Simpson et al. (2015) present recent reviews of tropospheric halogen
11 chemistry including chlorine. Sea-salt aerosols represent a large chloride flux to the atmosphere but most of that
12 chloride is removed rapidly by deposition. Only a small fraction is mobilized to the gas phase as HCl or other species.
13 Additional minor sources of tropospheric chlorine include open fires, coal combustion, waste incineration, industry,
14 road salt application, fugitive dust, and ocean emission of organochlorine compounds (Lobert et al., 1999; McCulloch
15 et al., 1999; Sarwar et al., 2012; WMO, 2014; Kolesar et al., 2018). It is useful to define Cl_y as total gas-phase inorganic
16 chlorine, excluding particle phase Cl^- . Most of this Cl_y is present as HCl, which is removed rapidly by deposition but
17 also serves as a source of chlorine radicals. Rapid cycling takes place between the chlorine radicals and other chlorine
18 gases, eventually returning HCl. Thus it is useful to define reactive chlorine Cl^* as the ensemble of Cl_y gases other
19 than HCl.

20 Cycling of chlorine affects tropospheric chemistry in a number of ways (Finlayson-Pitts, 2003; Saiz-Lopez and von
21 Glasow, 2012). Acid displacement of Cl^- by nitric acid (HNO_3) is a source of NO_3^- aerosol (Massucci et al., 1999). Cl
22 atoms provide a sink for methane, other volatile organic compounds (VOCs) (Atkinson, 1997), dimethyl sulfide (DMS)
23 (Hoffmann et al., 2016; Chen et al., 2017), and mercury (Horowitz et al., 2017). Cycling between Cl radicals and their
24 reservoirs drives catalytic ozone loss, and converts nitrogen oxide radicals ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$) to HNO_3 , decreasing
25 both ozone and OH. On the other hand, aqueous-phase reaction of Cl^- with N_2O_5 in polluted environments produces
26 ClNO_2 radicals that photolyze in the daytime to return Cl atoms and NO_2 , stimulating ozone production (Behnke et
27 al., 1997; Osthoff et al., 2008). Chlorine also interacts with other halogens (bromine, iodine), initiating further radical
28 chemistry that affects ozone, OH, and mercury.

29 A number of global modeling studies have investigated tropospheric halogen chemistry but most have focused on
30 bromine and iodine, which are more active than chlorine because of the lower chemical stability of HBr and HI
31 (Parrella et al., 2012; Sherwen et al., 2016a). Interest in global modeling of tropospheric chlorine has focused
32 principally on quantifying the Cl atom concentration as a sink for methane (Keene et al., 1990; Singh et al., 1996).
33 Previous global 3-D models found mean tropospheric Cl atom concentrations of the order of 10^3 cm^{-3} , with values up
34 to 10^4 cm^{-3} in the marine boundary layer (MBL), and contributing 2-3% of atmospheric methane oxidation (Long et
35 al., 2014; Hossaini et al., 2016; Sherwen et al., 2016b; Schmidt et al., 2016). A regional modeling study by Sarwar et

1 al. (2014) included ClNO₂ chemistry in a standard ozone mechanism and found increases in surface ozone mixing
2 ratios over the US of up to 7 ppb (ppb ≡ nmol mol⁻¹).

3 Here we present a more comprehensive analysis of global tropospheric chlorine chemistry and its implications,
4 building on previous model development of oxidant-aerosol-halogen chemistry in GEOS-Chem. A first capability for
5 modeling tropospheric bromine in GEOS-Chem was introduced by Parrella et al. (2012). Eastham et al. (2014)
6 extended it to describe stratospheric halogen chemistry including chlorine and bromine cycles. Schmidt et al. (2016)
7 updated the tropospheric bromine simulation to include a broader suite of heterogeneous processes, and extended the
8 Eastham et al. (2014) stratospheric chlorine scheme to the troposphere. Sherwen et al. (2016a;b) added iodine
9 chemistry and made further updates to achieve a consistent representation of tropospheric chlorine-bromine-iodine
10 chemistry in GEOS-Chem. Chen et al. (2017) added the aqueous-phase oxidation of SO₂ by HOBr and found a large
11 effect on the MBL bromine budget. Our work advances the treatment of tropospheric chlorine in GEOS-Chem to
12 include in particular a consistent treatment of SSA chloride and chlorine gases, SSA acid displacement
13 thermodynamics, improved representation of heterogeneous chemistry, and better accounting of chlorine sources. We
14 evaluate the model with a range of global observations for chlorine and related species. From there we quantify the
15 global tropospheric chlorine budgets, describe the principal chemical pathways, and explore the impacts on
16 tropospheric chemistry.

17 **2 Model description**

18 **2.1 GEOS-Chem model with Cl+Br+I halogen chemistry**

19 We build our new tropospheric chlorine simulation capability onto the standard version 11-02d of GEOS-Chem
20 (<http://www.geos-chem.org>). The standard version includes a detailed tropospheric oxidant-aerosol-halogen
21 mechanism as described by Sherwen et al. (2016b) and Chen et al. (2017). It includes 12 gas phase Cl_y species: Cl,
22 Cl₂, Cl₂O₂, ClNO₂, ClNO₃, ClO, ClOO, OCIO, BrCl, ICl, HOCl, and HCl. It allows for heterogeneous chemistry
23 initiated by SSA Cl⁻ but does not actually track the SSA Cl⁻ concentration and its exchange with gas-phase Cl_y. Here
24 we add two new transported reactive species to GEOS-Chem to describe Cl⁻ aerosol, one for the fine mode (< 1 μm
25 diameter) and one for the coarse mode (> 1 μm diameter). The standard GEOS-Chem wet deposition schemes for
26 water-soluble aerosols (Liu et al., 2001) and gases (Amos et al., 2012) are applied to Cl⁻ aerosol and Cl_y gases
27 respectively, the latter with Henry's law constants from Sander (2015). Dry deposition of Cl⁻ aerosol follows that of
28 SSA (Jaeglé et al., 2011), and dry deposition of Cl_y gases follows the resistance-in-series scheme of Wesely (1989) as
29 implemented in GEOS-Chem by Wang et al. (1998). We also add to the model two SSA alkalinity tracers in the fine
30 and coarse modes, and retain the inert SSA tracer to derive local concentrations of non-volatile SSA cations (Section
31 2.3). SSA debromination by oxidation of Br⁻ as described by Schmidt et al. (2016) was included only as an option in
32 standard version 11-02d of GEOS-Chem because of concern over excessive MBL BrO (Sherwen et al., 2016b).
33 However, Zhu et al. (2018) show that it allows in fact a successful simulation of MBL BrO when one accounts for
34 new losses in the standard model from aqueous-phase oxidation of SO₂ by HOBr (Chen et al., 2017) and oxidation of
35 marine acetaldehyde by Br atoms (Millet et al., 2010). We include SSA debromination in this work.

1 We present a 1-year global simulation for 2016 driven by GEOS-FP (forward processing) assimilated meteorological
2 fields from the NASA Global Modeling and Assimilation office (GMAO) with native horizontal resolution of 0.25°
3 $\times 0.3125^\circ$ and 72 vertical levels from the surface to the mesosphere. Our simulation is conducted at $4^\circ \times 5^\circ$ horizontal
4 resolution and meteorological fields are conservatively regridded for that purpose. Stratospheric chemistry is
5 represented using 3-D monthly mean production rates and loss rate constants from a fully coupled stratosphere-
6 troposphere GEOS-Chem simulation (Murray et al., 2012; Eastham et al., 2014).

7 **2.2 Sources of chlorine**

8 Table 1 lists the global sources and sinks of tropospheric gas-phase inorganic chlorine (Cl_y) and reactive chlorine (Cl^*)
9 in our model. The main source is mobilization of Cl^- from SSA. SSA emission is computed locally in GEOS-Chem
10 separately for fine and coarse as the integrals of the size-dependent source function over two size bins, fine ($0.2\text{-}1\ \mu\text{m}$
11 diameter) and coarse ($1\text{-}8\ \mu\text{m}$ diameter). The source function depends on wind speed and sea surface temperature
12 (Jaeglé et al., 2011). We obtain a global SSA source of $3230\ \text{Tg}\ \text{a}^{-1}$ for 2016, corresponding to $1780\ \text{Tg}\ \text{a}^{-1}\ \text{Cl}^-$
13 (assuming fresh SSA to be 55.05% Cl^- by mass (Lewis and Schwartz, 2013), of which 16% is in the fine mode and
14 84% is in the coarse mode. Only $64\ \text{Tg}\ \text{Cl}^- \text{a}^{-1}$ (3.6%) is mobilized to Cl_y by acid displacement and other heterogeneous
15 reactions, while the rest is deposited. 42% of the mobilization is from fine SSA and 58% is from coarse SSA. Details
16 of this mobilization are in Sections 2.3 and 2.4. 80% of the mobilization is by acid displacement to HCl, which is in
17 turn efficiently deposited. Only 19% of HCl is further mobilized to Cl^* by reaction with OH to drive chlorine radical
18 chemistry. Direct generation of Cl^* from SSA through heterogeneous chemistry provides a Cl^* source of comparable
19 magnitude to $\text{HCl} + \text{OH}$, with dominant contributions from $\text{HOBr} + \text{Cl}^-$ and $\text{N}_2\text{O}_5 + \text{Cl}^-$ (the latter in polluted high-
20 NO_x environments).

21 Cl^* can also be produced in the model by atmospheric degradation of the organochlorine gases CH_3Cl , CH_2Cl_2 , CHCl_3 ,
22 and CH_2ICl . These gases are mainly of biogenic marine origin, with the exception of CH_2Cl_2 which has a large
23 industrial solvent source (Simmonds et al., 2006). Mean tropospheric lifetimes are 520 days for CH_3Cl , 280 days for
24 CH_2Cl_2 , 260 days for CHCl_3 , and 0.4 days for CH_2ICl . Emissions of CH_3Cl , CH_2Cl_2 , and CHCl_3 are implicitly treated
25 in the model by specifying monthly mean surface air boundary conditions in 5 latitude bands ($60\text{-}90^\circ\text{N}$, $30\text{-}60^\circ\text{N}$, 0-
26 30°N , $0\text{-}30^\circ\text{S}$, and $30\text{-}90^\circ\text{S}$) from AGAGE observations (Prinn et al., 2018). Emission of CH_2ICl is from Ordóñez et
27 al. (2012), as described by Sherwen et al. (2016a). Tropospheric oxidation of hydrochlorofluorocarbons (HCFCs) is
28 neglected as a source of Cl^* because it is small compared to the other organochlorines. The stratospheric source of
29 Cl_y from chlorofluorocarbons (CFCs), HCFCs, and CCl_4 is included in the model on the basis of the Eastham et al.
30 (2014) GEOS-Chem stratospheric simulation as described in Section 2.1. Tropospheric organochlorines give a global
31 Cl^* source of $3.3\ \text{Tg}\ \text{Cl}\ \text{a}^{-1}$ in Table 1, smaller than that from heterogeneous SSA Cl^- reactions ($11.9\ \text{Tg}\ \text{Cl}\ \text{a}^{-1}$) or
32 oxidation of HCl by OH ($9.7\ \text{Tg}\ \text{Cl}\ \text{a}^{-1}$). The stratosphere is a minor global source of tropospheric Cl^* ($0.06\ \text{Tg}\ \text{Cl}\ \text{a}^{-1}$)
33 although it could be important in the upper troposphere (Schmidt et al., 2016).

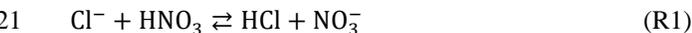
1 We also include primary HCl emissions from open fires. We apply the emission factors of (HCl + Cl⁻) from Lobert et
2 al. (1999) for different vegetation types to the GFED4 (Global Fire Emissions Database) biomass burned inventory
3 (van der Werf et al., 2010; Giglio et al., 2013), resulting in a global source of 7.6 Tg Cl a⁻¹ emitted as HCl.

4 Anthropogenic sources of HCl include coal combustion, waste incineration, and industrial activities. The only global
5 emission inventory is that of McCulloch et al. (1999), which gives a total of 6.7 Tg Cl a⁻¹. As shown in Section 4.2,
6 we find that this greatly overestimates atmospheric observations of HCl over the US. National inventories of HCl from
7 coal combustion available for China (236 Gg Cl a⁻¹ in 2012; (Liu et al., 2018)) and the US (69 Gg Cl a⁻¹ in 2014; (US
8 EPA, 2018)) are respectively six and seven times lower than McCulloch et al. (1999) for those countries. We choose
9 therefore not to include anthropogenic HCl emissions in our standard simulation, as they are small in any case from a
10 global budget perspective. We show in Section 4.2 that we can account for HCl observations in continental air largely
11 on the basis of the SSA Cl⁻ source. We also do not consider Cl* generation from snow/ice surfaces which could be
12 important in the Arctic spring MBL (Liao et al., 2014) but is highly uncertain and would only affect a small
13 atmospheric domain.

14 We do not include the anthropogenic Cl⁻ source from fugitive dust, although it might be important in contributing to
15 chloride levels in continental surface air (Sarwar et al., 2012). The global source of anthropogenic fugitive dust is
16 estimated to be less than 13 Tg a⁻¹ (Philip et al., 2017), of which 0.3% by mass is estimated to be chloride (Reff et al.,
17 2009). This corresponds to a chloride source of less than 0.39 Tg Cl a⁻¹, negligible on a global scale.

18 2.3 HCl/Cl⁻ acid displacement thermodynamics

19 SSA Cl⁻ can be displaced to HCl by strong acids (H₂SO₄, HNO₃) once the SSA is sufficiently aged that its initial
20 supply of alkalinity ($\equiv \text{HCO}_3^- + 2 \times \text{CO}_3^{2-}$) has been exhausted. The acid displacement is described by



23 with equilibrium constants from Fountoukis and Nenes, (2007). (R1) must be treated as an equilibrium because HNO₃
24 and HCl have comparable effective Henry's law constants. H₂SO₄ has a much lower vapor pressure so that (R2) fully
25 displaces HCl. Additional displacement of HCl by HSO₄⁻ does not take place because HSO₄⁻ is a much weaker acid
26 than HCl (Jacob et al., 1985).

27 Alkalinity initially prevents any acid displacement in freshly emitted SSA. Alkalinity is emitted as 0.07 mole
28 equivalents per kg of dry SSA (Gurciullo et al., 1999), and is transported in the model as two separate tracers for fine
29 and coarse SSA. It is consumed over time by uptake of acids (SO₂, H₂SO₄, HNO₃, and HCl) as described by Alexander
30 et al. (2005), and once fully consumed it is set to zero (titration). The SSA is then diagnosed as acidified, enabling
31 acid displacement by (R1)-(R2). In our simulation, alkalinity is titrated everywhere shortly after emission except in
32 some areas of the Southern Ocean, which is consistent with the model results of Alexander et al. (2005) and Kasibhatla
33 et al. (2018).

1 Observations in the MBL indicate that fine SSA is usually internally mixed with sulfate-nitrate-ammonium (SNA)
2 aerosols while coarse SSA is externally mixed (Fridlind and Jacobson, 2000; Dasgupta et al., 2007). Acid displacement
3 for the acidified fine SSA is thus computed by adding HCl/Cl⁻ to the SNA thermodynamics. The local thermodynamic
4 gas-aerosol equilibrium for the resulting H₂SO₄-HCl-HNO₃-NH₃-NVC system is calculated with ISORROPIA II
5 (Fountoukis and Nenes, 2007). The calculation is done assuming an aqueous aerosol even if relative humidity is below
6 the deliquescence point (metastable state). NVC (non-volatile cations) describes the sum of cations emitted as SSA
7 and is treated in ISORROPIA II using Na⁺ as proxy. Here NVC is emitted as 16.4 moles equivalent per kg of dry SSA
8 to balance the emission of SSA anions including Cl⁻, alkalinity, and sea-salt sulfate. The NVC concentration is
9 determined locally from the mass concentration of the inert SSA tracer.

10 Acid displacement for acidified coarse SSA is assumed to be driven by uptake of strong acids from the gas phase,
11 mainly HNO₃ (Kasibhatla et al., 2018). The ISORROPIA II calculation is conducted with 2 gas species (HNO₃ and
12 HCl) and 4 aerosol species (NVC, Cl⁻, SO₄²⁻, and NO₃⁻). Here the sulfate includes only the emitted sea-salt component
13 and that produced by heterogeneous SO₂ oxidation in coarse SSA (Alexander et al., 2005). In the case of coarse
14 aerosols, there may be significant mass transfer limitation to reaching gas-aerosol thermodynamic partitioning (Meng
15 and Seinfeld, 1996). To account for this limitation, the concentrations are adjusted after the ISORROPIA II calculation
16 following the dynamic method of Pilinis et al. (2000). This 2-step thermodynamics approach has been used in previous
17 studies (Koo et al., 2003; Kelly et al., 2010).

18 **2.4 Heterogeneous chemistry of Cl⁻**

19 Table 2 lists the heterogeneous reactions of Cl⁻ other than acid displacement. The loss rate of a gas species X due to
20 reaction with Cl⁻ is calculated following Jacob (2000):

$$21 \quad \frac{dn_X}{dt} = - \left(\frac{r}{D_g} + \frac{4}{c\gamma([\text{Cl}^-])} \right)^{-1} A n_X \quad (1)$$

22 Here n_X is the number density of species X (molecules of X per unit volume of air), A is the aerosol or cloud surface
23 area concentration per unit volume of air, r is the effective particle radius, D_g is the gas-phase molecular diffusion
24 coefficient of X, c is the average gas-phase thermal velocity of X, and γ is the reactive uptake coefficient which is a
25 function of the aqueous-phase molar Cl⁻ concentration [Cl⁻] (moles of Cl⁻ per liter of water). Values of γ in Table 2
26 are mostly from recommendations by the International Union of Pure and Applied Chemistry (IUPAC) (Ammann et
27 al., 2013).

28 The heterogeneous reactions take place in both clear-air aerosol and clouds. The GEOS-FP input meteorological data
29 include cloud fraction and liquid/ice water content for every grid cell. Concentrations per cm³ of air of aerosol-phase
30 species (including fine and coarse Cl⁻ and Br⁻) within a grid cell are partitioned between clear air and cloud as
31 determined by the cloud fraction. Clear-air aqueous-phase concentrations for use in calculating heterogeneous
32 reaction rates are derived from the RH-dependent liquid water contents of fine and coarse SSA using aerosol
33 hygroscopic growth factors from the Global Aerosol Database (GADS, (Koepke, 1997)) with update by Lewis and

1 Schwartz (2006). In-cloud aqueous-phase concentrations are derived using liquid and ice water content from the
2 GEOS-FP meteorological data. Values of r in equation (1) are specified as RH-dependent effective radii for the
3 different clear-air aerosol components (Martin et al., 2003), and are set to 10 μm for cloud droplets and 75 μm for ice
4 particles. These effective radii are also used to infer the area concentrations A on the basis of the mass concentrations.
5 Heterogeneous chemistry in ice clouds is restricted to the unfrozen layer coating the ice crystal, which is assumed to
6 be 1% of the ice crystal radius (Schmidt et al., 2016).

7 The reactions of HOBr, HOCl, and ClNO₂ with Cl⁻ in Table 2 are pH-dependent and require acidic conditions (Fickert
8 et al., 1999; Abbatt et al., 2012). They are considered only when SSA alkalinity has been titrated, and ClNO₂ + Cl⁻
9 further requires pH < 2. The pH of chloride-containing fine aerosol after alkalinity has been titrated is calculated by
10 ISORROPIA II. Liquid cloud water pH is calculated in GEOS-Chem following Alexander et al. (2012), with update
11 to include Cl⁻ and NVC. Coarse-mode SSA and ice cloud pH are assumed to be 5 and 4.5 respectively (Schmidt et al.,
12 2016).

13 3 Global budget and distribution of tropospheric chlorine

14 Figure 1 describes the global budget and cycling of tropospheric inorganic chlorine in GEOS-Chem. The dominant
15 source of Cl_y is acid displacement from SSA. The global rate of Cl_y generation from acid displacement is 52 Tg Cl a⁻¹
16 ¹, close to the observationally based estimate of 50 Tg Cl a⁻¹ by Graedel and Keene (1995), and lower than the model
17 estimate of 90 Tg Cl a⁻¹ from Hossaini et al. (2016), who treated displacement of Cl⁻ by HNO₃ as an irreversible rather
18 than thermodynamic equilibrium process. HCl is the largest reservoir of Cl_y in the troposphere, with a global mean
19 tropospheric mixing ratio of 60 ppt (ppt ≡ pmol/mol).

20 Acid displacement generates Cl_y as HCl, which is mostly removed by deposition. Broader effects of chlorine on
21 tropospheric chemistry take place through the cycling of radicals originating from production of reactive chlorine Cl*
22 ≡ Cl_y – HCl. HCl contributes 9.7 Tg Cl a⁻¹ to Cl* through the reaction between HCl and OH. Beside this source, Cl⁻
23 provides a Cl* source of 12 Tg Cl a⁻¹ through heterogeneous reactions with principal contributions from HOBr + Cl⁻
24 (8.6 Tg Cl a⁻¹) and N₂O₅ + Cl⁻ (1.8 Tg Cl a⁻¹). This heterogeneous source of 12 Tg Cl a⁻¹ is much higher than previous
25 estimates of 5.6 Tg Cl a⁻¹ (Hossaini et al., 2016) and 6.1 Tg Cl a⁻¹ (Schmidt et al., 2016). Schmidt et al. (2016) only
26 considered the HOBr + Cl⁻ reaction. Production of the chlorine radicals Cl and ClO is contributed by the HCl + OH
27 reaction (45%) and by photolysis of BrCl (40%), ClNO₂ (8%), Cl₂ (4%), and ICl (2%). Loss of Cl* is mainly through
28 the reaction of Cl with methane (46%) and other organic compounds (CH₃OH 15%, CH₃OOH 11%, C₂H₆ 8%, higher
29 alkanes 8%, and CH₂O 7%).

30 Conversion of Cl to ClO* drives some cycling of chlorine radicals, but the associated chain length versus Cl* loss is
31 short ($4.1 \times 10^4 / 2.5 \times 10^4 = 1.6$). Conversion of Cl to ClO is mainly by reaction with ozone (98%), while conversion of
32 ClO back to Cl is mostly by reaction with NO (72%), driving a null cycle as NO₂ photolyzes to regenerate NO and
33 ozone.

1 Figure 2 shows the annual mean global distributions of HCl mixing ratios and Cl atom concentrations. The mixing
2 ratio of HCl decreases from the surface to the middle troposphere, reflecting the SSA source, and then increases again
3 in the upper troposphere where it is supplied by transport from the stratosphere and has a long lifetime due to lack of
4 scavenging. Remarkably, Cl atom number densities show little decrease with altitude, contrary to the common
5 assumption that tropospheric Cl atoms should be mainly confined to the MBL where the SSA source resides (Singh
6 et al., 1996). We find that the effect of the SSA source is offset by the slower sink of Cl* at higher altitudes due to the
7 strong temperature dependence of the reactions between Cl atom and organic compounds. Transport of HCl and Cl*
8 from the stratosphere also contribute to the source of Cl atoms in the upper troposphere.

9 HCl mixing ratios in marine surface air are usually highest along polluted coastlines where the large sources of HNO₃
10 and H₂SO₄ from anthropogenic NO_x and SO₂ emissions drive acid displacement from SSA. By contrast, HCl mixing
11 ratios over the Southern Ocean are low because of the low supply of acid gases. The distribution of Cl atoms in surface
12 air reflects its sources from both HCl + OH and the heterogeneous production of Cl*. The highest concentrations are
13 in northern Europe due to production of ClNO₂ from the N₂O₅ + Cl⁻ reaction (R3). Cl atom concentrations in marine
14 air are shifted poleward relative to HCl because of increasing bromine radical concentrations (Parrella et al., 2012),
15 driving BrCl formation by the HOBr + Cl⁻ reaction (R5).

16 Figure 3 shows the global mean vertical distributions of reactive chlorine species (Cl*) in continental and marine air.
17 Mean boundary layer mixing ratios are higher over land than over the ocean because of the ClNO₂ source from N₂O₅
18 + Cl⁻ in high-NO_x polluted air (Thornton et al., 2010). ClNO₂ mixing ratios are much higher than in the Sherwen et al.
19 (2016b) model which restricted its production to SSA, reflecting the importance of HCl dissolved in SNA aerosol
20 which allows further transport inland. High mixing ratios of ClNO₃ in the upper troposphere are due to transport from
21 the stratosphere and inefficacy of the sinks from hydrolysis and heterogeneous chemistry. In the marine MBL we find
22 comparable contributions from HOCl (mainly in daytime) and Cl₂ and ClNO₂ (mainly at night). The BrCl mixing ratio
23 is much lower than in the previous model studies of Long et al. (2014) and Sherwen et al. (2016b) which had very
24 large sources from the HOBr + Cl⁻ reaction (R5). Our lower BrCl mixing ratio is due to competition from the HOBr +
25 S(IV) reaction (Chen et al., 2017) and to oceanic VOC emissions (Millet et al., 2010), both of which act to depress
26 bromine radical concentrations in the MBL (Zhu et al., 2018). Further discussion of the BrCl source is presented in
27 Section 5.2.

28 **4 Comparison to observations**

29 Here we compare the model simulation for 2016 to observations for gas-phase chlorine and related species collected
30 in different years, assuming interannual variability to be a minor factor in model error. Previous evaluation of the
31 GEOS-Chem sea salt source by Jaeglé et al. (2011) showed general skill in simulating SSA observations and we do
32 not repeat this evaluation here. We also do not consider data affected by local anthropogenic sources because they
33 would not be properly resolved at the 4°×5° grid resolution of our model.

1 4.1 Surface air observations

2 Table 3 compares our simulated Cl⁻ SSA deficits to an ensemble of marine air observations compiled by Graedel and
3 Keene (1995). The Cl⁻ deficit is relative to seawater composition and provides an indicator of the mobilization of Cl⁻
4 through acid displacement and heterogeneous chemistry. The observations show a wide range from -50% to +90%,
5 and Graedel and Keene (1995) emphasize that uncertainties are large. Slight negative deficits in the observations could
6 be caused by titration of alkalinity by HCl but large negative deficits are likely due to error. Mean model deficits
7 sampled for the regions and months of the observations range from +4% to +40%, not inconsistent with the
8 observations. The largest model deficits are in polluted coastal regions because of acid displacement and this is also
9 where the measured deficits are largest.

10 Figure 4 compares simulated HCl and HNO₃ mixing ratios to concurrent observations of both gases at coastal sites
11 and over oceans. The data are arranged from left to right by increasing latitude. Mean HCl mixing ratios average 323
12 ppt in the model and 347 ppt in the observations for the ensemble of regions. The HCl source in the model is mainly
13 acid displacement from SSA. A sensitivity simulation without acid displacement from SSA has less than 7 ppt HCl
14 in all regions. The model captures the spatial variability of the mean HCl mixing ratios across locations ($r = 0.88$),
15 which largely reflects the HCl enhancement at polluted coastal sites and northern mid-latitudes (Figure 2). Simulated
16 HNO₃ mixing ratios average 190 ppt across locations as compared to 137 ppt in the observations, again with good
17 simulation of spatial variability ($r = 0.96$) driven by NO_x emissions. HNO₃ mixing ratios are sensitive to acid
18 displacement from SSA, as the sensitivity simulation without acid displacement shows mean values of 441 ppt that
19 are much higher than observed. This could partly explain the general model problem of overestimating HNO₃ in
20 remote air (Bey et al., 2001).

21 Figure 5 shows 2016 annual mean observations of PM_{2.5} Cl⁻ (mass concentration in particles less than 2.5 μm diameter)
22 from the US Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Malm et al., 1994).
23 Corresponding model values are shown as background contours for fine Cl⁻ (< 1 μm diameter and internally mixed
24 with SNA aerosol) are for total Cl⁻. One would expect the IMPROVE concentrations to be higher than the model fine
25 Cl⁻ (because of the larger size cut) and lower than total Cl⁻, and this is generally the case. . The model is consistent
26 with observations in the continental interior, which we attribute to inland transport of marine HCl incorporated into
27 SNA aerosol. Fine Cl⁻ concentrations can actually be higher over the continent than over the ocean because of HCl
28 displacement from the coarse SSA followed by re-condensation on anthropogenic SNA aerosol. The model
29 underestimates the observations over the Southwest US and this may be due to a missing dust source. We find
30 IMPROVE Cl⁻ and dust concentrations are moderately to highly correlated ($R = 0.3-0.9$) at the sites in this region.

31 A number of surface air measurements have been made of Cl* as the water-soluble component of Cl_y after removal of
32 HCl (Keene et al., 1990), although most of these measurements are below the detection limit (Table 4, mostly from
33 Keene et al. (2009)). This Cl* has been commonly assumed to represent the sum of Cl₂ and HOCl (Pszenny et al.,
34 1993) but it would also include ClNO₂, ClNO₃, and minor components of Cl*. Table 4 shows that simulated Cl* mixing

1 ratios are consistent with the measurements to the extent that comparison is possible. Simulated Cl* over remote
2 oceans is dominated by HOCl, but ClNO₂ is responsible for the high values over the Atlantic Ocean near Europe.

3 Lawler et al. (2009) measured Cl₂ and BrCl mixing ratios at Cape Verde in the tropical Atlantic for 5 days in May-
4 June 2007, and Lawler et al. (2011) measured Cl₂ and HOCl mixing ratios at the same site for 7 days in May-June
5 2009. The observations show a diurnal cycle with mixing ratios of Cl₂ highest at night, and HOCl highest in the day,
6 consistent with the model. Observed mixing ratios in background marine air were in the range 0-30 ppt for Cl₂ and 0-
7 2 ppt for BrCl at night, and 0-5 ppt for HOCl in the daytime. Corresponding mean model values are 0.3 ppt for Cl₂,
8 1.8 ppt for BrCl, and 5 ppt for HOCl, with little day-to-day variability. Lawler et al. (2011) also sampled long-range
9 outflow from Europe for 3 days in 2009 with daytime HOCl and nighttime Cl₂ mixing ratio ranges of 40-200 ppt and
10 5-40 ppt respectively but the model does not capture these enhancements. Sommariva and von Glasow (2012)
11 suggested that a lower aerosol pH and/or slower rate for HOCl + Cl⁻ could explain the high HOCl in European outflow
12 but this would also cause Cl₂ to be lower. We have no explanation for the high Cl₂ values observed by Lawler et al.
13 (2009; 2011) in marine air or for the joint observed enhancements of HOCl and Cl₂ in European outflow.

14 Many surface observations of ClNO₂ have been made in nighttime urban environments. These are difficult to compare
15 to the model because of the 4° × 5° grid resolution and because of nighttime stratification of the surface layer (the
16 lowest model grid level extends up to 130 m above the surface). In addition, the publications usually report maxima
17 instead of means. Table 5 shows a comparison for representative sites, indicating that the model offers a credible
18 simulation within the above caveats. The previous GEOS-Chem simulation of Sherwen et al. (2016b) only considered
19 ClNO₂ production in SSA and as a result their ClNO₂ mixing ratios were consistently below a few ppt at continental
20 sites. Our simulation can reproduce the observed >100 ppt concentrations at these sites because it accounts for HCl
21 dissolved in SNA aerosol, allowing marine influence to extend further inland as also shown in the comparison to the
22 IMPROVE Cl⁻ data (Figure 5).

23 4.2 Comparison to aircraft measurements

24 The WINTER aircraft campaign over the eastern US and offshore in February-March 2015 provides a unique data set
25 for evaluating our model. Measurements included HCl, ClNO₂, HOCl, Cl₂, and ClNO₃ by Time of Flight Chemical
26 Ionization Mass Spectrometry (TOF-CIMS) (Lee et al., 2018). We focus on the first four measurements because
27 calibration for ClNO₃ needs further examination. The mean 1s detection limits for HCl, ClNO₂, HOCl, and Cl₂ were
28 100, 2, 2, and 1 ppt respectively (Lee et al., 2018). The estimated calibration uncertainty is ±30% for all chlorine
29 species. As discussed in Lee et al. (2018), labeled 15-N₂O₅ was added to the inlet tip during WINTER flights to
30 quantify inlet production of ClNO₂, which was found to be negligible (<<10% of measured ClNO₂), but inlet
31 production of Cl₂, for example, from surface reactions of HOCl with adsorbed HCl, was not evaluated.

32 Figure 6 compares the observed median vertical profiles of HCl, ClNO₂, HOCl, and Cl₂ in WINTER to the model
33 sampled along the flight tracks for the corresponding period. Figure 7 compares the median diurnal variations below

1 1 km altitude, separately over ocean and land. We exclude daytime (10:00-16:00 local) data for ClNO₂ in Figure 6
2 because its mixing ratios are near-zero (Figure 7).

3 The WINTER observations of HCl show median values of 380 ppt near the surface, dropping to a background of 100-
4 200 ppt in the free troposphere (Figure 6). The model is lower than the observations in the lowest 2 km but within the
5 calibration uncertainty. The free tropospheric background in the model is much lower than observed but the
6 observations are near the 100 ppt detection limit. HCl mixing ratios in the lowest km average 60% higher over ocean
7 than over land in both the observations and the model, reflecting the marine source.

8 Also shown in Figure 6 is a sensitivity simulation including anthropogenic HCl emissions from McCulloch et al. (1999)
9 as described in Section 2.2. The resulting model mixing ratios are too high though still within the calibration
10 uncertainty. Based on sampling of power plant plumes during WINTER campaign, Lee et al. (2018) inferred a
11 HCl:SO₂ emission mass ratio of 0.033 from power plants. Adding this emission to the standard simulation, scaled to
12 the SO₂ emissions in GEOS-Chem (from the EPA National Emission Inventory over the US) increases modeled
13 mixing ratios of HCl in the continental boundary layer by 18% along the WINTER flight tracks, improving agreement
14 with observations relative to the standard simulation but still representing a relatively minor source. ClNO₂, HOCl,
15 and Cl₂ mixing ratios increase by 12%, 8%, and 4% respectively.

16 Figure 8 compares the model HCl vertical profiles to measurements by the Georgia Tech CIMS instrument during the
17 SEAC⁴RS campaign over the Southeast US in August-September 2013 (Toon et al., 2016) and the KORUS-AQ
18 campaign over and around the Korea peninsula in May-June 2015. The standard model simulation without
19 anthropogenic chlorine successfully simulates the boundary layer HCl observations, but adding the McCulloch et al.
20 (1999) anthropogenic inventory results in large overestimates. Boundary layer HCl mixing ratios over land are much
21 lower in SEAC⁴RS than in WINTER and this is well reproduced by the model, where the difference is due to seasonal
22 contrast in the SSA source and in the inflow of marine air. The free tropospheric background observed in SEAC⁴RS
23 and KORUS-AQ data is only ~25 ppt, much lower than in WINTER (100-200 ppt), whereas the model free
24 tropospheric background is consistently 20-50 ppt in all three campaigns. The WINTER observations are near their
25 100 ppt detection limit as pointed out above.

26 Mixing ratios of ClNO₂ observed in WINTER are above the detection limit only in the lowest km of atmosphere at
27 night, and are much higher over the ocean than over land. This is well simulated by the model (Figures 6 and 7), and
28 reflects the nighttime source from the N₂O₅ + Cl⁻ heterogeneous reaction from the combined with the fast loss by
29 photolysis in daytime. Our results contrast with previous studies suggesting that the Bertram and Thornton (2009)
30 representation of ClNO₂ production from the N₂O₅ + Cl⁻ heterogeneous reaction (Table 2) results in an overestimate
31 of ClNO₂ observations (Riedel et al., 2013; Wagner et al., 2013; McDuffie et al., 2018a;b). By using a box model
32 applied to the WINTER observations, McDuffie et al. (2018a;b) found that both N₂O₅ uptake rate and ClNO₂
33 production yield were overestimated by the Bertram and Thornton (2009) parameterization. One important difference
34 with our simulation is the assumption of aerosol mixing state. When computing N₂O₅ reactive uptake with the
35 parameterization of Table 2, McDuffie et al. (2018a;b) assumed Cl⁻ to be internally mixed across all aerosol types

1 (including in particular organic aerosol). In contrast, GEOS-Chem assumes that Cl⁻ is present only in SNA and SSA
2 when doing the calculation of N₂O₅ reactive uptake rates, assuming an external mixture of aerosol types (Martin et al.,
3 2003; Evans and Jacob, 2005). This decreases both the N₂O₅ uptake rate and the ClNO₂ yield as compared to the
4 internal mixing assumption of McDuffie et al. (2018a;b), although it is not clear which assumption is best.

5
6 Nighttime Cl₂ mixing ratios in WINTER are greatly overestimated by the model. Under polluted wintertime conditions
7 such as in WINTER the ClNO₂ + Cl⁻ reaction greatly enhances Cl₂ production in the model:



9 The reactive uptake coefficient for (R7) in Table 2 is based on a single laboratory study (Roberts et al., 2008). It
10 requires an aerosol pH < 2 and this condition is generally met for our model simulation of the WINTER environment,
11 consistent with the observation-based analysis of aerosol pH by Guo et al. (2016) for the eastern US in winter. A
12 sensitivity simulation without (R7) is shown as dashed red lines in Figure 7 and can reproduce the low Cl₂ mixing
13 ratios observed over the ocean at night. The analysis of WINTER data by McDuffie et al. (2018b) finds that the
14 correlation between particle acidity and Cl₂ observations is opposite of the trend expected from (R7). Further study of
15 that reaction is needed.

16 The model underestimates the WINTER observations of HOCl and Cl₂ in daytime, over the ocean as well as over land.
17 These species have short lifetimes against photolysis (less than a few minutes). Direct anthropogenic emission from
18 coal combustion has been proposed (Chang et al., 2002) but would only be observed in plumes and not over the oceans.
19 Matching the >1 ppt Cl₂ observed during daytime is particularly problematic since it would require a large
20 photochemical source absent from the model. Lawler et al. (2011) suggested a fast daytime HOCl source from a
21 hypothetical light-dependent Cl⁻ oxidation. The measurements of Cl₂ are also possibly subject to positive artifact from
22 rapid heterogeneous conversion of chlorine species on the surface of the TOF-CIMS inlet (Lee et al., 2018).

23 **5 Global implications of tropospheric chlorine chemistry**

24 **5.1 Cl atom and its impact on VOCs**

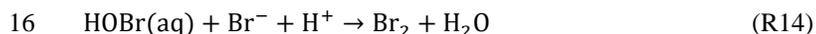
25 The global mean pressure-weighted tropospheric Cl atom concentration in our simulation is 620 cm⁻³, while the MBL
26 concentration averages 1200 cm⁻³ (Figure 2). Our global mean is lower than the previous global model studies of
27 Hossaini et al. (2016) (1300 cm⁻³) and Long et al. (2014) (3000 cm⁻³), which had excessive Cl* generation as discussed
28 above. It is consistent with the upper limit of 1000 cm⁻³ inferred by Singh et al. (1996) from global modeling of C₂Cl₄
29 observations (C₂Cl₄ is highly reactive with Cl atoms). Isotopic observations of methane have been used to infer a Cl
30 atom concentration in the MBL higher than 9000 cm⁻³ in the extra-tropical Southern Hemisphere (Platt et al., 2004;
31 Allan et al., 2007), much higher than our estimate of 800 cm⁻³ over this region. More recently, Gromov et al. (2018)
32 revisited these data together with added constraints from CO isotope measurements and concluded that extra-tropical

1 Southern Hemisphere concentrations of Cl atoms in the MBL should be lower than 900 cm^{-3} , consistent with our
2 estimate.

3 Tropospheric oxidation by Cl atoms drives a present-day methane loss rate of 5.3 Tg a^{-1} in our model, contributing
4 only 1.0% of total methane chemical loss. It has more significant impact on the oxidation of some other VOCs,
5 contributing 20% of the global loss for ethane, 14% for propane, 10% for higher alkanes, and 4% for methanol.

6 **5.2 Impact on bromine and iodine chemistry**

7 Bromine radicals ($\text{BrO}_x \equiv \text{Br} + \text{BrO}$) and iodine radicals ($\text{IO}_x \equiv \text{I} + \text{IO}$) affect global tropospheric chemistry by
8 depleting ozone and OH (Parrella et al., 2012; Sherwen et al., 2016b). Br atoms are also thought to drive the oxidation
9 of elemental mercury (Holmes et al., 2006). Chlorine chemistry increases IO_x mixing ratios by 16% due to the
10 reactions of HOI, INO_2 , and INO_3 with Cl^- (R11-R13), producing ICl which photolyzes rapidly to I atoms (Figure 1).
11 The effect on bromine is more complicated. Bromine radicals originate from photolysis and oxidation of
12 organobromines emitted by the ocean, as well as from SSA debromination (Yang et al., 2005). They are lost by
13 conversion to HBr which is efficiently deposited. Parrella et al. (2012) pointed out that heterogeneous chemistry of
14 HBr (dissolved as Br^-) is critical for recycling bromine radicals and explaining observed tropospheric BrO mixing
15 ratios in the background troposphere:



18 Chloride ions and dissolved SO_2 ($\text{S(IV)} \equiv \text{HSO}_3^- + \text{SO}_3^{2-}$) can however compete with Br^- for the available HOBr (Chen
19 et al., 2017):



22 Chen et al. (2017) pointed out that reaction (R16) effectively decreases BrO mixing ratios by producing HBr which is
23 rapidly deposited instead of contributing to BrO_x cycling. They found in a GEOS-Chem simulation that global
24 tropospheric BrO mixing ratios decreased by a factor of 2 as a result. Reaction (R5) may however have a compensating
25 or opposite effect. It propagates the cycling of BrO_x if BrCl volatilizes:

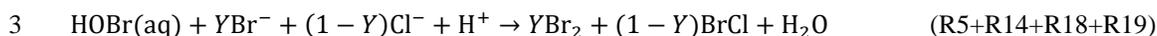


27 but it may also generate new BrO_x if BrCl reacts with Br^- in the aqueous phase to produce Br_2 (Wang et al., 1994):



30 The sequence (R5) + (R18) + (R19) with Cl^- as a catalyst has the same stoichiometry as (R14) and thus contributes to
31 HBr recycling in the same way. We find in the model that it is globally 30 times faster than (R14) and therefore much

1 more effective at regenerating bromine radicals. In GEOS-Chem, the rate of reaction (R5) computed from Table 2 is
2 applied to the following stoichiometry reflecting the ensemble of reactions (R5, R14, R18, and R19):



4 where Y is the yield of Br_2 and $1-Y$ is the yield of BrCl . Y is calculated following the laboratory study of Fickert et al.
5 (1999):

6 $Y = 0.41\log_{10}([\text{Br}^-]/[\text{Cl}^-]) + 2.25$ for $[\text{Br}^-]/[\text{Cl}^-] < 5 \times 10^{-4}$ (2)

7 $Y = 0.90$ for $[\text{Br}^-]/[\text{Cl}^-] > 5 \times 10^{-4}$ (3)

8 **This mechanism was first included in GEOS-Chem version 11-02d** by Chen et al. (2017), who did not however have
9 an explicit SSA Cl^- simulation (they instead assumed a fixed SSA $[\text{Cl}^-] = 0.5 \text{ M}$, and considered only dissolved HCl
10 in cloud).

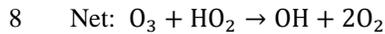
11 Chen et al. (2017) found in their GEOS-Chem simulation that the global tropospheric BrO burden was 8.7 Gg without
12 the $\text{HOBr} + \text{S(IV)}$ reaction (R16), and dropped to 3.6 Gg when the reaction was included. Previous GEOS-Chem
13 model estimates of the global tropospheric BrO burden were 3.8 Gg (Parrella et al., 2012), 5.7 Gg (Schmidt et al.,
14 2016), and 6.4 Gg (Sherwen et al., 2016b). Our simulation features many updates relative to Chen et al. (2017)
15 including not only explicit SSA Cl^- but also explicit calculation of aerosol pH with ISORROPIA II for the rates of
16 reactions in Table 2. By including explicit SSA Cl^- , the cloudwater $[\text{Cl}^-]$ in our model is much higher than that in Chen
17 et al. (2017) and more comparable to measurements ($\sim 10^{-4} \text{ M}$ in typical cloud; (Straub et al., 2007)). We find in our
18 standard simulation a global tropospheric BrO burden of 4.2 Gg, 17% higher than Chen et al. (2017).

19 Figure 9 shows the change of surface BrO mixing ratios due specifically to tropospheric chlorine chemistry, as
20 obtained by difference with a sensitivity simulation including none of the Cl_y chemistry shown in Figure 1. The
21 inclusion of chlorine chemistry increases the global tropospheric BrO burden by 85%. More than 80% of this change
22 is caused by the $\text{HOBr} + \text{Cl}^-$ reaction as discussed above. Other significant contributions include $\text{ClNO}_3 + \text{Br}^-$ and
23 $\text{ClNO}_2 + \text{Br}^-$. The largest BrO increases (1-2 ppt) are in surface air over the high northern latitudes oceans where SSA
24 emissions are high and acidic conditions promote $\text{HOBr} + \text{Cl}^-$ chemistry.

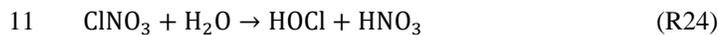
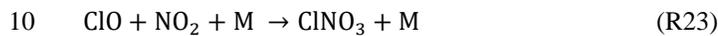
25 **5.3 Impact on tropospheric ozone and OH**

26 Figure 9 also shows the effects of chlorine chemistry on NO_x , OH , and ozone. The global tropospheric burdens
27 decrease by 5% for NO_x , 3% for OH , and 7% for ozone. The inter-hemispheric (N/S) ratio of tropospheric mean OH
28 decreases from 1.14 to 1.12. Models tend to overestimate global mean tropospheric OH and its inter-hemispheric ratio
29 relative to the constraint from methylchloroform which suggests a ratio of 0.85-0.98 (Naik et al., 2013; Voulgarakis et
30 al., 2013). The effect of chlorine chemistry on the N/S ratio is slight but in the right direction.

1 The chlorine-induced decreases in Figure 9 are mainly through bromine chemistry initiated by chlorine (Section 5.2),
2 and have spatial distributions characteristic of bromine chemistry with maxima at high latitudes as discussed by
3 Schmidt et al. (2016). There are specific chlorine mechanisms including catalytic ozone loss through HOCl formation
4 and photolysis:



9 and also loss of NO_x :



12 However, we find that the rates are very small compared to similar mechanisms involving bromine and iodine because
13 the stability of HCl quenches Cl^* radical cycling.

14

15 A particular situation arises over polluted continents due to ClONO_2 chemistry. Production of ClONO_2 at night from the
16 $\text{N}_2\text{O}_5 + \text{Cl}^-$ heterogeneous reaction, followed by photolysis in the morning to release Cl and NO_2 , provides a source of
17 radicals and ozone. This explains the increases of OH over North America and Europe in Figure 9. The effect is most
18 important at high northern latitudes in winter due to the longer night. To isolate the impact on ozone we conducted a
19 sensitivity simulation with no ClONO_2 production, setting $\phi = 0$ for reaction (R3) in Table 2. The surface air ozone
20 enhancement due to ClONO_2 chemistry is found to be the largest (~8 ppb) in European winter, due to the large supply
21 of Cl^- from the North Atlantic combined with high NO_x emissions. Other polluted continents see ozone increases of
22 1-5 ppb in winter. The effect in summer is less than 1 ppb. These results are similar to previous regional modeling
23 studies by Sarwar et al. (2014) and Sherwen et al. (2017).

24

25 Figure S1 shows the differences of BrO, NO_x , OH, and ozone concentrations between our model and the standard
26 GEOS-Chem model version 11-02d including SSA debromination. Our explicit treatment of chlorine chemistry and
27 thermodynamic representation of aerosol pH increases the global tropospheric BrO burden by 40%. Most of this
28 change is caused by faster $\text{HOBr} + \text{Cl}^-$ reaction at high latitudes, resulting from higher Cl^- concentration in our model
29 particularly in cloud. The decrease of BrO in the tropical MBL is caused by an increase in aerosol pH (pH was
30 previously assumed to be 0 for computation of bromine chemistry), which slows down the acid-catalyzed recycling
31 of bromine by reactions (R5) and (R14). Our computed global tropospheric burdens decrease by 4% for NO_x , 2% for
32 OH, and 4% for ozone relative to version 11-02d, again due to the more active bromine chemistry. The increase of
33 OH over continental regions is due to our accounting of HCl dissolved in SNA aerosol, allowing marine influence to
34 extend further inland to drive ClONO_2 chemistry.

1 **6 Conclusions**

2 We have added to the GEOS-Chem model a comprehensive and consistent representation of tropospheric chlorine
3 chemistry. This includes in particular explicit accounting of the mobilization of sea salt aerosol (SSA) chloride (Cl^-),
4 by acid displacement of HCl as well as by other heterogeneous processes. Cycling of inorganic gas-phase chlorine
5 species (Cl_y) generated from SSA and other sources is simulated and coupled to the model aerosol-oxidant-bromine-
6 iodine chemistry. With our work, GEOS-Chem now has a complete simulation of halogen ($\text{Cl}+\text{Br}+\text{I}$) chemistry in
7 both the troposphere and stratosphere.

8 Emission of chlorine in the model is mainly as sea-salt aerosol ($1780 \text{ Tg Cl a}^{-1}$). Other sources (combustion,
9 organochlorines, stratospheric input) are also included but are small in comparison. Most of the sea-salt aerosol
10 chloride is removed by deposition, but 3.6% is mobilized to inorganic gas-phase chlorine (Cl_y) through acid
11 displacement to HCl (52 Tg a^{-1}) and through other heterogeneous chemistry producing more reactive chlorine species
12 (12 Tg a^{-1}). We define reactive chlorine (Cl^*) as the ensemble of Cl_y species excluding HCl and including Cl, ClO,
13 Cl_2 , BrCl, HOCl, ClNO₂, ClNO₃, plus other minor species. Oxidation of HCl by OH provides a Cl^* source of 9.7 Tg
14 a^{-1} , comparable to the heterogeneous source from HOBr + Cl^- (8.6 Tg a^{-1}). $\text{N}_2\text{O}_5 + \text{Cl}^-$ (1.8 Tg a^{-1}) is also important
15 in polluted environments. Cycling between Cl^* species drives radical chlorine (Cl/ClO) chemistry but chain lengths
16 are limited by fast conversion to HCl and subsequent deposition.

17 HCl mixing ratios in the model are highest over the oceans downwind of polluted continents due to effective acid
18 displacement from sea-salt aerosol by HNO_3 and H_2SO_4 . Mixing ratios are much lower over the Southern Ocean where
19 the supply of acids is low. The dominant daytime Cl^* species is generally HOCl while BrCl, Cl_2 , and ClNO₂ dominate
20 at night. ClNO₃ dominates in the upper troposphere due to stratospheric input. Chlorine atom concentrations are
21 highest over Europe in winter due to ClNO₂ chemistry, and are otherwise high over the northern mid-latitudes oceans
22 where the supply of acidity promotes Cl formation both through HCl and through acid-catalyzed heterogeneous
23 processes.

24 Comparison of model results to observations in marine surface air show that the model is usually able to reproduce
25 the range and distributions of observed sea-salt aerosol chloride deficits, HCl mixing ratios, and Cl^* mixing ratios. In
26 particular, concurrent observations of HCl and HNO_3 in coastal/marine air worldwide show high correlation with the
27 model including high HCl mixing ratios at northern mid-latitudes combined with depressed HNO_3 . Consideration of
28 acid displacement greatly improves model agreement with HNO_3 observations in marine air. The model can also
29 successfully simulate observations of high ClNO₂ at night including in continental air. The chlorine in that case
30 originates from sea-salt aerosol transported far inland following uptake of volatilized HCl by sulfate-nitrate-
31 ammonium (SNA) aerosol. The model cannot reproduce the very high HOCl and Cl_2 concentrations observed by
32 Lawler et al. (2009;2011) at Cape Verde in the tropical Atlantic.

33 Comparisons of model results to aircraft campaign observations from WINTER (eastern US and offshore, Feb-Mar
34 2015), SEAC4RS (Southeast US, Aug-Sep 2013), and KORUS-AQ (Korean Peninsula, April-Jun 2016) show general

1 consistency for HCl vertical profiles. Continental boundary layer HCl mixing ratios in these campaigns can be mostly
2 accounted for by the marine source transported inland, though power plants could make a minor contribution.
3 WINTER observations also include ClNO₂ and Cl₂, and HOCl. The observed ClNO₂ is mainly confined to the
4 nighttime marine boundary layer and is consistent with the model. Observed Cl₂ concentrations at night are much
5 lower than the model, which has a large source under the WINTER conditions from the ClNO₂ + Cl⁻ heterogeneous
6 reaction. The rate coefficient for this reaction is from only one laboratory study.

7 The model simulates a global mean Cl atom concentration of 620 cm⁻³ in the troposphere and 1200 cm⁻³ in the marine
8 boundary layer (MBL), lower than previous global model studies that had excessive generation of Cl* but consistent
9 with independent proxy constraints. We find that oxidation by Cl atoms accounts for only 1.0% of the global loss of
10 atmospheric methane but has larger effects on the global losses of ethane (20%), propane (14%), and methanol (4%).
11 Chlorine chemistry increases global tropospheric BrO by 85%, and decreases ozone and OH by 7% and 3%
12 respectively, relative to a sensitivity simulation with no chlorine chemistry. The large effect on BrO is due to
13 production of bromine radicals by the HOBr + Cl⁻ heterogeneous reaction, and the decreases of ozone and OH are
14 mainly through the induced bromine chemistry. An exception is winter conditions over polluted regions, where ClNO₂
15 chemistry increases ozone mixing ratios by up to 8 ppb.

16 **Author contributions.** XW, DJJ, and HL designed the study. XW developed the chlorine model code, performed the
17 simulations and analyses. SDE, MPS, LZ, QC, BA, TS, and MJE contributed to the GEOS-Chem halogen model
18 development. BHL, JDH, FDL, and JAT conducted and processed the measurement during WINTER campaign. GLH
19 conducted and processed the measurement during SEAC⁴RS and KORUS-AQ campaigns. XW and DJJ prepared the
20 manuscript with contributions from all co-authors.

21 **Data availability.** The model code is available from the corresponding author upon request, and will be made available
22 to the community through the standard GEOS-Chem (<http://www.geos-chem.org>) in the future. Data of WINTER
23 campaign are available to the general public at https://www.eol.ucar.edu/field_projects/winter. Data of NASA
24 SEAC⁴RS AND KORUS-AQ missions and are available to the general public through the NASA data archive
25 (<https://www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs> and [https://www-air.larc.nasa.gov/cgi-](https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq)
26 [bin/ArcView/korusaq](https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq)). IMPROVE data are available through the Federal Land Manager Environmental database
27 (<http://views.cira.colostate.edu/fed>).

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4

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1 **Table 1: Global sources and sinks of gas-phase inorganic (Cl_y) and reactive (Cl^*) tropospheric chlorine ^a.**

	Cl_y (Gg Cl a^{-1})	Cl^* (Gg Cl a^{-1})
Total source	75200	25000
Sea Salt	63900	11900
Acid displacement ^b	52000	-
HOBr + Cl^-	8590	8590
N_2O_5 + Cl^-	1810	1810
HOI, IONO_x ^c + Cl^-	641	641
ClNO_2 + Cl^-	327	327
OH + Cl^-	403	403
ClNO_3 + Cl^-	64	64
HOCl + Cl^-	61	61
HCl + OH	-	9720
Organochlorines	3320	3300
CH_3Cl + OH ^d	2200	2180
CH_2Cl_2 + OH	780	780
CHCl_3 + OH	298	298
CH_2ClCl + OH	46	46
Stratosphere ^e	380	64
Anthropogenic HCl ^f	(6660)	-
Open fires	7640	-
Total sink	75200	25000
Deposition	71400	346
Dry	35200	170
Wet	36200	176
Uptake by alkaline SSA	3800	-
Conversion to HCl ^g	-	24600
Tropospheric mass (Gg)	316	12
Lifetime (hours)	37	3.8

2 ^a Annual totals for 2016 computed from GEOS-Chem. Gas-phase inorganic chlorine is defined as $\text{Cl}_y \equiv \text{Cl} + 2 \times \text{Cl}_2 + 2 \times \text{Cl}_2\text{O}_2 +$
3 $\text{ClNO}_2 + \text{ClNO}_3 + \text{ClO} + \text{ClOO} + \text{OCIO} + \text{BrCl} + \text{ICl} + \text{HOCl} + \text{HCl}$. Reactive chlorine is defined as $\text{Cl}^* \equiv \text{Cl}_y - \text{HCl}$. Thus the
4 source of HCl can be inferred from the Table entries as $\text{Cl}_y - \text{Cl}^*$. The definition of Cl_y excludes aerosol Cl^- , which has a very large
5 sea salt source of 1780 Tg Cl a^{-1} but is mainly removed by deposition, HCl is the dominant component of Cl_y but is also mostly
6 removed by deposition. Reactive chlorine Cl^* is the chemical family principally involved in radical cycling.

7 ^c $\text{IONO}_x \equiv \text{IONO} + \text{IONO}_2$

8 ^b Net production minus loss of HCl from acid aerosol displacement by HNO_3 and H_2SO_4 computed as thermodynamic equilibrium.

9 ^d The source from $\text{CH}_3\text{Cl} + \text{Cl}$ is not shown since it contributes < 1% of CH_3Cl oxidation. Same for other organochlorines.

10 ^e Net stratospheric input to the troposphere.

11 ^f Coal combustion, waste incineration, and industrial activities. These emissions are only included in a sensitivity simulation (see
12 Section 2.2 and 4.2 for details) and are therefore listed here in parentheses. Emissions of anthropogenic fugitive dust are estimated
13 as less than 390 Gg a^{-1} (Section 2,2) and are not included in the model.

14 ^g From reactions of Cl atoms (see Figure 1).

1 **Table 2: Heterogeneous reactions of Cl⁻ and reactive uptake coefficients (γ)^a.**

Reaction	Reactive uptake coefficient (γ)	Footnote
R3	$\gamma = Bk'_{2f} \left(1 - \frac{1}{\left(\frac{k_3[\text{H}_2\text{O}]}{k_{2b}[\text{NO}_3^-]} \right) + 1 + \left(\frac{k_4[\text{Cl}^-]}{k_{2b}[\text{NO}_3^-]} \right)} \right)$ $k'_{2f} = \beta(1 - e^{-\delta[\text{H}_2\text{O}]}) ; \varphi = \left(\frac{k_2[\text{H}_2\text{O}]}{k_3[\text{Cl}^-]} + 1 \right)^{-1}$ $B = 3.2 \times 10^{-8} \text{ s} ; k_3/k_2 = 450$ $\beta = 1.15 \times 10^6 \text{ s}^{-1} ; \delta = 0.13 \text{ M}^{-1}$ $k_3/k_{2b} = 0.06 ; k_4/k_{2b} = 29$	b
R4	$\gamma = 0.04[\text{Cl}^-]$	c
R5	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}$ $\Gamma_b = 4H_{\text{HOBr}}RTI_r k_b [\text{Cl}^-][\text{H}^+]f(r, I_r)/c$ $I_r = \sqrt{D_l/(k_b[\text{Cl}^-][\text{H}^+])} ; \alpha_b = 0.6$ $k_b = 2.3 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1} ; D_l = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	d
R6	$\gamma = 0.0244$	e
R7	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1} \text{ (pH} < 2), \quad \gamma = 0 \text{ (pH} > 2)$ $\Gamma_b = 4H_{\text{ClNO}_2}RTI_r k^{II} [\text{Cl}^-]f(r, I_r)/c$ $I_r = \sqrt{D_l/(k^{II}[\text{Cl}^-])} ; \alpha_b = 0.01$ $k^{II} = 10^7 \text{ M}^{-2} \text{ s}^{-1} ; D_l = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
R8	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}$ $\Gamma_b = 4H_{\text{ClNO}_2}RTI_r k^{II} [\text{Br}^-]f(r, I_r)/c$ $I_r = \sqrt{D_l/(k^{II}[\text{Br}^-])} ; \alpha_b = 0.01$ $H_{\text{ClNO}_2}^2 D_l k^{II} = 0.101 \text{ M cm}^2 \text{ s}^{-2}$	
R9	$\gamma = \min\left(\left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}, 2 \times 10^{-4} \right)$ $\Gamma_b = 4H_{\text{HOCl}}RTI_r k_t [\text{Cl}^-][\text{H}^+]f(r, I_r)/c$ $I_r = \sqrt{D_l/(k_t[\text{Cl}^-][\text{H}^+])} ; \alpha_b = 0.8$ $k_t = 1.5 \times 10^4 \text{ M}^{-2} \text{ s}^{-1} ; D_l = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
R10	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}$ $\Gamma_b = 4H_{\text{NO}_3}RTI_r k' [\text{Cl}^-]f(r, I_r)/c$ $I_r = \sqrt{D_l/(k'[\text{Cl}^-])} ; \alpha_b = 0.013$ $k' = 2.76 \times 10^6 \text{ M}^{-2} \text{ s}^{-1} ; D_l = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
R11	$\gamma = 8.5 \times 10^{-3}$	f
R12	$\gamma = 0.017$	f
R13	$\gamma = 8.5 \times 10^{-3}$	f

1 ^aFormulations for the reactive uptake coefficient γ are from IUPAC (Ammann et al., 2013) unless stated otherwise in the footnote
2 column. Brackets denote aqueous-phase concentrations in unit of M (moles per liter of water). R is the ideal gas constant. c is the
3 average gas-phase thermal velocity for the reactant with Cl^- . The reactive uptake coefficient is used to calculate the reaction rate
4 following equation (1). $f(r, I_r) = \coth(r/I_r) - (I_r/r)$ is a spherical correction to mass transfer where I_r is a reacto-diffusive length
5 scale and r is the radius of the aerosol particle or cloud droplet.
6 ^b Bertram and Thornton (2009); Roberts et al. (2009).
7 ^c Knipping and Dabdub (2002)
8 ^d k_b is based on Liu and Margerum (2001). R5 competes with the heterogeneous reactions $\text{HOBr} + \text{Br}^-$ and $\text{HOBr} + \text{S(IV)}$ as given by
9 Chen et al. (2017). The BrCl product may either volatilize or react with Br^- to produce Br_2 and return Cl^- following Fickert et al.
10 (1999), as described in Section 5.2.
11 ^e Assumes that Cl^- is present in excess so that γ does not depend on $[\text{Cl}^-]$. However, R6 competes with the heterogeneous
12 reaction $\text{ClNO}_3 + \text{Br}^-$ as given by Schmidt et al. (2016), with the branching ratio determined by the relative rates.
13 ^f These reactions are based on Sherwen et al. (2016a) and only take place in SSA.
14

1 **Table 3: Chloride deficits in sea salt aerosol.^a**

Location	Modeled Cl ⁻ deficit (%)	Measured Cl ⁻ deficit (%)
North Carolina coast	+40	-1 to +90
Townsville coast, Australia	+23	+33
California coast	+21	+2 to +75
Greenland Sea	+18	+6 to +22
North Atlantic Ocean	+14	-24 to +54
Equatorial Atlantic	+12	+11 to +64
Puerto Rico coast	+9	+7 to +25
Pacific Ocean	+6	-22 ~ +40
Cape Grim, Australia	+4	-50~+15

2 ^a Deficits relative to seawater composition. Observations compiled by Graedel and Keene (1995) are reported there as ranges for
 3 individual regions and months, with the ranges likely reflecting measurement uncertainty rather than physical variability. Model
 4 values are means for the regions and months of observations.

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9 **Table 4: Surface air mixing ratios of reactive chlorine (Cl*)^a**

Location	Modeled Cl* (ppt)	Measured mean Cl* (ppt)	Reference
Atlantic cruise near Europe	43	27 ^b	Keene et al. (2009)
Appledore Island (US east coast)	17	< 20	Keene et al. (2007)
Atlantic cruise near North Africa	5	< 24	Keene et al. (2009)
Southern Ocean cruise	4	< 24	Keene et al. (2009)
Hawaii	4	6	Pszenny et al. (2004)
Tropical Atlantic cruise	2	< 24	Keene et al. (2009)
Alert (Canada)	0.2	< 14	Impey et al. (1999)

10 ^a Reactive chlorine Cl* is the ensemble of gas-phase inorganic chlorine species excluding HCl. Measurements are 24- hour
 11 averages. Model values are monthly means in 2016 taken for the same month and location as the observations.

12 ^b Median value

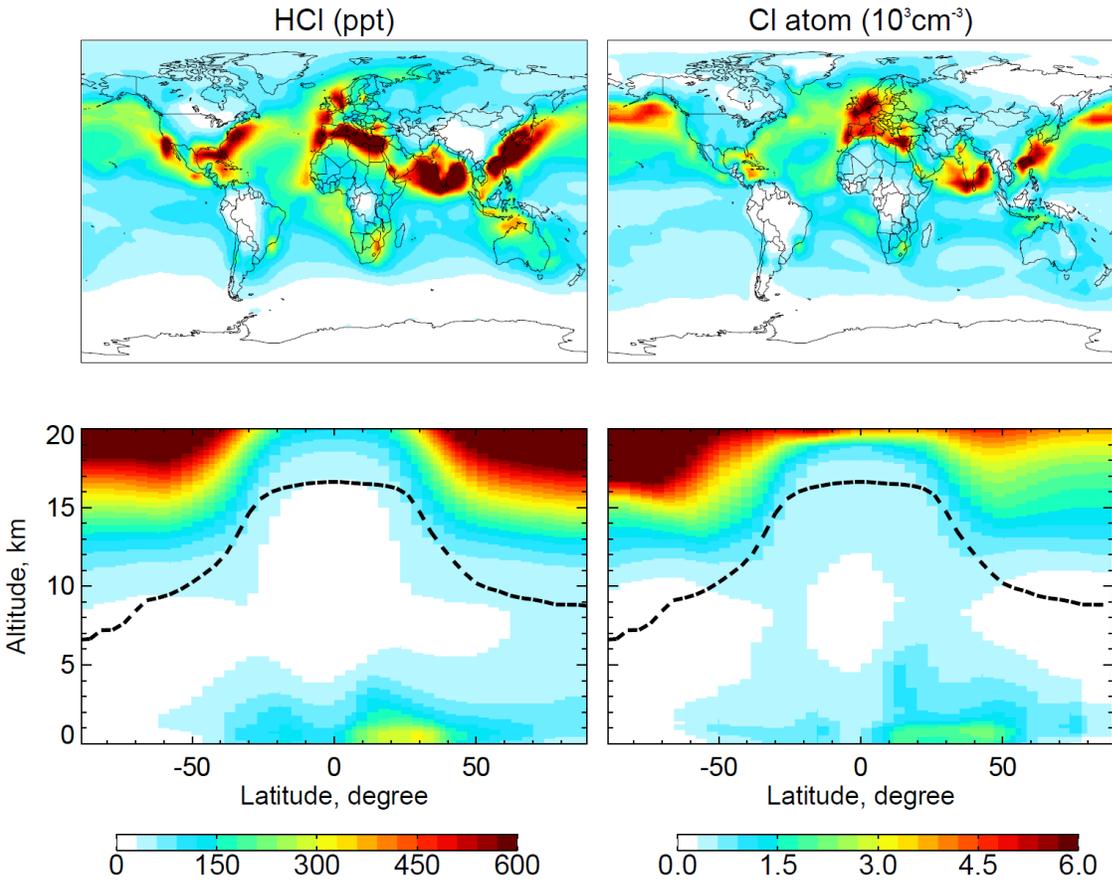
13

1 **Table 5: Comparison of modeled maximum CINO₂ mixing ratios to surface observations ^a**

Location	Date	Observed (ppt)	Simulated (ppt)	References
Manchester, UK	Oct-Nov 2014	510	400	Priestley et al. (2018)
Weybourne, UK	Jun-Aug 2015	1100	1200	Sommariva et al. (2018)
East Anglia Coast, UK	Jan 2014	100	400	Bannan et al. (2017)
Leicester, UK	Feb 2016	730	760	Sommariva et al. (2018)
London, UK	July-Aug 2012	730	510	Bannan et al. (2015)
Calgary, Canada	Apr 2010	240	130	Mielke et al. (2011)
Calgary, Canada	Sep 2010-Mar 2011	340	170	Mielke et al. (2015)
Penlee Point, UK	Apr-May 2015	920	870	Sommariva et al. (2018)
Kleiner Feldberg, Germany	Aug-Sep 2011	850	400	Phillips et al. (2012)
Long Island Sound	Mar 2008	200	210	Kercher et al. (2009)
Olympic Park, South Korea	May-Jun 2016	780	520	Jeong et al. (2018)
Taehwa Research Forest, South Korea	May-Jun 2016	2600	220	Jeong et al. (2018)
Boulder, Colorado	Feb 2009	440	130	Thornton et al. (2010)
Pasadena, California	May-Jun 2010	3500	360	Mielke et al. (2013)
Offshore of Los Angeles, California	May-Jun 2010	1800	500	Riedel et al. (2013)
La Jolla, California	Feb 2013	65	65	Kim et al. (2014)
Houston, Texas	Aug-Sep 2006	1200	150	Osthoff et al. (2008)
Houston, Texas	Sep 2013	140	18	Faxon et al. (2015)
Hong Kong, China	Aug, 2012	1900	200	Tham et al. (2014)
Hong Kong, China	Nov-Dec, 2013	4700	410	Wang et al. (2016)

2 ^a Observed and modeled values are maxima for the reporting period. Model maxima are based on hourly values sampled at the
3 same location and time period as the observations. **The sites are listed in order of decreasing latitude.**
4

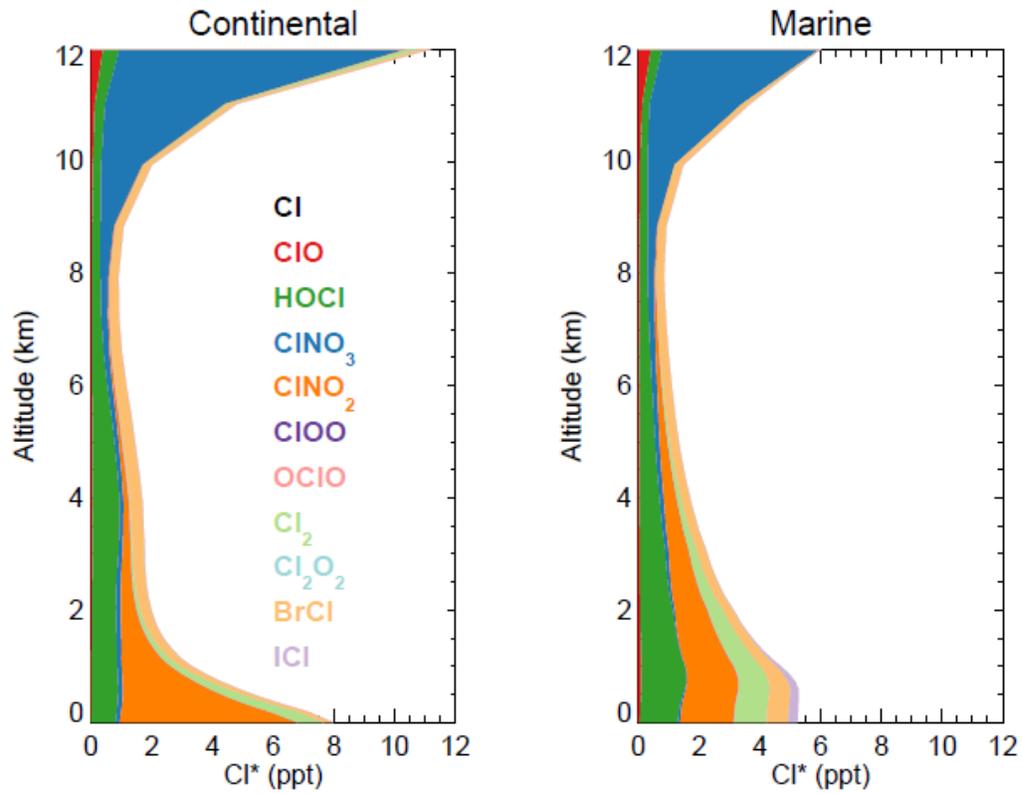
Surface and zonal mean HCl mixing ratios and Cl atom concentrations



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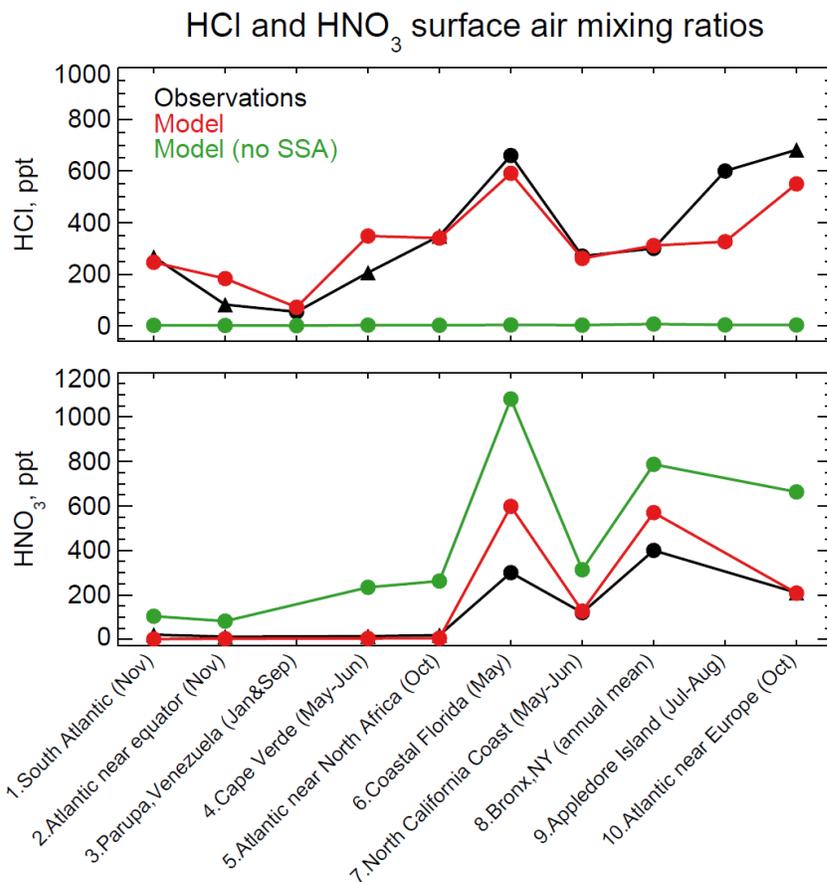
Figure 2: Global distributions of annual mean HCl mixing ratios and Cl atom concentrations in GEOS-Chem. The top panels show surface air mixing ratios/concentrations. The bottom panels show zonal mean mixing ratios/concentrations as a function of latitude and altitude. Dashed lines indicate the tropopause.

Global vertical distribution of reactive chlorine gases



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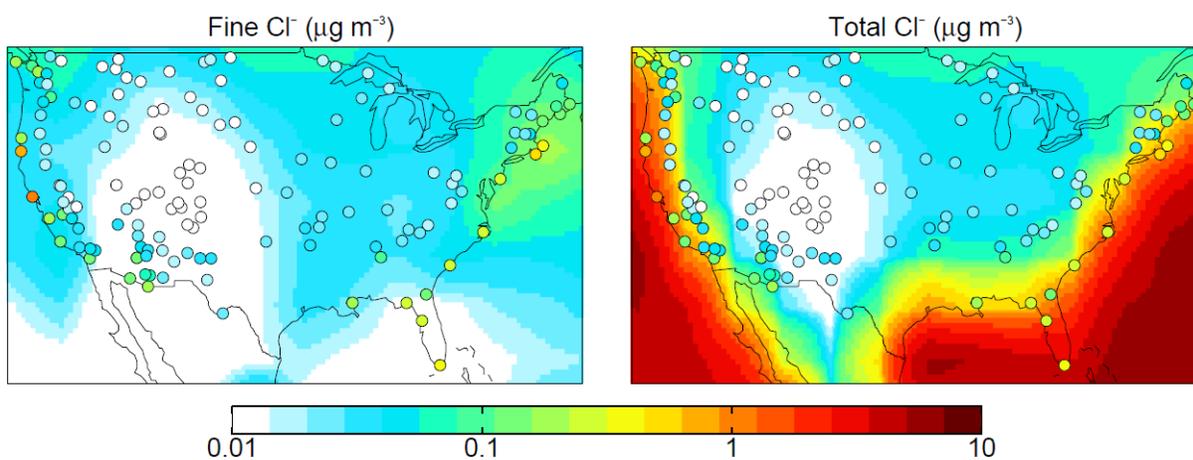
Figure 3: Global annual mean vertical distributions of reactive chlorine species (Cl*) in GEOS-Chem for continental and marine air. Stratospheric conditions are excluded.



1
 2 **Figure 4: HCl and HNO₃ surface air mixing ratios at coastal/island sites and from ocean cruises, arranged from left to right**
 3 **in order of increasing latitude. Observations are means (black circles) or medians (black triangles) depending on availability.**
 4 **Model values are monthly means for the sampling locations. Also shown are results from a sensitivity simulation with no**
 5 **mobilization of Cl⁻ from sea salt aerosol (SSA). References: (1, 2, 5, 10) Keene et al. (2009); (3) Sanhueza and Garaboto**
 6 **(2002); (4) Sander et al. (2013); (6) Dasgupta et al. (2007); (7) Crisp et al. (2014); (8) Bari et al. (2003); (9) Keene et al. (2007).**

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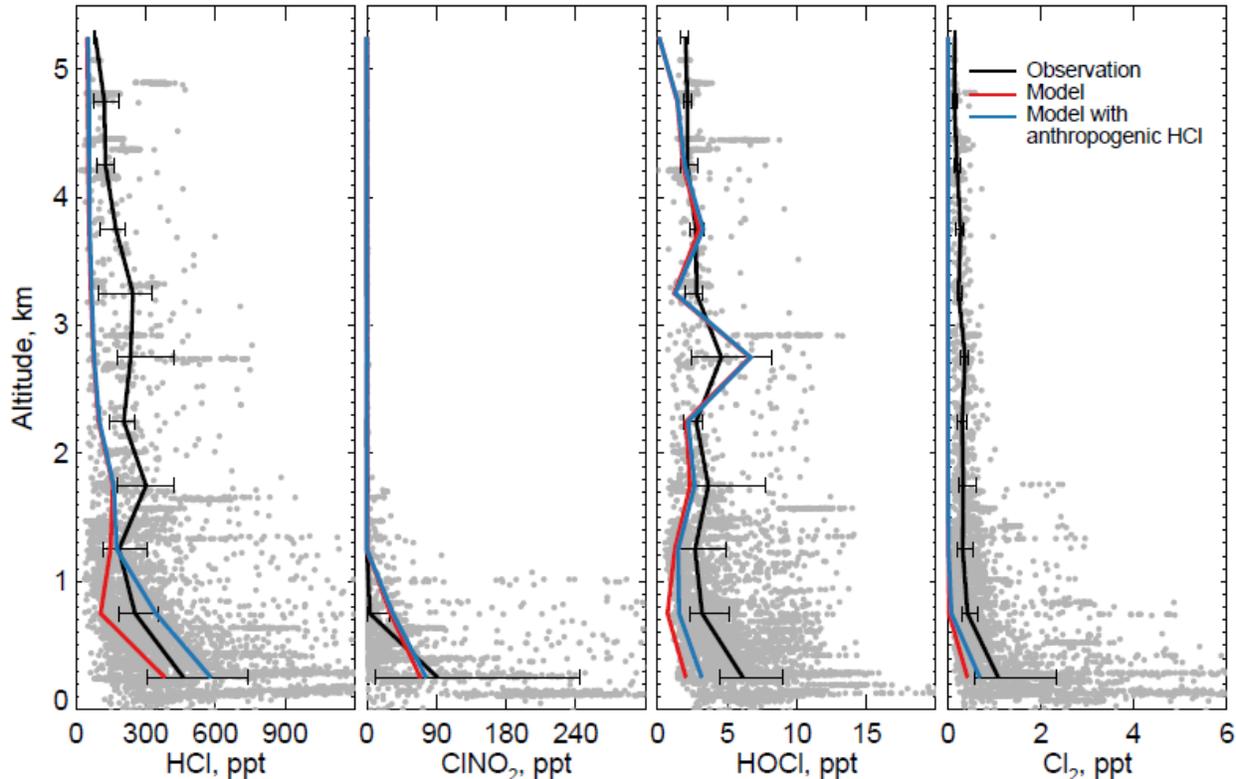
Cl⁻ concentrations in surface air over the US



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Figure 5: Aerosol Cl⁻ concentrations in surface air over the contiguous US. Values are annual means for 2016. GEOS-Chem model values are shown as contours separately for fine Cl⁻ (<1 μm diameter) and total Cl⁻. Observations from the IMPROVE network (<2.5 μm diameter) are shown as circles and are the same in both panels; one would expect them to be higher than the model fine Cl⁻ but lower than total Cl⁻.

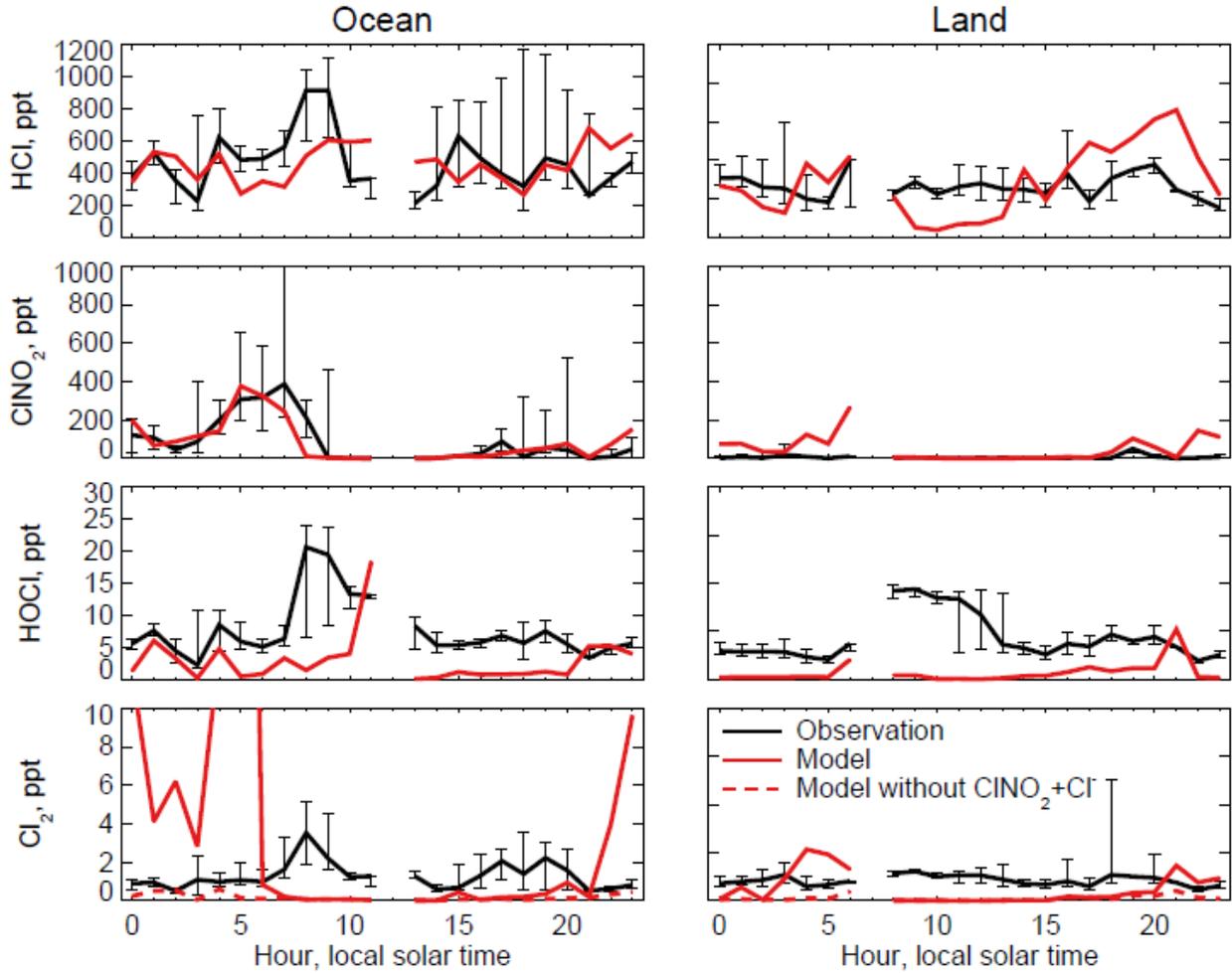
Median vertical profiles of chlorine species during WINTER



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 2 **Figure 6:** Vertical profiles of HCl, nighttime ClNO₂, HOCl, and Cl₂ mixing ratios during the WINTER campaign over the
 3 eastern US and offshore in February-March 2015. Observations from Haskins et al. (2018) are shown as individual 1-minute
 4 data points, with medians and 25th-75th percentiles in 500-m vertical bins. Measurements below the detection limit are
 5 treated as the median of 0 and detection limit. ClNO₂ data exclude daytime (10:00-16:00 local) when mixing ratios are near
 6 zero both in the observations and in the model (Figure 7). Model values are shown as medians sampled along the flight
 7 tracks. Also shown are results from a sensitivity simulation including the anthropogenic chlorine inventory of McCulloch
 8 et al. (1999).

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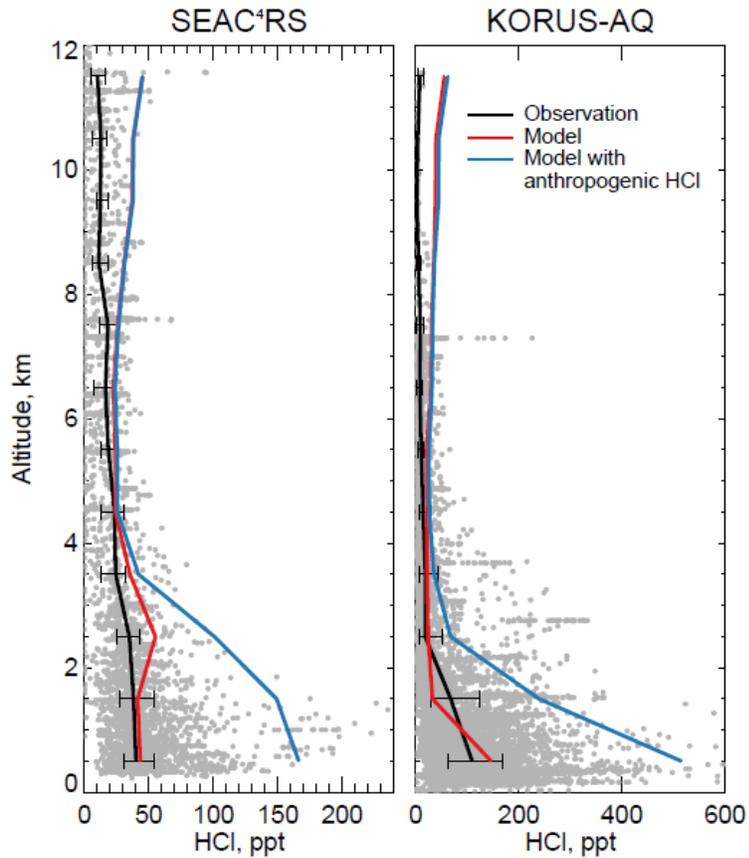
Diurnal variations of chlorine species during WINTER



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 2 **Figure 7: Median diurnal variations of HCl, ClNO₂, and Cl₂ mixing ratios below 1 km altitude during the WINTER aircraft**
 3 **campaign over the eastern US and offshore in February-March 2015. The data are separated between ocean (left panels)**
 4 **and land (right panels). Model values are compared to observations from Haskins et al. (2018). Vertical bars show the 25th-**
 5 **75th percentiles in the observations. Measurements below the detection limit are treated as the median of 0 and detection**
 6 **limit. Also shown are results from a sensitivity simulation excluding ClNO₂+Cl, which has negligible effect on HCl, ClNO₂,**
 7 **and HOCl, but brings the Cl₂ simulation in much better agreement with observations at night.**

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HCl vertical profiles

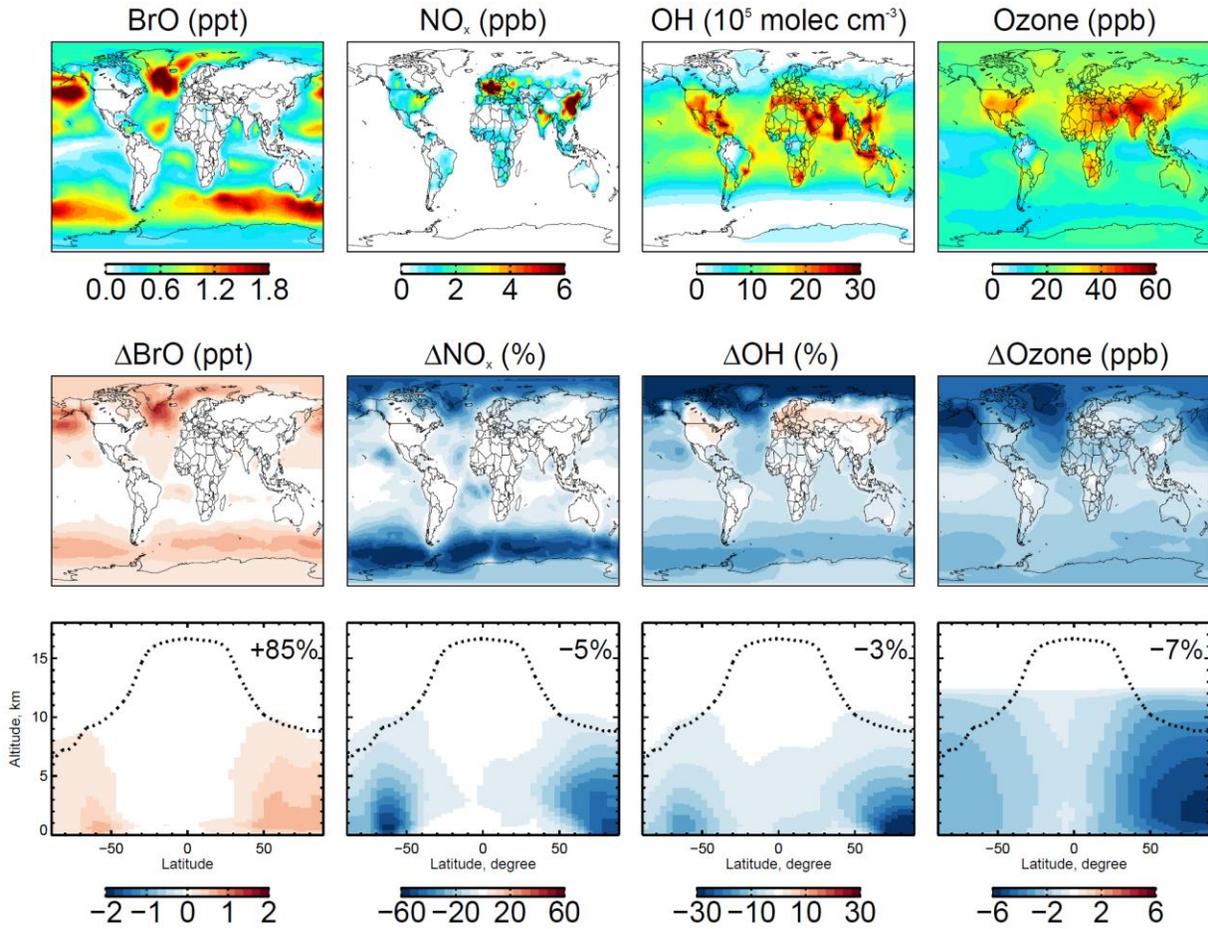


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2 **Figure 8: Vertical profiles of HCl mixing ratios during the SEAC⁴RS aircraft campaign over the Southeast US (95°-81.5°W,**
3 **30.5°-39°N) in August-September 2013 and during the KORUS-AQ aircraft campaign over and around the Korean**
4 **peninsula (120°-132°E, 32°-38°N) in May-June 2015. Observations from the Georgia Tech CIMS instrument are shown as**
5 **gray points (1-minute averages), with medians and 25th-75th percentiles in 1-km vertical bins. Model values are sampled**
6 **along the flight tracks and for the measurement period. Measurements below the detection limit are treated as the median**
7 **of 0 and detection limit.**

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Chlorine driven changes in BrO, NO_x, OH, and ozone



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3 **Figure 9: Effects of tropospheric chlorine chemistry on BrO, NO_x, OH, and ozone. The top panels show the annual mean**
 4 **surface concentrations of BrO, NO_x, OH, and ozone simulated in our standard model including tropospheric chlorine**
 5 **chemistry. The lower panels show the changes in annual mean mixing ratios/concentrations due to tropospheric chlorine**
 6 **chemistry, as determined by difference with a sensitivity simulation including no Cl_y production and cycling. The middle**
 7 **panels show the changes in surface air concentrations and the bottom panels show the changes in zonal mean mixing**
 8 **ratios/concentrations as a function of latitude and altitude. Black dashed lines indicate the tropopause. Numbers in bottom panels**
 9 **show the global tropospheric mean differences.**

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