

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

Reviewer #1

The authors answered most of the previous comments/issues except for the following:

The authors point out the fact that Kim et al., 2008 was not carried through to publication as the reason for not doing a comparison. Aren't the data still available on the NASA data site? Are the authors (one of whom was the senior author on the Kim paper) saying that they don't believe the HCl measurements? They should state that or do the comparison.

We now include model comparison to INTEX-B data in Figure 8 and in the fourth paragraph on page 11.

The authors are mistaken that Young et al. 2012 only repeated the data of Mielke et al., 2013. The Young et al., paper, and it turns out Wagner et al., 2012, also have vertical profiles from the NOAA WP3 measurements that were part of CalNex 2010. Again, the whole data set is available: <https://www.esrl.noaa.gov/csd/projects/calnex/>.

There is no chlorine measurement available to public from the NOAA WP3 measurements during CalNex 2010 (<https://esrl.noaa.gov/csd/groups/csd7/measurements/2010calnex/P3/datainfo.html>). We do not include this dataset.

Reviewer #2

The authors have thoughtfully modified the manuscript to address many of the comments received during the review. There remain three sections that should be addressed prior to publication.

Page 11, Line 29

The authors have chosen to retain the $\Phi(\text{ClNO}_2)$ parameterization based on previous laboratory results. The authors state that agreement of resulting simulated ClNO_2 with WINTER observations is in contrast with previous results (McDuffie et al., 2018a; Riedel et al., 2013; Wagner et al., 2013), that have shown the Bertram and Thornton (2009) parameterization over-predicts ClNO_2 production. Two minor points, 1) the cited references report that the *yield of ClNO_2* ($\Phi(\text{ClNO}_2)$) is over-predicted by the parameterization, not necessarily the absolute amount of ClNO_2 , 2) only McDuffie et al., 2018a (ClNO_2 yields) should be cited here as McDuffie et al., 2018b only reports $\gamma(\text{N}_2\text{O}_5)$ results from WINTER.

We now clarify these points on page 11 line 35 – page 12 line 2.

My bigger concern is that the authors have not sufficiently discussed the extent of the disagreement that exists in the literature between field and laboratory-derived Φ (CINO₂) results. I want to reiterate that while all laboratory-based studies have reported similar parameterizations of Φ (CINO₂) (Behnke et al., 1997; Bertram & Thornton, 2009; Roberts et al., 2009; Ryder et al., 2015), *every single* field study has shown that this Φ (CINO₂) parameterization over-predicts Φ (CINO₂) on ambient aerosol (see references in my initial review). There is currently no consensus on the source of this disagreement. In this analysis, it remains concerning that the authors have chosen to implement a parameterization that has been repeatedly shown to disagree with field results, especially without providing sufficient recognition of this disagreement or sufficient motivation for its inclusion.

As already stated in our last response, although our parameterization of N₂O₅ uptake on SNA is based on Bertram and Thornton, (2009), our simulation of N₂O₅ uptake and CINO₂ yield also combines the uptake on other aerosols. By assuming externally mixing of aerosol types when doing N₂O₅ uptake, the overall N₂O₅ uptake rate and CINO₂ yield on all aerosols are different from Bertram and Thornton, (2009). The mean CINO₂ yield below 1 km in our model is 0.20 during WINTER campaign. This agrees with the field results of McDuffie et al., (2018a) (0.218). We now edit the text in the first paragraph on page 12 and add a note in the footnote in Table 2 to make it clearer.

Page 11, Line 33

The added discussion of γ (N₂O₅) and Φ (CINO₂) results from (McDuffie et al., 2018a; McDuffie et al., 2018b) is useful here as these values were derived for the same campaign that is used to evaluate the model performance here. First, it would be better, in my opinion, to recognize the uncertainty in the γ (N₂O₅) parameterization (as the authors have done), but then cite the γ (N₂O₅) agreement between GEOS-Chem and the McDuffie et al. (2018b) box model that was previously presented in Jaeglé et al. (2018). As the authors have noted in their response, the γ (N₂O₅) parameterization is the same here in Jaeglé et al. (2018) (though the particle chloride concentrations were calculated differently and Jaeglé et al. (2018)/Shah et al. (2018) also updated the organic aerosol uptake coefficient), so the reported agreement in γ (N₂O₅) could help to validate the γ (N₂O₅) calculation here.

We now cite Jaeglé et al. (2018) and edit the text in the first paragraph on page 12 to make our comparison clearer.

My second comment is that the discussion of mixing state and chloride distributions across different aerosol types does not explain the overestimation of γ (N₂O₅) or Φ (CINO₂) by Bertram and Thornton (2009) parameterization that was reported by (McDuffie et al., 2018a; McDuffie et al., 2018b), nor does it help validate their use here. For instance, since the γ (N₂O₅) and Φ (CINO₂) parameterizations do not explicitly account of organic aerosol concentrations, γ (N₂O₅) and Φ (CINO₂) would only be lower here relative to the McDuffie

results if there were additional organic-associated chloride that was not being accounted for in GEOS-Chem by the assumption that chloride is only present in the SSA and SNA aerosol types. In addition, the authors may be further complicating this discussion by introducing the concept of mixing state because Bertram and Thornton (2009) explicitly state that their parameterization was ‘designed to address an internally mixed particle population’ (granted, SNA particles are assumed internally mixed in GEOS-Chem). Rather than discussing mixing state assumptions, I suggest simply citing and Jaeglé et al. (2018) to validate the $\gamma(\text{N}_2\text{O}_5)$ parameterization as described above.

The discussion of mixing state is not used for explaining the overestimation of N_2O_5 or ClNO_2 by Bertram and Thornton (2009) parameterization. We include the discussion of mixing state to state that our model parametrization of N_2O_5 uptake on all aerosols is different from Bertram and Thornton (2009) parameterization. We agree with the reviewer regarding the overestimation of Bertram and Thornton (2009) parameterization. We have edited the text in the first paragraph on page 12 to make this clearer.

Page 12, line 9 –

The discussion of the $\text{ClNO}_2 + \text{Cl}^- \rightarrow \text{Cl}_2$ reaction has greatly improved with the addition of the sensitivity test where R7 is removed. May I also suggest citing Fickert et al. (1998), Schweitzer et al. (1998), and Frenzel et al. (1998) who report ClNO_2 uptake coefficients for similar reactions with Br^- and I^- that are ~ 2 orders of magnitude lower than coefficients presented in Roberts et al. (2008). This could help to provide additional context for the magnitude of direct ClNO_2 uptake/reactions.

We add a sentence and cite these references on page 12, line 22-24.

Minor Comments:

Page 7, line 7/8: Add reference to Roberts et al. (2008).

I would also suggest changing this sentence to: “The heterogeneous uptake of HOBr , HOCl , and ClNO_2 , and further aqueous-phase reaction with Cl^- has been shown to be pH-dependent, with a higher efficiency in acidic solutions.

We have referenced Roberts et al. (2008) and changed this sentence following the reviewer’s suggestion.

Page 7, line 8/9 -

Change to: “They are considered... , and the reaction of $\text{ClNO}_2 + \text{Cl}^-$ further requires $\text{pH} < 2$, following laboratory results presented in Roberts et al. (2008).”

Changed.

Page 9, line 25 –

remove the extra period at the end of the sentence.

Removed.

Page 10, line 25 –

Change to: “...by an Iodide, Time of Flight, Chemical Ionization Mass Spectrometer (I-TOF-CIMS).

Changed.

Line 14 –

Suggest adding: “... is opposite of the trend expected from (R7), though there may be no trend on sufficiently acidic (i.e., pH < 2) aerosol.

Added.

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). Here we present a
8 more comprehensive analysis of this chemistry within the framework of the GEOS-Chem chemical transport model
9 (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 (Yang
31 et al., 2005; Saiz-Lopez et al., 2014). Interest in global modeling of tropospheric chlorine has focused principally on
32 quantifying the Cl atom concentration as a sink for methane (Keene et al., 1990; Singh et al., 1996). Previous global
33 3-D models found mean tropospheric Cl atom concentrations of the order of 10^3 cm^{-3} , with values up to 10^4 cm^{-3} in
34 the marine boundary layer (MBL), and contributing 2-3% of atmospheric methane oxidation (Long et al., 2014;
35 Hossaini et al., 2016; Sherwen et al., 2016b; Schmidt et al., 2016). A regional modeling study by Sarwar et al. (2014)

1 included ClNO₂ chemistry in a standard ozone mechanism and found increases in surface ozone mixing ratios over
2 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 (0.2-1 μm
11 diameter) and coarse (1-8 μm 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 Tg a^{-1} for 2016, corresponding to $1780 \text{ Tg a}^{-1} \text{ Cl}^-$
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 $64 \text{ Tg Cl}^- \text{ a}^{-1}$ (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 (60-90°N, 30-60°N, 0-
26 30°N, 0-30°S, and 30-90°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 Tg Cl a^{-1} in Table 1, smaller than that from heterogeneous SSA Cl^- reactions ($11.9 \text{ Tg Cl a}^{-1}$) or
32 oxidation of HCl by OH (9.7 Tg Cl a^{-1}). The stratosphere is a minor global source of tropospheric Cl^* ($0.06 \text{ Tg Cl a}^{-1}$)
33 although it could be important in the upper troposphere (Schmidt et al., 2016).

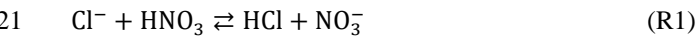
1 We also include primary HCl emissions from open fires. We apply the emission factors of (HCl + Cl⁻) from Lobert et
2 al. (1999) for different vegetation types to the GFED4 (Global Fire Emissions Database) biomass burned inventory
3 (van der Werf et al., 2010; Giglio et al., 2013), resulting in a global 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 heterogeneous uptake of HOBr, HOCl, and ClNO₂ as well as further aqueous-phase reaction with Cl⁻ in Table 2
8 are pH-dependent, with a higher efficiency in acidic solutions (Fickert et al., 1999; Roberts et al., 2008; Abbatt et al.,
9 2012). They are considered only when SSA alkalinity has been titrated, and ClNO₂ + Cl⁻ further requires pH < 2,
10 following laboratory results presented in Roberts et al. (2008). The pH of chloride-containing fine aerosol after
11 alkalinity has been titrated is calculated by ISORROPIA II. Liquid cloud water pH is calculated in GEOS-Chem
12 following Alexander et al. (2012), with update to include Cl⁻ and NVC. Coarse-mode SSA and ice cloud pH are
13 assumed to be 5 and 4.5 respectively (Schmidt et al., 2016).

14 3 Global budget and distribution of tropospheric chlorine

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

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

31 Conversion of Cl to ClO* drives some cycling of chlorine radicals, but the associated chain length versus Cl* loss is
32 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

1 ClO back to Cl is mostly by reaction with NO (72%), driving a null cycle as NO₂ photolyzes to regenerate NO and
2 ozone.

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

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

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

30 **4 Comparison to observations**

31 Here we compare the model simulation for 2016 to observations for gas-phase chlorine and related species collected
32 in different years, assuming interannual variability to be a minor factor in model error. Previous evaluation of the
33 GEOS-Chem sea salt source by Jaeglé et al. (2011) showed general skill in simulating SSA observations and we do

1 not repeat this evaluation here. We also do not consider data affected by local anthropogenic sources because they
2 would not be properly resolved at the $4^{\circ} \times 5^{\circ}$ grid resolution of our model.

3 **4.1 Surface air observations**

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

12 Figure 4 compares simulated HCl and HNO_3 mixing ratios to concurrent observations of both gases at coastal sites
13 and over oceans. The data are arranged from left to right by increasing latitude. Mean HCl mixing ratios average 323
14 ppt in the model and 347 ppt in the observations for the ensemble of regions. The HCl source in the model is mainly
15 acid displacement from SSA. A sensitivity simulation without acid displacement from SSA has less than 7 ppt HCl
16 in all regions. The model captures the spatial variability of the mean HCl mixing ratios across locations ($r = 0.88$),
17 which largely reflects the HCl enhancement at polluted coastal sites and northern mid-latitudes (Figure 2). Simulated
18 HNO_3 mixing ratios average 190 ppt across locations as compared to 137 ppt in the observations, again with good
19 simulation of spatial variability ($r = 0.96$) driven by NO_x emissions. HNO_3 mixing ratios are sensitive to acid
20 displacement from SSA, as the sensitivity simulation without acid displacement shows mean values of 441 ppt that
21 are much higher than observed. This could partly explain the general model problem of HNO_3 overestimation in
22 remote air (Bey et al., 2001).

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

33 A number of surface air measurements have been made of Cl^* as the water-soluble component of Cl_y after removal of
34 HCl (Keene et al., 1990), although most of these measurements are below the detection limit (Table 4, mostly from

1 Keene et al. (2009)). This Cl* has been commonly assumed to represent the sum of Cl₂ and HOCl (Pszenny et al.,
2 1993) but it would also include ClNO₂, ClNO₃, and minor components of Cl*. Table 4 shows that simulated Cl* mixing
3 ratios are consistent with the measurements to the extent that comparison is possible. Simulated Cl* over remote
4 oceans is dominated by HOCl, but ClNO₂ is responsible for the high values over the Atlantic Ocean near Europe.

5 Lawler et al. (2009) measured Cl₂ and BrCl mixing ratios at Cape Verde in the tropical Atlantic for 5 days in May-
6 June 2007, and Lawler et al. (2011) measured Cl₂ and HOCl mixing ratios at the same site for 7 days in May-June
7 2009. The observations show a diurnal cycle with mixing ratios of Cl₂ highest at night, and HOCl highest in the day,
8 consistent with the model. Observed mixing ratios in background marine air are in the range 0-30 ppt for Cl₂ and 0-2
9 ppt for BrCl at night, and 0-5 ppt for HOCl in the daytime. Corresponding mean model values are 0.3 ppt for Cl₂, 1.8
10 ppt for BrCl, and 5 ppt for HOCl, with little day-to-day variability. Lawler et al. (2011) also sampled long-range
11 outflow from Europe for 3 days in 2009 with daytime HOCl and nighttime Cl₂ mixing ratio ranges of 40-200 ppt and
12 5-40 ppt respectively but the model does not capture these enhancements. Sommariva and von Glasow (2012)
13 suggested that a lower aerosol pH and/or slower rate for HOCl + Cl⁻ could explain the high HOCl in European outflow
14 but this would also cause Cl₂ to be lower. We have no explanation for the high Cl₂ values observed by Lawler et al.
15 (2009, 2011) in marine air or for the joint observed enhancements of HOCl and Cl₂ in European outflow.

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

25 **4.2 Comparison to aircraft measurements**

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

1 Figure 6 compares the observed median vertical profiles of HCl, ClNO₂, HOCl, and Cl₂ in WINTER to the model
2 sampled along the flight tracks for the corresponding period. Figure 7 compares the median diurnal variations below
3 1 km altitude, separately over ocean and land. We exclude daytime (10:00-16:00 local) data for ClNO₂ in Figure 6
4 because its mixing ratios are near-zero (Figure 7).

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

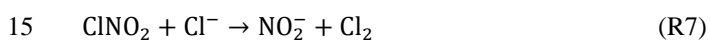
10 Also shown in Figure 6 is a sensitivity simulation including anthropogenic HCl emissions from McCulloch et al. (1999)
11 as described in Section 2.2. The resulting model mixing ratios are too high though still within the calibration
12 uncertainty. Based on sampling of power plant plumes during WINTER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

18 Figure 8 compares the model HCl vertical profiles to measurements by the Georgia Tech CIMS instrument during the
19 SEAC⁴RS campaign over the Southeast US in August-September 2013 (Toon et al., 2016), the KORUS-AQ campaign
20 over and around the Korea peninsula in May-June 2015, and the INTEX-B campaign over the North Pacific in May
21 2006 (Kim et al., 2008). The standard model simulation without anthropogenic chlorine successfully simulates the
22 boundary layer HCl observations during SEAC⁴RS and KORUS-AQ, but adding the McCulloch et al. (1999)
23 anthropogenic inventory results in large overestimates. Boundary layer HCl mixing ratios over land are much lower
24 in SEAC⁴RS than in WINTER and this is well reproduced by the model, where the difference is due to seasonal
25 contrast in the SSA source and in the inflow of marine air. The free tropospheric background observed in SEAC⁴RS,
26 KORUS-AQ, and INTEX-B data is only ~25 ppt, much lower than in WINTER (100-200 ppt), whereas the model
27 free tropospheric background is consistently 20-50 ppt in all four campaigns. The WINTER observations are near
28 their 100 ppt detection limit as pointed out above. Modeled vertical profile of HCl during INTEX-B is very similar to
29 that of KORUS-AQ, but overestimates observed boundary layer HCl by a factor of 5. The median value of observed
30 surface HCl mixing ratio is 24 ppt during INTEX-B, which is much lower than all the surface air observations in
31 Section 4.1.

32 Mixing ratios of ClNO₂ observed in WINTER are above the detection limit only in the lowest km of atmosphere at
33 night, and are much higher over the ocean than over land. This is well simulated by the model (Figures 6 and 7), and
34 reflects the nighttime source from the N₂O₅ + Cl⁻ heterogeneous reaction from the combined with the fast loss by
35 photolysis in daytime. Previous studies have suggested that the Bertram and Thornton (2009) representation of the

1 ClNO₂ production yield from the N₂O₅ + Cl⁻ heterogeneous reaction in Table 2 is too high (Riedel et al., 2013; Wagner
2 et al., 2013; McDuffie et al., 2018a). By using a box model applied to the WINTER observations, McDuffie et al.
3 (2018a;b) found that both the N₂O₅ uptake rate and the ClNO₂ production yield were overestimated by the Bertram
4 and Thornton (2009) parameterization. One important difference with these previous studies is the assumption of
5 aerosol mixing state. GEOS-Chem assumes that Cl⁻ is present only in SNA and SSA when doing the calculation of
6 N₂O₅ reactive uptake rates, assuming an external mixture of aerosol types (Martin et al., 2003; Evans and Jacob, 2005;
7 Jaeglé et al., 2018). This decreases both the N₂O₅ uptake rate and the ClNO₂ yield as compared to using the
8 parameterization of Bertram and Thornton (2009) on internally mixed aerosols. Jaeglé et al. (2018) reported that using
9 this external mixing assumption leads to good agreement between modeled and observed N₂O₅ during WINTER
10 campaign. The mean ClNO₂ yield (ϕ in R3) below 1 km in our model is 0.20 during the WINTER campaign, very
11 close to that calculated from observation (0.218) by McDuffie et al., (2018a).

12
13 Nighttime Cl₂ mixing ratios in WINTER are greatly overestimated by the model. Under polluted wintertime conditions
14 such as in WINTER the ClNO₂ + Cl⁻ reaction greatly enhances Cl₂ production in the model:



16 The reactive uptake coefficient for (R7) in Table 2 is based on a single laboratory study (Roberts et al., 2008). It
17 requires an aerosol pH < 2 and this condition is generally met for our model simulation of the WINTER environment,
18 consistent with the observation-based analysis of aerosol pH by Guo et al. (2016) for the eastern US in winter. A
19 sensitivity simulation without (R7) is shown as dashed red lines in Figure 7 and can reproduce the low Cl₂ mixing
20 ratios observed over the ocean at night. The analysis of WINTER data by McDuffie et al. (2018b) finds that the
21 correlation between particle acidity and Cl₂ observations is opposite of the trend expected from (R7), though there
22 may be no trend on sufficiently acidic (i.e. pH < 2) aerosol. Further study of that reaction is needed. Similar reactions
23 such as ClNO₂ + Br⁻ (R8) and ClNO₂ + I⁻ are also very uncertain as their reaction rate coefficients are very different
24 in different studies (Fickert et al., 1998; Frenzel et al., 1998; Schweitzer et al., 1998).

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

1 **5 Global implications of tropospheric chlorine chemistry**

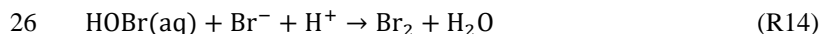
2 **5.1 Cl atom and its impact on VOCs**

3 The global mean pressure-weighted tropospheric Cl atom concentration in our simulation is 620 cm^{-3} , while the MBL
4 concentration averages 1200 cm^{-3} (Figure 2). Our global mean is lower than the previous global model studies of
5 Hossaini et al. (2016) (1300 cm^{-3}) and Long et al. (2014) (3000 cm^{-3}), which had excessive Cl* generation as discussed
6 above. It is consistent with the upper limit of 1000 cm^{-3} inferred by Singh et al. (1996) from global modeling of C_2Cl_4
7 observations (C_2Cl_4 is highly reactive with Cl atoms). Isotopic observations of methane have been used to infer a Cl
8 atom concentration in the MBL higher than 9000 cm^{-3} in the extra-tropical Southern Hemisphere (Platt et al., 2004;
9 Allan et al., 2007), much higher than our estimate of 800 cm^{-3} over this region. More recently, Gromov et al. (2018)
10 revisited these data together with added constraints from CO isotope measurements and concluded that extra-tropical
11 Southern Hemisphere concentrations of Cl atoms in the MBL should be lower than 900 cm^{-3} , consistent with our
12 estimate.

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

16 **5.2 Impact on bromine and iodine chemistry**

17 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
18 depleting ozone and OH (Parrella et al., 2012; Sherwen et al., 2016b). Br atoms are also thought to drive the oxidation
19 of elemental mercury (Holmes et al., 2006). Chlorine chemistry increases IO_x mixing ratios by 16% due to the
20 reactions of HOI, INO_2 , and INO_3 with Cl (R11-R13), producing ICl which photolyzes rapidly to I atoms (Figure 1).
21 The effect on bromine is more complicated. Bromine radicals originate from photolysis and oxidation of
22 organobromines emitted by the ocean, as well as from SSA debromination (Yang et al., 2005). They are lost by
23 conversion to HBr which is efficiently deposited. Parrella et al. (2012) pointed out that heterogeneous chemistry of
24 HBr (dissolved as Br) is critical for recycling bromine radicals and explaining observed tropospheric BrO mixing
25 ratios in the background troposphere:



28 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
29 et al., 2017):



32 Chen et al. (2017) pointed out that reaction (R16) effectively decreases BrO mixing ratios by producing HBr which is
33 rapidly deposited instead of contributing to BrO_x cycling. They found in a GEOS-Chem simulation that global

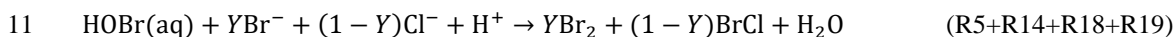
1 tropospheric BrO mixing ratios decreased by a factor of 2 as a result. Reaction (R5) may however have a compensating
2 or opposite effect. It propagates the cycling of BrO_x if BrCl volatilizes:



4 but it may also generate new BrO_x if BrCl reacts with Br⁻ in the aqueous phase to produce Br₂ (Wang et al., 1994):



7 The sequence (R5) + (R18) + (R19) with Cl⁻ as a catalyst has the same stoichiometry as (R14) and thus contributes to
8 HBr recycling in the same way. We find in the model that it is globally 30 times faster than (R14) and therefore much
9 more effective at regenerating bromine radicals. In GEOS-Chem, the rate of reaction (R5) computed from Table 2 is
10 applied to the following stoichiometry reflecting the ensemble of reactions (R5, R14, R18, and R19):



12 where Y is the yield of Br₂ and $1 - Y$ is the yield of BrCl. Y is calculated following the laboratory study of Fickert et al.
13 (1999):

$$14 \quad Y = 0.41 \log_{10}([\text{Br}^-]/[\text{Cl}^-]) + 2.25 \quad \text{for } [\text{Br}^-]/[\text{Cl}^-] < 5 \times 10^{-4} \quad (2)$$

$$15 \quad Y = 0.90 \quad \text{for } [\text{Br}^-]/[\text{Cl}^-] > 5 \times 10^{-4} \quad (3)$$

16 This mechanism was first included in GEOS-Chem version 11-02d by Chen et al. (2017), who did not however have
17 an explicit SSA Cl⁻ simulation (they instead assumed a fixed SSA [Cl⁻] = 0.5 M, and considered only dissolved HCl
18 in cloud).

19 Chen et al. (2017) found in their GEOS-Chem simulation that the global tropospheric BrO burden was 8.7 Gg without
20 the HOBr + S(IV) reaction (R16), and dropped to 3.6 Gg when that reaction was included. Previous GEOS-Chem
21 model estimates of the global tropospheric BrO burden were 3.8 Gg (Parrella et al., 2012), 5.7 Gg (Schmidt et al.,
22 2016), and 6.4 Gg (Sherwen et al., 2016b). Our simulation features many updates relative to Chen et al. (2017)
23 including not only explicit SSA Cl⁻ but also explicit calculation of aerosol pH with ISORROPIA II for the rates of
24 reactions in Table 2. By including explicit SSA Cl⁻, the cloudwater [Cl⁻] in our model is much higher than that in Chen
25 et al. (2017) and more comparable to measurements (~10⁻⁴ M in typical cloud; (Straub et al., 2007)). We find in our
26 standard simulation a global tropospheric BrO burden of 4.2 Gg, 17% higher than Chen et al. (2017).

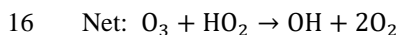
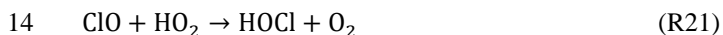
27 Figure 9 shows the change of surface BrO mixing ratios due specifically to tropospheric chlorine chemistry, as
28 obtained by difference with a sensitivity simulation including none of the Cl_y chemistry shown in Figure 1. The
29 inclusion of chlorine chemistry increases the global tropospheric BrO burden by 85%. More than 80% of this change
30 is caused by the HOBr + Cl⁻ reaction as discussed above. Other significant contributions include ClNO₃ + Br⁻ and

1 ClNO₂ + Br⁻. The largest BrO increases (1-2 ppt) are in surface air over the high northern latitudes oceans where SSA
2 emissions are high and acidic conditions promote HOBr + Cl⁻ chemistry.

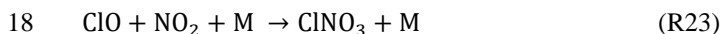
3 **5.3 Impact on tropospheric ozone and OH**

4 Figure 9 also shows the effects of chlorine chemistry on NO_x, OH, and ozone concentrations. The global tropospheric
5 burdens decrease by 5% for NO_x, 3% for OH, and 7% for ozone. The inter-hemispheric (N/S) ratio of tropospheric
6 mean OH decreases from 1.14 to 1.12. Models tend to overestimate global mean tropospheric OH and its inter-
7 hemispheric ratio relative to the constraint from methylchloroform which suggests a ratio of 0.85-0.98 (Naik et al.,
8 2013; Voulgarakis et al., 2013). The effect of chlorine chemistry on the N/S ratio is slight but in the right direction.

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



17 and also loss of NO_x:



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

22
23 A particular situation arises over polluted continents due to ClNO₂ chemistry. Production of ClNO₂ at night from the
24 N₂O₅ + Cl⁻ heterogeneous reaction, followed by photolysis in the morning to release Cl and NO₂, provides a source of
25 radicals and ozone. This explains the increases of OH over North America and Europe in Figure 9. The effect is most
26 important at high northern latitudes in winter due to the longer night. To isolate the impact on ozone we conducted a
27 sensitivity simulation with no ClNO₂ production, setting φ = 0 for reaction (R3) in Table 2. The surface air ozone
28 enhancement due to ClNO₂ chemistry is found to be the largest (~8 ppb) in European winter, due to the large supply
29 of Cl⁻ from the North Atlantic combined with high NO_x emissions. Other polluted continents see ozone increases of
30 1-5 ppb in winter. The effect in summer is less than 1 ppb. These results are similar to previous regional modeling
31 studies by Sarwar et al. (2014) and Sherwen et al. (2017).

32

1 Figure S1 shows the differences of BrO, NO_x, OH, and ozone concentrations between our model and the standard
2 GEOS-Chem model version 11-02d including SSA debromination. Our explicit treatment of chlorine chemistry and
3 thermodynamic representation of aerosol pH increases the global tropospheric BrO burden by 40%. Most of this
4 change is caused by faster HOBr + Cl⁻ reaction at high latitudes, resulting from higher Cl⁻ concentration in our model
5 particularly in cloud. The decrease of BrO in the tropical MBL is caused by an increase in aerosol pH (pH was
6 previously assumed to be 0 for computation of bromine chemistry), which slows down the acid-catalyzed recycling
7 of bromine by reactions (R5) and (R14). Our computed global tropospheric burdens decrease by 4% for NO_x, 2% for
8 OH, and 4% for ozone relative to version 11-02d, again due to the more active bromine chemistry. The increase of
9 OH over continental regions is due to our accounting of HCl dissolved in SNA aerosol, allowing marine influence to
10 extend further inland to drive ClNO₂ chemistry.

11 **6 Conclusions**

12 We have added to the GEOS-Chem model a comprehensive and consistent representation of tropospheric chlorine
13 chemistry. This includes in particular explicit accounting of the mobilization of sea salt aerosol (SSA) chloride (Cl⁻),
14 by acid displacement of HCl as well as by other heterogeneous processes. Cycling of inorganic gas-phase chlorine
15 species (Cl_y) generated from SSA and other sources is simulated and coupled to the model aerosol-oxidant-bromine-
16 iodine chemistry. With our work, GEOS-Chem now has a complete simulation of halogen (Cl+Br+I) chemistry in
17 both the troposphere and stratosphere.

18 Emission of chlorine in the model is mainly as sea-salt aerosol (1780 Tg Cl a⁻¹). Other sources (combustion,
19 organochlorines, stratospheric input) are also included but are small in comparison. Most of the sea-salt aerosol
20 chloride is removed by deposition, but 3.6% is mobilized to inorganic gas-phase chlorine (Cl_y) through acid
21 displacement to HCl (52 Tg a⁻¹) and through other heterogeneous chemistry producing more reactive chlorine species
22 (12 Tg a⁻¹). We define reactive chlorine (Cl*) as the ensemble of Cl_y species excluding HCl and including Cl, ClO,
23 Cl₂, BrCl, HOCl, ClNO₂, ClNO₃, plus other minor species. Oxidation of HCl by OH provides a Cl* source of 9.7 Tg
24 a⁻¹, comparable to the heterogeneous source from HOBr + Cl⁻ (8.6 Tg a⁻¹). N₂O₅ + Cl⁻ (1.8 Tg a⁻¹) is also important
25 in polluted environments. Cycling between Cl* species drives radical chlorine (Cl/ClO) chemistry but chain lengths
26 are limited by fast conversion to HCl and subsequent deposition.

27 HCl mixing ratios in the model are highest over the oceans downwind of polluted continents due to effective acid
28 displacement from sea-salt aerosol by HNO₃ and H₂SO₄. Mixing ratios are much lower over the Southern Ocean where
29 the supply of acids is low. The dominant daytime Cl* species is generally HOCl while BrCl, Cl₂, and ClNO₂ dominate
30 at night. ClNO₃ dominates in the upper troposphere due to stratospheric input. Chlorine atom concentrations are
31 highest over Europe in winter due to ClNO₂ chemistry, and are otherwise high over the northern mid-latitudes oceans
32 where the supply of acidity promotes Cl formation both through HCl and through acid-catalyzed heterogeneous
33 processes.

1 Comparison of model results to observations in marine surface air show that the model is usually able to reproduce
2 the range and distributions of observed sea-salt aerosol chloride deficits, HCl mixing ratios, and Cl* mixing ratios. In
3 particular, concurrent observations of HCl and HNO₃ in coastal/marine air worldwide show high correlation with the
4 model including high HCl mixing ratios at northern mid-latitudes combined with depressed HNO₃. Consideration of
5 acid displacement greatly improves model agreement with HNO₃ observations in marine air. The model can also
6 successfully simulate observations of high ClNO₂ at night including in continental air. The chlorine in that case
7 originates from sea-salt aerosol transported far inland following uptake of volatilized HCl by sulfate-nitrate-
8 ammonium (SNA) aerosol. The model cannot reproduce the very high HOCl and Cl₂ concentrations observed by
9 Lawler et al. (2009;2011) at Cape Verde in the tropical Atlantic.

10 Comparisons of model results to aircraft campaign observations from WINTER (eastern US and offshore, Feb-Mar
11 2015), SEAC⁴RS (Southeast US, Aug-Sep 2013), and KORUS-AQ (Korean Peninsula, April-Jun 2016) show general
12 consistency for HCl vertical profiles. Continental boundary layer HCl mixing ratios in these campaigns can be mostly
13 accounted for by the marine source transported inland, though power plants could make a minor contribution.
14 WINTER observations also include ClNO₂ and Cl₂, and HOCl. The observed ClNO₂ is mainly confined to the
15 nighttime marine boundary layer and is consistent with the model. Observed Cl₂ concentrations at night are much
16 lower than the model, which has a large source under the WINTER conditions from the ClNO₂ + Cl⁻ heterogeneous
17 reaction. The rate coefficient for this reaction is from only one laboratory study.

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

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

32 **Data availability.** The model code is available from the corresponding author upon request, and will be made available
33 to the community through the standard GEOS-Chem (<http://www.geos-chem.org>) in the future. Data of WINTER
34 campaign are available to the general public at https://www.eol.ucar.edu/field_projects/winter. Data of NASA
35 SEAC⁴RS AND KORUS-AQ missions and are available to the general public through the NASA data archive

1 (<https://www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs> and <https://www-air.larc.nasa.gov/cgi->
2 [bin/ArcView/korusaq](https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq)). IMPROVE data are available through the Federal Land Manager Environmental database
3 (<http://views.cira.colostate.edu/fed>).

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

8 ^c $\text{IONO}_x \equiv \text{IONO} + \text{IONO}$

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 ^bBertram and Thornton (2009); Roberts et al. (2009). This parametrization is only applied for SNA and SSA aerosols. For N_2O_5
7 uptake on other aerosols, we assume $\varphi = 0$ and follow Jaeglé et al., (2018).
8 ^cKnipping and Dabdub (2002)
9 ^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
10 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.
11 (1999), as described in Section 5.2.
12 ^eAssumes that Cl^- is present in excess so that γ does not depend on $[\text{Cl}^-]$. However, R6 competes with the heterogeneous
13 reaction $\text{ClNO}_3 + \text{Br}^-$ as given by Schmidt et al. (2016), with the branching ratio determined by the relative rates.
14 ^fThese reactions are based on Sherwen et al. (2016a) and only take place in SSA.
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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

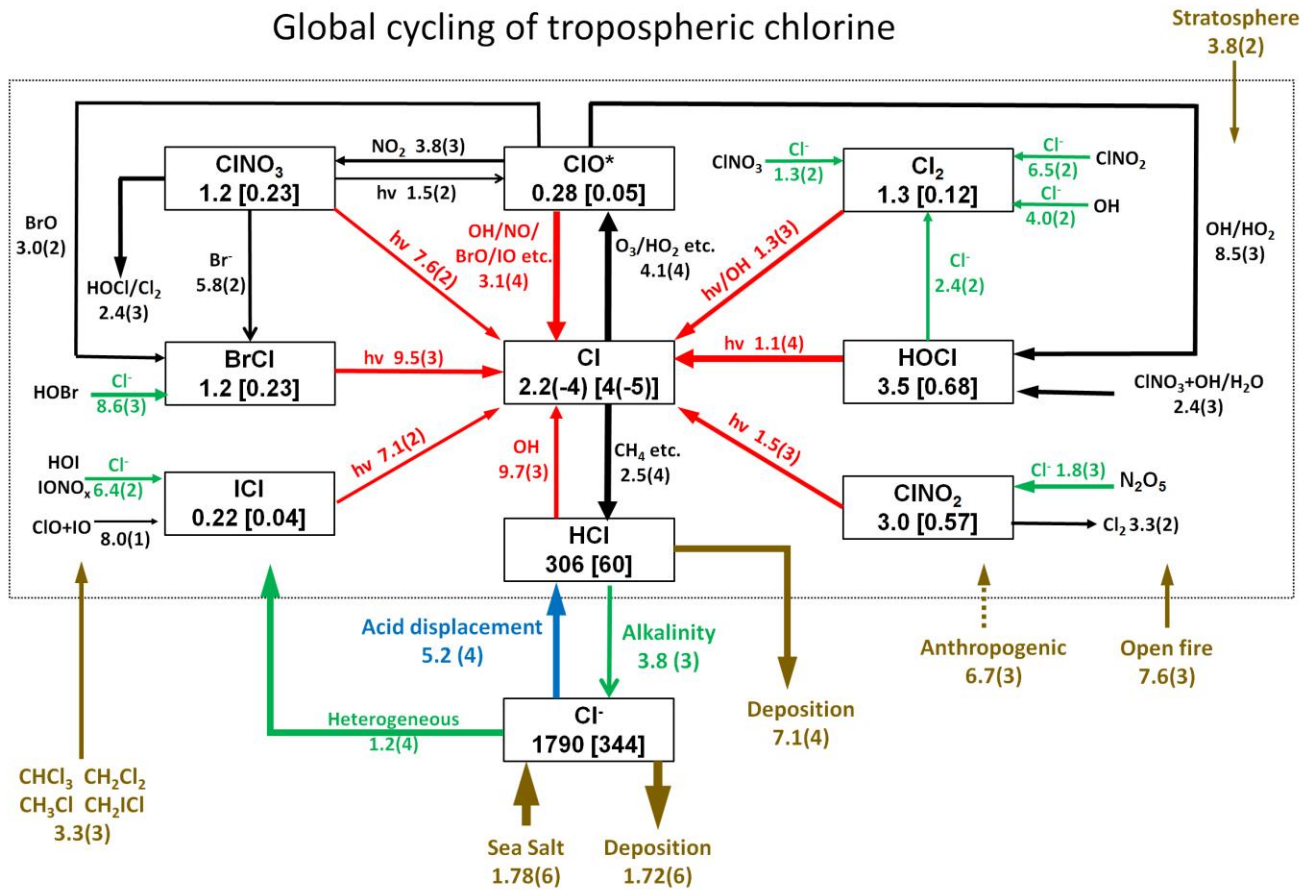
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1 **Table 5: Comparison of modeled maximum CINO₂ mixing ratios to surface observations ^a**

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.
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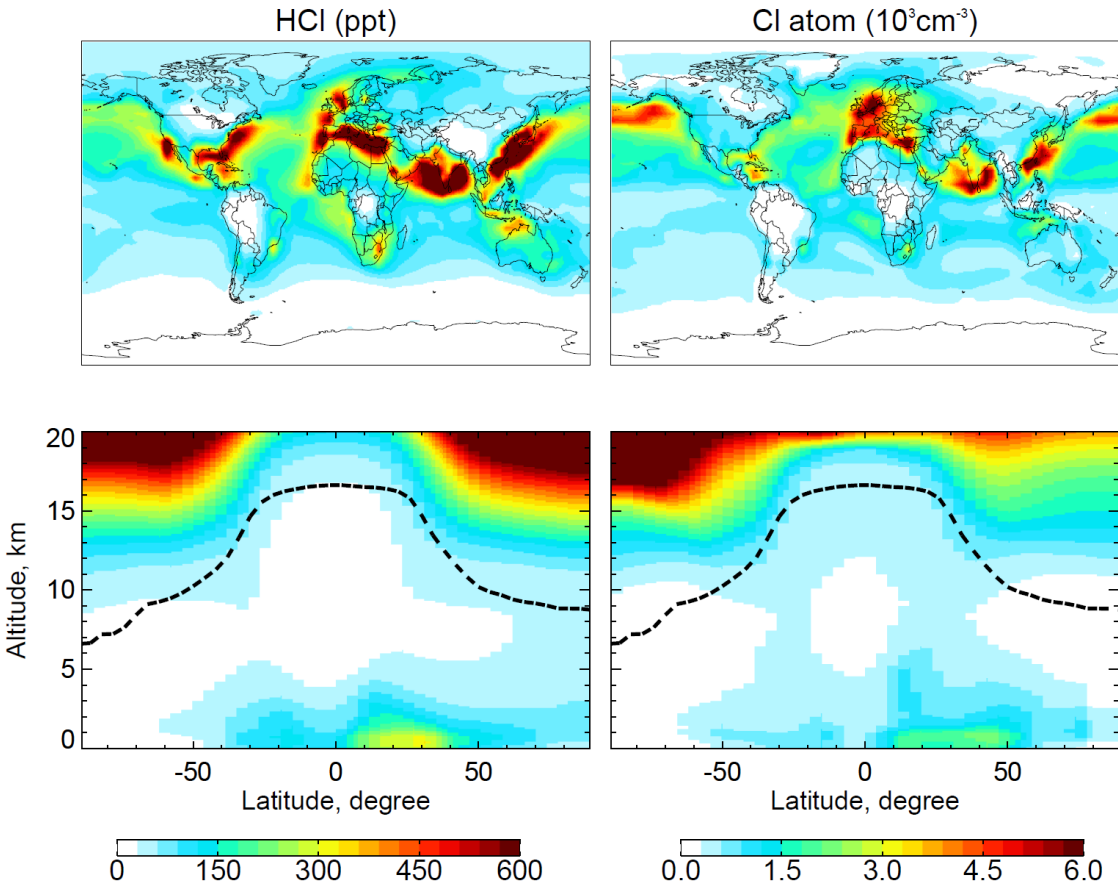
Global cycling of tropospheric chlorine



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Figure 1: Global budget and cycling of tropospheric inorganic chlorine (Cl_y) in GEOS-Chem. The figure shows global annual mean rates (Gg Cl a^{-1}), masses (Gg), and mixing ratios (ppt, in brackets) for simulation year 2016. Read 2.5(4) as 2.5×10^4 . ClO^* stands for $\text{ClO} + \text{OCIO} + \text{ClO}_2 + 2 \times \text{Cl}_2\text{O}_2$; 84% is present as ClO . Reactions producing Cl atoms and related to Cl^- heterogeneous chemistry are shown in red and green, respectively. The dotted box indicates the Cl_y family, and arrows into and out of that box represent general sources and sinks of Cl_y . Reactions with rate < 100 Gg Cl a^{-1} are not shown. Anthropogenic emissions of HCl as indicated by a dashed line are only included in a sensitivity simulation (see Section 2.2 and 4.2 for details).

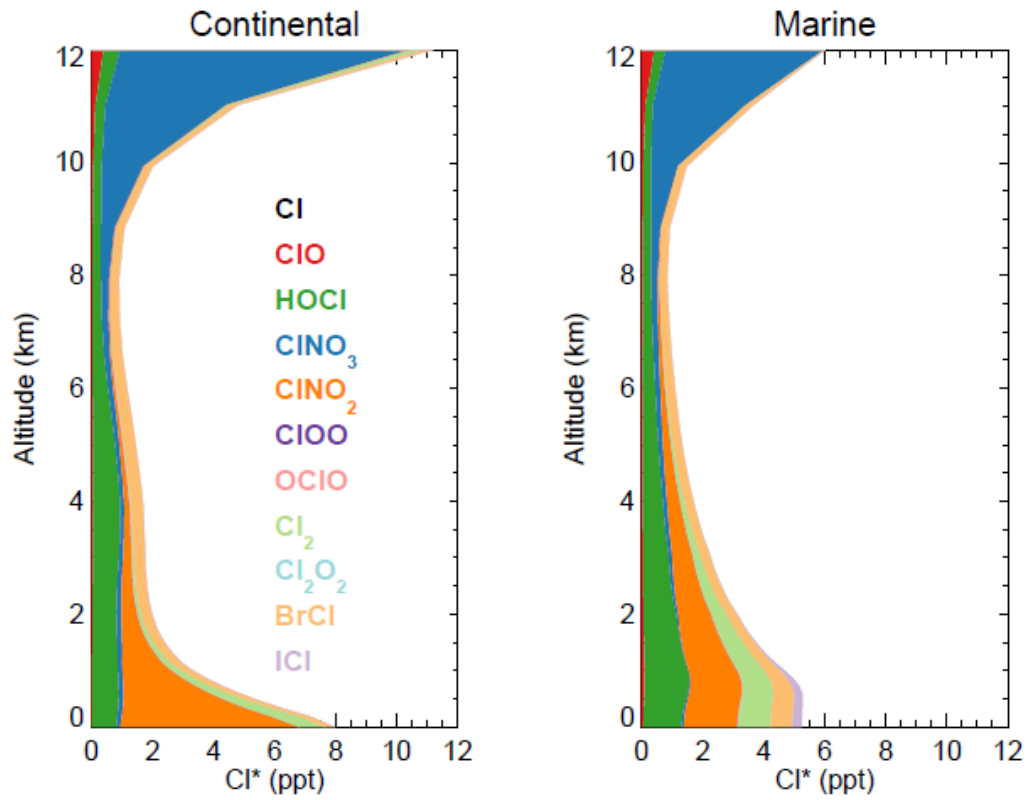
Surface and zonal mean HCl mixing ratios and Cl atom concentrations



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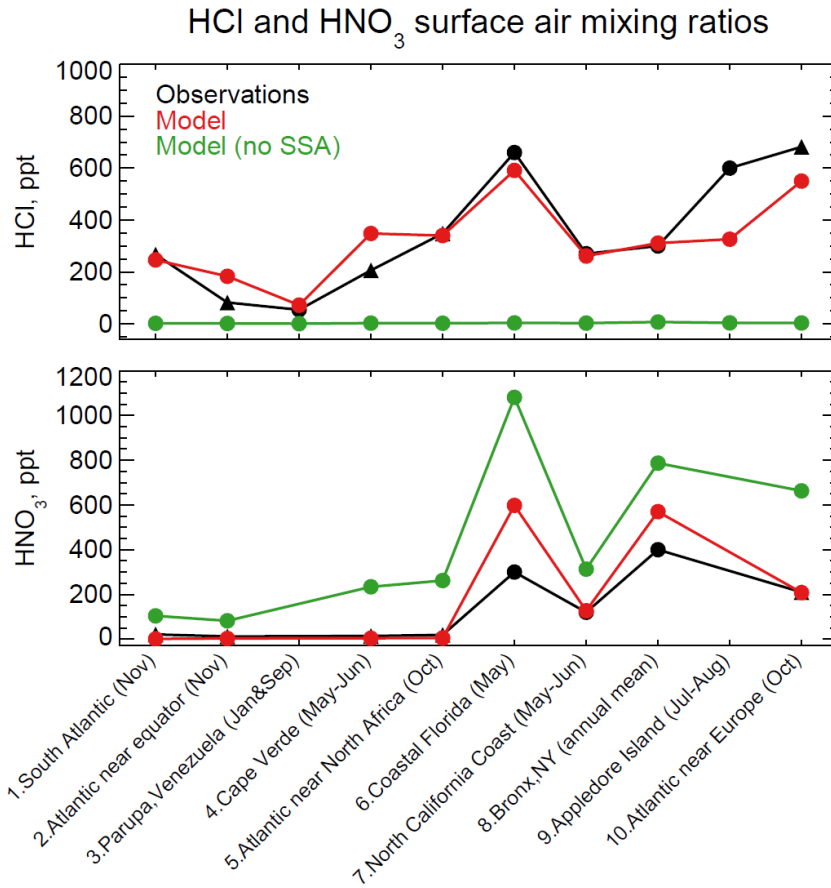
Figure 2: Global distributions of annual mean HCl mixing ratios and Cl atom concentrations in GEOS-Chem. The top panels show surface air mixing ratios/concentrations. The bottom panels show zonal mean mixing ratios/concentrations as a function of latitude and altitude. Dashed lines indicate the tropopause.

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.



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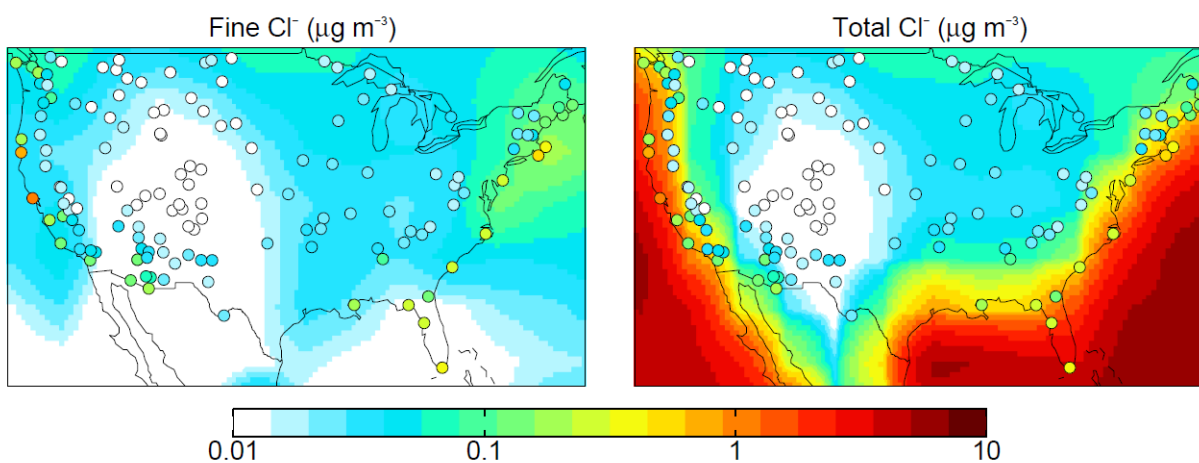
2 **Figure 4: HCl and HNO₃ surface air mixing ratios at coastal/island sites and from ocean cruises, arranged from left to right**
 3 **in order of increasing latitude. Observations are means (black circles) or medians (black triangles) depending on availability**
 4 **from the publications. Model values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

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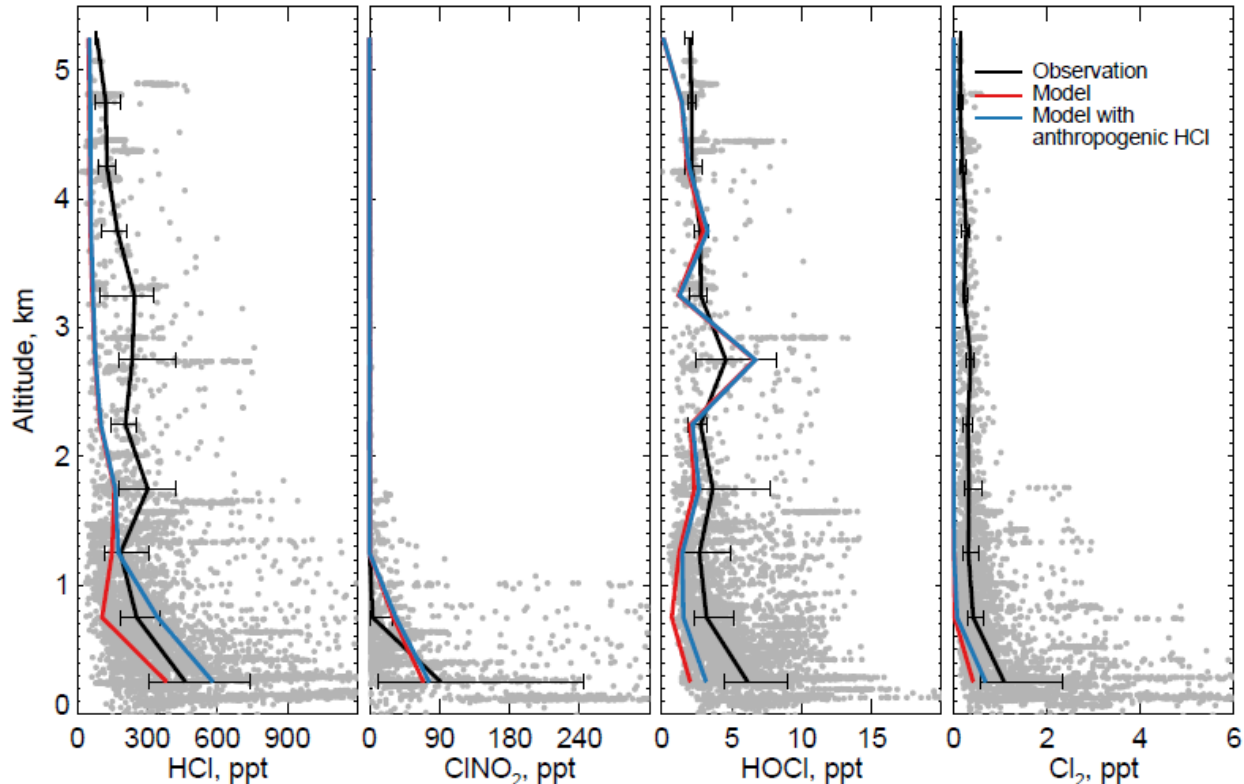
Cl⁻ concentrations in surface air over the US



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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⁻.

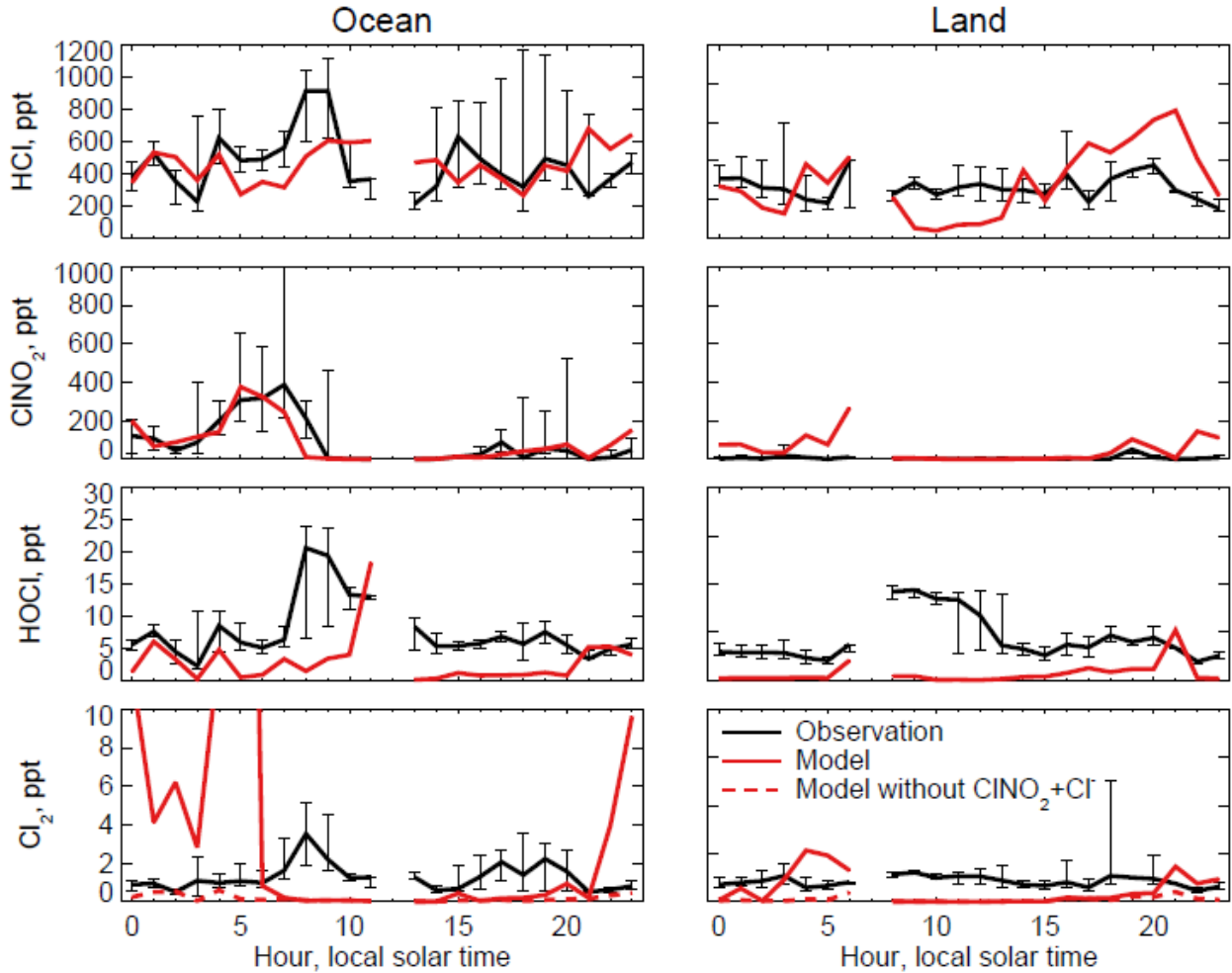
Median vertical profiles of chlorine species during WINTER



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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).

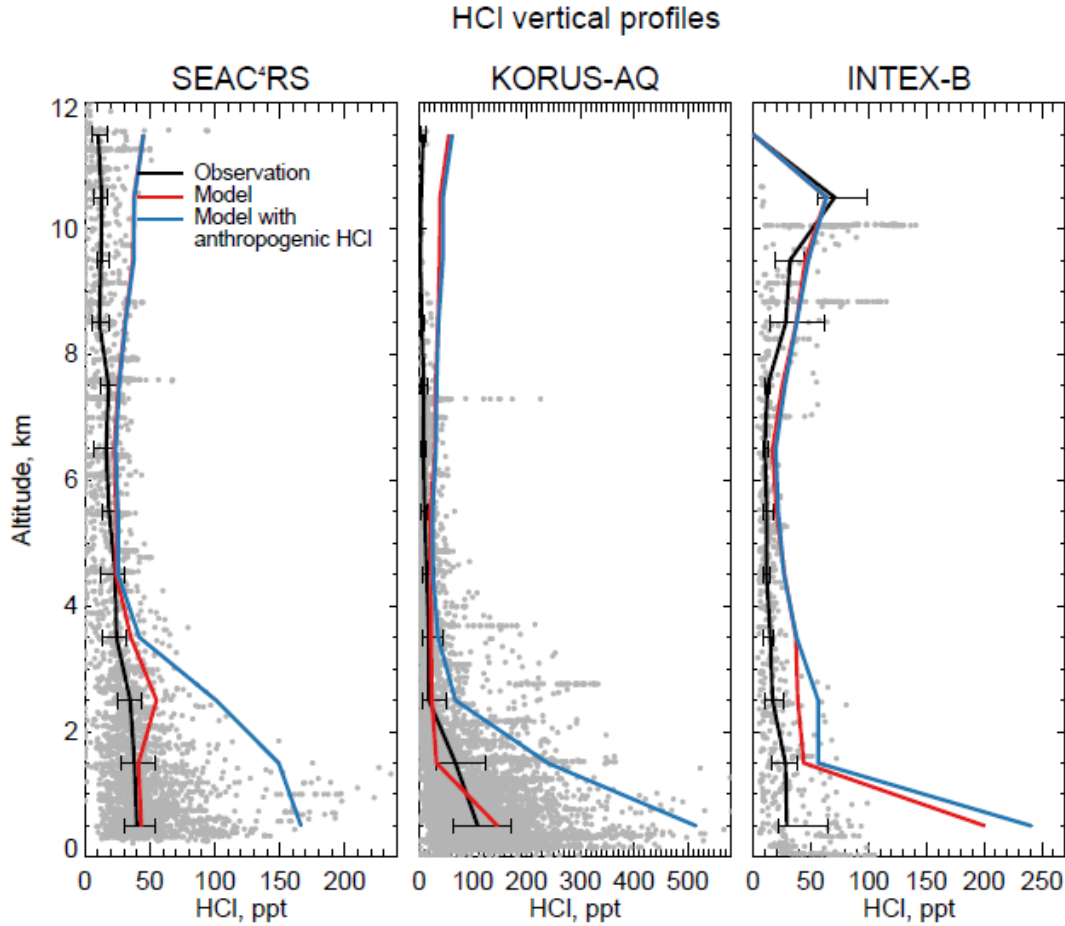
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Diurnal variations of chlorine species during WINTER



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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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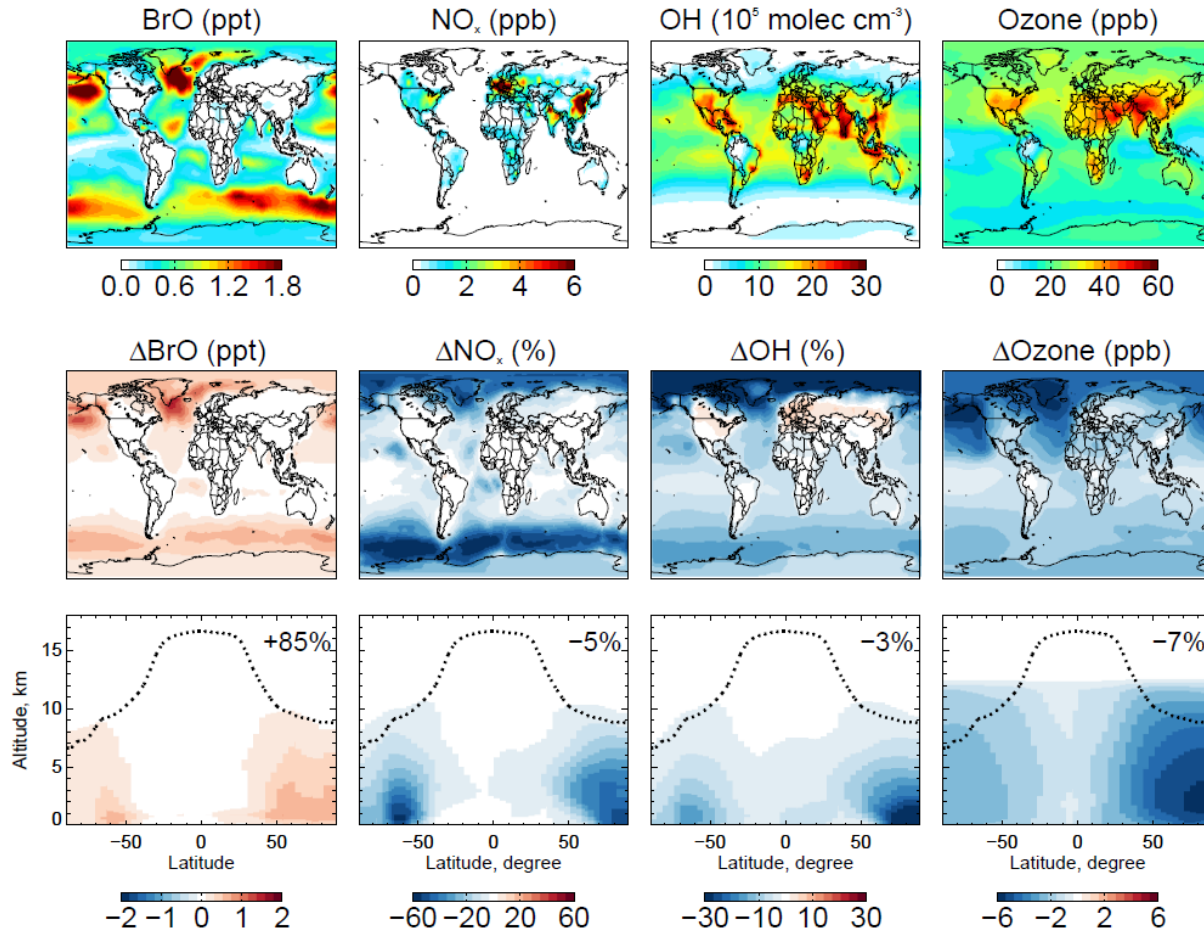


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 2 **Figure 8: Vertical profiles of HCl mixing ratios during the SEAC⁴RS aircraft campaign over the Southeast US (95°-81.5°W,**
 3 **30.5°-39°N) in August-September 2013, during the KORUS-AQ aircraft campaign over and around the Korean peninsula**
 4 **(120°-132°E, 32°-38°N) in May-June 2015, and during the INTEX-B aircraft campaign over North Pacific (175°E-50°W,**
 5 **40°-61°N) in May 2006.** Observations from the Georgia Tech CIMS instrument are shown as gray points (1-minute
 6 averages), with medians and 25th-75th percentiles in 1-km vertical bins. Model values are sampled along the flight tracks
 7 and for the measurement period. Measurements below the detection limit are treated as the median of 0 and detection limit.
 8 Note the difference in scales between panels.

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



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

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