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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 successfully simulates the observed mixing ratios of HCl in marine air (highest at northern midlatitudes) 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 successfully simulates 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 Introduction

Mobilization of chloride (Cl⁻) from sea salt aerosol (SSA) is a large source of chlorine gases to the troposphere (Graedel and Keene, 1995; Finlayson-Pitts, 2003). These gases may generate chlorine radicals with a broad range of implications for tropospheric chemistry including the budgets of ozone, OH (the main tropospheric oxidant), volatile organic com-

pounds (VOCs), nitrogen oxides, other halogens, and mercury (Saiz-Lopez and von Glasow, 2012; Simpson et al., 2015). Only a few global models have attempted to examine the implications of tropospheric chlorine chemistry on a global scale (Singh and Kasting, 1988; Long et al., 2014; Hossaini et al., 2016). Here we present a more comprehensive analysis of this chemistry within the framework of the GEOS-Chem chemical transport model (CTM).

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

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

A number of global modeling studies have investigated tropospheric halogen chemistry but most have focused on bromine and iodine, which are more active than chlorine because of the lower chemical stability of HBr and HI (Yang et al., 2005; Saiz-Lopez et al., 2014). Interest in global modeling of tropospheric chlorine has focused principally on quantifying the Cl atom concentration as a sink for methane (Keene et al., 1990; Singh et al., 1996). Previous global 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 the marine boundary layer (MBL), and contributing 2%–3% of atmospheric methane oxidation (Long et al., 2014; Hossaini

et al., 2016; Sherwen et al., 2016b; Schmidt et al., 2016). A regional modeling study by Sarwar et al. (2014) included ClNO_2 chemistry in a standard ozone mechanism and found increases in surface ozone mixing ratios over the US of up to 7 ppb ($\text{ppb} \equiv \text{nmol mol}^{-1}$).

Here we present a more comprehensive analysis of global tropospheric chlorine chemistry and its implications, building on previous model development of oxidant–aerosol–halogen chemistry in GEOS-Chem. A first capability for modeling tropospheric bromine in GEOS-Chem was introduced by Parrella et al. (2012). Eastham et al. (2014) extended it to describe stratospheric halogen chemistry including chlorine and bromine cycles. Schmidt et al. (2016) updated the tropospheric bromine simulation to include a broader suite of heterogeneous processes and extended the Eastham et al. (2014) stratospheric chlorine scheme to the troposphere. Sherwen et al. (2016a, b) added iodine chemistry and made further updates to achieve a consistent representation of tropospheric chlorine–bromine–iodine chemistry in GEOS-Chem. Chen et al. (2017) added the aqueous-phase oxidation of SO_2 by HOBr and found a large effect on the MBL bromine budget. Our work advances the treatment of tropospheric chlorine in GEOS-Chem to include, in particular, a consistent treatment of SSA chloride and chlorine gases, SSA acid displacement thermodynamics, improved representation of heterogeneous chemistry, and better accounting of chlorine sources. We evaluate the model with a range of global observations for chlorine and related species. From there we quantify the global tropospheric chlorine budgets, describe the principal chemical pathways, and explore the impacts on tropospheric chemistry.

2 Model description

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

We build our new tropospheric chlorine simulation capability onto the standard version 11-02d of GEOS-Chem (<http://www.geos-chem.org>, last access: 1 March 2019). The standard version includes a detailed tropospheric oxidant–aerosol–halogen mechanism as described by Sherwen et al. (2016b) and Chen et al. (2017). It includes 12 gas-phase Cl_y species: Cl, Cl_2 , Cl_2O_2 , ClNO_2 , ClNO_3 , ClO, ClOO, OClO, BrCl, ICl, HOCl, and HCl. It allows for heterogeneous chemistry initiated by SSA Cl^- but does not actually track the SSA Cl^- concentration and its exchange with gas-phase Cl_y . Here we add two new transported reactive species to GEOS-Chem to describe Cl^- aerosol, one for the fine mode ($< 1 \mu\text{m}$ diameter) and one for the coarse mode ($> 1 \mu\text{m}$ diameter). The standard GEOS-Chem wet deposition schemes for water-soluble aerosols (Liu et al., 2001) and gases (Amos et al., 2012) are applied to Cl^- aerosol and Cl_y gases, respectively, the latter with Henry's law con-

starts from Sander (2015). Dry deposition of Cl^- aerosol follows that of SSA (Jaeglé et al., 2011), and dry deposition of Cl_y gases follows the resistance-in-series scheme of Wesely (1989) as implemented in GEOS-Chem by Wang et al. (1998). We also add to the model two SSA alkalinity tracers in the fine and coarse modes and retain the inert SSA tracer to derive local concentrations of non-volatile SSA cations (Sect. 2.3). SSA de-bromination by oxidation of Br^- as described by Schmidt et al. (2016) was included only as an option in standard version 11-02d of GEOS-Chem because of concern over excessive MBL BrO (Sherwen et al., 2016b). However, Zhu et al. (2018) show that it in fact allows a successful simulation of MBL BrO when one accounts for new losses in the standard model from aqueous-phase oxidation of SO_2 by HOBr (Chen et al., 2017) and oxidation of marine acetaldehyde by Br atoms (Millet et al., 2010). We include SSA de-bromination in this work.

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

2.2 Sources of chlorine

Table 1 lists the global sources and sinks of tropospheric gas-phase inorganic chlorine (Cl_y) and reactive chlorine (Cl^*) in our model. The main source is mobilization of Cl^- from SSA. SSA emission is computed locally in GEOS-Chem separately for fine and coarse modes as the integrals of the size-dependent source function over two size bins, fine (0.2–1 μm diameter) and coarse (1–8 μm diameter). The source function depends on wind speed and sea surface temperature (Jaeglé et al., 2011). We obtain a global SSA source of 3230 Tg a^{-1} for 2016, corresponding to $1780 \text{ Tg a}^{-1} \text{ Cl}^-$ (assuming fresh SSA to be 55.05 % Cl^- by mass (Lewis and Schwartz, 2014), of which 16 % is in the fine mode and 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 reactions, while the rest is deposited. A total of 42 % of the mobilization is from fine SSA and 58 % is from coarse SSA. Details of this mobilization are in Sect. 2.3 and 2.4. About 80 % of the mobilization is by acid displacement to HCl, which is in turn efficiently deposited. Only 19 % of HCl is further mobilized to Cl^* by reaction with OH to drive chlorine radical chemistry. Direct generation of Cl^* from SSA through heterogeneous chemistry provides a Cl^* source of comparable magnitude to $\text{HCl} + \text{OH}$, with dominant contri-

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	75 200	25 000
Sea Salt	63 900	11 900
Acid displacement ^b	52 000	–
HOBr + Cl^-	8590	8590
$\text{N}_2\text{O}_5 + \text{Cl}^-$	1810	1810
HOI, $\text{IONO}_x^c + \text{Cl}^-$	641	641
$\text{ClNO}_2 + \text{Cl}^-$	327	327
OH + Cl^-	403	403
$\text{ClNO}_3 + \text{Cl}^-$	64	64
HOCl + Cl^-	61	61
HCl + OH	–	9720
Organochlorines	3320	3300
$\text{CH}_3\text{Cl} + \text{OH}^d$	2200	2180
$\text{CH}_2\text{Cl}_2 + \text{OH}$	780	780
$\text{CHCl}_3 + \text{OH}$	298	298
$\text{CH}_2\text{ICl} + \text{OH}$	46	46
Stratosphere ^e	380	64
Anthropogenic HCl ^f	(6660)	–
Open fires	7640	–
Total sink	75 200	25 000
Deposition	71 400	346
Dry	35 200	170
Wet	36 200	176
Uptake by alkaline SSA	3800	–
Conversion to HCl ^g	–	24 600
Tropospheric mass (Gg)	316	12
Lifetime (h)	37	3.8

^a Annual totals for 2016 computed from GEOS-Chem. Gas-phase inorganic chlorine is defined as $\text{Cl}_y \equiv \text{Cl} + 2 \times \text{Cl}_2 + 2 \times \text{Cl}_2\text{O}_2 + \text{ClNO}_2 + \text{ClNO}_3 + \text{ClO} + \text{ClOO} + \text{OCIO} + \text{BrCl} + \text{ICl} + \text{HOCl} + \text{HCl}$. Reactive chlorine is defined as $\text{Cl}^* \equiv \text{Cl}_y - \text{HCl}$. Thus the 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 sea salt source of $1780 \text{ Tg Cl a}^{-1}$ but is mainly removed by deposition, HCl is the dominant component of Cl_y but is also mostly removed by deposition. Reactive chlorine Cl^* is the chemical family principally involved in radical cycling. ^b Net production minus loss of HCl from acid aerosol displacement by HNO_3 and H_2SO_4 computed as thermodynamic equilibrium. ^c $\text{IONO}_x \equiv \text{IONO} + \text{IONO}_2$. ^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. ^e Net stratospheric input to the troposphere. ^f Coal combustion, waste incineration, and industrial activities. These emissions are only included in a sensitivity simulation (see Sects. 2.2 and 4.2 for details) and are therefore listed here in parentheses. Emissions of anthropogenic fugitive dust are estimated as less than 390 Gg a^{-1} (Sect. 2.2) and are not included in the model. ^g From reactions of Cl atoms (see Fig. 1).

butions from HOBr + Cl^- and $\text{N}_2\text{O}_5 + \text{Cl}^-$ (the latter in polluted high- NO_x environments).

Cl^* can also be produced in the model by atmospheric degradation of the organochlorine gases CH_3Cl , CH_2Cl_2 , CHCl_3 , and CH_2ICl . These gases are mainly of biogenic marine origin, with the exception of CH_2Cl_2 , which has a large industrial solvent source (Simmonds et al., 2006). Mean tropospheric lifetimes are 520 days for CH_3Cl , 280 days for 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 in the model by specifying monthly mean surface air boundary conditions in five latitude bands (60–90, 30–60, and 0–30° N, 0–30, and 30–90° S) from AGAGE observations (Prinn et al., 2018). Emission of CH₂ICl is from Ordóñez et al. (2012), as described by Sherwen et al. (2016a). Tropospheric oxidation of hydrochlorofluorocarbons (HCFCs) is neglected as a source of Cl* because it is small compared to the other organochlorines. The stratospheric source of Cl_y from chlorofluorocarbons (CFCs), HCFCs, and CCl₄ is included in the model on the basis of the Eastham et al. (2014) GEOS-Chem stratospheric simulation as described in Sect. 2.1. Tropospheric organochlorines give a global Cl* source of 3.3 Tg Cl a⁻¹ in Table 1, smaller than that from heterogeneous SSA Cl⁻ reactions (11.9 Tg Cl a⁻¹) or oxidation of HCl by OH (9.7 Tg Cl a⁻¹). The stratosphere is a minor global source of tropospheric Cl* (0.06 Tg Cl a⁻¹) although it could be important in the upper troposphere (Schmidt et al., 2016).

We also include primary HCl emissions from open fires. We apply the emission factors of (HCl + Cl⁻) from Lobert et al. (1999) for different vegetation types to the GFED4 (Global Fire Emissions Database) biomass burned inventory (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.

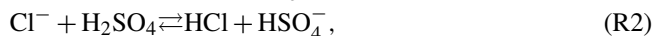
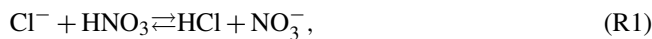
Anthropogenic sources of HCl include coal combustion, waste incineration, and industrial activities. The only global emission inventory is that of McCulloch et al. (1999), which gives a total of 6.7 Tg Cl a⁻¹. As shown in Sect. 4.2, we find that this greatly overestimates atmospheric observations of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

We do not include the anthropogenic Cl⁻ source from fugitive dust, although it might be important in contributing to chloride levels in continental surface air (Sarwar et al., 2012). The global source of anthropogenic fugitive dust is 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., 2009). This corresponds to a chloride source of less than 0.39 Tg Cl a⁻¹, negligible on a global scale.

2.3 HCl/Cl⁻ acid displacement thermodynamics

SSA Cl⁻ can be displaced to HCl by strong acids (H₂SO₄, HNO₃) once the SSA is sufficiently aged that its initial sup-

ply of alkalinity ($\equiv \text{HCO}_3^- + 2 \times \text{CO}_3^{2-}$) has been exhausted. The acid displacement is described by



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

Alkalinity initially prevents any acid displacement in freshly emitted SSA. Alkalinity is emitted as 0.07 mol equivalents kg⁻¹ of dry SSA (Gurciullo et al., 1999) and is transported in the model as two separate tracers for fine and coarse SSA. It is consumed over time by uptake of acids (SO₂, H₂SO₄, HNO₃, and HCl) as described by Alexander et al. (2005), and once fully consumed it is set to zero (titration). The SSA is then diagnosed as acidified, enabling acid displacement by Reactions (R1)–(R2). In our simulation, alkalinity is titrated everywhere shortly after emission except in some areas of the Southern Ocean, which is consistent with the model results of Alexander et al. (2005) and Kasibhatla et al. (2018).

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

Acid displacement for acidified coarse SSA is assumed to be driven by uptake of strong acids from the gas phase, mainly HNO₃ (Kasibhatla et al., 2018). The ISORROPIA II calculation is conducted with two gas species (HNO₃ and HCl) and four aerosol species (NVC, Cl⁻, SO₄²⁻, and NO₃⁻). Here the sulfate includes only the emitted sea salt component and that produced by heterogeneous SO₂ oxidation in coarse SSA (Alexander et al., 2005). In the case of coarse aerosols, there may be significant mass transfer limitation to reaching gas–aerosol thermodynamic partitioning (Meng

and Seinfeld, 1996). To account for this limitation, the concentrations are adjusted after the ISORROPIA II calculation following the dynamic method of Pilinis et al. (2000). This two-step thermodynamics approach has been used in previous studies (Koo et al., 2003; Kelly et al., 2010).

2.4 Heterogeneous chemistry of Cl^-

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

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

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 area concentration per unit volume of air, r is the effective particle radius, D_g is the gas-phase molecular diffusion coefficient of X , c is the average gas-phase thermal velocity of X , and γ is the reactive uptake coefficient, which is a function of the aqueous-phase molar Cl^- concentration $[\text{Cl}^-]$ (moles of Cl^- per liter of water). Values of γ in Table 2 are mostly from recommendations by the International Union of Pure and Applied Chemistry (IUPAC) (Ammann et al., 2013).

The heterogeneous reactions take place in both clear-air aerosol and clouds. The GEOS-FP input meteorological data include cloud fraction and liquid/ice water content for every grid cell. Concentrations per cubic centimeter of air of aerosol-phase species (including fine and coarse Cl^- and Br^-) within a grid cell are partitioned between clear air and cloud as determined by the cloud fraction. Clear-air aqueous-phase concentrations for use in calculating heterogeneous reaction rates are derived from the relative-humidity-dependent liquid water contents of fine and coarse SSA using aerosol hygroscopic growth factors from the Global Aerosol Database (GADS, Koepke, 1997) with an update by Lewis and Schwartz (2006). In-cloud aqueous-phase concentrations are derived using liquid and ice water content from the GEOS-FP meteorological data. Values of r in Eq. (1) are specified as relative-humidity-dependent effective radii for the different clear-air aerosol components (Martin et al., 2003), and are set to $10 \mu\text{m}$ for cloud droplets and $75 \mu\text{m}$ for ice particles. These effective radii are also used to infer the area concentrations A on the basis of the mass concentrations. Heterogeneous chemistry in ice clouds is restricted to the unfrozen layer coating the ice crystal, which is assumed to be 1 % of the ice crystal radius (Schmidt et al., 2016).

The heterogeneous uptake of HOBr, HOCl, and ClNO_2 as well as further aqueous-phase reaction with Cl^- in Table 2 are pH dependent, with a higher efficiency in acidic solutions (Fickert et al., 1999; Roberts et al., 2008; Abbatt et al., 2012). They are considered only when SSA alkalinity has been titrated, and $\text{ClNO}_2 + \text{Cl}^-$ further requires $\text{pH} < 2$, following laboratory results presented in Roberts et

al. (2008). The pH of chloride-containing fine aerosol after alkalinity has been titrated is calculated by ISORROPIA II. Liquid cloud water pH is calculated in GEOS-Chem following Alexander et al. (2012), with update to include Cl^- and NVC. Coarse-mode SSA and ice cloud pH are assumed to be 5 and 4.5, respectively (Schmidt et al., 2016).

3 Global budget and distribution of tropospheric chlorine

Figure 1 describes the global budget and cycling of tropospheric inorganic chlorine in GEOS-Chem. The dominant 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} , close to the observationally based estimate of 50 Tg Cl a^{-1} by Graedel and Keene (1995) and lower than the model estimate of 90 Tg Cl a^{-1} from Hossaini et al. (2016), who treated displacement of Cl^- by HNO_3 as an irreversible rather than thermodynamic equilibrium process. HCl is the largest reservoir of Cl_y in the troposphere, with a global mean tropospheric mixing ratio of 60 ppt (ppt \equiv pmol mol $^{-1}$).

Acid displacement generates Cl_y as HCl, which is mostly removed by deposition. Broader effects of chlorine on tropospheric chemistry take place through the cycling of radicals originating from production of reactive chlorine $\text{Cl}^* \equiv \text{Cl}_y - \text{HCl}$. HCl contributes 9.7 Tg Cl a^{-1} to Cl^* through the reaction between HCl and OH. In addition to this source, Cl^- provides a Cl^* source of 12 Tg Cl a^{-1} through heterogeneous reactions with principal contributions from $\text{HOBr} + \text{Cl}^-$ (8.6 Tg Cl a^{-1}) and $\text{N}_2\text{O}_5 + \text{Cl}^-$ (1.8 Tg Cl a^{-1}). This heterogeneous source of 12 Tg Cl a^{-1} is much higher than previous 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 considered the $\text{HOBr} + \text{Cl}^-$ reaction. Production of the chlorine radicals Cl and ClO is by the $\text{HCl} + \text{OH}$ reaction (45 %) and by photolysis of BrCl (40 %), ClNO_2 (8 %), Cl_2 (4 %), and ICl (2 %). Loss of Cl^* is mainly through the reaction of Cl with methane (46 %) and other organic compounds (CH_3OH 15 %, CH_3OOH 11 %, C_2H_6 8 %, higher alkanes 8 %, and CH_2O 7 %).

Conversion of Cl to ClO^* drives some cycling of chlorine radicals, but the associated chain length versus Cl^* loss is 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 ClO back to Cl is mostly by reaction with NO (72 %), driving a null cycle as NO_2 photolyzes to regenerate NO and ozone.

Figure 2 shows the annual mean global distributions of HCl mixing ratios and Cl atom concentrations. The mixing ratio of HCl decreases from the surface to the middle troposphere, reflecting the SSA source, and then increases again in the upper troposphere where it is supplied by transport from the stratosphere and has a long lifetime due to lack of scavenging. Remarkably, Cl atom concentrations show little decrease with altitude, contrary to the common assumption

Table 2. Heterogeneous reactions of Cl^- and reactive uptake coefficients (γ)^a.

Reaction	Reactive uptake coefficient (γ)	Footnote
R3 $\text{N}_2\text{O}_5 + \varphi\text{Cl}^- + (1-\varphi)\text{H}_2\text{O} \rightarrow \varphi\text{ClNO}_2 + (2-\varphi)\text{NO}_3^- + 2(1-\varphi)\text{H}^+$	$\gamma = Bk'_{2f} \left(1 - \frac{1}{\left(\frac{k_3[\text{H}_2\text{O}]}{k_{2b}[\text{NO}_3^-]} \right) + 1 + \left(\frac{k_4[\text{Cl}^-]}{k_{2b}[\text{NO}_3^-]} \right)} \right)$ $k'_{2f} = \beta \left(1 - e^{-\delta[\text{H}_2\text{O}]} \right); \varphi = \left(\frac{k_2[\text{H}_2\text{O}]}{k_3[\text{Cl}^-]} + 1 \right)^{-1}$ $B = 3.2 \times 10^{-8} \text{ s}; k_3/k_2 = 450$ $\beta = 1.15 \times 10^6 \text{ s}^{-1}; \delta = 0.13 \text{ M}^{-1}$ $k_3/k_{2b} = 0.06; k_4/k_{2b} = 29$	b
R4 $\text{OH} + \text{Cl}^- \rightarrow 0.5\text{Cl}_2 + \text{OH}^-$	$\gamma = 0.04 [\text{Cl}^-]$	c
R5 $\text{HOBr} + \text{Cl}^- + \text{H}^+ \rightarrow \text{BrCl} + \text{H}_2\text{O}$	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}$ $\Gamma_b = 4H_{\text{HOBr}}RTl_rk_b[\text{Cl}^-][\text{H}^+]/c$ $l_r = \sqrt{D_l/(k_b[\text{Cl}^-][\text{H}^+])}; \alpha_b = 0.6$ $k_b = 2.3 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1}; D_l = 1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	d
R6 $\text{ClNO}_3 + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{NO}_3^-$	$\gamma = 0.0244$	e
R7 $\text{ClNO}_2 + \text{Cl}^- \rightarrow \text{NO}_2^- + \text{Cl}_2$	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1} \text{ (pH} < 2), \gamma = 0 \text{ (pH} > 2)$ $\Gamma_b = 4H_{\text{ClNO}_2}RTl_rk^{II}[\text{Cl}^-]f(r, l_r)/c$ $l_r = \sqrt{D_l/(k^{II}[\text{Cl}^-])}; \alpha_b = 0.01$ $k^{II} = 10^7 \text{ M}^{-2} \text{ s}^{-1}; D_l = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
R8 $\text{ClNO}_2 + \text{Br}^- \rightarrow \text{NO}_2^- + \text{BrCl}$	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}$ $\Gamma_b = 4H_{\text{ClNO}_2}RTl_rk^{II}[\text{Br}^-]f(r, l_r)/c$ $l_r = \sqrt{D_l/(k^{II}[\text{Br}^-])}; \alpha_b = 0.01$ $H_{\text{ClNO}_2}^2D_lk^{II} = 0.101 \text{ M cm}^2 \text{ s}^{-2}$	
R9 $\text{HOCl} + \text{Cl}^- + \text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	$\gamma = \min \left(\left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}, 2 \times 10^{-4} \right)$ $\Gamma_b = 4H_{\text{HOCl}}RTl_rk_t[\text{Cl}^-][\text{H}^+]/c$ $l_r = \sqrt{D_l/(k_t[\text{Cl}^-][\text{H}^+])}; \alpha_b = 0.8$ $k_t = 1.5 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}; D_l = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
R10 $\text{NO}_3 + \text{Cl}^- \rightarrow \text{NO}_3^- + \text{Cl}^-$	$\gamma = \left(\frac{1}{\Gamma_b} + \frac{1}{\alpha_b} \right)^{-1}$ $\Gamma_b = 4H_{\text{NO}_3}RTl_rk'[\text{Cl}^-]f(r, l_r)/c$ $l_r = \sqrt{D_l/(k'[\text{Cl}^-])}; \alpha_b = 0.013$ $k' = 2.76 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}; D_l = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
R11 $\text{IONO}_2 + \text{Cl}^- \rightarrow \text{ICl} + \text{NO}_3^-$	$\gamma = 8.5 \times 10^{-3}$	f
R12 $\text{IONO} + \text{Cl}^- \rightarrow \text{ICl} + \text{NO}_2^-$	$\gamma = 0.017$	f
R13 $\text{HOI} + \text{Cl}^- \rightarrow \text{ICl} + \text{OH}^-$	$\gamma = 8.5 \times 10^{-3}$	f

^a Formulations for the reactive uptake coefficient γ are from IUPAC (Ammann et al., 2013) unless stated otherwise in the footnote column. Brackets denote aqueous-phase concentrations in molarity (moles per liter of water). R is the ideal gas constant. c is the average gas-phase thermal velocity for the reactant with Cl^- . The reactive uptake coefficient is used to calculate the reaction rate following Eq. (1). $f(r, l_r) = \coth(r/l_r) - (l_r/r)$ is a spherical correction to mass transfer for which l_r is a reacto-diffusive length scale and r is the radius of the aerosol particle or cloud droplet. ^b Bertram and Thornton (2009); Roberts et al. (2009). This parametrization is only applied for SNA and SSA aerosols. For N_2O_5 uptake on other aerosols, we assume $\varphi = 0$ and follow Jaeglé et al. (2018). ^c Knipping and Dabdub (2002). ^d k_b is based on Liu and Margerum (2001). Reaction (R5) competes with the heterogeneous reactions $\text{HOBr} + \text{Br}^-$ and $\text{HOBr} + \text{S(IV)}$ as given by 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. (1999), as described in Sect. 5.2. ^e Assumes that Cl^- is present in excess so that γ does not depend on $[\text{Cl}^-]$. However, Reaction (R6) competes with the heterogeneous reaction $\text{ClNO}_3 + \text{Br}^-$ as given by Schmidt et al. (2016), with the branching ratio determined by the relative rates. ^f These reactions are based on Sherwen et al. (2016a) and only take place in SSA.

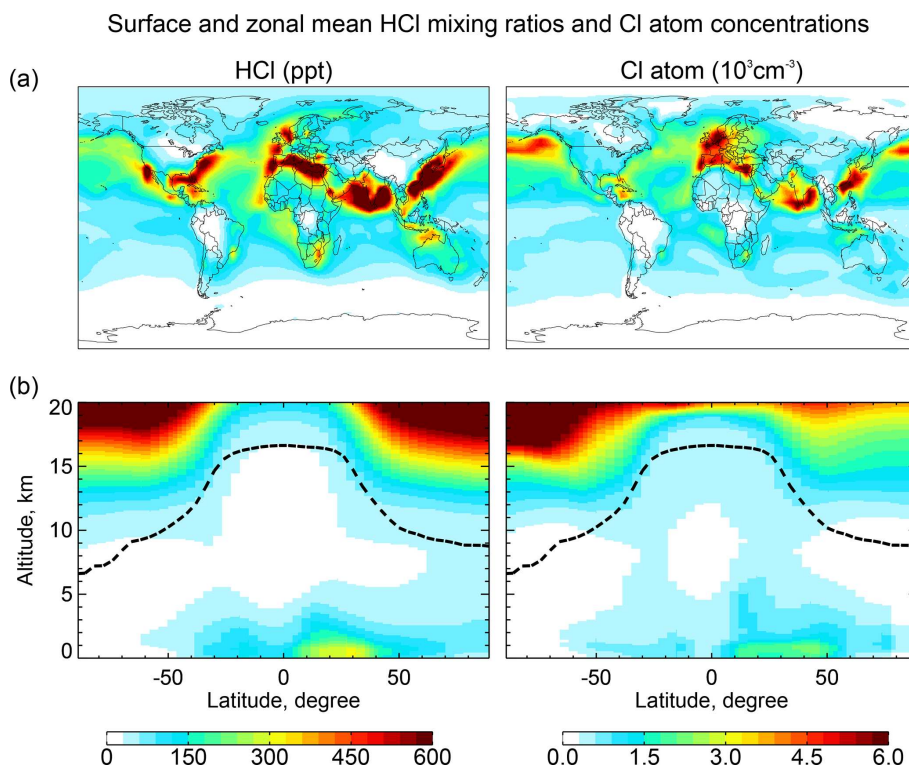


Figure 2. Global distributions of annual mean HCl mixing ratios and Cl atom concentrations in GEOS-Chem. Panel (a) shows surface air mixing ratios and concentrations. Panel (b) shows zonal mean mixing ratios and concentrations as a function of latitude and altitude. Dashed lines indicate the tropopause.

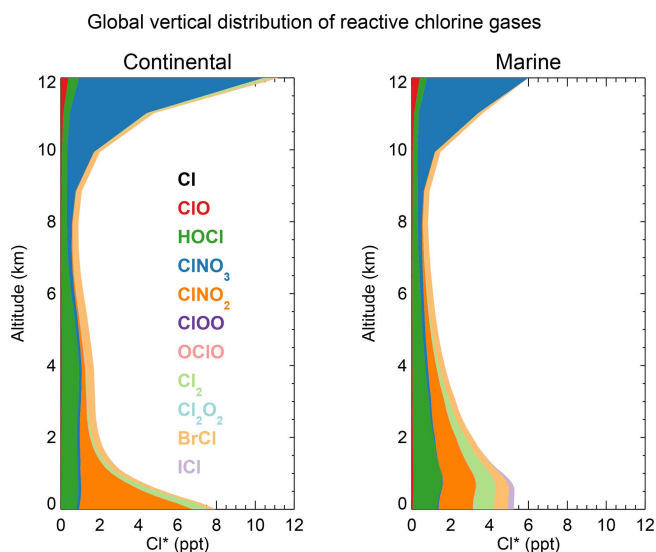


Figure 3. Global annual mean vertical distributions of reactive chlorine species (Cl^*) in GEOS-Chem for continental and marine air. Stratospheric conditions are excluded.

nor factor in model error. Previous evaluation of the GEOS-Chem sea salt source by Jaeglé et al. (2011) showed general skill in simulating SSA observations and we do not repeat

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

4.1 Surface air observations

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

Figure 4 compares simulated HCl and HNO_3 mixing ratios to concurrent observations of gases both at coastal sites and over oceans. The data are arranged from left to right by increasing latitude. Mean HCl mixing ratios average 323 ppt in the model and 347 ppt in the observations for the ensemble

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

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

of regions. The HCl source in the model is mainly acid displacement from SSA. A sensitivity simulation without acid displacement from SSA has less than 7 ppt HCl in all regions. The model captures the spatial variability of the mean HCl mixing ratios across locations ($r = 0.88$), which largely reflects the HCl enhancement at polluted coastal sites and northern midlatitudes (Fig. 2). Simulated HNO₃ mixing ratios average 190 ppt across locations compared to 137 ppt in the observations, again with good simulation of spatial variability ($r = 0.96$) driven by NO_x emissions. HNO₃ mixing ratios are sensitive to acid displacement from SSA, as the sensitivity simulation without acid displacement shows mean values of 441 ppt that are much higher than observed. This could partly explain the general model problem of HNO₃ overestimation in remote air (Bey et al., 2001).

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

A number of surface air measurements have been made of Cl* as the water-soluble component of Cl_y after removal of HCl (Keene et al., 1990), although most of these measure-

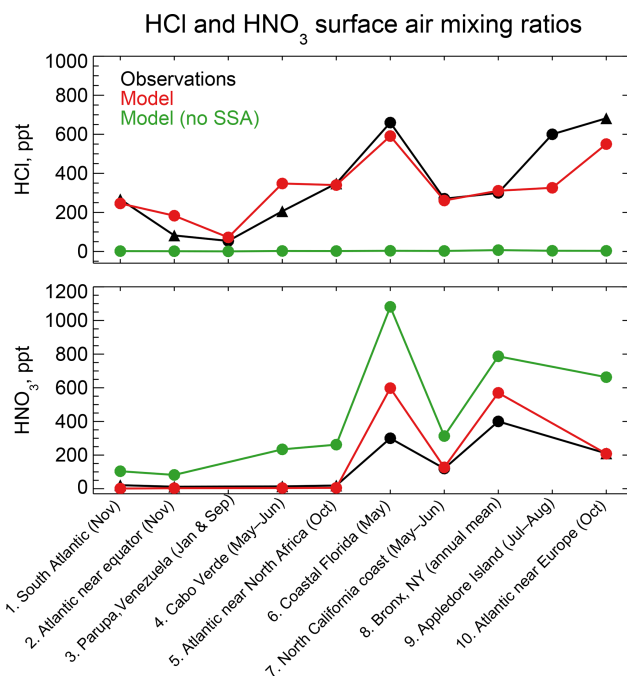


Figure 4. HCl and HNO₃ surface air mixing ratios at coastal and island sites and from ocean cruises, arranged from left to right in order of increasing latitude. Observations are means (black circles) or medians (black triangles) depending on availability from the publications. Model values are monthly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

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

Lawler et al. (2009) measured Cl₂ and BrCl mixing ratios at Cabo Verde in the tropical Atlantic for 5 days in May–June 2007, and Lawler et al. (2011) measured Cl₂ and HOCl mixing ratios at the same site for 7 days in May–June 2009. The observations show a diurnal cycle with mixing ratios of Cl₂ highest at night, and HOCl highest in the day, consistent with the model. Observed mixing ratios in background marine air are in the range 0–30 ppt for Cl₂ and 0–2 ppt for BrCl at night and 0–5 ppt for HOCl in the daytime. Corresponding mean model values are 0.3 ppt for Cl₂, 1.8 ppt for BrCl, and 5 ppt for HOCl, with little day-to-day variability. Lawler et al. (2011) also sampled long-range outflow from Europe for 3 days in 2009 with daytime HOCl and nighttime Cl₂ mix-

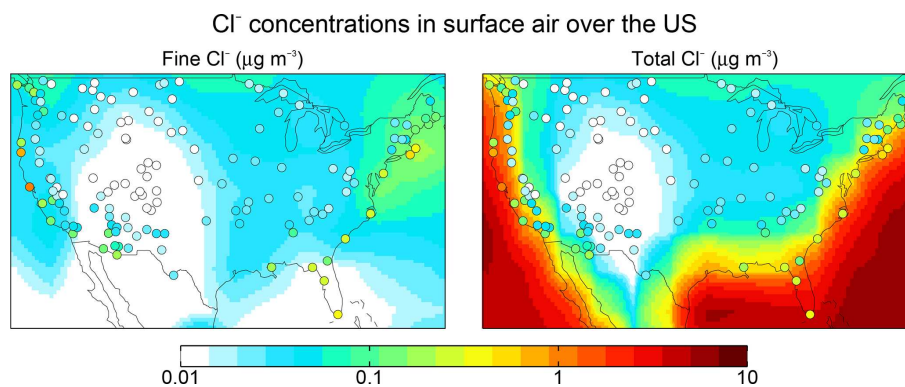


Figure 5. Aerosol Cl^- concentrations in surface air over the contiguous US. Values are annual means for 2016. GEOS-Chem model values are shown as contours separately for fine Cl^- ($<1 \mu\text{m}$ diameter) and total Cl^- . Observations from the IMPROVE network ($<2.5 \mu\text{m}$ diameter) are shown 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^- .

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)

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

^b Median value.

ing ratio ranges of 40–200 and 5–40 ppt, respectively, but the model does not capture these enhancements. Sommariva and von Glasow (2012) suggested that a lower aerosol pH and/or slower rate for $\text{HOCl} + \text{Cl}^-$ could explain the high HOCl in European outflow but this would also cause Cl_2 to be lower. We have no explanation for the high Cl_2 values observed by Lawler et al. (2009, 2011) in marine air or for the joint observed enhancements of HOCl and Cl_2 in European outflow.

Many surface observations of ClNO_2 have been made in nighttime urban environments. These are difficult to compare to the model because of the $4^\circ \times 5^\circ$ grid resolution and because of nighttime stratification of the surface layer (the lowest model grid level extends up to 130 m above the surface). In addition, the publications usually report maxima instead of means. Table 5 shows a comparison for representative sites, indicating that the model offers a credible simulation within the above caveats. The previous GEOS-Chem simulation of Sherwen et al. (2016b) only considered ClNO_2 production in SSA and as a result their ClNO_2 mixing ratios were consistently below a few parts per trillion at continental sites. Our simulation can reproduce the observed >100 ppt concentrations at these sites because it accounts for HCl dissolved in SNA aerosol, allowing marine influence to extend further in-

land as also shown in the comparison to the IMPROVE Cl^- data (Fig. 5).

4.2 Comparison to aircraft measurements

The WINTER aircraft campaign over the eastern US and offshore in February–March 2015 provides a unique data set for evaluating our model. Measurements included HCl, ClNO_2 , HOCl, Cl_2 , and ClNO_3 by iodide, time of flight, chemical ionization mass spectrometry (I-TOF-CIMS) (Lee et al., 2018). We focus on the first four measurements because calibration for ClNO_3 needs further examination. The mean 1 s detection limits for HCl, ClNO_2 , HOCl, and Cl_2 were 100, 2, 2, and 1 ppt, respectively (Lee et al., 2018). The estimated calibration uncertainty is $\pm 30\%$ for all chlorine species. As discussed in Lee et al. (2018), labeled $15\text{-N}_2\text{O}_5$ was added to the inlet tip during WINTER flights to quantify inlet production of ClNO_2 , which was found to be negligible ($\ll 10\%$ of measured ClNO_2), but inlet production of Cl_2 , for example from surface reactions of HOCl with adsorbed HCl, was not evaluated.

Figure 6 compares the observed median vertical profiles of HCl, ClNO_2 , HOCl, and Cl_2 in WINTER to the model

Table 5. Comparison of modeled maximum ClNO₂ mixing ratios to surface observations^a.

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

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

sampled along the flight tracks for the corresponding period. Figure 7 compares the median diurnal variations below 1 km in altitude, separately over ocean and land. We exclude daytime (10:00–16:00 local) data for ClNO₂ in Fig. 6 because its mixing ratios are near zero (Fig. 7).

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

Also shown in Fig. 6 is a sensitivity simulation including anthropogenic HCl emissions from McCulloch et al. (1999) as described in Sect. 2.2. The resulting model mixing ratios are too high though still within the calibration uncertainty. Based on sampling of power plant plumes during the WINTER campaign, Lee et al. (2018) inferred a HCl : SO₂ emission mass ratio of 0.033 from power plants. Adding this emission to the standard simulation scaled to the SO₂ emissions in GEOS-Chem (from the EPA National Emission Inventory over the US) increases modeled mixing ratios of HCl in the continental boundary layer by 18 % along the WINTER flight tracks, improving agreement with observations relative to the standard simulation but still representing a rel-

atively minor source. ClNO₂, HOCl, and Cl₂ mixing ratios increase by 12 %, 8 %, and 4 %, respectively.

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

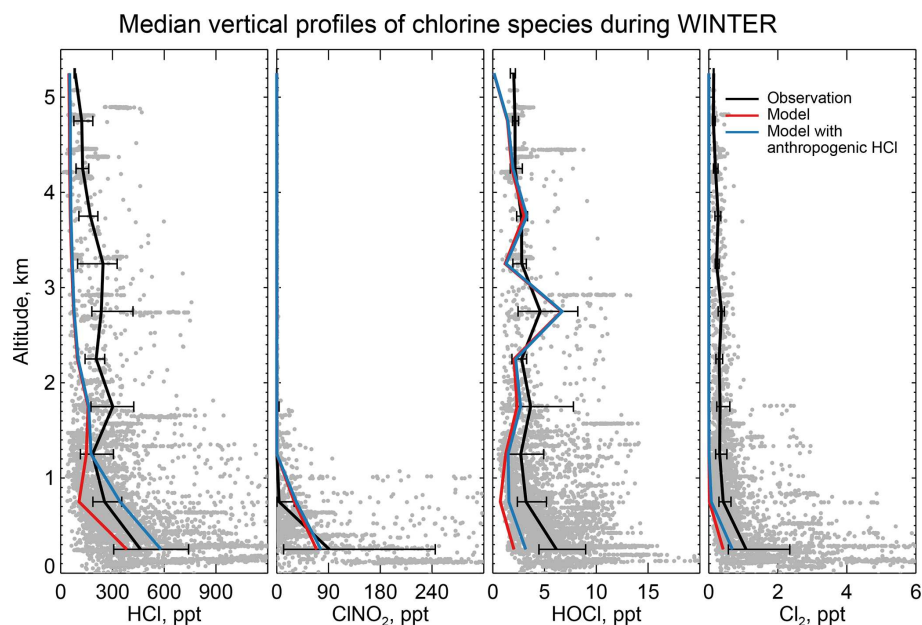
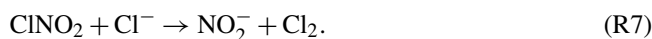


Figure 6. Vertical profiles of HCl, nighttime ClNO_2 , HOCl, and Cl_2 mixing ratios during the WINTER campaign over the eastern US and offshore in February–March 2015. Observations from Haskins et al. (2018) are shown as individual 1 min data points, with medians and 25th–75th percentiles in 500 m vertical bins. Measurements below the detection limit are treated as the median of 0 and detection limit. ClNO_2 data exclude daytime (10:00–16:00 local) when mixing ratios are near zero in both the observations and the model (Fig. 7). Model values are shown as medians sampled along the flight tracks. Also shown are results from a sensitivity simulation including the anthropogenic chlorine inventory of McCulloch et al. (1999).

Mixing ratios of ClNO_2 observed in WINTER are above the detection limit only in the lowest kilometer of atmosphere at night and are much higher over the ocean than over land. This is well simulated by the model (Figs. 6 and 7) and reflects the nighttime source from the $\text{N}_2\text{O}_5 + \text{Cl}^-$ heterogeneous reaction combined with the fast loss by photolysis in daytime. Previous studies have suggested that the Bertram and Thornton (2009) representation of the ClNO_2 production yield from the $\text{N}_2\text{O}_5 + \text{Cl}^-$ heterogeneous reaction in Table 2 is too high (Riedel et al., 2013; Wagner et al., 2013; McDuffie et al., 2018a). By using a box model applied to the WINTER observations, McDuffie et al. (2018a, b) found that both the N_2O_5 uptake rate and the ClNO_2 production yield were overestimated by the Bertram and Thornton (2009) parameterization. One important difference with these previous studies is the assumption of aerosol mixing state. GEOS-Chem assumes that Cl^- is present only in SNA and SSA when doing the calculation of N_2O_5 reactive uptake rates, assuming an external mixture of aerosol types (Martin et al., 2003; Evans and Jacob, 2005; Jaeglé et al., 2018). This decreases both the N_2O_5 uptake rate and the ClNO_2 yield compared to using the parameterization of Bertram and Thornton (2009) on internally mixed aerosols. Jaeglé et al. (2018) reported that using this external mixing assumption leads to good agreement between modeled and observed N_2O_5 during the WINTER campaign. The mean ClNO_2 yield (φ in Reaction R3) below 1 km in our model is 0.20 during the WINTER cam-

paing, very close to that calculated from observation (0.218) by McDuffie et al. (2018a).

Nighttime Cl_2 mixing ratios in WINTER are greatly overestimated by the model. Under polluted wintertime conditions such as in WINTER the $\text{ClNO}_2 + \text{Cl}^-$ reaction greatly enhances Cl_2 production in the model:



The reactive uptake coefficient for Reaction (R7) in Table 2 is based on a single laboratory study (Roberts et al., 2008). It requires an aerosol $\text{pH} < 2$ and this condition is generally met for our model simulation of the WINTER environment, consistent with the observation-based analysis of aerosol pH by Guo et al. (2016) for the eastern US in winter. A sensitivity simulation without Reaction (R7) is shown as dashed red lines in Fig. 7 and can reproduce the low Cl_2 mixing ratios observed over the ocean at night. The analysis of WINTER data by McDuffie et al. (2018b) finds that the correlation between particle acidity and Cl_2 observations is opposite of the trend expected from Reaction (R7), though there may be no trend on sufficiently acidic (i.e., $\text{pH} < 2$) aerosol. Further study of that reaction is needed. Similar reactions such as $\text{ClNO}_2 + \text{Br}^-$ (Reaction R8) and $\text{ClNO}_2 + \text{I}^-$ are also very uncertain as their reaction rate coefficients are very different in different studies (Fickert et al., 1998; Frenzel et al., 1998; Schweitzer et al., 1998).

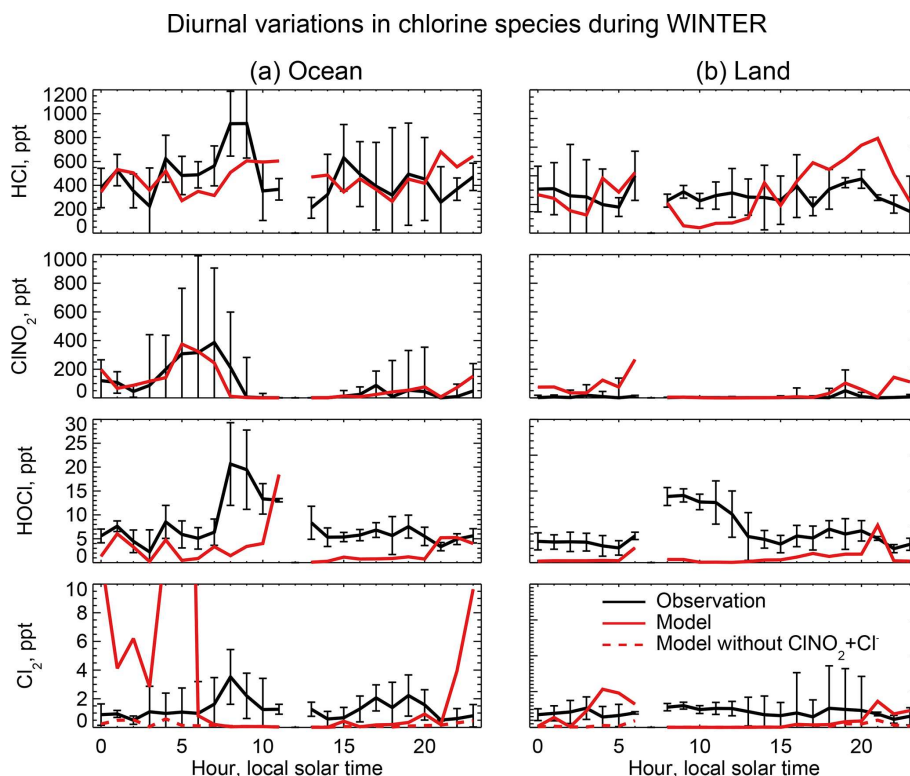


Figure 7. Median diurnal variations in HCl, ClNO₂, and Cl₂ mixing ratios below 1 km in altitude during the WINTER aircraft campaign over the eastern US and offshore in February–March 2015. The data are separated between ocean (a) and land (b). Model values are compared to observations from Haskins et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

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

5 Global implications of tropospheric chlorine chemistry

5.1 Cl atom and its impact on VOCs

The global mean pressure-weighted tropospheric Cl atom concentration in our simulation is 620 cm^{−3}, while the MBL concentration averages 1200 cm^{−3} (Fig. 2). Our global mean

is lower than the previous global model studies of Hossaini et al. (2016) (1300 cm^{−3}) and Long et al. (2014) (3000 cm^{−3}), which had excessive Cl* generation as discussed above. It is consistent with the upper limit of 1000 cm^{−3} inferred by Singh et al. (1996) from global modeling of C₂Cl₄ observations (C₂Cl₄ is highly reactive with Cl atoms). Isotopic observations of methane have been used to infer a Cl atom concentration in the MBL higher than 9000 cm^{−3} in the extratropical Southern Hemisphere (Platt et al., 2004; Allan et al., 2007), much higher than our estimate of 800 cm^{−3} over this region. More recently, Gromov et al. (2018) revisited these data together with added constraints from CO isotope measurements and concluded that extratropical Southern Hemisphere concentrations of Cl atoms in the MBL should be lower than 900 cm^{−3}, consistent with our estimate.

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

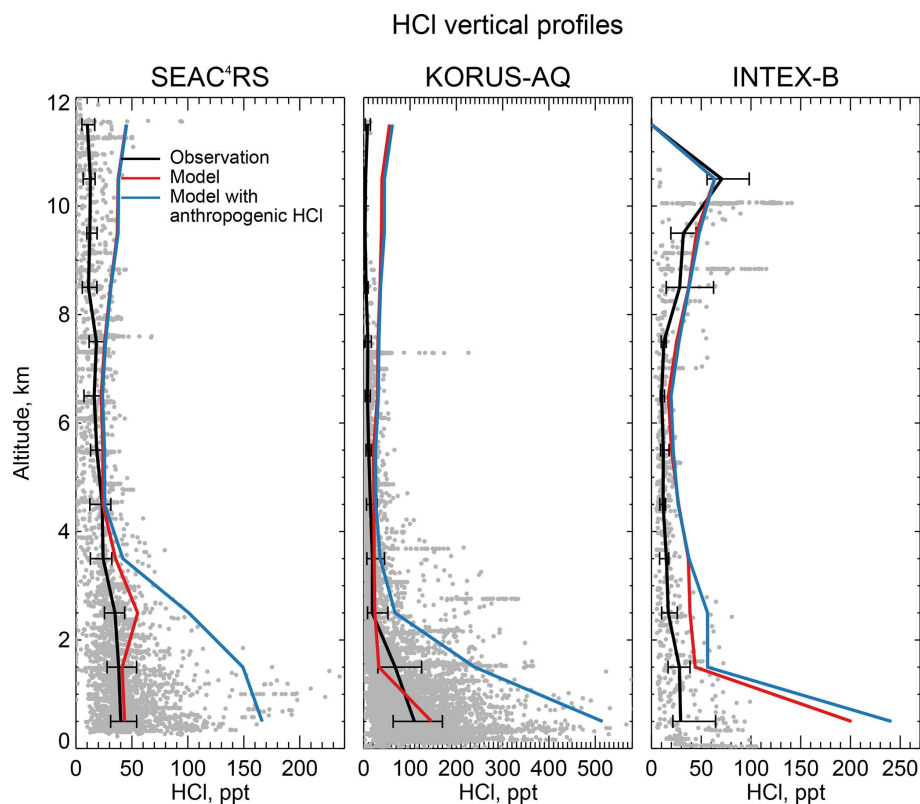
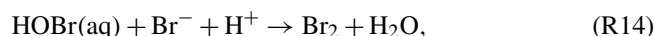


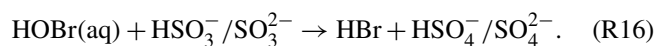
Figure 8. Vertical profiles of HCl mixing ratios during the SEAC⁴RS aircraft campaign over the Southeast US (95–81.5° W, 30.5–39° N) in August–September 2013, during the KORUS-AQ aircraft campaign over and around the Korean peninsula (120–132° E, 32–38° N) in May–June 2015 and during the INTEX-B aircraft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

5.2 Impact on bromine and iodine chemistry

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



Chloride ions and dissolved SO_2 can however compete with Br^- for the available HOBr (Chen et al., 2017):



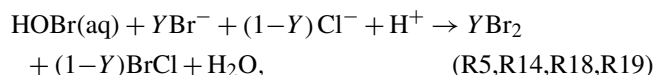
Chen et al. (2017) pointed out that Reaction (R16) effectively decreases BrO mixing ratios by producing HBr, which is rapidly deposited instead of contributing to BrO_x cycling. They found in a GEOS-Chem simulation that global tropospheric BrO mixing ratios decreased by a factor of 2 as a result. Reaction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



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):



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



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. (1999).

$$Y = 0.41 \log_{10}([\text{Br}^-]/[\text{Cl}^-]) + 2.25$$

$$\text{for } [\text{Br}^-]/[\text{Cl}^-] < 5 \times 10^{-4} \quad (2)$$

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

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

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

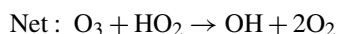
Figure 9 shows the change in surface BrO mixing ratios due specifically to tropospheric chlorine chemistry, as obtained by difference with a sensitivity simulation including none of the Cl_y chemistry shown in Fig. 1. The inclusion of chlorine chemistry increases the global tropospheric BrO burden by 85 %. More than 80 % of this change is caused by

the $\text{HOBr} + \text{Cl}^-$ reaction as discussed above. Other significant contributions include $\text{ClNO}_3 + \text{Br}^-$ and $\text{ClNO}_2 + \text{Br}^-$. The largest BrO increases (1–2 ppt) are in surface air over the high-northern-latitude oceans where SSA emissions are high and acidic conditions promote $\text{HOBr} + \text{Cl}^-$ chemistry.

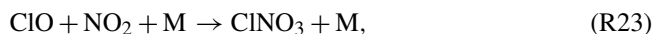
5.3 Impact on tropospheric ozone and OH

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

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



and also loss of NO_x :



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

A particular situation arises over polluted continents due to ClNO_2 chemistry. Production of ClNO_2 at night from the $\text{N}_2\text{O}_5 + \text{Cl}^-$ heterogeneous reaction, followed by photolysis in the morning to release Cl and NO_2 , provides a source of radicals and ozone. This explains the increases in OH over North America and Europe in Fig. 9. The effect is most important at high northern latitudes in winter due to the longer night. To isolate the impact on ozone we conducted a sensitivity simulation with no ClNO_2 production, setting $\varphi = 0$ for Reaction (R3) in Table 2. The surface air ozone enhancement due to ClNO_2 chemistry is found to be the largest ($\sim 8 \text{ ppb}$) in European winter, due to the large supply of Cl^- from the North Atlantic combined with high NO_x emissions. Other polluted continents see ozone increases of 1–5 ppb in winter. The effect in summer is less than 1 ppb. These results are

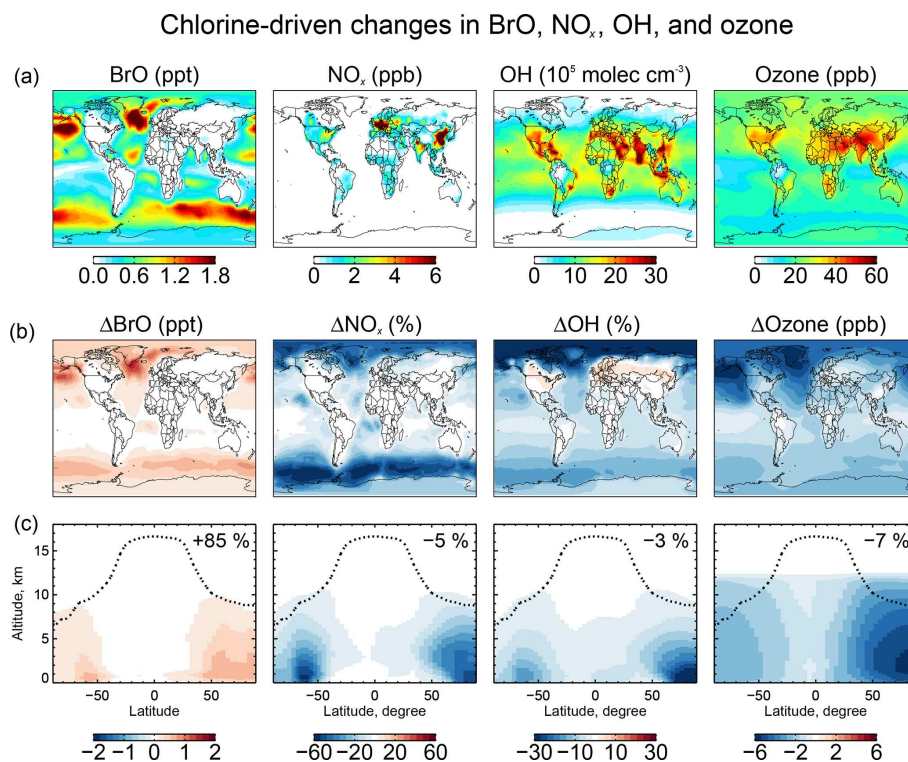


Figure 9. Effects of tropospheric chlorine chemistry on BrO, NO_x, OH, and ozone concentrations. Panel (a) shows the annual mean surface concentrations of BrO, NO_x, OH, and ozone simulated in our standard model including tropospheric chlorine chemistry. Panels (b) and (c) show the changes in annual mean mixing ratios and concentrations due to tropospheric chlorine chemistry, as determined by the difference with a sensitivity simulation including no Cl_y production and cycling. Panel (b) shows the changes in surface air concentrations and panel (c) shows the changes in zonal mean mixing concentrations as a function of latitude and altitude. Black dashed lines indicate the tropopause. Numbers in (c) show the global tropospheric mean differences.

similar to previous regional modeling studies by Sarwar et al. (2014) and Sherwen et al. (2017).

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

6 Conclusions

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

Emission of chlorine in the model is mainly as sea salt aerosol (1780 Tg Cl a⁻¹). Other sources (combustion, organochlorines, stratospheric input) are also included but are small in comparison. Most of the sea salt aerosol chloride is removed by deposition, but 3.6% is mobilized to inorganic gas-phase chlorine (Cl_y) through acid displacement to HCl (52 Tg a⁻¹) and through other heterogeneous chemistry producing more reactive chlorine species (12 Tg a⁻¹). We define reactive chlorine (Cl*) as the ensemble of Cl_y species excluding HCl and including Cl, ClO, Cl₂, BrCl, HOCl,

CINO₂, and CINO₃ plus other minor species. Oxidation of HCl by OH provides a Cl* source of 9.7 Tg 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 in polluted environments. Cycling among Cl* species drives radical chlorine (Cl/CIO) chemistry but chain lengths are limited by fast conversion to HCl and subsequent deposition.

HCl mixing ratios in the model are highest over the oceans downwind of polluted continents due to effective acid displacement from sea salt aerosol by HNO₃ and H₂SO₄. Mixing ratios are much lower over the Southern Ocean where the supply of acids is low. The dominant daytime Cl* species is generally HOCl while BrCl, Cl₂, and CINO₂ dominate at night. CINO₃ dominates in the upper troposphere due to stratospheric input. Chlorine atom concentrations are highest over Europe in winter due to CINO₂ chemistry and are otherwise high over the northern midlatitude oceans where the supply of acidity promotes Cl formation through both HCl and acid-catalyzed heterogeneous processes.

Comparison of model results to observations in marine surface air shows that the model is usually able to reproduce the range and distributions of observed sea salt aerosol chloride deficits, HCl mixing ratios, and Cl* mixing ratios. In particular, concurrent observations of HCl and HNO₃ in coastal/marine air worldwide show high correlation with the model including high HCl mixing ratios at northern midlatitudes combined with depressed HNO₃. Consideration of acid displacement greatly improves model agreement with HNO₃ observations in marine air. The model can also successfully simulate observations of high CINO₂ at night including in continental air. The chlorine in that case originates from sea salt aerosol transported far inland following uptake of volatilized HCl by sulfate–nitrate–ammonium (SNA) aerosol. The model cannot reproduce the very high HOCl and Cl₂ concentrations observed by Lawler et al. (2009, 2011) at Cabo Verde in the tropical Atlantic.

Comparisons of model results to aircraft campaign observations from WINTER (eastern US and offshore, February–March 2015), SEAC4RS (Southeast US, August–September 2013), and KORUS-AQ (Korean peninsula, April–June 2016) show general consistency for HCl vertical profiles. Continental boundary layer HCl mixing ratios in these campaigns can be mostly accounted for by the marine source transported inland, though power plants could make a minor contribution. WINTER observations also include CINO₂, Cl₂, and HOCl. The observed CINO₂ is mainly confined to the nighttime marine boundary layer and is consistent with the model. Observed Cl₂ concentrations at night are much lower than the model, which has a large source under the WINTER conditions from the CINO₂ + Cl⁻ heterogeneous reaction. The rate coefficient for this reaction is from only one laboratory study.

The model simulates a global mean Cl atom concentration of 620 cm⁻³ in the troposphere and 1200 cm⁻³ in the marine boundary layer (MBL), lower than previous global

model studies that had excessive generation of Cl* but consistent with independent proxy constraints. We find that oxidation by Cl atoms accounts for only 1.0 % of the global loss of atmospheric methane but has larger effects on the global losses of ethane (20 %), propane (14 %), and methanol (4 %). Chlorine chemistry increases global tropospheric BrO by 85 % and decreases ozone and OH by 7 % and 3 %, respectively, relative to a sensitivity simulation with no chlorine chemistry. The large effect on BrO is due to production of bromine radicals by the HOBr + Cl⁻ heterogeneous reaction, and the decreases in ozone and OH are mainly through the induced bromine chemistry. An exception is winter conditions over polluted regions, for which CINO₂ chemistry increases ozone mixing ratios by up to 8 ppb.

Data availability. The model code is available from the corresponding author upon request and will be made available to the community through the standard GEOS-Chem (<http://www.geos-chem.org>) in the future. Data of the WINTER campaign are available to the general public at https://www.eol.ucar.edu/field_projects/winter. Data of NASA SEAC⁴RS, KORUS-AQ, and INTEX-B missions are available to the general public through the NASA data archive (<https://www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs>, <https://www-air.larc.nasa.gov/cgi-bin/ArcView/korusaq>, and <https://www-air.larc.nasa.gov/cgi-bin/ArcView/intexb>). IMPROVE data are available through the Federal Land Manager Environmental database (<http://views.cira.colostate.edu/fed>). All links mentioned here were last accessed on 1 March 2019.

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

Competing interests. The authors declare that they have no conflict of interest.

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