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Anthropogenic Impacts on Tropospheric Reactive Chlorine since the Preindustrial

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Key Points:

- Greenland ice-core records showed non-sea-salt chlorine increased from the 1940s–1970s, and decreased leveled off afterwards.
- Historical simulations by a global model qualitatively capture the observed trends when only considering changes in anthropogenic emissions.
- Modeled trends are driven by anthropogenic emissions of sulfur dioxide, nitrogen oxides, and coal combustion-emitted hydrochloric acid.

Abstract

Tropospheric reactive gaseous chlorine (Cl_y) impacts the atmosphere's oxidation capacity with implications for chemically reduced gases such as methane. Here we use Greenland ice-core records of chlorine, sodium, and acidity, and global model simulations to show how tropospheric Cl_y has been impacted by anthropogenic emissions since the 1940s. We show that anthropogenic contribution of non-sea-salt chlorine significantly influenced total chlorine and its trends after the 1940s. The modeled regional 170% Cl_y increase from preindustrial to the 1970s was driven by acid displacement from sea-salt-aerosol, direct emission of hydrochloric acid (HCl) from combustion, and chemical reactions driven by anthropogenic nitrogen oxide (NO_x) emissions. Since the 1970s, the modeled 6% Cl_y decrease was caused mainly by reduced anthropogenic HCl emissions from air pollution mitigation policies. Our findings suggest that anthropogenic emissions of acidic gases and their emission control strategies have substantial impacts on Cl_y with implications for tropospheric oxidants, methane, and mercury.

Plain Language Summary

Greenland ice cores preserve information from past atmospheres and provide information on how human activities have changed the composition of the atmosphere. While ice-core chlorine mainly originates from deposited sea-salt particles in the air, we found that emissions from human activities also influence ice-core chlorine. Using six Greenland ice cores and global model simulations, we show that the observed increasing trend in non-sea-salt chlorine during the 1940s–1970s was caused by enhanced human emissions of acidic gases and the resulting chemical reactions involving atmospheric sea-salt particles, and the observed decrease after the 1970s is largely attributed to air pollution control strategies that are widely applied in North America and Europe.

1 Introduction

Chlorine (Cl) in polar ice cores can provide information about past SSA abundance since the main source of ice-core Cl is from the emission and transport of sea-salt-aerosol (SSA). Reactive gaseous chlorine ($Cl_y = BrCl + HCl + Cl + ClO + HOCl + ClNO_3 + ClNO_2 + ClOO + OClO + 2\cdot Cl_2 + 2\cdot Cl_2O_2 + ICl$) from anthropogenic emissions, mainly in the form HCl, may also be a significant source of ice-core Cl (Legrand et al., 2002; Pasteris et al., 2014). The impact of anthropogenic emissions on tropospheric reactive chlorine since the preindustrial has not been quantified. Formation of HCl through acid displacement on SSA is thought to be the largest (85%) source of Cl_y in the troposphere (X. Wang et al., 2019), and is influenced by anthropogenic emissions of acid gas precursors such as sulfur dioxide (SO_2) and nitrogen oxides ($NO_x = NO + NO_2$). HCl is also emitted directly from combustion, mainly coal (Fu et al., 2018; Keene et al., 1999; Kolesar et al., 2018; Y. Liu et al., 2018; McCulloch et al., 1999). HCl contributes to acid deposition, causing damage to lakes and ecosystems, altering atmospheric acidity (Evans et al., 2011), and leads to severe haze and fog through co-condensation on aerosol (Gunthe et al., 2021). Oxidation of HCl and sea-salt chloride ($_{SSA}Cl^-$) produces more reactive forms of chlorine species, such as the chlorine radical (Cl•) (Bryukov et al., 2006), nitryl chloride ($ClNO_2$) (Finlayson-Pitts et al., 1989; Kercher et al., 2009; Raff et al., 2009), and hypochlorous acid (HOCl) (Watson, 1977). Despite the much lower abundance, these highly reactive chlorine species has potentially large local influence for ozone (Finlayson-Pitts, 2003; Knipping & Dabdub, 2003), nitrogen oxides (Haskins et al., 2019; Thornton et al., 2010), secondary organic aerosol (Choi et al., 2020), methane (Allan et al., 2007; Platt et al., 2004), non-methane hydrocarbons (Aschmann & Atkinson, 1995; Pszenny et al., 2007), and elemental mercury (Donohoue et al., 2005; Horowitz et al., 2017).

Anthropogenic emissions and acid displacement of HCl can lead to enrichment or depletion of Cl relative to sodium (Na) compared to their ratio in sea water, denoted as Cl_{exc} (Eq.2 in Methods). Legrand et al. (2002) calculated ice-core HCl after removing sea-salt and continental chloride from the measured total chloride, and attributed the increases in alpine ice cores to enhanced coal combustion and waste incineration in western Europe during 1925–1970. Observations show decreasing trends of non-SSA Cl^- deposition over the past 20–30 years in the US (Haskins et al., 2020) and UK (Evans et al., 2011), suggesting that the post-1970s air pollution mitigation policies targeting SO_2 and NOx emissions have reduced emissions of HCl. At Summit (central Greenland), Legrand et al. (2002) found that Cl_{exc} originates mainly from acid displacement of HCl from SSA, which increased by a factor of 2–3 over the 20th century due to enhanced aerosol acidity resulting from growing anthropogenic NO_x and SO_2 emissions. Greenland ice-core records of sulfate and nitrate, the main sinks for NO_x and SO_2, show increases beginning in the 1900s, peaking in the 1970s, followed by a rapid decline in sulfate and a more gradual decline in nitrate (Geng et al., 2014), consistent with trends of anthropogenic SO_2 and NO_x emissions from combustion (Smith et al., 2011).

2 Methods

2.1 Ice-core records

We present ice-core chlorine, sodium, and acidity records from the six Greenland ice cores (Figure S1). Precise locations and other information are summarized in Table S1, and details on core extraction and dating are described in previous publications (Geng et al., 2014; Iizuka et al., 2018; McConnell et al., 2019; Opel et al., 2013; Spolaor et al., 2016). Measurements of ice-core Na and Cl were using either a continuous flow analysis with an online ion chromatography system (CFA-IC) with an accuracy of 5% at annual resolution (for Summit07) (Geng et al., 2014; Iizuka et al., 2018), or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (McConnell et al., 2014; Spolaor et al., 2016) with an uncertainty of ±10% (for NEEM, NGT_B19, Tunu, ACT_11d and Summit10). For NEEM, NGT_B19, Tunu, ACT_11d and Summit10 cores, acidity (H^+) was measured directly using a flow-through bubbling chamber method described in Pasteris et al. (2012), with an error less than 5%. For Summit07 ice core, acidity was calculated based on the ion balance, according to **Eq. 1**:

$$[H^+] = [Cl^-] + [NO_3^-] + [SO_4^{2-}] - [Na^+] - [NH_4^+] - [K^+] - [Mg^{2+}] - [Ca^{2+}] \qquad \textbf{(Eq. 1)}$$

with concentrations in units of $\mu eq\ L^{-1}$ (Geng et al., 2014). Note that this calculation may underestimate snow acidity because it does not consider organic-acid anions (e.g., formate and acetate), which were measured to be $0.3\pm0.1\mu M$ at Summit during 1767–1945 (Legrand & Mayewski, 1997).

To separate the contribution of SSA relative to more reactive forms (e.g., HCl) of Cl, we calculated the chlorine excess (Cl_{exc}) relative to what would be expected from SSA alone, which is defined with a sea water Cl/Na mass ratio ($([Cl]/[Na])_{\text{sea water}}$) of 1.796 (Riley & Tongudai, 1967) (**Eq. 2**).

$$Cl_{exc} = [Cl]_{\text{ice core}} - ([Cl]/[Na])_{\text{sea water}} \times [Na]_{\text{ice core}} \qquad \textbf{(Eq. 2)}$$

ICP-MS measurements may lead to an underestimate of Cl_{exc} because it measures both the soluble Na and the insoluble Na fraction which may originate from non-sea-salt aerosol (e.g., dust), whereas IC measures the soluble Na and a small fraction of leachable Na from dust.

To analyze the relationship between measured species in the ice cores, we adopt the Passing-Bablok (PB) regression model (Passing & Bablok, 1983). In contrast to the traditional Ordinary Least Squares regression (OLS) which only considers measurement errors on the y-axis variable, PB regression assumes both x- and y-axis variables contain measurement errors and is insensitive to outliers (e.g., due to volcanic eruptions). We use the Pearson's correlation coefficient (*r*) to show the relationships between species, and *r* is not affected by the choice of the regression model.

2.2 GEOS-Chem simulations

To estimate impacts of anthropogenic emissions on tropospheric HCl and reactive chlorine abundances, we use a global 3-D chemical transport model GEOS-Chem (version 11-02d, Text S1) described in Bey et al. (2001) with updates described in the SI. The model is driven by MERRA-2 assimilated meteorological observations from the Goddard Earth Observing System (GEOS) (Gelaro et al., 2017). The model simulates detailed HO_x-NO_x-VOC-ozone-halogen-aerosol tropospheric chemistry, which includes SSA (Jaeglé et al., 2011) and tropospheric gas-, liquid-, and heterogeneous-phase reactive chlorine chemistry (X. Wang et al., 2019), and fully coupled stratospheric chemistry (Eastham et al., 2014).

Model simulations are performed using three emission scenarios: preindustrial (PI, year 1750), peak atmospheric acidity (PA, year 1975), and present day (PD, year 2007), as summarized in SI (Text S1 and Table S2). We run each simulation for 5 years to equilibrate stratosphere-troposphere exchange, and use only the fifth year for analysis. All simulations are conducted at 4°×5° horizontal resolution and 72 vertical levels up to 0.01hPa. We use MERRA-2 meteorological fields of the same year (2007) for all three simulations to isolate changes induced by anthropogenic emissions. This configuration will also keep emissions that are dependent on meteorological parameters, such as wind-blown dust, lightning and soil NO_x, biogenic VOCs, and SSA from the open ocean and sea-ice, constant. Only anthropogenic and biomass-burning emissions are allowed to vary between simulations in order to isolate their impacts on tropospheric chlorine.

2.3 Backward trajectory analysis

To determine the source regions of Cl_y at the six Greenland ice-core sites, we run backward trajectory analysis using the HYSPLIT model (Hybrid Single-Particle Lagrangian Integrated Trajectory) (Stein et al., 2015). We calculate the cumulative air mass probability for the 5-day backward trajectories, considering the modeled lifetime of acidic gases (e.g., SO_2 and NO_x of about 1 day), accumulation-mode aerosol (up to 6 days) (Alexander et al., 2005), and gas phase HCl (2.5 days), as well as possible seasonal variations in transport. To retrieve the source regions across the ice-core covered time periods, we conduct the backward trajectory analysis for 1959-2010, and present the averaged results. Initial altitudes of air masses are at 10, 500, 1000 and 1500 m above ground level (a.g.l.), and the calculation was constrained within 1500 m a.g.l., which was assumed to be the depth of the mixing layer. Daily precipitation from the reanalysis data sets (ERA-40 and ERA-Interim (Dee et al., 2011; Uppala et al., 2005)) was used for weighting the probability of air masses. Considering the proximity of the two Summit cores, and

Tunu and NGT_B19, we only conduct the analysis for four locations: NEEM, Tunu, ACT_11d, and Summit, and chose a region that covers most of the backward trajectory probabilities as the backward trajectory region (TRJ) (Figure S2).

3 Results

3.1 Ice-core observations

Figure 1 shows annual concentrations of Na, Cl, Cl_{exc}, and acidity from six Greenland ice cores (Figure S1). Positive mean Cl_{exc} values (1.0–5.9 ng g^{-1}) over the reported time periods (1750 or 1776–end of the records) in all records are consistent with negligible loss of HCl from the snowpack after atmospheric deposition where snow accumulation rates are greater than 40 kg m^{-2} yr^{-1} (Röthlisberger, 2003) (Table S1). Cl_{exc} represents a higher fraction of total Cl in lower latitude (medians of 9–49% over the full records) compared to higher latitude ice cores (medians of 8–17% over the full records) (Figure S3) likely due to closer proximity to North American (NA) and Western European (WE) anthropogenic source regions, as determined by back trajectory analysis (Figure S2). For all ice cores, Cl_{exc} records show no trends before 1940, followed by a 2-to-7-fold increase until ~1975. After 1975, Cl_{exc} either declined (Summit07, ACT_11d) or leveled off (Summit10, Tunu, NEEM, and NGT_B19). Ice-core acidity is similar to Cl_{exc}, with no long-term trends before the 1900s (lower latitude cores) or 1940s (higher latitude cores), an increase from 1940 to 1975, followed by a leveling off or decrease. Acidity trends are consistent with previous Greenland ice-core sulfate records (Geng et al., 2014) and trends in anthropogenic sulfur emissions in NA and WE (Smith et al., 2011).

Figure 2 and Table S3 show relationships between annual ice-core Na and Cl, and between ice-core acidity and Cl_{exc}. Na and Cl were strongly correlated in all ice cores, with a stronger relationship in higher-latitude ($r = 0.86$–0.94) compared to lower-latitude ($r = 0.49$–0.80) cores. Continued strong correlation after the 1940s (Table S3) suggests that SSA was the dominant source of chlorine throughout the records. Correlations between acidity and Cl_{exc} were stronger in post-1940s ($r = 0.33$–0.72), compared to pre-1940s ($r = -0.02$–0.43) when acidity was relatively low (Table S3). Lower latitude cores show a higher correlation ($r = 0.67$–0.72) post-1940s than higher latitude cores ($r = 0.33$–0.38) due to their closer proximity to anthropogenic source regions.

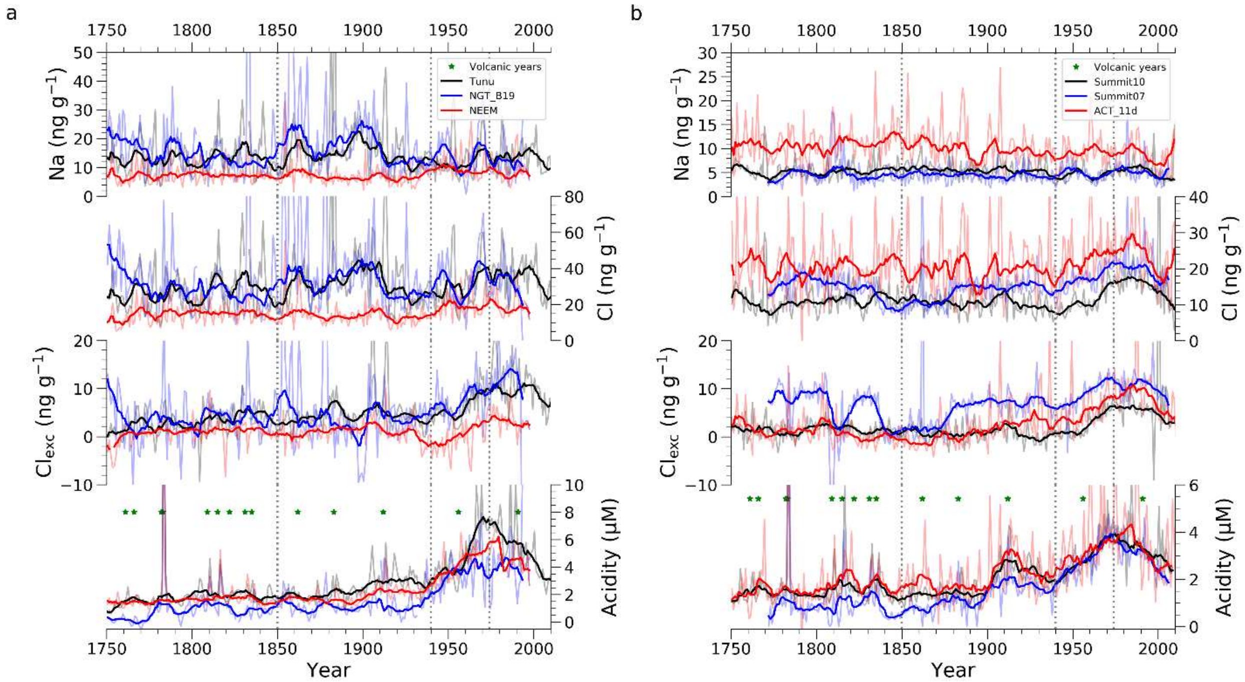

Figure 1 Annual concentrations of Na, Cl, Cl$_{exc}$, and acidity of the six ice cores in Greenland. **a**, records from higher-latitude Greenland ice cores Tunu (black), NGT_B19 (blue), and NEEM (red). **b**, records from lower-latitude Greenland ice cores Summit10 (black), Summit07 (blue), and ACT_11d (red). Grey, light blue, and pink lines represent the annual-mean concentrations. Black, blue and red lines represent the 9-year running average concentrations after removing the outliers that are outside of 1.5×IQR (interquartile range). Green stars mark volcanic eruption years (Text S2). Ion concentrations are reported for Summit07, whereas elemental concentrations are reported for other ice cores. Vertical grey dotted lines mark the years 1850, 1940, and 1975.

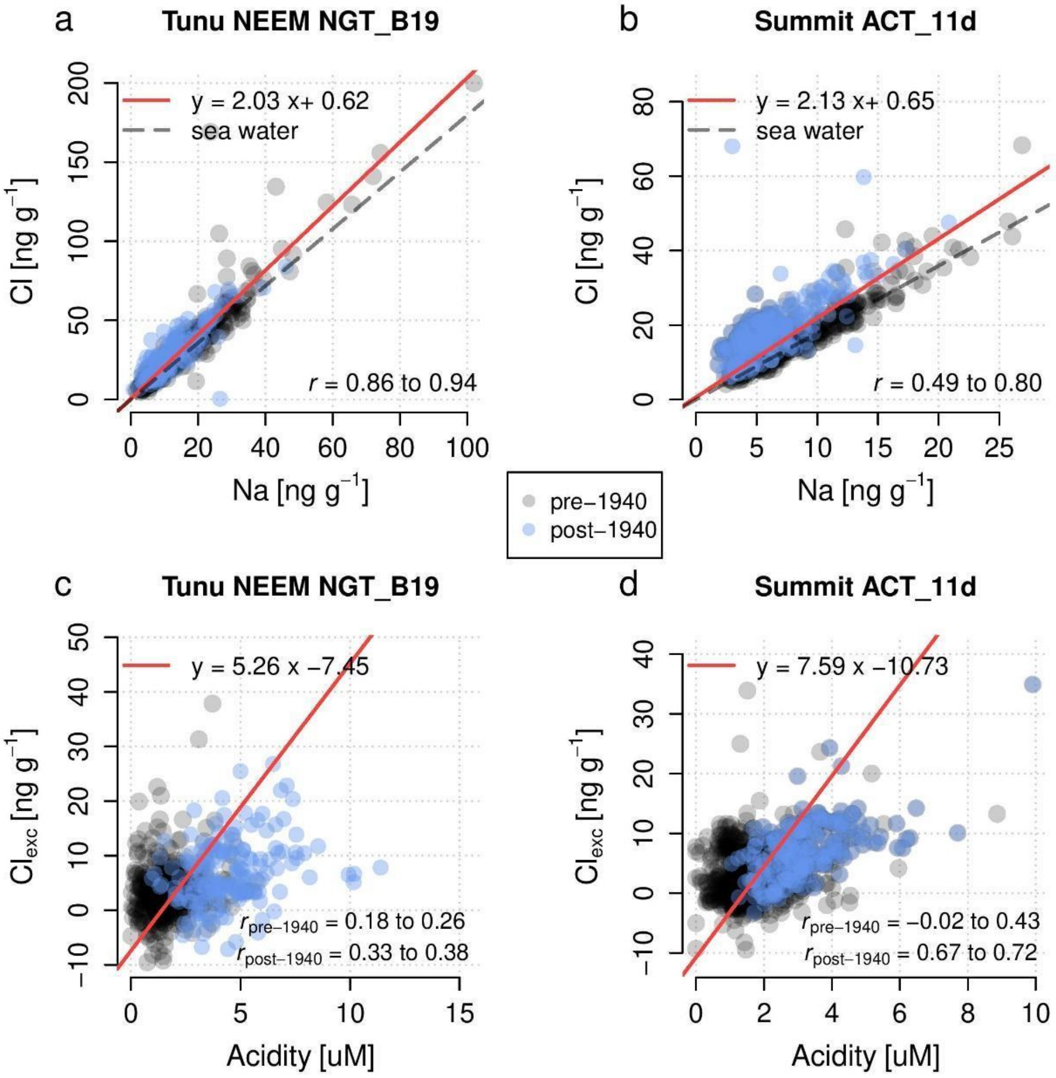

Figure 2 Relationships between annual ice-core (**a** and **b**) Na and Cl concentrations, and (**c** and **d**) snow acidity and Cl_{exc} from the six Greenland ice-core records. **a** and **c** show higher-latitude cores including Tunu, NEEM, NGT_B19, **b** and **d** show the lower-latitude cores including Summit07, Summit10, and ACT_11d. Black circles are the pre-1940 record and blue circles represent post-1940 records. Red lines and the equation show the PB regression for the full record. Dashed black lines show the relationship between Na and Cl in sea water. r, $r_{\text{pre-1940}}$ and $r_{\text{post-1940}}$ represent respectively the Pearson's correlation coefficients for the full records, pre-1940 and post-1940 records, and the range of r values is from individual ice cores in the group. Outliers outside the 1.5×IQR (interquartile range) are removed. All r values are significant with p values lower than 0.05.

3.2 Model-observation comparisons

Figure 3 shows the 30–90ºN regional distribution of modeled annual mean surface Cl_y in PI, PA, and PD, where the model considers past changes in anthropogenic emissions (Methods, and Text S1). Surface Cl_y is shown because most tropospheric Cl_y is confined to lower altitudes (2 km) due to the dominance of direct surface emissions and near-surface chemistry sources (Figure S4). The highest surface Cl_y concentrations in PA and PD are distributed in continental outflow regions where anthropogenic acids encounter $_{SSA}Cl^-$, leading to acid-displacement of HCl. The tropospheric burden of Cl_y in the 30–90ºN region increased 132% from PI to PA and 7% from PA to PD. While surface Cl_y increases everywhere in the region from PI to PA and PI to PD, the trend from PA to PD shows spatial variability that is consistent with regional trends in anthropogenic emissions of SO_2 and NO_x.

The simulated trends in Cl_y in the calculated 5-day back trajectory region (TRJ, green dashed region in Figure 3) are qualitatively consistent with and within the ranges of the observed trends in Greenland ice-core Cl_{exc} (Figure 4a). On average, the modeled Cl_y burden in TRJ increased by 170% from PI to PA, and decreased by 6% from PA to PD. From PI to PA, ice-core Cl_{exc} showed increases ranging from 105% to 631%, with an average increase of 335%. Although modeled average trends from PI to PA lie below the 25th percentile of observations, the modeled increase in Cl_y in continental outflow regions of NA (276%) and WE (203%) lie within the interquartile range (IQR) of the observations, suggesting that trends in chlorine deposition in inland Greenland may be more influenced by these source regions. From PI to PD, the simulated average TRJ Cl_y increased 153%, similar to the median increase (163%) in the observations, and was within the IQR range of the ice-core trends. The average modeled trend (+153%) fell on the lower end of the observed range, but again the simulated trends in NA and WE continental outflow regions (223% and 185%, respectively) showed a more robust comparison with the average change in ice-core Cl_{exc} (253%). From PA to PD, most inland Greenland ice cores showed a decreasing trend in Cl_{exc}, with an average decrease of 20%, and a median decrease of 41%. The magnitude of the average modeled Cl_y trends from PA to PD in the TRJ region (−6%) was smaller than the average of ice-core observations, but the modeled changes in the NA and WE continental source regions (−13%) were more similar to the observations. The range of PA to PD changes in the model (−46% to 19%) fell within the range of the ice-core observations (–114% to 102%). The modeled PI-to-PA (210%) and PA-to-PD (−25%) change in Cl_y at the location of the Col du Dome ice core in the French Alps also was qualitatively consistent with ice-core Cl_{exc} changes (383% from PI to PA, −71% from PA to PD) from Legrand et al. (2002). Model underestimation of the trends may be due in part to uncertainties in anthropogenic HCl emissions (Methods).

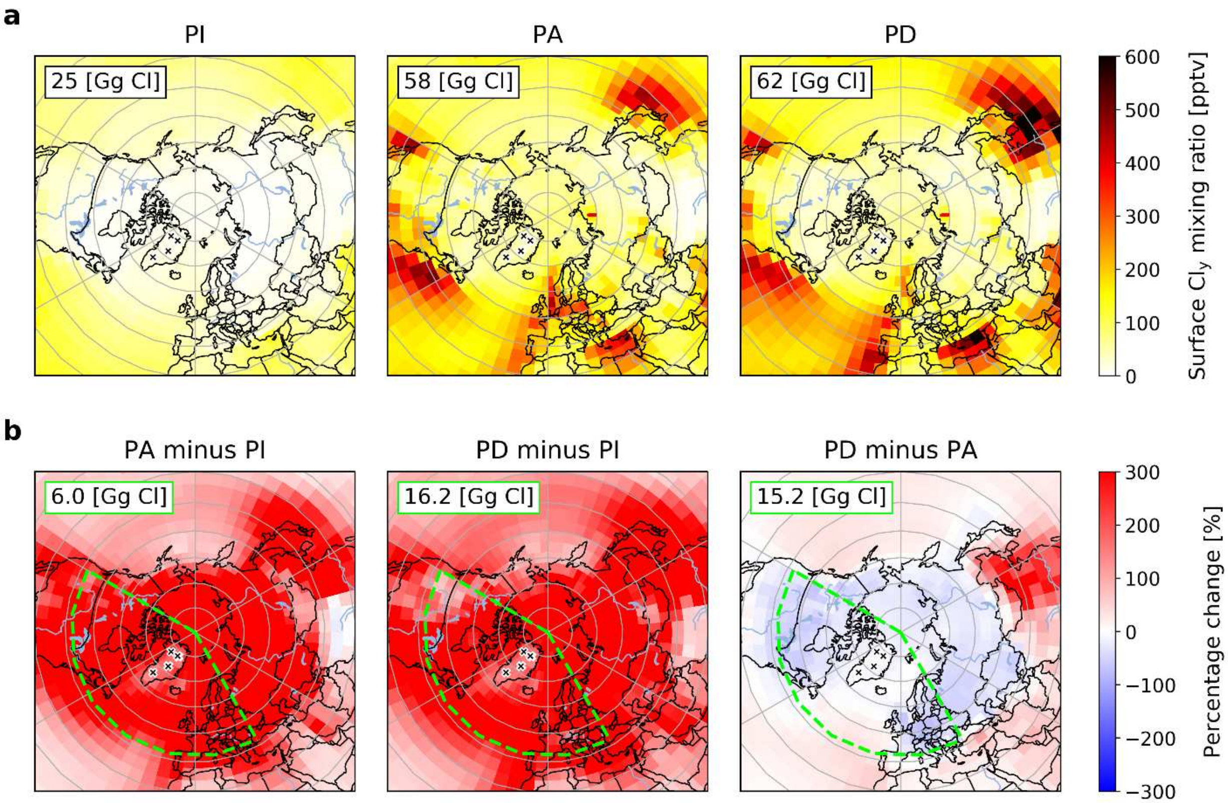

Figure 3 30–90°N regional distributions of annual mean surface mixing ratios of Cl_y in the three time periods in GEOS-Chem (**a**), and the percentage difference of Cl_y surface mixing ratio between the three time periods (**b**). Grey grid lines show 10° latitude and 60° longitude distance. Black crosses mark the ice-core sites. Dashed green lines show the back trajectory region (TRJ, 120°W–30°E, 42°N–90°N) for the six Greenland ice cores based on the 5-day back trajectory analysis. The annual mean tropospheric Cl_y burdens for 30–90°N regions are shown on the top-left corners of subplots in **a**, and the burdens for the TRJ region are shown similarly in **b**.

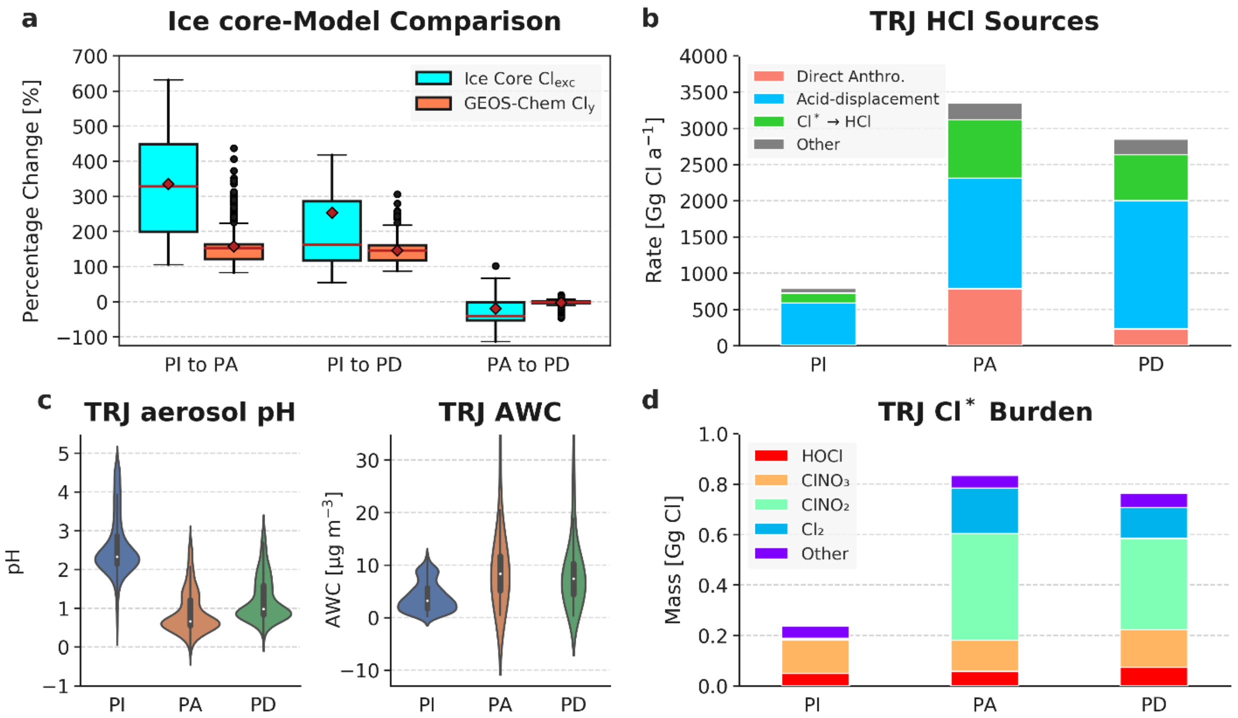

Figure 4 Model-observation comparison of non-SSA chlorine and model interpretation of the trends. **a**, Comparison of percentage changes in the Cl$_{exc}$ concentrations from the six Greenland ice cores (blue boxes) and modeled Cl$_y$ burdens in TRJ (orange boxes) between PI, PA and PD. Ice core statistics are calculated from 1750-1760 for PI, 1970-1980 for PA, and the last 10 years of the records for PD. Boxplots show the range of percentage changes, red diamonds mark the mean values and red lines represent the medians. Black dots are model grid boxes outside the range of 1.5 IQR. **b**, Modeled HCl sources in TRJ for PI, PA, and PD. 'Direct Anthro.' refers to direct anthropogenic emissions of HCl. 'Cl^* → HCl' represents the net conversion of Cl^* into HCl. 'Other' sources include the stratosphere to troposphere exchange and transport from outside of TRJ (<7%), biomass burning (<2%), and HCl formed from organochlorines (<0.1%). **c**, Violin plots for modeled accumulation mode aerosol pH in TRJ (left panel) and aerosol water content (AWC) in TRJ for PI, PA and PD. **d**, Modeled annual mean tropospheric Cl^* burden (in Gg Cl) in TRJ for PI, PA, and PD. 'Other' Cl^* species include BrCl, Cl, ClO, ClOO, Cl_2O_2, and ICl.

3.3 Anthropogenic impacts on reactive gaseous chlorine

Simulated trends in Cl_y reflect trends in HCl, since >94% of the burden and 99% of deposition is of the form HCl (Figure S5). The dominant source of HCl in all three time periods is acid displacement of $_{SSA}Cl^-$, contributing 73%, 47%, and 61% to the total source in PI, PA, and PD, respectively (Figure 4b). Chemical reactions that convert Cl^* (= Cl_y − HCl) to HCl is the second largest source (20%, 27% and 26% in PI, PA and PD, respectively). In PA, the Cl^* source is closely followed by direct anthropogenic HCl emissions, which contributes 21% of the total source. Other sources are minor (<10%). The increase in HCl from PI to PA in the TRJ region (mean of 238%) is driven by increases in direct anthropogenic emissions of HCl (35%), acid-displacement (29%), and heterogeneous reactions involving Cl^* (29%). The 12% decrease in HCl from PA to PD is driven by decreases in the direct anthropogenic source of HCl (71%) and in conversion of Cl^* to HCl (16%), and is partly compensated by a continued increase (15%) in acid displacement.

HCl acid displacement is controlled by thermodynamic equilibrium between gas phase (HCl) and aerosol phase ($_{SSA}Cl^-$). Lower aerosol pH and aerosol water content (AWC) both favor acid displacement of HCl (Haskins et al., 2018), but the relationship is non-linear. At higher pH in PI, the equilibrium is more sensitive to pH than to AWC. At lower pH in PA and PD, AWC becomes more important (Haskins et al., 2018). From PI to PA, the mean aerosol pH in TRJ decreased 1.7 pH units, resulting in a large increase in HCl displacement despite the increase in AWC (223%) (Figure 4c). From PA to PD, continued increase in HCl displacement is driven by lower AWC in the PD relative to the PA. Although accumulation mode aerosol pH increases slightly from PA to PD (0.3 pH units), the equilibrium is less sensitive to aerosol pH at the lower pH values during the PA and PD (Haskins et al., 2018) (Figure 4c).

The HCl source from Cl^* chemistry originates from reactions between Cl• with hydrocarbons and the in-cloud reaction between dissolved SO_2 and HOCl (Figure S5). Trends in the Cl^* source of HCl reflect trends in Cl^* abundance. The Cl^* burden increased by 252% from PI to PA, and decreased by −9% from PA to PD in TRJ (Figure 4d). Enhanced formation of $ClNO_2$ (395-fold) from heterogeneous reaction of N_2O_5 with particulate chloride, driven by elevated NO_x emissions (Figure S6), dominates the increase in Cl^* from PI to PA. The decrease in Cl^* from PA to PD is caused by the decrease of $ClNO_2$ (−14%) and Cl_2 (−32%) from PA to PD due to less N_2O_5 in continental outflow regions (Figure S7) driven by a decrease in NO_x emissions (Figure S6), consistent with satellite observations (Kim et al., 2006; Konovalov et al., 2010).

Changes in $ClNO_2$ production from PI to PA and PA to PD drive changes in total Cl^* abundance and in all individual Cl^* species except Cl• (Figure S5). Opposite to the Cl^* trends, Cl• abundance decreased 27% from PI to PA and increased 20% from PA to PD in the TRJ region. These changes are driven by their reactions with alkanes producing HCl (Figure S5, Table S4). Enhanced emissions of alkanes from transportation and energy extraction (Hoesly et al., 2018) and increasing methane from PI to PA (Murray, 2016) increased conversion rate of Cl• to HCl, driving the Cl• decrease. From PA to PD, although methane levels continue to increase, anthropogenic emissions of alkanes in NA and WE decrease (Hoesly et al., 2018), resulting in an increase in Cl• from PA to PD. Changes in sink reactions of Cl• are driving the conversion of Cl^* to HCl, which shows an increase from PI to PA and a decrease from PA to PD (Figure 4d).

4 Conclusions and Implications

This study investigates total and non-sea-salt chlorine (Cl_{exc}) trends since pre-industrial time using six Greenland ice cores and examines the contribution of anthropogenic emissions to these trends using the GEOS-Chem model. Observed trends in inland Greenland ice-core Cl_{exc} are captured by historical model simulations that isolate the impact of changes in anthropogenic emissions while holding meteorology constant. Model results indicate that from PI to PA, the increases in acid-displacement of HCl from SSA, direct anthropogenic HCl emissions and enhanced Cl^* production were responsible for the increasing trend in Cl_y. From PA to PD, acid-displacement continued to increase, but was overcompensated by reduced direct anthropogenic HCl emissions and chemical conversion of Cl^* to HCl. Although direct anthropogenic emissions of HCl represent <21% of the total HCl source, it is required to explain the decreasing trends in Cl_{exc} observed in ice cores since PA.

Cycling of Cl_y species can destroy O_3 directly through catalytic cycles, and indirectly through reducing NO_x abundance (X. Wang et al., 2019). Consequently, increases in Cl_y lead to decreases in OH due to reduction in ozone. The implications of Cl_y for ozone, OH and NO_x have been demonstrated previously (X. Wang et al., 2019). This study shows that anthropogenic emissions of HCl, SO_2 and NO_x have had significant impacts on tropospheric Cl_y abundance (up to +170%), which should be considered in the estimation of anthropogenic impacts on changes in tropospheric oxidation capacity.

In addition to the impact of Cl_y on oxidants such as OH, Cl• serves as an oxidant itself (Sherwen et al., 2016; X. Wang et al., 2019), with reactivity 1–2 orders of magnitude higher than OH in oxidizing alkanes (Atkinson et al., 2006; Finlayson-Pitts & Pitts, 1999; Ji et al., 2013; Xie et al., 2017; Young et al., 2014). Although a minor sink for methane, reaction with Cl• has a large impact on methane’s isotopic composition (Strode et al., 2020), which is used to constrain the methane budget in present and past climates (Allan et al., 2001, 2007; Bock et al., 2017; Strode et al., 2020; Whiticar & Schaefer, 2007). Our model simulations suggest that anthropogenic emissions alone have changed the global Cl• abundance by up to −16% since preindustrial times, which will influence the isotopic composition of methane and potentially the isotope-based interpretation of the methane budget.

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Open Research

Data Availability Statement

Ice-core data for this research is available at the Arctic Data Center via https://doi.org/10.18739/A2XS5JJ1N with Creative Commons Attribution. GEOS-Chem is open software and available on https://doi.org/10.5281/zenodo.5047976. GEOS-Chem historical simulation output is archived in the University of Washington ResearchWorks repository via http://hdl.handle.net/1773/46969.

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