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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 ( $\text{Cl}_y$ ) 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  $\text{Cl}_y$  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%  $\text{Cl}_y$  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 ( $\text{NO}_x$ ) emissions. Since the 1970s, the modeled 6%  $\text{Cl}_y$  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  $\text{Cl}_y$  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 ( $\text{Cl}_y = \text{BrCl} + \text{HCl} + \text{Cl} + \text{ClO} + \text{HOCl} + \text{ClNO}_3 + \text{ClNO}_2 + \text{ClOO} + \text{OCIO} + 2 \cdot \text{Cl}_2 + 2 \cdot \text{Cl}_2\text{O}_2 + \text{ICl}$ ) 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  $\text{Cl}_y$  in the troposphere (X. Wang et al., 2019), and is influenced by anthropogenic emissions of acid gas precursors such as sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). 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 ( $\text{SSACl}^-$ ) produces more reactive forms of chlorine species, such as the chlorine radical ( $\text{Cl}\cdot$ ) (Bryukov et al., 2006), nitryl chloride ( $\text{ClNO}_2$ ) (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  $NO_x$  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 20<sup>th</sup> 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  $\pm 10\%$  (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**:

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

with concentrations in units of  $\mu\text{eq L}^{-1}$  (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  $0.3 \pm 0.1 \mu\text{M}$  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**).

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

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  $4^\circ \times 5^\circ$  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



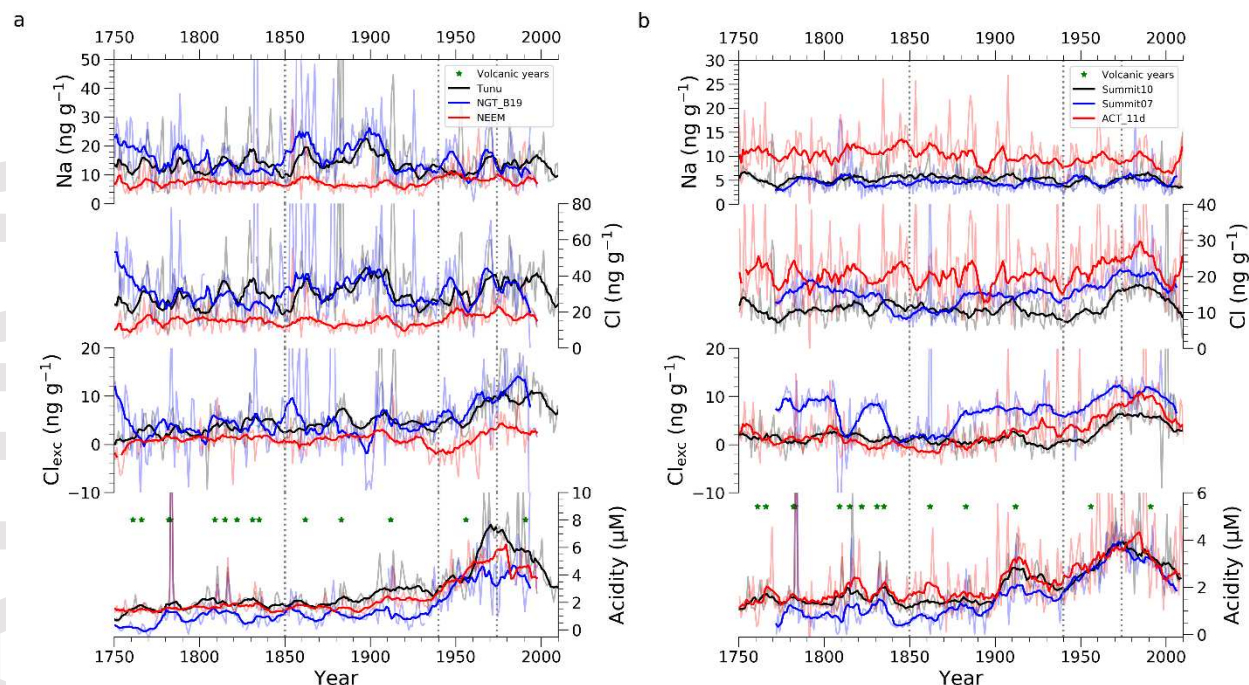
Tunu and NGT\_B19, we only conduct the analysis for four locations: NEEM, Tunu, ACT\_11d, and Summit, and chose a region that covers most of the backward trajectory probabilities as the backward trajectory region (TRJ) (Figure S2).

### 3 Results

#### 3.1 Ice-core observations

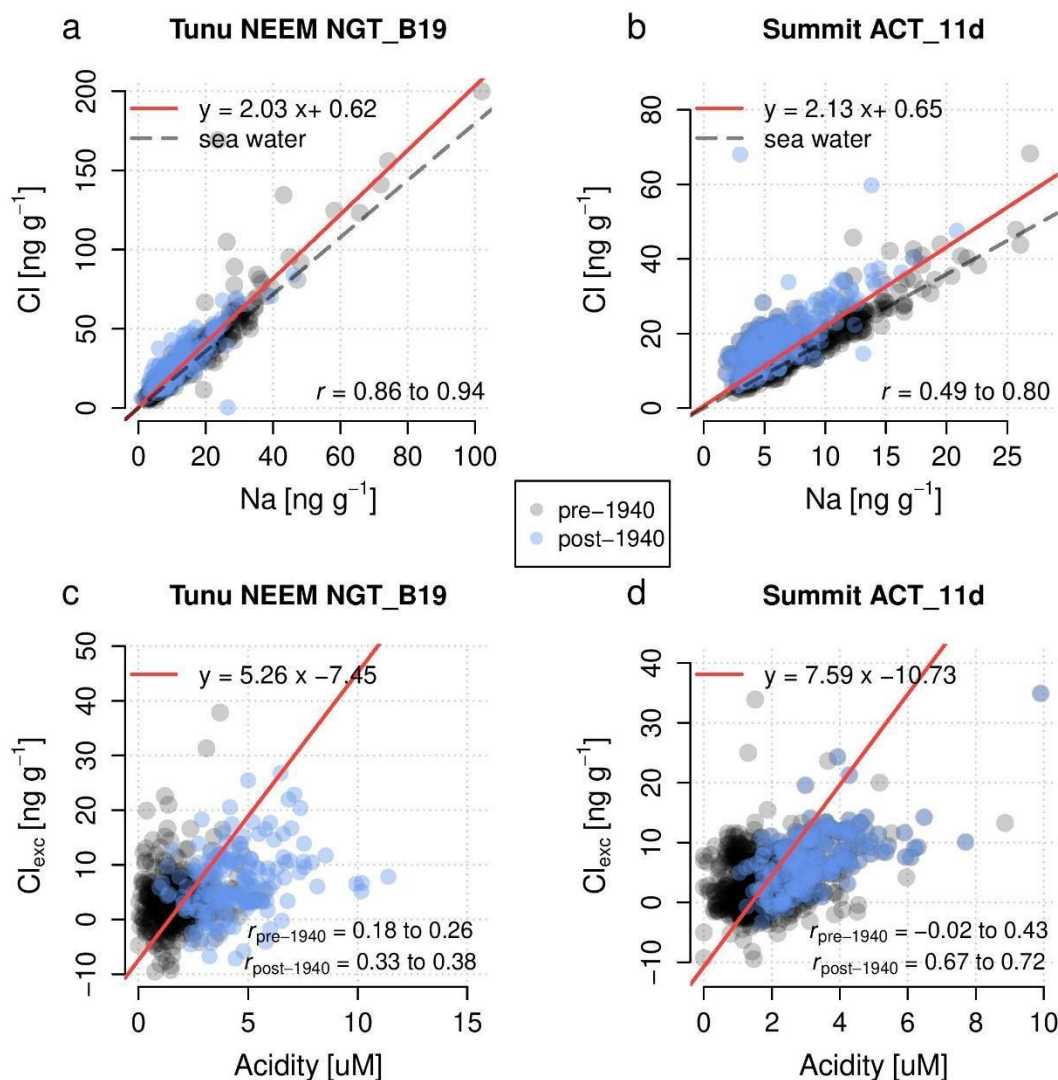
Figure 1 shows annual concentrations of Na, Cl, Cl<sub>exc</sub>, and acidity from six Greenland ice cores (Figure S1). Positive mean Cl<sub>exc</sub> values (1.0–5.9 ng g<sup>-1</sup>) over the reported time periods (1750 or 1776–end of the records) in all records are consistent with negligible loss of HCl from the snowpack after atmospheric deposition where snow accumulation rates are greater than 40 kg m<sup>-2</sup> yr<sup>-1</sup> (Röthlisberger, 2003) (Table S1). Cl<sub>exc</sub> 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<sub>exc</sub> records show no trends before 1940, followed by a 2-to-7-fold increase until ~1975. After 1975, Cl<sub>exc</sub> either declined (Summit07, ACT\_11d) or leveled off (Summit10, Tunu, NEEM, and NGT\_B19). Ice-core acidity is similar to Cl<sub>exc</sub>, 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<sub>exc</sub>. 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<sub>exc</sub> 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,  $\text{Cl}_{\text{exc}}$ , 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  $1.5 \times \text{IQR}$  (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.



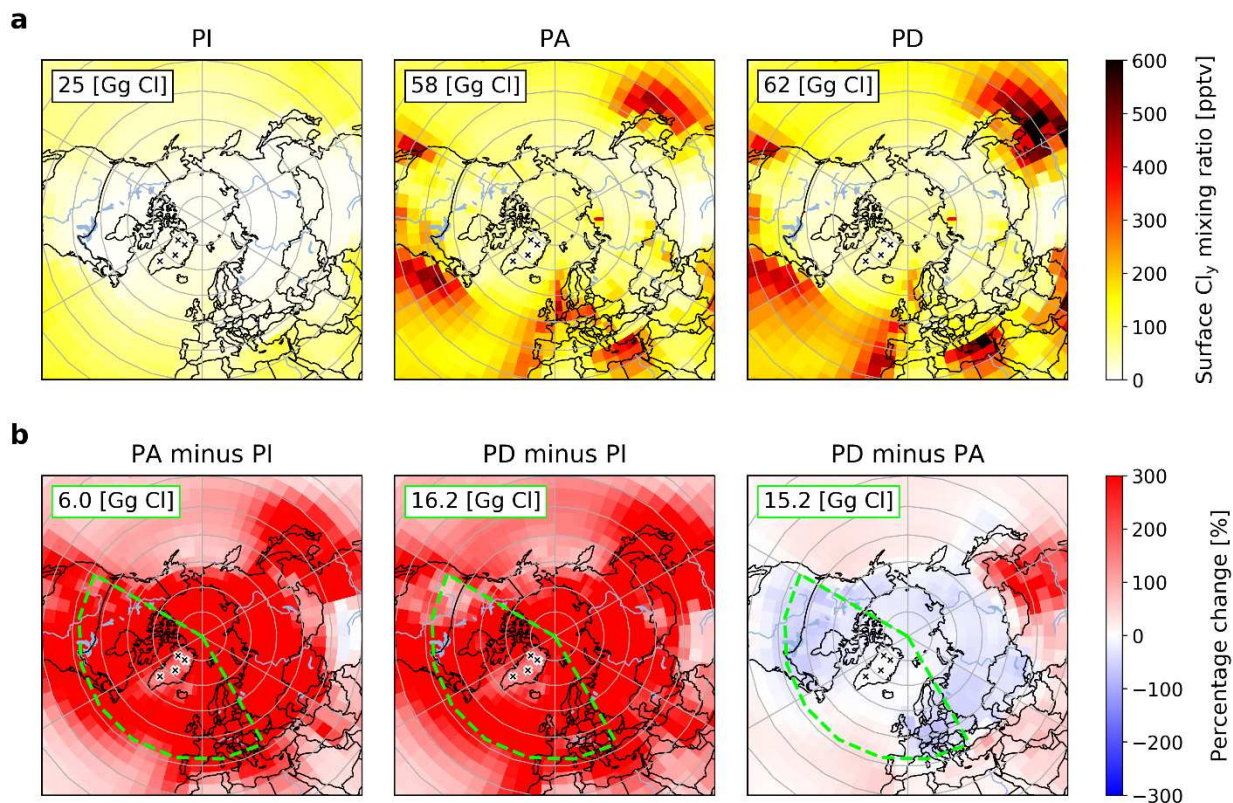


**Figure 2** Relationships between annual ice-core (**a** and **b**) Na and Cl concentrations, and (**c** and **d**) snow acidity and Cl<sub>exc</sub> from the six Greenland ice-core records. **a** and **c** show higher-latitude cores including Tunu, NEEM, NGT\_B19, **b** and **d** show the lower-latitude 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.

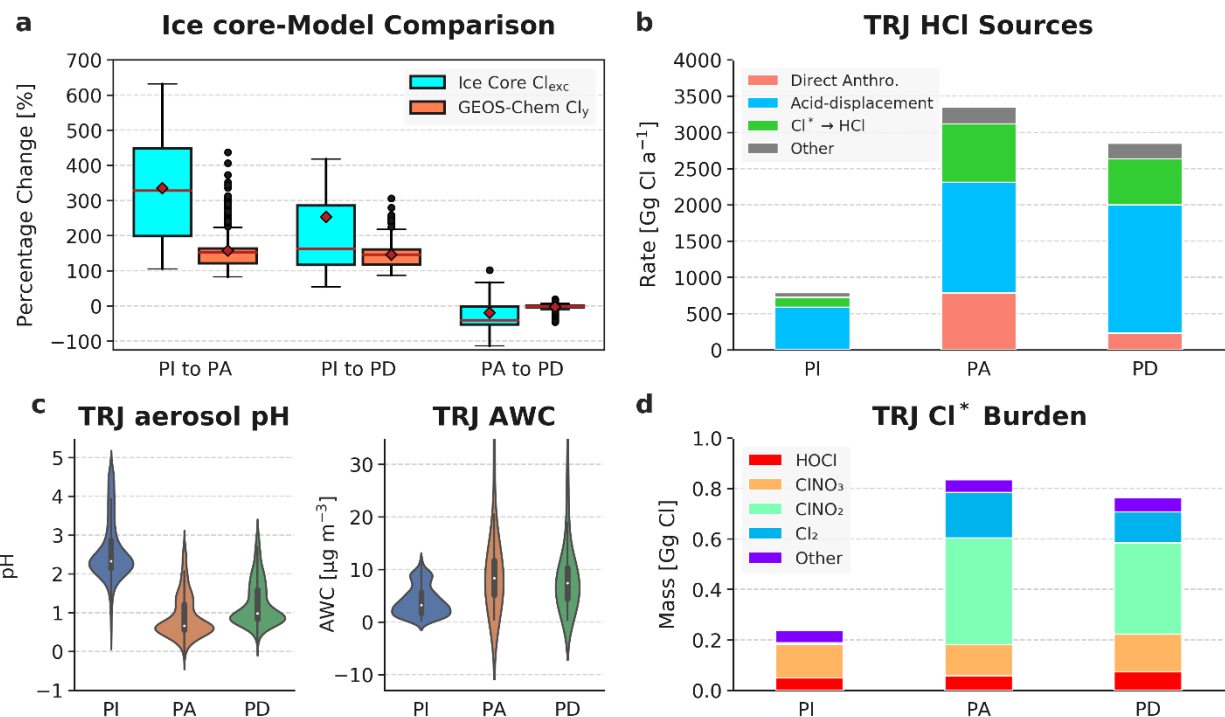
### 3.2 Model-observation comparisons

Figure 3 shows the 30–90°N regional distribution of modeled annual mean surface  $\text{Cl}_y$  in PI, PA, and PD, where the model considers past changes in anthropogenic emissions (Methods, and Text S1). Surface  $\text{Cl}_y$  is shown because most tropospheric  $\text{Cl}_y$  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  $\text{Cl}_y$  concentrations in PA and PD are distributed in continental outflow regions where anthropogenic acids encounter  $\text{SSA-Cl}^-$ , leading to acid-displacement of HCl. The tropospheric burden of  $\text{Cl}_y$  in the 30–90°N region increased 132% from PI to PA and 7% from PA to PD. While surface  $\text{Cl}_y$  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  $\text{SO}_2$  and  $\text{NO}_x$ .

The simulated trends in  $\text{Cl}_y$  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  $\text{Cl}_{\text{exc}}$  (Figure 4a). On average, the modeled  $\text{Cl}_y$  burden in TRJ increased by 170% from PI to PA, and decreased by 6% from PA to PD. From PI to PA, ice-core  $\text{Cl}_{\text{exc}}$  showed increases ranging from 105% to 631%, with an average increase of 335%. Although modeled average trends from PI to PA lie below the 25<sup>th</sup> percentile of observations, the modeled increase in  $\text{Cl}_y$  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  $\text{Cl}_y$  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  $\text{Cl}_{\text{exc}}$  (253%). From PA to PD, most inland Greenland ice cores showed a decreasing trend in  $\text{Cl}_{\text{exc}}$ , with an average decrease of 20%, and a median decrease of 41%. The magnitude of the average modeled  $\text{Cl}_y$  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  $\text{Cl}_y$  at the location of the Col du Dome ice core in the French Alps also was qualitatively consistent with ice-core  $\text{Cl}_{\text{exc}}$  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  $\text{Cl}_y$  in the three time periods in GEOS-Chem (a), and the percentage difference of  $\text{Cl}_y$  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  $\text{Cl}_y$  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. ‘ $Cl^* \rightarrow HCl$ ’ 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  $\text{Cl}_y$  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  $\text{SSACl}^-$ , contributing 73%, 47%, and 61% to the total source in PI, PA, and PD, respectively (Figure 4b). Chemical reactions that convert  $\text{Cl}^*$  ( $= \text{Cl}_y - \text{HCl}$ ) to HCl is the second largest source (20%, 27% and 26% in PI, PA and PD, respectively). In PA, the  $\text{Cl}^*$  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  $\text{Cl}^*$  (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  $\text{Cl}^*$  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 ( $\text{SSACl}^-$ ). 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  $\text{Cl}^*$  chemistry originates from reactions between  $\text{Cl}^\bullet$  with hydrocarbons and the in-cloud reaction between dissolved  $\text{SO}_2$  and HOCl (Figure S5). Trends in the  $\text{Cl}^*$  source of HCl reflect trends in  $\text{Cl}^*$  abundance. The  $\text{Cl}^*$  burden increased by 252% from PI to PA, and decreased by -9% from PA to PD in TRJ (Figure 4d). Enhanced formation of  $\text{ClNO}_2$  (395-fold) from heterogeneous reaction of  $\text{N}_2\text{O}_5$  with particulate chloride, driven by elevated  $\text{NO}_x$  emissions (Figure S6), dominates the increase in  $\text{Cl}^*$  from PI to PA. The decrease in  $\text{Cl}^*$  from PA to PD is caused by the decrease of  $\text{ClNO}_2$  (-14%) and  $\text{Cl}_2$  (-32%) from PA to PD due to less  $\text{N}_2\text{O}_5$  in continental outflow regions (Figure S7) driven by a decrease in  $\text{NO}_x$  emissions (Figure S6), consistent with satellite observations (Kim et al., 2006; Konovalov et al., 2010).

Changes in  $\text{ClNO}_2$  production from PI to PA and PA to PD drive changes in total  $\text{Cl}^*$  abundance and in all individual  $\text{Cl}^*$  species except  $\text{Cl}^\bullet$  (Figure S5). Opposite to the  $\text{Cl}^*$  trends,  $\text{Cl}^\bullet$  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  $\text{Cl}^\bullet$  to HCl, driving the  $\text{Cl}^\bullet$  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  $\text{Cl}^\bullet$  from PA to PD. Changes in sink reactions of  $\text{Cl}^\bullet$  are driving the conversion of  $\text{Cl}^*$  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 ( $\text{Cl}_{\text{exc}}$ ) 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  $\text{Cl}_{\text{exc}}$  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  $\text{Cl}^*$  production were responsible for the increasing trend in  $\text{Cl}_y$ . From PA to PD, acid-displacement continued to increase, but was overcompensated by reduced direct anthropogenic HCl emissions and chemical conversion of  $\text{Cl}^*$  to HCl. Although direct anthropogenic emissions of HCl represent <21% of the total HCl source, it is required to explain the decreasing trends in  $\text{Cl}_{\text{exc}}$  observed in ice cores since PA.

Cycling of  $\text{Cl}_y$  species can destroy  $\text{O}_3$  directly through catalytic cycles, and indirectly through reducing  $\text{NO}_x$  abundance (X. Wang et al., 2019). Consequently, increases in  $\text{Cl}_y$  lead to decreases in OH due to reduction in ozone. The implications of  $\text{Cl}_y$  for ozone, OH and  $\text{NO}_x$  have been demonstrated previously (X. Wang et al., 2019). This study shows that anthropogenic emissions of HCl,  $\text{SO}_2$  and  $\text{NO}_x$  have had significant impacts on tropospheric  $\text{Cl}_y$  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  $\text{Cl}_y$  on oxidants such as OH,  $\text{Cl}\cdot$  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  $\text{Cl}\cdot$  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  $\text{Cl}\cdot$  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>.

## References

- Alexander, B., Park, R. J., Jacob, D. J., Li, Q. B., Yantosca, R. M., Savarino, J., et al. (2005). Sulfate formation in sea-salt aerosols: Constraints from oxygen isotopes. *Journal of Geophysical Research*, 110(D10). <https://doi.org/10.1029/2004jd005659>
- Allan, W., Lowe, D. C., & Cainey, J. M. (2001). Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of  $\delta^{13}\text{C}$  in methane. *Geophysical Research Letters*, 28(17), 3239–3242. <https://doi.org/10.1029/2001gl013064>
- Allan, W., Struthers, H., & Lowe, D. C. (2007). Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with Southern Hemisphere measurements. *Journal of Geophysical Research*, 112(D4), 467. <https://doi.org/10.1029/2006JD007369>
- Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., et al. (2012). Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition. *Atmospheric Chemistry and Physics*, 12(1), 591–603. <https://doi.org/10.5194/acp-12-591-2012>
- Aschmann, S. M., & Atkinson, R. (1995). Rate constants for the gas-phase reactions of alkanes with Cl atoms at  $296 \pm 2$  K. *International Journal of Chemical Kinetics*, 27(6), 613–622. <https://doi.org/10.1002/kin.550270611>
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., et al. (2006). Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II--gas phase reactions of organic species. *Atmospheric Chemistry and Physics*, 6(11), 3625–4055. Retrieved from <https://acp.copernicus.org/articles/6/3625/2006/>
- Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., et al. (2001). Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation. *Journal of Geophysical Research*, 106(D19), 23073–23095. <https://doi.org/10.1029/2001jd000807>
- Bock, M., Schmitt, J., Beck, J., Seth, B., Chappellaz, J., & Fischer, H. (2017). Glacial/interglacial wetland, biomass burning, and geologic methane emissions constrained by dual stable isotopic CH<sub>4</sub> ice core records. *Proceedings of the National Academy of Sciences of the United States of America*, 114(29), E5778–E5786. <https://doi.org/10.1073/pnas.1613883114>
- Bryukov, M. G., Dellinger, B., & Knyazev, V. D. (2006). Kinetics of the gas-phase reaction of OH with HCl. *The Journal of Physical Chemistry. A*, 110(3), 936–943. <https://doi.org/10.1021/jp053615x>
- Chen, Q., Schmidt, J. A., Shah, V., Jaeglé, L., Sherwen, T., & Alexander, B. (2017). Sulfate production by reactive bromine: Implications for the global sulfur and reactive bromine budgets: Sulfur-Halogen Interactions. *Geophysical Research Letters*, 44(13), 7069–7078. <https://doi.org/10.1002/2017GL073812>
- Choi, M. S., Qiu, X., Zhang, J., Wang, S., Li, X., Sun, Y., et al. (2020). Study of Secondary Organic Aerosol Formation from Chlorine Radical-Initiated Oxidation of Volatile Organic Compounds in a Polluted Atmosphere Using a 3D Chemical Transport Model. *Environmental Science & Technology*, 54(21), 13409–13418. <https://doi.org/10.1021/acs.est.0c02958>
- Cole-Dai, J., Ferris, D. G., Lanciki, A. L., Savarino, J., Thiemens, M. H., & McConnell, J. R. (2013). Two likely stratospheric volcanic eruptions in the 1450s C.E. found in a bipolar, subannually dated 800 year ice core record: TWO VOLCANIC ERUPTIONS IN THE

- 1450s. *Journal of Geophysical Research, D: Atmospheres*, 118(14), 7459–7466.  
<https://doi.org/10.1002/jgrd.50587>
- Custard, K. D., Raso, A. R. W., Shepson, P. B., Staebler, R. M., & Pratt, K. A. (2017). Production and Release of Molecular Bromine and Chlorine from the Arctic Coastal Snowpack. *ACS Earth and Space Chemistry*, 1(3), 142–151.  
<https://doi.org/10.1021/acsearthspacechem.7b00014>
- Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., et al. (2011). The ERA-Interim reanalysis: configuration and performance of the data assimilation system. *Quarterly Journal of the Royal Meteorological Society*, 137(656), 553–597. <https://doi.org/10.1002/qj.828>
- Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., et al. (2011). The ERA-Interim reanalysis: configuration and performance of the data assimilation system. *Quarterly Journal of the Royal Meteorological Society*, 137(656), 553–597.  
<https://doi.org/10.1002/qj.828>
- Dlugokencky, E. J. (2016). Atmospheric Methane Dry Air Mole Fractions (1983-2015) and Atmospheric Carbon Dioxide Dry Air Mole Fractions (1968-2015) from the NOAA ESRL Carbon Cycle Cooperative Global Air Sampling Network, original data files. Retrieved from <https://epic.awi.de/id/eprint/44810/>
- van Donkelaar, A., Martin, R. V., Leaitch, W. R., Macdonald, A. M., Walker, T. W., Streets, D. G., et al. (2008). Analysis of aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada. *Atmospheric Chemistry and Physics*, 8, 2999–3014. Retrieved from <https://acp.copernicus.org/articles/8/2999/2008/acp-8-2999-2008.pdf>
- Donohoue, D. L., Bauer, D., & Hynes, A. J. (2005). Temperature and pressure dependent rate coefficients for the reaction of Hg with Cl and the reaction of Cl with Cl: a pulsed laser photolysis-pulsed laser induced fluorescence study. *The Journal of Physical Chemistry. A*, 109(34), 7732–7741. <https://doi.org/10.1021/jp051354l>
- Eastham, S. D., Weisenstein, D. K., & Barrett, S. R. H. (2014). Development and evaluation of the unified tropospheric–stratospheric chemistry extension (UCX) for the global chemistry-transport model GEOS-Chem. *Atmospheric Environment*, 89, 52–63.  
<https://doi.org/10.1016/j.atmosenv.2014.02.001>
- Evans, C. D., Monteith, D. T., Fowler, D., Cape, J. N., & Brayshaw, S. (2011). Hydrochloric acid: an overlooked driver of environmental change. *Environmental Science & Technology*, 45(5), 1887–1894. <https://doi.org/10.1021/es103574u>
- Finlayson-Pitts, B. J. (2003). The tropospheric chemistry of sea salt: a molecular-level view of the chemistry of NaCl and NaBr. *Chemical Reviews*, 103(12), 4801–4822.  
<https://doi.org/10.1021/cr020653t>
- Finlayson-Pitts, B. J., & Pitts, J. N., Jr. (1999). *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*. Elsevier. Retrieved from <https://play.google.com/store/books/details?id=mRoJUB5fxRwC>
- Finlayson-Pitts, B. J., Ezell, M. J., & Pitts, J. N. (1989). Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>. *Nature*. <https://doi.org/10.1038/337241a0>
- Fisher, J. A., Jacob, D. J., Wang, Q., Bahreini, R., Carouge, C. C., Cubison, M. J., et al. (2011). Sources, distribution, and acidity of sulfate–ammonium aerosol in the Arctic in winter–spring. *Atmospheric Environment*, 45(39), 7301–7318.  
<https://doi.org/10.1016/j.atmosenv.2011.08.030>

- Fountoukis, C., & Nenes, A. (2007). ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K–Ca–Mg–NH–Na–SO–NO–Cl–HO aerosols. *Atmospheric Chemistry and Physics*, 7, 4639–4659. Retrieved from <https://www.atmos-chem-phys.net/7/4639/2007/acp-7-4639-2007.pdf>
- Fu, X., Wang, T., Wang, S., Zhang, L., Cai, S., Xing, J., & Hao, J. (2018). Anthropogenic Emissions of Hydrogen Chloride and Fine Particulate Chloride in China. *Environmental Science & Technology*, 52(3), 1644–1654. <https://doi.org/10.1021/acs.est.7b05030>
- Gelaro, R., McCarty, W., Suárez, M. J., Todling, R., Molod, A., Takacs, L., et al. (2017). The Modern-Era Retrospective Analysis for Research and Applications, Version 2 (MERRA-2). *Journal of Climate*, 30(Iss 13), 5419–5454. <https://doi.org/10.1175/JCLI-D-16-0758.1>
- Geng, L., Alexander, B., Cole-Dai, J., Steig, E. J., Savarino, J., Sofen, E. D., & Schauer, A. J. (2014). Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change. *Proceedings of the National Academy of Sciences of the United States of America*, 111(16), 5808–5812. <https://doi.org/10.1073/pnas.1319441111>
- Gunthe, S. S., Liu, P., Panda, U., Raj, S. S., Sharma, A., Darbyshire, E., et al. (2021). Enhanced aerosol particle growth sustained by high continental chlorine emission in India. *Nature Geoscience*, 1–8. <https://doi.org/10.1038/s41561-020-00677-x>
- Halfacre, J. W., Shepson, P. B., & Pratt, K. A. (2019). pH-dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces. *Atmospheric Chemistry and Physics*, 19(7), 4917–4931. <https://doi.org/10.5194/acp-19-4917-2019>
- Haskins, J. D., Jaeglé, L., Shah, V., & Lee, B. H. (2018). Wintertime Gas-Particle Partitioning and Speciation of Inorganic Chlorine in the Lower Troposphere Over the Northeast United States and Coastal Ocean. *Journal of*. Retrieved from <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/2018JD028786>
- Haskins, J. D., Lee, B. H., Lopez-Hilfiker, F. D., Peng, Q., Jaeglé, L., Reeves, J. M., et al. (2019). Observational Constraints on the Formation of Cl<sub>2</sub> From the Reactive Uptake of ClNO<sub>2</sub> on Aerosols in the Polluted Marine Boundary Layer. *Journal of Geophysical Research, D: Atmospheres*. <https://doi.org/10.1029/2019JD030627>
- Haskins, J. D., Jaeglé, L., & Thornton, J. A. (2020). Significant decrease in wet deposition of anthropogenic chloride across the Eastern United States, 1998–2018. *Geophysical Research Letters*, 47(22). <https://doi.org/10.1029/2020gl090195>
- Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., et al. (2018). Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS). *Geoscientific Model Development*, 11(1), 369–408. <https://doi.org/10.5194/gmd-11-369-2018>
- Holmes, C. D., Bertram, T. H., Confer, K. L., Graham, K. A., Ronan, A. C., Wirks, C. K., & Shah, V. (2019). The Role of Clouds in the Tropospheric NO<sub>x</sub> Cycle: A New Modeling Approach for Cloud Chemistry and Its Global Implications. *Geophysical Research Letters*, 46(9), 4980–4990. <https://doi.org/10.1029/2019GL081990>
- Horowitz, H. M., Jacob, D. J., Zhang, Y., Dibble, T. S., Slemr, F., Amos, H. M., et al. (2017). A new mechanism for atmospheric mercury redox chemistry: implications for the global mercury budget. *Atmospheric Chemistry and Physics*, 17(10), 6353–6371. <https://doi.org/10.5194/acp-17-6353-2017>
- Huang, J., & Jaeglé, L. (2017). Wintertime enhancements of sea salt aerosol in polar regions consistent with a sea ice source from blowing snow. *Atmospheric Chemistry and Physics*, 17(5), 3699–3712. <https://doi.org/10.5194/acp-17-3699-2017>

- Iizuka, Y., Uemura, R., Fujita, K., Hattori, S., Seki, O., Miyamoto, C., et al. (2018). A 60 Year Record of Atmospheric Aerosol Depositions Preserved in a High-Accumulation Dome Ice Core, Southeast Greenland. *Journal of Geophysical Research, D: Atmospheres*, 123(1), 574–589. <https://doi.org/10.1002/2017JD026733>
- Jacob, D. J., Waldman, J. M., Munger, J. W., & Hoffmann, M. R. (1985). Chemical composition of fogwater collected along the California coast. *Environmental Science & Technology*, 19(8), 730–736. <https://doi.org/10.1021/es00138a013>
- Jaeglé, L., Quinn, P. K., Bates, T. S., Alexander, B., & Lin, J.-T. (2011). Global distribution of sea salt aerosols: new constraints from in situ and remote sensing observations. *Atmospheric Chemistry and Physics*, 11(7), 3137–3157. <https://doi.org/10.5194/acp-11-3137-2011>
- Ji, Y. M., Wang, H. H., Gao, Y. P., Li, G. Y., & An, T. C. (2013). A theoretical model on the formation mechanism and kinetics of highly toxic air pollutants from halogenated formaldehydes reacted with halogen atoms. *Atmospheric Chemistry and Physics Discussions: ACPD*, 13(7), 18205–18231. <https://doi.org/10.5194/acpd-13-18205-2013>
- Keene, W. C., Khalil, M. A. K., Erickson, D. J., III, McCulloch, A., Graedel, T. E., Lobert, J. M., et al. (1999). Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research*, 104(D7), 8429–8440. <https://doi.org/10.1029/1998JD100084>
- Kercher, J. P., Riedel, T. P., & Thornton, J. A. (2009). Chlorine activation by NO: simultaneous, in situ detection of ClNO and NO by chemical ionization mass spectrometry. Retrieved January 14, 2021, from <https://core.ac.uk/download/pdf/194272417.pdf>
- Kim, S.-W., Heckel, A., McKeen, S. A., Frost, G. J., Hsie, E.-Y., Trainer, M. K., et al. (2006). Satellite-observed U.S. power plant NO<sub>x</sub> emission reductions and their impact on air quality. *Geophysical Research Letters*, 33(22), 127. <https://doi.org/10.1029/2006GL027749>
- Knipping, E. M., & Dabdub, D. (2003). Impact of chlorine emissions from sea-salt aerosol on coastal urban ozone. *Environmental Science & Technology*, 37(2), 275–284. <https://doi.org/10.1021/es025793z>
- Kolesar, K. R., Mattson, C. N., Peterson, P. K., May, N. W., Prendergast, R. K., & Pratt, K. A. (2018). Increases in wintertime PM<sub>2.5</sub> sodium and chloride linked to snowfall and road salt application. *Atmospheric Environment*, 177, 195–202. <https://doi.org/10.1016/j.atmosenv.2018.01.008>
- Kononov, I. B., Beekmann, M., Richter, A., Burrows, J. P., & Hilboll, A. (2010). Multi-annual changes of NO<sub>x</sub> emissions in megacity regions: nonlinear trend analysis of satellite measurement based estimates. *Atmospheric Chemistry and Physics*, 10(17), 8481. Retrieved from [http://search.proquest.com/openview/17df78241e59ef4f030b4ae7dc9fc011/1?pq-origsite=gscholar&cbl=105744&casa\\_token=LbjF86FaKZ0AAAAA:Z7mxXO\\_XwpQDgERA8H4khqhY7NRYy7kcJ2ICn4oCbxD-RL0ZgwgIkWaDpE6AV6qdD7y\\_cR0YA](http://search.proquest.com/openview/17df78241e59ef4f030b4ae7dc9fc011/1?pq-origsite=gscholar&cbl=105744&casa_token=LbjF86FaKZ0AAAAA:Z7mxXO_XwpQDgERA8H4khqhY7NRYy7kcJ2ICn4oCbxD-RL0ZgwgIkWaDpE6AV6qdD7y_cR0YA)
- Lee, B. H., Lopez-Hilfiker, F. D., Schroder, J. C., Campuzano-Jost, P., Jimenez, J. L., McDuffie, E. E., et al. (2018). Airborne Observations of Reactive Inorganic Chlorine and Bromine Species in the Exhaust of Coal-Fired Power Plants. *Journal of Geophysical Research, D: Atmospheres*, 123(19), 11225–11237. <https://doi.org/10.1029/2018JD029284>
- Legrand, M., & Mayewski, P. (1997). Glaciochemistry of polar ice cores: A review. *Reviews of Geophysics*, 35(3), 219–243. <https://doi.org/10.1029/96RG03527>
- Legrand, M., Preunkert, S., Wagenbach, D., & Fischer, H. (2002). Seasonally resolved Alpine and Greenland ice core records of anthropogenic HCl emissions over the 20th century. *Journal of Geophysical Research*, 107(D12). <https://doi.org/10.1029/2001jd001165>



- Liang, Q., Stolarski, R. S., Kawa, S. R., Nielsen, J. E., Douglass, A. R., Rodriguez, J. M., et al. (2010). Finding the missing stratospheric Br<sub>y</sub>: a global modeling study of CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub>. *Atmospheric Chemistry and Physics*, 10(5), 2269–2286. <https://doi.org/10.5194/acp-10-2269-2010>
- Liao, J., Huey, L. G., Liu, Z., Tanner, D. J., Cantrell, C. A., Orlando, J. J., et al. (2014). High levels of molecular chlorine in the Arctic atmosphere. *Nature Geoscience*, 7(2), 91–94. <https://doi.org/10.1038/ngeo2046>
- Li, M., Zhang, Q., Streets, D. G., He, K. B., Cheng, Y. F., Emmons, L. K., et al. (2014). Mapping Asian anthropogenic emissions of non-methane volatile organic compounds to multiple chemical mechanisms. *Atmospheric Chemistry and Physics*, 14(11), 5617–5638. <https://doi.org/10.5194/acp-14-5617-2014>
- Liu, H., Jacob, D. J., Bey, I., & Yantosca, R. M. (2001). Constraints from <sup>210</sup>Pb and <sup>7</sup>Be on wet deposition and transport in a global three-dimensional chemical tracer model driven by assimilated meteorological fields. *Journal of Geophysical Research*, 106(D11), 12109–12128. <https://doi.org/10.1029/2000jd900839>
- Liu, T., & Abbatt, J. P. D. (2020). An Experimental Assessment of the Importance of S(IV) Oxidation by Hypohalous Acids in the Marine Atmosphere. *Geophysical Research Letters*, 47(4), D23202. <https://doi.org/10.1029/2019GL086465>
- Liu, Y., Fan, Q., Chen, X., Zhao, J., Ling, Z., Hong, Y., et al. (2018). Modeling the impact of chlorine emissions from coal combustion and prescribed waste incineration on tropospheric ozone formation in China. *Atmospheric Chemistry and Physics*, 18(4), 2709–2724. <https://doi.org/10.5194/acp-18-2709-2018>
- Marais, E. A., & Wiedinmyer, C. (2016). Air Quality Impact of Diffuse and Inefficient Combustion Emissions in Africa (DICE-Africa). *Environmental Science & Technology*, 50(19), 10739–10745. <https://doi.org/10.1021/acs.est.6b02602>
- van Marle, M. J. E., Kloster, S., Magi, B. I., Marlon, J. R., Daniau, A.-L., Field, R. D., et al. (2017). Historic global biomass burning emissions for CMIP6 (BB4CMIP) based on merging satellite observations with proxies and fire models (1750–2015). *Geoscientific Model Development*, 10(9), 3329–3357. <https://doi.org/10.5194/gmd-10-3329-2017>
- Maselli, O. J., Chellman, N. J., Grieman, M., Layman, L., McConnell, J. R., Pasteris, D., et al. (2017). Sea ice and pollution-modulated changes in Greenland ice core methanesulfonate and bromine. *Climate of the Past*, 13(1), 39–59. <https://doi.org/10.5194/cp-13-39-2017>
- McConnell, J. R., Maselli, O. J., Sigl, M., Vallelonga, P., Neumann, T., Anshütz, H., et al. (2014). Antarctic-wide array of high-resolution ice core records reveals pervasive lead pollution began in 1889 and persists today. *Scientific Reports*, 4, 5848. <https://doi.org/10.1038/srep05848>
- McConnell, J. R., Chellman, N. J., Wilson, A. I., Stohl, A., Arienzo, M. M., Eckhardt, S., et al. (2019). Pervasive Arctic lead pollution suggests substantial growth in medieval silver production modulated by plague, climate, and conflict. *Proceedings of the National Academy of Sciences of the United States of America*, 116(30), 14910–14915. <https://doi.org/10.1073/pnas.1904515116>
- McCulloch, A., Aucott, M. L., Benkovitz, C. M., Graedel, T. E., Kleiman, G., Midgley, P. M., & Li, Y.-F. (1999). Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research*, 104(D7), 8391–8403. <https://doi.org/10.1029/1999JD900025>



- McCulloch, A., Aucott, M. L., Graedel, T. E., Kleiman, G., Midgley, P. M., & Li, Y.-F. (1999). Industrial emissions of trichloroethene, tetrachloroethene, and dichloromethane: Reactive Chlorine Emissions Inventory. *Journal of Geophysical Research*, 104(D7), 8417–8427. <https://doi.org/10.1029/1999jd900011>
- Meinshausen, M., Vogel, E., Nauels, A., Lorbacher, K., Meinshausen, N., Etheridge, D. M., et al. (2017). Historical greenhouse gas concentrations for climate modelling (CMIP6). *Geoscientific Model Development*, 10(5), 2057–2116. <https://doi.org/10.5194/gmd-10-2057-2017>
- Moch, J. M., Dovrou, E., Mickley, L. J., Keutsch, F. N., Liu, Z., Wang, Y., et al. (2020). Global Importance of Hydroxymethanesulfonate in Ambient Particulate Matter: Implications for Air Quality. *Journal of Geophysical Research, D: Atmospheres*, 125(18), e2020JD032706. <https://doi.org/10.1029/2020JD032706>
- Murray, L. T. (2016). Lightning NO<sub>x</sub> and Impacts on Air Quality. *Current Pollution Reports*, 2(2), 115–133. <https://doi.org/10.1007/s40726-016-0031-7>
- Opel, T., Fritzsche, D., & Meyer, H. (2013). Eurasian Arctic climate over the past millennium as recorded in the Akademii Nauk ice core (Severnaya Zemlya). *Climate of the Past*, 9(5), 2379–2389. <https://doi.org/10.5194/cp-9-2379-2013>
- Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., E. L. Atlas, Blake, D. R., et al. (2012). Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources. *Atmospheric Chemistry and Physics*, 12(3), 1423–1447. <https://doi.org/10.5194/acp-12-1423-2012>
- Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., et al. (2012). Tropospheric bromine chemistry: implications for present and pre-industrial ozone and mercury. *Atmospheric Chemistry and Physics*, 12(15), 6723–6740. <https://doi.org/10.5194/acp-12-6723-2012>
- Passing, H., & Bablok. (1983). A new biometrical procedure for testing the equality of measurements from two different analytical methods. Application of linear regression procedures for method comparison studies in clinical chemistry, Part I. *Journal of Clinical Chemistry and Clinical Biochemistry. Zeitschrift Fur Klinische Chemie Und Klinische Biochemie*, 21(11), 709–720. <https://doi.org/10.1515/cclm.1983.21.11.709>
- Pasteris, D., McConnell, J. R., Edwards, R., Isaksson, E., & Albert, M. R. (2014). Acidity decline in Antarctic ice cores during the Little Ice Age linked to changes in atmospheric nitrate and sea salt concentrations. *Journal of Geophysical Research, D: Atmospheres*, 119(9), 5640–5652. <https://doi.org/10.1002/2013JD020377>
- Pasteris, D. R., McConnell, J. R., & Edwards, R. (2012). High-resolution, continuous method for measurement of acidity in ice cores. *Environmental Science & Technology*, 46(3), 1659–1666. <https://doi.org/10.1021/es202668n>
- Platt, U., Allan, W., & Lowe, D. (2004). Hemispheric average Cl atom concentration from <sup>13</sup>C/<sup>12</sup>C ratios in atmospheric methane. *Atmospheric Chemistry and Physics*. Retrieved from <https://www.atmos-chem-phys.net/4/2393/2004/acp-4-2393-2004.html>
- Pszenny, A. A. P., Fischer, E. V., Russo, R. S., Sive, B. C., & Varner, R. K. (2007). Estimates of Cl atom concentrations and hydrocarbon kinetic reactivity in surface air at Appledore Island, Maine (USA), during International Consortium for Atmospheric Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals: Cl-NHMC CHEMISTRY DURING ICARTT/CHAIOS. *Journal of Geophysical Research*, 112(D10), 1. <https://doi.org/10.1029/2006JD007725>

- Raff, J. D., Njegic, B., Chang, W. L., Gordon, M. S., Dabdub, D., Gerber, R. B., & Finlayson-Pitts, B. J. (2009). Chlorine activation indoors and outdoors via surface-mediated reactions of nitrogen oxides with hydrogen chloride. *Proceedings of the National Academy of Sciences of the United States of America*, 106(33), 13647–13654. <https://doi.org/10.1073/pnas.0904195106>
- Riley, J. P., & Tongudai, M. (1967). The major cation/chlorinity ratios in sea water. *Chemical Geology*, 2, 263–269. [https://doi.org/10.1016/0009-2541\(67\)90026-5](https://doi.org/10.1016/0009-2541(67)90026-5)
- Röthlisberger, R. (2003). Limited dechlorination of sea-salt aerosols during the last glacial period: Evidence from the European Project for Ice Coring in Antarctica (EPICA) Dome C ice core. *Journal of Geophysical Research*, 108(D16), 3645. <https://doi.org/10.1029/2003JD003604>
- Sigl, M., McConnell, J. R., Layman, L., Maselli, O., McGwire, K., Pasteris, D., et al. (2013). A new bipolar ice core record of volcanism from WAIS Divide and NEEM and implications for climate forcing of the last 2000 years: A 2000YR BIPOLAR VOLCANO RECORD. *Journal of Geophysical Research*, 118(3), 1151–1169. <https://doi.org/10.1029/2012jd018603>
- Sherwen, T., Schmidt, J. A., Evans, M. J., Carpenter, L. J., Großmann, K., Eastham, S. D., et al. (2016). Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem. *Atmospheric Chemistry and Physics*, 16(18), 12239–12271. <https://doi.org/10.5194/acp-16-12239-2016>
- Sherwen, T., Evans, M. J., Carpenter, L. J., Schmidt, J. A., & Mickley, L. J. (2017). Halogen chemistry reduces tropospheric O<sub>3</sub> radiative forcing. *Atmospheric Chemistry and Physics*, 17(2), 1557–1569. <https://doi.org/10.5194/acp-17-1557-2017>
- Smith, S. J., van Aardenne, J., Klimont, Z., Andres, R. J., Volke, A., & Delgado Arias, S. (2011). Anthropogenic sulfur dioxide emissions: 1850–2005. *Atmospheric Chemistry and Physics*, 11(3), 1101–1116. <https://doi.org/10.5194/acp-11-1101-2011>
- Spolaor, A., Opel, T., McConnell, J. R., Maselli, O. J., Spreen, G., Varin, C., et al. (2016). Halogen-based reconstruction of Russian Arctic sea ice area from the Akademii Nauk ice core (Severnaya Zemlya). *The Cryosphere*, 10(1), 245–256. <https://doi.org/10.5194/tc-10-245-2016>
- Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., & Ngan, F. (2015). NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bulletin of the American Meteorological Society*. <https://doi.org/10.1175/bams-d-14-00110.1>
- Strode, S. A., Wang, J. S., Manyin, M., Duncan, B., Hossaini, R., Keller, C. A., et al. (2020). Strong sensitivity of the isotopic composition of methane to the plausible range of tropospheric chlorine [Data set]. <https://doi.org/10.5194/acp-20-8405-2020>
- Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., et al. (2010). A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature*, 464(7286), 271–274. <https://doi.org/10.1038/nature08905>
- Travis, K. R., Jacob, D. J., Fisher, J. A., Kim, P. S., Marais, E. A., Zhu, L., et al. (2016). Why do Models Overestimate Surface Ozone in the Southeastern United States? *Atmospheric Chemistry and Physics*, 16(21), 13561–13577. <https://doi.org/10.5194/acp-16-13561-2016>
- Uppala, S. M., Kållberg, P. W., Simmons, A. J., Andrae, U., Bechtold, V. D. C., Fiorino, M., et al. (2005). The ERA-40 re-analysis. *Quarterly Journal of the Royal Meteorological Society*, 131(612), 2961–3012. <https://doi.org/10.1256/qj.04.176>
- US EPA. (2016, September 22). 2014 national emissions inventory (NEI) data. Retrieved

- February 1, 2021, from <https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data>
- Wang, Q., Jacob, D. J., Fisher, J. A., Mao, J., Leibensperger, E. M., Carouge, C. C., et al. (2011). Sources of carbonaceous aerosols and deposited black carbon in the Arctic in winter-spring: implications for radiative forcing. *Atmospheric Chemistry and Physics*, 11(23), 12453–12473. <https://doi.org/10.5194/acp-11-12453-2011>
- Wang, Q., Jacob, D. J., Spackman, J. R., Perring, A. E., Schwarz, J. P., Mote, N., et al. (2014). Global budget and radiative forcing of black carbon aerosol: Constraints from pole-to-pole (HIPPO) observations across the Pacific: GLOBAL BC BUDGET AND RADIATIVE FORCING. *Journal of Geophysical Research*, 119(1), 195–206. <https://doi.org/10.1002/2013jd020824>
- Wang, X., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Zhu, L., Chen, Q., et al. (2019). The role of chlorine in global tropospheric chemistry. *Atmospheric Chemistry and Physics*, 19(6), 3981–4003. <https://doi.org/10.5194/acp-19-3981-2019>
- Wang, Y., Jacob, D. J., & Logan, J. A. (1998). Global simulation of tropospheric O<sub>3</sub>-NO<sub>x</sub>-hydrocarbon chemistry: 1. Model formulation. *Journal of Geophysical Research*, 103(D9), 10713–10725. <https://doi.org/10.1029/98jd00158>
- Watson, R. T. (1977). Rate constants for reactions of ClO<sub>x</sub> of atmospheric interest. *Journal of Physical and Chemical Reference Data*, 6(3), 871–918. <https://doi.org/10.1063/1.555558>
- Wesely, M. L. (1989). Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment*, 23(6), 1293–1304. [https://doi.org/10.1016/0004-6981\(89\)90153-4](https://doi.org/10.1016/0004-6981(89)90153-4)
- Whiticar, M., & Schaefer, H. (2007). Constraining past global tropospheric methane budgets with carbon and hydrogen isotope ratios in ice. *Philosophical Transactions. Series A, Mathematical, Physical, and Engineering Sciences*, 365(1856), 1793–1828. <https://doi.org/10.1098/rsta.2007.2048>
- Xie, H.-B., Ma, F., Yu, Q., He, N., & Chen, J. (2017). Computational Study of the Reactions of Chlorine Radicals with Atmospheric Organic Compounds Featuring NH<sub>x</sub>- $\pi$ -Bond (x = 1, 2) Structures. *The Journal of Physical Chemistry. A*, 121(8), 1657–1665. <https://doi.org/10.1021/acs.jpca.6b11418>
- Young, C. J., Washenfelder, R. A., Edwards, P. M., Parrish, D. D., Gilman, J. B., Kuster, W. C., et al. (2014). Chlorine as a primary radical: evaluation of methods to understand its role in initiation of oxidative cycles. *Atmospheric Chemistry and Physics*, 14(7), 3427–3440. <https://doi.org/10.5194/acp-14-3427-2014>
- Zhang, L., Gong, S., Padro, J., & Barrie, L. (2001). A size-segregated particle dry deposition scheme for an atmospheric aerosol module. *Atmospheric Environment*, 35(3), 549–560. [https://doi.org/10.1016/S1352-2310\(00\)00326-5](https://doi.org/10.1016/S1352-2310(00)00326-5)
- Zhu, L., Jacob, D. J., Eastham, S. D., Sulprizio, M. P., Wang, X., Sherwen, T., et al. (2019). Effect of sea salt aerosol on tropospheric bromine chemistry. *Atmospheric Chemistry and Physics*, 19(9), 6497–6507. <https://doi.org/10.5194/acp-19-6497-2019>