Significant Decrease in Wet Deposition of Anthropogenic Chloride Across the Eastern United States, 1998–2018

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Abstract

Using deposition observations from precipitation samples collected by the National Atmospheric Deposition Program at 125 sites across the United States, we show that the mean wet deposition flux of non-sea-salt chloride (NSS Cl\(^{-}\)) has decreased by 83% throughout the eastern United States between 1998 and 2018. We find that 30% of the sites switch from having excess Cl\(^{-}\) to being depleted in Cl\(^{-}\). We attribute the observed decreases in NSS Cl\(^{-}\) deposition to a 95% decrease in U.S. anthropogenic HCl emissions since 1998. We propose that industry emission controls that remove HCl as a co-benefit of NO\(_x\) and SO\(_2\) have caused significant decreases in NSS Cl\(^{-}\) deposition throughout the eastern United States, in addition to shifts from coal to natural gas and to coal with lower Cl\(^{-}\) content. Our analysis implies that the lower tropospheric reactive inorganic chlorine burden was larger over the United States in the past than it is today.

Plain Language Summary

Comparing the relative ratio of sodium and chloride that is deposited in rainwater, it is possible to separate out whether that chloride is from anthropogenic sources, like burning coal, or from natural sources, like seawater. Using rainwater samples collected at 125 sites by the National Atmospheric Deposition Program between 1998 and 2018, we show that the amount of chloride deposited in rainwater from anthropogenic sources has decreased by 83% across the eastern United States. Power plant scrubbers designed to reduce emissions of SO\(_2\) and NO\(_x\), which lead to acid rain and smog, also remove emissions of HCl from burning coal, as a co-benefit. The widespread installation of these emission control technologies, together with a switch from coal to natural gas and to coal with lower chloride content, has resulted in a decrease in emissions of anthropogenic HCl by 95% in the last 21 years.

We show that these anthropogenic HCl emission decreases are closely correlated with decreases of non-sea-salt sources of chloride in rainwater. Our results suggest that the impacts of chloride on air quality and climate were significantly larger in the past over the United States than they are today.

1. Introduction

The multiphase photochemical cycling of chlorine (Cl) has a widespread influence on the chemical composition of the troposphere, affecting climate, the oxidant budget, acid deposition to the biosphere, and the chemistry of primary and secondary pollutants such as nitrogen oxides (NO\(_x\) ≡ NO + NO\(_2\)), nitrate aerosols, and ozone (O\(_3\)) (Evans et al., 2011; Finlayson-Pitts, 2003; Massucci et al., 1999; Osthoff et al., 2008; Pszenny et al., 1993; Saiz-Lopez & von Glasow, 2012; Sherwen et al., 2016; Thornton et al., 2010; Young et al., 2012).

The broad influence of chlorine chemistry stems from the high reactivity of Cl atoms with many gas phase species, including methane (Atkinson, 1997), many volatile organic compounds (VOCs) (Simpson et al., 2015), dimethyl sulfide (Chen et al., 2017; Hoffmann et al., 2016), and mercury (Horowitz et al., 2017). Cl atoms can even be the dominant early-morning oxidative agent in the winter, serving to increase OH production by enhancing formaldehyde through Cl atom-initiated VOC oxidation and enhancing O\(_3\) production from NO\(_x\) recycling (Haskins et al., 2019).

Beyond its broad impacts on atmospheric chemistry, the deposition of Cl\(^{-}\) can negatively influence ecosystems (Svensson et al., 2011). Evans et al. (2011) showed that the decrease in Cl\(^{-}\) deposition across the United Kingdom could account for 30–40% of the chemical recovery from ecosystem acidification since the 1990s and highlighted the broader impact Cl\(^{-}\) deposition had on disrupting the peatland carbon cycle. Given the impact of Cl both within the atmosphere and on ecosystems upon deposition, the trends in sources of Cl are critically important to constrain.
The main source of tropospheric gas phase inorganic chlorine (Cl\(_g\) = HCl + ClNO\(_2\) + ClNO\(_3\) + HOCI + 2Cl\(_2\) + Cl) is mobilization of Cl\(^-\) from sea-salt aerosol (SSA) (Graedel & Keene, 1995; Keene et al., 1999). Wang et al. (2019) estimate that 3.6% of the global flux of SSA is mobilized as Cl\(_g\) through acid displacement and heterogeneous reactions, resulting in a source of 64 Tg Cl year\(^{-1}\). They find that nearly 80% of the mobilized SSA Cl\(_g\) is released as hydrochloric acid (HCl) (51 Tg Cl year\(^{-1}\)). Over continents, HCl can be directly emitted into the atmosphere through coal combustion, industrial processes, waste incineration, road salt application, fugitive dust, and biomass burning (Andreae, 2019; Keene et al., 1999; Kolesar et al., 2018; Lobert et al., 1999; McCulloch et al., 1999; Sarwar et al., 2012; World Meteorological Organization [WMO], 2014). Although these non-sea-salt (NSS) emissions of Cl\(_g\) are much smaller in magnitude (together <6.6 Tg Cl year\(^{-1}\), Keene et al., 1999) relative to the source from SSA, they are potentially important as inland sources of HCl and thus reactive Cl\(_g\) (Haskins et al., 2018; Thornton et al., 2010).

Since the 1990 U.S. Clean Air Act Amendments, anthropogenic emissions from power generation, industry, transportation, and waste incineration have decreased significantly, thereby affecting the direct anthropogenic sources of Cl\(_g\). Additionally, decreases in anthropogenic SO\(_2\) and NO\(_x\) emissions have led to reduced concentrations of HNO\(_3\), H\(_2\)SO\(_4\), and N\(_2\)O\(_5\), which may have weakened the mobilization of Cl\(^-\) from SSA via acid displacement and heterogeneous reactions. Between 1998 and 2018 in the United States, anthropogenic HCl emissions have decreased by 95%, SO\(_2\) emissions have decreased by more than 59% (U.S. EPA, 2018a). These anthropogenic emission changes have led to significant and well-documented decreases in SO\(_4^{2-}\) deposition to the environment, increases in rainwater pH, and the recovery of previously devastated ecosystems (Butler et al., 2001; Giang & Selin, 2016; Fedkin et al., 2019; Lajtha & Jones, 2013; Lehmann et al., 2007; Paulot et al., 2017).

These emission reductions stem from the widespread installation of emission control measures. Other contributing factors include the shift from coal to natural gas in electricity generation after 2005 (de Gouw et al., 2014; U.S. EPA, 2020) and the increasing use of coal sourced from west of the Mississippi River, which has lower chlorine and sulfur content than that sourced in the eastern United States (U.S. Energy Information Administration, 2020; U.S. EPA, 2014). Emission control technologies, such as flue-gas desulphurization (FGD) and selective catalytic reactors (SCRs), were designed to remove SO\(_2\), NO\(_x\), and mercury as part of the 1990 Acid Rain Program, the 2005 Clean Air Interstate Rule (CAIR), the 2011 Cross State Air Pollution Rule, and the 2012 Mercury and Air Toxics Standards (MATS) rule. As a beneficent of NO\(_x\), SO\(_2\), and mercury targeted reductions, emission control technologies have been shown to be effective at removing gas phase HCl, which can be emitted from burning chloride-containing items (e.g., coal, waste, and biomass) (Lee et al., 2004; McCulloch et al., 1999). FGD uses an alkaline sorbent to remove SO\(_2\) which also reacts readily with other acid gases such as HCl, and is used to control SO\(_2\) and HCl emissions at municipal and industrial facilities with a removal efficiency estimated to be greater than 95% (McCulloch et al., 1999). Emission controls through SCR, originally designed to remove NO\(_x\) before emission, can be coupled with FGD in order to convert insoluble elemental mercury (Hg\(^{0}\)) to oxidized mercury (Hg\(^{2+}\)). This conversion is achieved via the heterogeneous reaction of Hg\(^{0}\) with HCl on various metal oxide surfaces to form HgCl\(_2\), which is then captured, thereby removing not only mercury but also HCl within flue gases (Lee et al., 2004).

In this work, we examine whether these anthropogenic HCl emission decreases are reflected in observations of wet deposition fluxes of total chlorine (HCl and particulate Cl\(^-\)) in the United States over the last two decades. We assess how changes in direct anthropogenic HCl emissions as well as in the secondary mobilization of Cl\(_g\) from SSA (from reduced NO\(_x\) and SO\(_2\) concentrations) have affected observed trends in chlorine wet deposition.

**2. Methodology**

The National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) has measured the concentrations of acids, nutrients, and base cations in weekly precipitation samples since 1978 to characterize the chemical composition of rain in the United States and its temporal and spatial trends (Lamb & Bowersox, 2000; NADP, 2020). As of 1 January 2020 there are 380 NADP sites. In this work, we use
NADP reported weekly measurements of total Cl\(^-\) (\(\tilde{\text{Cl}}^-\)), sodium (Na\(^+\)), total sulfate (\(\tilde{\text{SO}}_4^{2-}\)), and precipitation (NADP, 2020). In order to separate natural and anthropogenic contributions to \(\tilde{\text{Cl}}^-\) deposition, we calculate the NSS contribution using NADP observations of Na\(^+\). The mass ratio of Cl\(^-\) to Na\(^+\) ratio in fresh sea spray has a value of 1.80, corresponding to bulk seawater composition (Keene et al., 1986). NSS Cl\(^-\) is thus calculated as follows:

\[
\text{NSS Cl}^- = \tilde{\text{Cl}}^- - \text{Na}^+(\text{Cl}^-/\text{Na}^+)_{\text{seawater}} \tag{1}
\]

Similarly, NSS SO\(_4^{2-}\) can be calculated using the SO\(_4^{2-}\)/Na\(^+\) mass ratio in seawater (0.507; Keene et al., 1986):

\[
\text{NSS SO}_4^{2-} = \tilde{\text{SO}}_4^{2-} - \text{Na}^+(\text{SO}_4^{2-}/\text{Na}^+)_{\text{seawater}} \tag{2}
\]

Using observed \(\tilde{\text{SO}}_4^{2-}\), \(\tilde{\text{Cl}}^-\), Na\(^+\), and precipitation data from the NADP/NTN, we calculate weekly NSS Cl\(^-\) and NSS SO\(_4^{2-}\) wet deposition fluxes for 1998–2018. Only samples flagged as valid by the NADP were used in our analysis. Valid samples are defined as those collected following standard procedures: not flagged as being contaminated, those not exposed to excess dry deposition, those with a sampling interval less than 8 days, and those samples with a reported rain gauge depth or sample volume (NADP, 2016). We require data to meet three completeness criteria as defined by the NADP for each week throughout the year, throughout the period of analysis (NADP, 2016): (1) that there are valid samples for at least 75% of the summary period, (2) that there must be precipitation amounts for at least 90% of the summary period, either from the rain gage or from the sample volume, and (3) that there must be valid samples for at least 75% of the total precipitation amount reported for the month. The first two criteria ensure that measurements on valid wet deposition samples and of precipitation amounts were reported for a minimum acceptable fraction of the summary period (i.e., functioning equipment), while the third ensures that there are valid precipitation chemistry data to represent a majority of the precipitation that was estimated to have occurred.

We performed a seasonal Kendall test (SKT) using Sen’s method on the weekly data at individual sites to detect trends underlying seasonal deposition patterns from 1998–2018 (Burkey, 2020; Marchetto et al., 2013). The SKT trends were applied to NADP sites that fulfilled the three criteria described above, and in addition, we excluded sites that had more than a 3-month gap in meeting the completeness criteria. For the 1998–2018 period considered here, 125 sites met these criteria, and we only show analysis and summary statistics for these 125 sites throughout this work. Seasons in the SKT test are based on the annual year, so seasonality trends are assessed from January–December. The null hypotheses were that the trend was 0 (Kendall’s tau-b statistic was 0), and the statistical significance level was set at 90%. The magnitude of the trend was determined by taking the Sen’s slope of the weekly deposition data.

We are particularly interested in analyzing trends at sites where NSS Cl\(^-\) is a significant portion of the \(\tilde{\text{Cl}}^-\) wet deposition flux. However, SS can often be a very large component of the \(\tilde{\text{Cl}}^-\) wet deposition flux. In order to distinguish sites of interest from those where sea-salt (SS) trends dominate \(\tilde{\text{Cl}}^-\) wet deposition, we will refer to sites where the NSS Cl\(^-\) deposition flux exceeds 5% of \(\tilde{\text{Cl}}^-\) wet deposition flux as sites with nonnegligible NSS Cl\(^-\) deposition flux. These sites tend to be located near industrial centers where anthropogenic Cl\(^-\) sources might be expected to contribute to \(\tilde{\text{Cl}}^-\) deposition or over inland regions where the SS Cl\(^-\) deposition is so small that even a small amount of deposited NSS Cl\(^-\) would be relevant. Sites with less than 5% contributions from NSS Cl\(^-\) to \(\tilde{\text{Cl}}^-\) are referred to as sites with negligible NSS Cl\(^-\) and tend to be located in coastal regions where direct SS deposition is large or where there is little anthropogenic Cl\(^-\) contribution to deposition.

The deposition flux of NSS Cl\(^-\) can be positive or negative because the concentration of NSS Cl\(^-\) is calculated as a difference (Equation 1). Positive values of NSS Cl\(^-\) deposition flux show that excess Cl\(^-\) was measured relative to what would be expected from SSA, thus indicating the influence of anthropogenic sources of Cl\(_p\). Negative values of NSS Cl\(^-\) deposition flux show that the measured rainwater sample was depleted in
Cl\(^{-}\) relative to what would be expected in SS aerosols. Therefore, negative deposition fluxes of NSS Cl\(^{-}\) suggest that SS Cl\(^{-}\) was displaced into the gas phase as Cl\(^{y}\) either through acid displacement by HNO\(_3\) or H\(_2\)SO\(_4\) or through heterogeneous reactions with N\(_2\)O\(_5\). Inherent in our calculation of NSS Cl\(^{-}\) (Equation 1) is the assumption that all measured Na\(^{+}\) is from SS. Other potential sources of Na\(^{+}\) include road salt, soil, and refuse incineration (Ooki et al., 2002). By using correlations between Na\(^{+}\) and Mg\(^{2+}\) (Text S1 in the supporting information), we determined that only 11 NADP sites showed evidence of a persistent NSS Na\(^{+}\) source (for less than 25% of the 1998–2018 time period). At these 11 sites, the calculated NSS Cl\(^{-}\) concentration could thus be an underestimate during some weeks. Results excluding these sites were consistent with those including them (see supporting information Text S1); therefore, we have chosen to keep these sites in our analysis.

3. Results and Discussion

Figures 1e and 1f show the 1998–2018 anthropogenic emission changes reported by the U.S. Environmental Protection Agency (EPA) as part of the National Emissions Inventory (U.S. EPA, 2014) for SO\(_2\) and by the Toxic Release Inventory (TRI) for HCl (U.S. EPA, 2018b). These emissions are aggregated into the 10 EPA regions. The reduction in SO\(_2\) emissions, from 17 Tg in 1998 to 2.2 Tg in 2018, is driven by large decreases in EPA Regions 3–5, which include the Midwest, southeast, and mid-Atlantic states, with the steepest
decreases occurring between 2005 and 2011. Anthropogenic HCl emissions have also decreased across the United States, from a maximum in 1999 of 303 to 15 Gg year\(^{-1}\) in 2018 (U.S. EPA, 2018b, Figure 1f). The most significant decreases in HCl have also occurred in EPA Regions 3–5. Compared to SO\(_2\) emissions, the reduction in HCl emissions is steeper. One explanation for this trend is the widespread installation of emission control technologies across industries (including those that do not coemit SO\(_2\)) in anticipation of the 2012 MATS rule and the 2009 enactment of CAIR regulations. CAIR required scrubbing technologies to run year-round, and not just in the summer months, for all states in EPA Regions 2–6 except 5. He et al. (2013) show that prior to 2009, anthropogenic NO\(_x\) emissions from point sources exhibited a square wave seasonality with peaks in the winter in Maryland, Ohio, and Pennsylvania from SCR only being turned on during summer months. After the 2009 enactment of CAIR, NO\(_x\) emissions (and thus HCl emissions) were controlled all year round, leading to the steep decrease in Figure 1f.

Figures 1a–1d contrast the spatial distribution of the 3-year mean wet deposition fluxes of NSS SO\(_4^{2-}\) and NSS Cl\(^-\) for the beginning (1998–2000) and end (2016–2018) of our analysis period at 125 sites. Figures 1a–1c highlight the well-documented reduction in NSS SO\(_4^{2-}\) deposition from anthropogenic SO\(_2\) emissions controls across the eastern United States (Fedkin et al., 2019; Lajtha & Jones, 2013; Lehmann et al., 2007; Paulot et al., 2017). The largest decreases in NSS SO\(_4^{2-}\) occur over the Ohio River Valley and downwind regions in the eastern United States. We find that mean annual NSS SO\(_4^{2-}\) wet deposition fluxes at sites in EPA Regions 2–5 decreased from an average of 8.85 kg S ha\(^{-1}\) (1998–2000) to 2.58 kg S ha\(^{-1}\) (2016–2018), with changes at individual sites from 1998–2018 upward of 19 kg S ha\(^{-1}\). This is consistent with results from Fedkin et al. (2019), who reported decreases up to 17 kg S ha\(^{-1}\) in annual wet SO\(_4^{2-}\) deposition between 2005 and 2015 centered around the Ohio, West Virginia, and Pennsylvania borders.

Reductions in NSS Cl\(^-\) wet deposition fluxes (Figures 1b and 1d) are also observed throughout the eastern United States, with the largest decreases occurring in Pennsylvania, North Carolina, New York, New Jersey, and Ohio, mirroring those of NSS SO\(_4^{2-}\). Between 1998 and 2000, 47 sites had positive values of nonnegligible NSS Cl\(^-\) deposition (red circles), indicative of anthropogenic sources of Cl\(_p\). These sites were mostly located near power plant sources in the eastern United States (Figure 1b), often colocated with high values of NSS SO\(_4^{2-}\) deposition (Figure 1a), suggesting a common source. By 2016–2018, only 15 sites had positive values of nonnegligible NSS Cl\(^-\) deposition flux (red circles), suggesting that fewer sites’ deposition patterns were being impacted by anthropogenic sources of Cl\(_p\). Considering all sites in EPA Regions 1–5, the mean NSS Cl\(^-\) wet deposition flux decreased from +0.12 kg Cl ha\(^{-1}\) (1998–2000) to −0.06 kg Cl ha\(^{-1}\) (2016–2018). This decrease in deposition of NSS Cl\(^-\) is largely driven by a switch of 37 sites (30% of the 125 sites) from positive (enhanced from anthropogenic sources) NSS Cl\(^-\) wet deposition fluxes in 1998–2000 to negative (depleted via heterogeneous chemistry) NSS Cl\(^-\) deposition fluxes in 2016–2018. These 37 sites, mostly located in the Midwest, have gone from having excess Cl\(^-\) deposited from anthropogenic emission contributions to having less Cl\(^-\) deposited than would be expected from a SSA source alone, signaling a significant decrease in anthropogenic emissions of Cl\(^-\).

In 1998–2000, 34 sites had negative values in NSS Cl\(^-\) deposition flux (blue markers, Figure 1b), which increased to 56 sites by 2016–2018 (blue markers, Figure 1d). Areas with significant negative values of
NSS Cl\(^-\) deposition fluxes are those where Cl\(^-\) from SSA was displaced into the gas phase as Cl\(_2\), via heterogeneous chemistry involving HNO\(_3\), H\(_2\)SO\(_4\), or N\(_2\)O\(_5\). The sites with the largest depletion in Cl\(^-\) relative to Na\(^+\) are located in the south and southeast, particularly in Missouri, Arkansas, Mississippi, and Texas. By 2016–2018, these sites are generally less depleted in Cl\(^-\) than in 1998–2000, likely reflecting decreases in NO\(_x\) and SO\(_2\) reducing heterogeneous mobilization of SS Cl\(^-\). This will be discussed further below.

Additionally, in this two-decade span, the number of sites with nonnegligible NSS Cl\(^-\) (NSS Cl\(^-\)/\(^4\)Cl\(^+\) > 0.05) decreased from 91 to 68 indicating that fewer sites now experience either (1) a significant contribution from anthropogenic sources of Cl\(_2\) or (2) significant heterogeneous chemistry mobilizing natural SS Cl\(^-\). This reflects that the number of sites experiencing a significant anthropogenic influence on the observed Cl\(^-\) wet deposition flux has significantly decreased over time.

Figure 2a shows the 1998–2018 trends in NSS SO\(_4^{2-}\) wet deposition as calculated with Sen’s method. All but 3 of the 125 NADP sites analyzed display negative trends in NSS SO\(_4^{2-}\) deposition, reflecting decreases in anthropogenic SO\(_2\) emissions. Sites having the largest decreases in NSS SO\(_4^{2-}\) wet deposition are in the midwestern and northeastern United States (EPA Regions 2–5). The mean change in annual NSS SO\(_4^{2-}\) wet deposition at sites with statistically significant trends (circles, \(n = 110\)) is \(-115 \text{ g } \text{S ha}^{-1} \text{ year}^{-1}\), with changes at individual sites in the Ohio River Valley being exceeding \(-300 \text{ g } \text{S ha}^{-1} \text{ year}^{-1}\), broadly consistent with other studies (Fedkin et al., 2019; Lehmann et al., 2007).

The largest statistically significant trends in NSS Cl\(^-\) deposition are also seen in the midwestern and northeastern United States (Figure 2b), again mirroring spatial patterns of NSS SO\(_4^{2-}\). The mean change at all sites with statistically significant trends in NSS Cl\(^-\) is \(-6.6 \text{ g } \text{Cl ha}^{-1} \text{ year}^{-1}\), with decreases at 85% of these sites. Considering only sites with statistically significant decreases and nonnegligible NSS Cl\(^-\), the mean change is \(-10.8 \text{ g } \text{Cl ha}^{-1} \text{ year}^{-1}\), with these sites largely located in Maryland, New Jersey, New York, North Carolina, Ohio, and Pennsylvania.

In contrast to the eastern United States, several sites in the southeastern United States had heavily depleted NSS Cl\(^-\) wet deposition fluxes (negative NSS Cl\(^-\)) in the late 1990s (Figure 1b). Thirteen of these sites displayed statistically significant increases (+3.8 g Cl ha\(^{-1}\) year\(^{-1}\)) in NSS Cl\(^-\) wet deposition flux. Of these 13 sites, only 6 had nonnegligible NSS Cl\(^-\) between 1998 and 2000 (blue circles in Figure 2b). For the remaining seven sites in the Pacific Northwest and coastal Florida (blue diamonds), the amount of NSS Cl\(^-\) deposited is negligible relative to the SS signal, such that the increases are occurring for a very small amount of deposited NSS Cl\(^-\) relative to \(^4\)Cl\(^+\) deposited. The average trend in NSS Cl\(^-\) at the six sites with nonnegligible NSS Cl\(^-\) wet deposition flux was +7.8 g Cl ha\(^{-1}\) year\(^{-1}\), increasing from a mean deposition of \(-174 \text{ g } \text{Cl ha}^{-1}\) in 1998–2000 to \(-104 \text{ g } \text{Cl ha}^{-1}\) in 2016–2018 (Figures 1b and 1c). Despite these increases in NSS Cl\(^-\) wet deposition, by 2018 these sites in the southeastern United States were still depleted in NSS Cl\(^-\), just to a lesser degree than in 1998. We attribute these positive trends in NSS Cl\(^-\) deposition in the southeast to stricter emission controls having decreased both SO\(_2\) and NO\(_x\), thus weakening displacement of Cl\(^-\) from SSA via anthropogenically driven secondary chemistry.

The larger pattern exhibited at all other 112 NADP sites is a negative trend in NSS Cl\(^-\) deposition. Sites with the largest decreases in NSS Cl\(^-\) and NSS SO\(_4^{2-}\) wet deposition are colocated as shown by the correlation plot on Figure 2c. Sites with statistically significant decreases in NSS Cl\(^-\) (and NSS Cl\(^-\) > 0.05 \(^4\)Cl\(^+\)) are spatially correlated with those having the largest decreases in NSS SO\(_4^{2-}\) deposition (\(r^2 = 0.70\)). Correlated decreases in NSS SO\(_4^{2-}\) and NSS Cl\(^-\) wet deposition fluxes are what would be expected from decreasing anthropogenic emissions of SO\(_2\) and HCl at common point sources but would not be expected if trends in other potential sources of NSS Cl\(^-\) like road-salting practices were driving the decreases in NSS Cl\(^-\) wet deposition flux.

Figure 3 shows the 1998–2018 evolution in NSS Cl\(^-\) wet deposition and compares them to changes in anthropogenic emissions of HCl for EPA Regions 1–5 in the eastern United States. For each site, we take a 3-year running mean in observed NSS Cl\(^-\) wet deposition and calculate the percent change in NSS Cl\(^-\) deposition relative to the 1998–2000 mean and then take the median of the percent changes across all sites considered. Here, we only consider deposition data from NADP sites with nonnegligible NSS Cl\(^-\) for the 1998–2000 period and statistically significant negative Sen’s slopes. The resulting percentage change in
deposition compares well to the trends calculated from the Sen’s slopes (blue “X” in Figure 3; see supporting information Text S2). In total, wet deposition of NSS Cl\(^-\) has decreased by 83% on average since 1998 across the eastern United States (Regions 1–5) at sites with significant trends. Figure 3. Percent decrease in anthropogenic HCl emissions (orange line) and NSS Cl\(^-\) wet deposition (blue line) relative to 1998–2000 for EPA (a–e) Regions 1–5. We only consider deposition data from NADP sites with nonnegligible NSS Cl\(^-\) for 1998–2000 as well as statistically significant negative Sen’s slopes. The inlays display the 1998–2018 change in annual NSS Cl\(^-\) (from Figure 2) at the individual sites included in our calculations. The emission trends are calculated by taking the 3-year running time average of the HCl emission change in a given region from all emission sectors, relative to the first 3-year mean (1998–2000), centered around 1999. Similarly, the NSS Cl\(^-\) wet deposition changes are calculated by taking the 3-year running time average centered around each year at each site and then taking the median trend of all sites included and the 25th and 75th percentiles of this trend (gray shading). The median of all sites’ individual change magnitudes as percentage of mean in wet deposition flux of NSS Cl\(^-\), calculated from the Sen’s slopes, is shown as a blue “X” at 2017.
Figure 3 illustrates that the observed NSS Cl\textsuperscript{−} wet deposition flux declines at a rate similar to the 3-year moving mean decrease in HCl emissions throughout the comparison period. For these five EPA regions, anthropogenic HCl emissions decrease by 95%–100%. Between 1998 and 2018, NSS Cl\textsuperscript{−} wet deposition decreases by 72%–95%. The time series of HCl emissions and NSS Cl\textsuperscript{−} wet deposition decrease are well correlated temporally, with \( r^2 \) ranging from 0.76 to 0.96 depending on the region. Temporal correlations between HCl emissions and NSS Cl\textsuperscript{−} deposition are largest in Region 3 (\( r^2 = 0.96, n = 8 \)). Over this region, anthropogenic HCl emissions were 61 Gg year\textsuperscript{−}1 in 1998, or 22% of the national anthropogenic HCl emissions that year, and NSS Cl\textsuperscript{−} wet deposition flux decreased from +0.59 g Cl ha\textsuperscript{−}1 (1998–2000) to –0.14 g Cl ha\textsuperscript{−}1 (2016–2018) at sites with nonnegligible NSS Cl\textsuperscript{−}. This is the largest absolute value change in NSS Cl\textsuperscript{−} wet deposition flux seen across all EPA regions. The impact of upwind HCl emissions can be seen at NADP sites in New York and New Jersey in Region 2, which has minimal direct anthropogenic HCl emissions from industry but experiences some of the largest decreases in the wet deposition flux of NSS Cl\textsuperscript{−} both in absolute value and percentage (Figure 3b). Regions 1 and 5 both show a slight difference between their trends in HCl emissions and NSS Cl\textsuperscript{−} deposition fluxes (Figures 3a and 3e). This difference could be due to the fact that not all regional anthropogenic HCl emissions are necessarily deposited within that region and that transport of upwind HCl emissions can influence the local deposition flux. Overall, the very similar temporal evolution in NSS Cl\textsuperscript{−} and HCl emissions in EPA Region 1–5, together with the spatial correlation between SO\textsubscript{4}\textsuperscript{2−} and NSS Cl\textsuperscript{−} deposition, suggests that decreases in anthropogenic HCl emissions are driving the observed NSS Cl\textsuperscript{−} wet deposition decreases in near source regions.

To determine the extent to which anthropogenic HCl emissions can explain the observed trends in NSS Cl\textsuperscript{−} wet deposition, we estimated the decrease in NSS Cl\textsuperscript{−} wet deposition by multiplying the weekly observed NSS SO\textsubscript{4}\textsuperscript{2−} wet deposition by the mean HCl/SO\textsubscript{2} anthropogenic emission ratio (ER) in each region, considering only electric utility sources and then taking the Sen’s slope of the predicted NSS Cl\textsuperscript{−} to estimate the decrease from HCl emission changes only, as described in supporting information Text S2 (Figures S4 and S5). The best agreement between observed and predicted change in NSS Cl\textsuperscript{−} deposition flux was found in EPA Region 3, with a mean 16% (+0.935 g Cl ha\textsuperscript{−}1 year\textsuperscript{−}1) overestimation from the predictions (Figure S5), consistent with our finding that Region 3 has the strongest temporal correlation between decreases in anthropogenic HCl emissions and NSS Cl\textsuperscript{−} wet deposition flux (Figure 3c). Overall, anthropogenic HCl emission decreases were enough to explain observed NSS Cl\textsuperscript{−} wet deposition decreases particularly in large source regions (see supporting information Text S2 for discussion) but were unable to capture increasing trends in the southeast influenced more strongly by Cl\textsuperscript{−} mobilization through acid displacement and heterogeneous reactions.

Together, the 1998–2018 decrease in excess NSS Cl\textsuperscript{−} deposited across the Midwestern and northeastern United States and the increase in depleted NSS Cl\textsuperscript{−} deposited in the southeastern United States represent a return to Cl\textsuperscript{−} deposition patterns less impacted by anthropogenic activities. Therefore, regardless of the exact mechanism for the decrease in the absolute value of NSS Cl\textsuperscript{−} wet deposition flux across the United States (reductions in primary emissions of anthropogenic HCl or reductions in emissions of SO\textsubscript{2} and NO\textsubscript{x} promoting less Cl\textsuperscript{−} mobilization from SS aerosols), we find that decreases in anthropogenic emissions have reduced the anthropogenic impact on the wet deposition of NSS Cl\textsuperscript{−} across the eastern United States. A similar decrease in anthropogenic HCl emissions from coal burning (~95%) in the United Kingdom has been shown to have resulted in a 66% decrease in deposition of NSS Cl\textsuperscript{−} between 1990 and 2007 (Evans et al., 2011).

4. Conclusions

Between 1998 and 2018, anthropogenic HCl emissions across the United States have decreased by 95% from a maximum in 1999 of 303 to 15 Gg year\textsuperscript{−}1 in 2018. We have shown that the observed NSS Cl\textsuperscript{−} wet deposition flux at NADP sites has decreased by 83% on average in the Midwest and northeastern United States between 1998 and 2018 and slightly increased in the southeastern United States, with evidence that both changes are driven by decreases in anthropogenic HCl, SO\textsubscript{2}, and NO\textsubscript{x} emissions. We found statistically sig-
nificant decreases in NSS Cl$^{−}$ deposition flux at 61% of the 125 NADP sites analyzed with an average decrease of −9.2 g Cl ha year$^{−1}$ between 1998 and 2018.

Observed decreases in NSS Cl$^{−}$ wet deposition were spatially well correlated with SO$_4^{2−}$ wet deposition decreases across the United States ($r^2 = 0.70$) and were temporally well correlated with observed HCl emission decreases ($r^2 ≥ 0.76$). We propose that the 95% decrease in anthropogenic HCl emissions across the United States has driven an observable decrease in NSS Cl$^{−}$ wet deposition in the Midwest and eastern United States. The negative trends in NSS Cl$^{−}$ deposition reflect a reduced anthropogenic impact on Cl$^{−}$ deposition, with more Cl$^{−}$ deposition explained by a SS source alone in 2016–2018 than in 1998–2000 and with sites switching from having excess NSS Cl$^{−}$ deposition in the late 1990s to having either depleted or near-zero NSS Cl$^{−}$ patterns by 2018. A small number of sites in the southeastern United States were depleted in NSS Cl$^{−}$ in 1998 and saw statistically significant increases in NSS Cl$^{−}$ deposition but remained depleted in Cl$^{−}$ by 2018. We attribute this positive trend to a decrease in displacement of NSS Cl$^{−}$ as stricter emission controls decreased both SO$_3$ and NO$_x$, which in turn decreased the amount of Cl$^{−}$ from SSA that was displaced into the gas phase as Cl$_2$.

Overall, our results suggest that the tropospheric Cl$_p$ burden was distinctly larger over the United States in the past than it is today, both from higher direct HCl emissions and larger mobilization of SS Cl$^{−}$. Global model simulations by Wang et al. (2019) recently showed that displacement of Cl$^{−}$ from SS aerosol provided a reactive Cl$_p$ (Cl$_p$-HCl) source of 12 Tg Cl year$^{−1}$ via heterogeneous reactions with HNO$_3$, H$_2$SO$_4$, and N$_2$O$_5$ in the year 2015, higher than previous estimates of 5.6 Tg Cl year$^{−1}$ (Hossaini et al., 2016) and 6.1 Tg Cl year$^{−1}$ (Schmidt et al., 2016). Our results suggest that this number may have been even higher in the past 20 years in the United States, when HNO$_3$ and H$_2$SO$_4$ production was larger and when anthropogenic HCl concentrations were a more significant inland source of Cl$_p$. The past impacts of Cl$_p$ on the oxidant budget, downwind O$_3$ formation, methane and VOC oxidation, dimethyl sulfide, and mercury concentrations remain to be quantified. Given that observations have shown Cl atoms can be the dominant early morning oxidant in winter in select polluted coastal regions as recently as 2015 (Haskins et al., 2018), our results suggest that the impact of tropospheric halogens may have played an even larger role on air quality and climate prior to large anthropogenic emission reductions.

**Data Availability Statement**

Deposition data used in this work from the National Atmospheric Deposition Program are available to the public at the website (http://nadp.slh.wisc.edu/data/ntn/ntnAllsites.aspx). HCl emission data used in this work from the EPA's Toxic Release Inventory are available to the public at the website (https://bit.ly/3ocV99g). Facility level SO$_3$ emission data used in this work from the EPA's National Emissions Inventory are available to the public at the website (https://www.epa.gov/air-emissions-inventories/2017-national-emissions-inventory-nei-data).

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