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3 Stratospheric chlorine processing after the 2020 Australian wildfires
4 derived from satellite data

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11 **Author Contributions:** P.W., S.S. designed research; P.W., K.S. performed research; P.W.
12 analyzed data; P.W., S.S., K.S. wrote the paper.

13 **Competing Interest Statement:** The authors declare no compete of interest.

14 **Classification:** Physical Sciences-Earth, Atmospheric, and Planetary Sciences

15 **Keywords:** stratospheric ozone, chlorine activation, wildfire

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17 **This PDF file includes:**

18 Main Text

19 Figures 1 to 6

20 Figures S1 to S9

Abstract

The 2019 – 2020 Australian summer wildfires injected an amount of organic gases and particles into the stratosphere unprecedented in the satellite record since 2002, causing large unexpected changes in HCl and ClONO₂. These fires provided a novel opportunity to evaluate heterogeneous reactions on organic aerosols in the context of stratospheric chlorine and ozone depletion chemistry. It has long been known that heterogeneous chlorine (Cl) activation occurs on the polar stratospheric clouds (PSCs; liquid and solid particles containing water, sulfuric acid, and in some cases nitric acid) that are found in the stratosphere, but these are only effective for ozone depletion chemistry at temperatures below about 195 K (i.e., largely in the polar regions during winter). Here, we develop a new approach to quantitatively assess atmospheric evidence for these reactions using satellite data. We show that heterogeneous reactions apparently even happened at temperatures above 220 K during autumn on the organic aerosols present in 2020, in contrast to earlier years. Further, increased variability in HCl was also found after the wildfires, suggesting diverse chemical properties among the 2020 aerosols. We also confirm the expectation based upon laboratory studies that heterogeneous Cl activation has a strong dependence upon water vapor partial pressure and hence atmospheric altitude, becoming much faster close to the tropopause. Our analysis improves the understanding of heterogeneous reactions that are important for stratospheric ozone chemistry under both background and wildfire conditions.

Significance Statement

Heterogeneous chlorine activation is a major driver for stratospheric ozone depletion and is understood to happen on polar stratospheric clouds (PSCs) at temperatures below about 195 K. The 2020 Australian wildfire released large amounts of organic aerosols, whose chemical properties under stratospheric conditions are virtually unknown. Here, we developed a novel approach to analyze the temperature dependency of atmospheric chlorine heterogeneous chemistry using satellite data. We found that such reactions can happen at temperatures even above 220 K on wildfire aerosols in 2020. Organic aerosols are present to some degree in the lower stratosphere even under background conditions. This result indicates that Cl processes on organic aerosols likely need to be considered in future stratospheric ozone simulations.

Main Text

Introduction

The Australian wildfire black summer was the largest such event in the satellite era. It produced on the order of 1 Tg of aerosols in the stratosphere from about Dec 31, 2019 to Jan 5, 2020 (1), equivalent to a small volcanic eruption. These aerosols and their precursors are brought into the lower stratosphere by pyrocumulonimbus convection, where they can be expected to decay over time. Volcanic aerosols typically display an e-folding time of about 18 months (2, 3). Model simulations (which assumed wildfire-released aerosols behave like sulfuric acid and water particles) (4), satellite observations (5–7), and *in-situ* measurements (8) all found significant ozone decreases in the lower stratosphere at southern hemisphere mid-latitudes in 2020 after the wildfire. Unusually low ozone abundances even continued into 2021 (6, 9). While there is evidence for some dynamical contributions to the ozone variations observed in that year (6, 10), averaged mid-latitude values presented in (6) indicate record low local abundances near 20 km, suggesting additional chemistry is likely. In addition, unprecedented and completely unexpected changes in mid-latitude chlorine (Cl) reservoir species (HCl and ClONO₂) were also found in satellite and *in-situ* observations (6–8), suggestive of Cl surface chemistry, e.g., via the following heterogeneous reaction of $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$ (11). The Cl₂ subsequently photolyzes rapidly in sunlit air, and can form Cl and ClO which deplete ozone. The fingerprint of N₂O₅ hydrolysis, another key heterogeneous reaction that contributes to depletion in the ozone layer, was also found in the satellite data (12) but cannot explain the unusual changes in HCl and ClONO₂. Here we provide a

fresh approach to the analysis of the Cl chemistry inspired by the unexpected HCl and ClONO₂ data that sheds light on its temperature-dependent chemistry not only for wildfires but also for background conditions.

Laboratory measurements (13, 14), *in-situ* observations (15), and model simulation (16) all suggest that the heterogeneous Cl reaction between HCl and ClONO₂ is only effective on the surfaces of typical stratospheric aerosols at temperatures below 195 K. In contrast to stratospheric background sulfuric acid and water aerosols, wildfire-released particles contain a wide variety of organic compounds (17, 18), which could have different chemical properties. Limited laboratory studies suggest that organic aerosols can enhance HCl uptake (19) and at warmer temperatures

The new approach presented here quantifies the temperature for Cl activation using satellite data from ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer; ACE for short) (21) combined with temperatures from a back trajectory model named Lagranto (Lagrangian Analysis Tool) (22), driven by meteorological conditions from ERA5 (European Centre for Medium-Range Weather Forecasts) reanalysis data (23). We focus on the southern hemisphere mid-latitudes defined as 40 – 55 °S and polar vortex region defined as 65 – 90 °S. The most significant changes in HCl and ClONO₂ in 2020 are observed at altitude ranges between 15 – 22 km (Fig. S1). Unless otherwise specified, we mainly focus on 18.5 km in our analysis to maximize the effects.

Results

Separating dynamical and chemical processes

Fig. 1A shows the monthly mean ACE data for CO (an indicator of biomass burning) at the lower stratosphere mid-latitudes. CO in 2020 reached a record high (6, 7), suggesting a significant amount of biomass burning and its long-lasting effect continuing throughout the entire year. CO in 2021 is within the range of climatology, indicating no significant wildfire or new particles injected into the lower stratosphere in that year. 2012 is also highlighted in Fig. 1 since we use it here as a typical reference year in later analysis, given no known large volcanic eruptions nor big biomass burning events in that year.

While HCl displayed remarkable anomalies in 2020, HF was within the range of past years, confirming the role of chemistry (Fig. 1). Once anthropogenically produced CFCs (chlorofluorocarbons) reach the stratosphere, they decompose into the fluorine (Fy) and chlorine (Cly) families of compounds. Nearly all of the Fy is in the form of HF because there are no known chemical loss pathways of HF in the stratosphere; hence it has long been used as an inactive tracer (24, 25). Insofar as the breakdown of CFCs is the dominant source of both stratospheric chlorine and fluorine, Cly and Fy should be proportional to one another. Viewed in this context, HCl and HF behavior also suggests unusual chemistry lasting into 2021, but with much smaller magnitude than 2020.

Correlation between chemical species or “tracer-tracer” analysis is a powerful tool to analyze dynamical and chemical interactions (26–28). The basis of the analysis is that dynamical transport should affect inactive and active species similarly, so departures from correlation in the active species are indicative of chemical processes. The availability of simultaneous ACE observations of HF, HCl, and ClONO₂ along a common line of sight ensures consistency and is key to such an analysis. To separate dynamical from chemical effects on specific Cly species, we perform the tracer-tracer analysis between HF and HCl, ClONO₂, and their sum (Fig. 2 for mid-latitude and Fig. S2 for the polar region).

Fig. 2 shows tracer-tracer scatter plots of ACE HF and HCl, ClONO₂, and HCl+ClONO₂ in each month from March to July. This spans months when no or little heterogeneous chemistry normally occurs (~March-April) to months with rapid chemistry on PSCs in polar regions (June-July) and in between (May). All the data align on a nearly straight line in March, suggesting little or no chemistry in this month. We therefore construct a baseline relationship between HF and the Cly

species from March 2004 – 2019 data using linear regression (indicated by the dark solid lines in Fig. 2 and Fig. S2).

The shaded regions in Fig. 2 and Fig. S2 quantify the baseline uncertainty. There are mainly two types of uncertainties in such analysis, one is the instrumental bias, and the other is the interannual variability. As the tracer-tracer correlation mainly focuses on the relative difference of Cl to HF , which are measured by ACE at the same occultation, instrumental bias on both molecules will largely cancel. To quantify the uncertainty of interannual variability and noise, we construct a baseline for each year in 2004 – 2019 to represent the range of variability in baselines. The shading areas indicate a conservative full range of variability bounded by the maximum and minimum baselines using data in individual years.

ACE has limited data coverage. To validate whether the results are robust, we compare ACE (at 18.5 km) with the MLS (Microwave Limb Sounder at 68.2 hPa) in Figs. S3 and S4 (mid-latitude and polar vortex region, respectively) for tracer-tracer analysis between N_2O and HCl (since MLS does not have measurements for HF and ClONO_2). MLS has much more spatial coverage, but with a lower signal-to-noise ratio on individual points (as shown in Figs. S3C and S4C). The zonally averaged MLS data (Figs. S3B and S4B) agree well with ACE (Figs. S3A and S4A), suggesting that even though ACE coverage is limited, it is consistent with MLS regarding the changes in HCl from tracer-tracer analysis. Note that the zonal averaging process in MLS reduces the noise but it also clusters measurements towards the mean values. Therefore, the baseline slope becomes more sensitive to small changes in N_2O and HCl in the clustered region, and the uncertainty range expands at those values where no or few data are fed into the linear regression. MLS N_2O also has experienced a ~3% instrumental drift in the past decade, which could also broaden the spread of the baseline uncertainty range (29). We therefore focus on the results from ACE measurements.

Fig. 2 shows that substantial deviations in HCl and ClONO_2 from their respective “no-chemistry” baseline occur in July for every year, indicating the known Cl activation mechanism on PSCs (11). More important, in 2020, HCl and ClONO_2 start to deviate from the “no-chemistry” baseline even in March, when the temperature is far too warm for heterogeneous Cl reactions to happen on PSCs. HCl and ClONO_2 in 2021 also display some deviations from the “no-chemistry” baseline, but the magnitudes are considerably smaller than in 2020.

Interestingly, the decrease in HCl is roughly compensated by increases in ClONO_2 in both 2020 and 2021 (e.g. April and May in Fig. 2 and Fig. S2, respectively) and in other years. The decrease in HCl suggests that anomalous heterogeneous Cl reactions occurred in these two years. However, at these latitudes outside the polar vortex, ample solar radiation is available to drive HNO_3 photolysis (and reaction with OH also occurs), making NO_2 available to deactivate the activated Cl , forming ClONO_2 . With a rich supply of NO_2 , the net reaction thus largely transfers HCl into ClONO_2 . Similar Cl deactivation forms the ClONO_2 “collar” (30), a slice of enhanced ClONO_2 surrounding the polar vortex in late spring as noted in past literature. Fig. 3 shows May HCl and ClONO_2 anomalies in 2020 compared to the May climatology from 2004 – 2019. The figure makes clear that the ClONO_2 “collar” mechanism is significantly enhanced in 2020 as early as May, as more Cl has been converted from HCl into ClONO_2 on wildfire-released particles. Similar processes continued to occur in 2021, but with a smaller magnitude (Fig. S5). HCl and ClONO_2 are both considered to be reservoirs for active chlorine species that deplete ozone (mainly Cl and ClO). It may be useful to consider such a process to represent Cl processing instead of Cl activation, since the sum of $\text{HCl} + \text{ClONO}_2$ is nearly conserved. Nonetheless, a small amount of enhanced ClO will be present as well, since ClONO_2 and ClO are essentially in photochemical balance in the sunlit atmosphere, and enhanced ClONO_2 therefore implies enhanced ClO and associated ozone loss. Indeed, evidence of enhanced ClO has been shown in both ACE and MLS measurements (6, 7).

Cl processing in the mid-latitudes

To estimate the temperatures that are likely to drive the heterogeneous chemistry, we first calculate the deviation of each data point in Fig. 2 from the “no-chemistry” baseline as a function of ACE-measured temperature (Fig. 4A-C). Thick lines show the averages of data points in 2 K

temperature bins from the baseline that is constructed by all available data from 2004 – 2019. The shaded regions represent the full range of Cl deviation from individual “no-chemistry” baselines that are constructed from data in individual years, representing the uncertainty due to variability. Negative values in ClONO₂ at warmer temperatures indicate that available ClO has been deactivated to form ClONO₂, and the sum of HCl and ClONO₂ in Fig. 4C thus indicates that a large amount of the Cl activated from HCl in 2020 and 2021 has almost all formed ClONO₂ at warmer temperatures. As we focus on 40 – 55 °S where the temperature is well above 195 K, activation on the PSCs is not likely to take place. This is supported by the 2004 – 2019 climatology, in which the average Cl activation remains close to zero. However, HCl data in 2020 and 2021 suggest that significant Cl activation occurred at temperatures even well above 220 K, but not in any other years (although the magnitude of Cl activation in 2021 is smaller than in 2020).

However, one pitfall of Figs. 2 and 4A-C is that the temperatures shown reflect only the state of the atmosphere at the satellite overpass, while Cl activation could have occurred at a different temperature along air parcel trajectories. We therefore use Lagranto (22) driven by ERA5 (23) to evaluate 5-day back trajectories for each data point in 2020 and 2021, as well as the reference year of 2012. The radiative relaxation time for the lower stratosphere is on the order of 195 – 20 – 30 days (31, 32); we pick a rather conservative estimate of 5 days to avoid potential effects of radiatively-driven ascent/descent of particles in the stratosphere. The ACE-measured instantaneous temperature is then replaced with the minimum temperature from the 5-day back trajectories of each data point (referred to as ERA5 T_{min} in Fig. 4D-F), providing an estimate of the air parcel's recent minimum temperature exposure. ERA5 temperatures at the co-located ACE observations agree well with each other (Fig. S6), and we find that the 5-day minimum temperature is rather insensitive to small perturbations in the starting position (Fig. S7). We also verified that the minimum temperature is similar between 5-day and 10-day back trajectories for the air parcels released at 18.5 km (detailed discussion in the **Altitude-dependent Cl activation** section). Back trajectories going beyond 10-days would require calculation of the air parcel's radiative field including the effect of the wildfire particles and thus was not considered in this analysis.

Fig. 4D-F shows Cl activation as a function of the 5-day minimum temperature calculated from Lagranto. The 5-day minimum temperature exposure for these measurements is still mainly above 195 K. This further strengthens the idea that wildfire-released organic aerosols can allow heterogeneous reactions to happen at warmer temperatures, which differs from the PSC mechanism that requires the temperature to be lower than 195 K. Further, the PDFs shown in Fig. 4D-F for temperatures ≥ 195 K indicate that not only do 2020 and 2021 have different mean values than in 2012, but the spread after the wildfire is also much wider than that in 2012. One plausible explanation for this behavior is variability in the composition and/or abundances of organic aerosols from the wildfire, displaying different chemical properties. Note that the PDF for the sum of HCl+ClONO₂ is centered very close to zero for 2012 but displays a distinct offset from zero in 2020 and to a lesser extent in 2021, indicating significant enhancements in other species including e.g. HOCl (7) and ClO in those years only (6).

Cl processing in the polar vortex region

Fig. 5 shows Cl activation in the polar vortex region at 65 – 90 °S. Cl activation for the total Cly in 2012 shows a sharp transition at 195 K (Fig. 5F), which matches remarkably well with the current understanding of Cl activation on PSCs as first observed with aircraft methods (15). It is noteworthy that even in 2012 when the background CO and aerosol extinctions are at the lower end in the climatology, there is still some ClONO₂ being converted from HCl at temperatures between 195 – 205 K (Fig. 5D-E). Observations show that organic aerosols are widespread in the lower stratosphere. Among other sources, tropical biomass burning produces organic aerosols in the upper troposphere (33) that may be transported into the stratosphere. Thus, early-season Cl processing on organic aerosols could occur to some extent every year, albeit with smaller magnitudes than in 2020.

Data in 2020 and 2021 show that a similar Cl processing mechanism also took place in the south polar vortex region at temperatures above 195 K. HCl in 2020 and 2021 continues to indicate

more active CI compared to other years at all temperatures until the temperature falls below 195 K, when the PSCs likely dominate the CI activation, and these two years merge into the 2004 – 2019 climatology. While CI activation in 2020 was lower at temperatures well below 195 K (Fig. 5F) compared to other years, this does not necessarily mean less total active CI being present in that year. In particular, the results show that a large amount of CI has already been activated earlier in the season (at warmer temperatures) and likely stayed in the forms of e.g. HOCl, ClO, and Cl₂O₂ in the polar vortex region (6, 7). Because of less solar radiation at higher latitudes, less NO₂ is available from HNO₃ photochemistry to transfer these more reactive forms of CI back to ClONO₂. This is supported by the evidence of large non-zero values of the mean of PDFs for ΔHCl+ClONO₂ at temperatures above 195 K in Fig. 5F (0.22 ± 0.12 ppb in 2020 and 0.18 ± 0.10 ppb in 2021, compared to 0.02 ± 0.10 ppb in 2012; $\pm$ sign followed by 1 standard deviation).

Note that most of the ACE data points in the polar region are over 65 – 70 °S (especially in colder seasons) and may not represent the conditions in the core of the polar vortex. Fig. S8 shows the limited data available for CI activation between 70 – 90 °S (ACE observations for March and April only). The general behavior of CI processing at warmer temperatures remains apparent in these months at high latitudes.

Altitude-dependent CI activation in the polar vortex region

The reaction efficiency of HCl+ClONO₂ can be affected not only by different types of surfaces (e.g. organic aerosols and PSCs), but also by water vapor content and pressure, which vary with altitude (34), which has been suggested as a potential mid-latitude ozone depletion mechanism (35, 36). We therefore expand the focus to the range of altitudes from 14.5 km to 18.5 km for 2020, 2021 and 2012 (Fig. 6). Note that data quality may be affected at lower altitudes, with more missing values at lower levels. An air parcel's recent minimum temperature exposure becomes more sensitive to the number of days considered in back trajectories at lower altitudes, where wind speed is slower, and the distance traveled by the air parcel might be too short to adequately reflect the lowest temperature experienced by the parcel. Therefore, even in a reference year in 2012, Fig. 6A shows CI activation occurred at temperatures well above 195 K at altitudes below 18.5 km. However, minimum temperatures from 5-day and 10-day back trajectories are not affected much at 18.5 km where wind speed is fast enough to allow air parcel to travel enough distance.

It is noteworthy that in a year without the impact of organic aerosols from large wildfires (2012), a systematic gradient of the onset temperature for CI activation is indicated, from 200 K at 14.5 km to 195 K at 18.5 km using the 10-day back trajectories (Fig. 6D). This agrees surprisingly well with current understanding, as indicated by a numerical calculation using the kinetics code and composition data from WACCM (Whole Atmosphere Community Climate Model) (14). For example, the reaction efficiency for HCl+ClONO₂ is about 80 times more efficient at 14.5 km than at 18.5 km (Fig. S9B), providing observational evidence for this effect in the atmosphere. But such altitude-dependency is significantly disturbed by organic aerosols after the 2020 Australian wildfire. Neither 2020 nor 2021 demonstrate a clear relationship between CI activation and altitude. Instead, large amounts of CI activation took place at all altitudes ranging from 14.5 km to 18.5 km in these years at temperatures warmer than 195 K.

Discussion

In conclusion, we have examined the heterogeneous reactions affecting the HCl and ClONO₂ reservoir species in the southern hemisphere fall and winter (March-July) for both the Australian wildfire-released organic aerosols and background conditions using satellite data. Our method confirms a sharp increase in CI activation for temperatures below about 195 K along 5-day air parcel trajectories characterizing the data, consistent with current understanding (11, 16, 37). This finding highlights the importance of relatively small temperature perturbations (i.e., less than 1 K) on this chemistry (e.g., those due to planetary or gravity waves). The method also successfully demonstrates the altitude-dependency of CI activation for a reference non-wildfire year (34). These

results illustrate the power of this method for both background conditions and wildfire perturbations in testing chemical understanding.

We find evidence for Cl processing at much warmer temperatures (above 220 K) than the current understanding for PSCs after the Australian fires. When such Cl processing happens at mid-latitudes, HCl decreases but nearly all of the active Cl is turned into ClONO₂ rapidly because of ongoing supply of NO₂ from HNO₃ photolysis and reaction with OH. However, PDFs of the sum of HCl+ClONO₂ activation reveal that some enhanced Cl does remain in active forms at temperatures above 195 K in 2020, which can be expected to produce some ozone loss. Importantly, the data suggest that the remaining aerosols from the 2020 wildfire apparently even continued to affect the Cl species (albeit to a lesser extent) into 2021. Further, diversity in wildfire-released organic aerosols (17, 18) with different chemical properties is suggested by an observed increase in the width of the distribution, i.e., varying amounts of Cl activation.

The total Cl budget could be closed by including other species, particularly ClO and Cl₂O₂. However, one drawback of this tracer-tracer method is that it works well for the rather long-lived species (e.g. HCl and ClONO₂), but the large variance in more short-lived species (e.g. ClO and HOCl) can impede the calculation. Furthermore, the ACE satellite produces twilight measurements (which do not indicate daytime ClO values) and it does not have measurements for Cl₂O₂; although (6) shows enhanced daytime ClO using MLS data, and twilight ClO enhancement is also found from ACE data albeit with larger noise (7). Further studies are needed to evaluate the total Cl budget and to fully quantify to what extent the ozone layer is affected by wildfire-triggered Cl processing. The frequency of wildfires is projected to increase in the future due to climate change (38). A better understanding of the range of composition of organic aerosols, and of heterogeneous reaction rates upon them, is needed to estimate any associated ozone impacts, including potential delay of the recovery in the stratospheric ozone layer in the future.

Materials and Methods

Satellite datasets

Level 2 satellite data from ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer) version 4.1 for molecules (39) is used in this study. Data range from 2004 to 2021. ACE provides measurements at twilight; both the sunrise and sunset data are used. We remove outliers defined as 3 standard deviations apart from the mean for each month (40).

Daily level 3 satellite data from MLS (Microwave Limb Sounder) version 5.0 (41) for N₂O, HCl and temperature are used in this study. Data range from 2005 to 2021. Both the ascending and descending modes are used, which provide measurements for daytime and nighttime.

Back trajectory calculation

Lagranto (Lagrangian Analysis Tool) version 2.0 (22) is used in this study to calculate the back trajectories for each data point in 2020, 2021, and 2012. It iterates three times in each time interval to calculate the average velocity between the starting and ending locations (from every iteration). Lagranto is driven by the ERA5 (European Centre for Medium-Range Weather Forecasts) reanalysis data (23) for pressure, temperature, and 3D wind fields. We used an ERA5 configuration that has 137 vertical model levels, a 1-degree horizontal resolution, and a 3-hour temporal resolution. Subgrid scale gravity waves can introduce temperature variability. ERA5 has been shown to resolve a large portion of that variability (42–44) and will be sampled irrespective of the time interval chosen for transport in the trajectory model. However, short horizontal wavelength disturbances could lead to effective chlorine activation at somewhat colder temperatures than those shown here, which should be considered an upper limit to the activation temperature.

HCl+ClONO₂ reaction efficiency

The HCl+ClONO₂ reactive uptake probabilities (in Fig. S9B) are calculated using the parameterization described in (14), which is used in the WACCM model. This calculation uses model values of temperature and pressure over an altitude range of 14.5–19.5 km during July at ~63°S. HCl and ClONO₂ volume mixing ratios are held constant at 0.3 and 0.05 ppb respectively. Water vapor volume mixing ratio is held constant at 3.5, 4, and 4.5 ppm. This allows for the effect of water vapor partial pressure over the above altitude to range to be investigated.

Data availability

Data and code used in this study are available at <https://doi.org/10.5281/zenodo.7338322> (45).

Acknowledgments

The authors appreciate Hongwei Sun (Harvard University) for the guidance in using Lagranto. SS, PW, and KS gratefully acknowledge partial support by NSF-1906719 and NASA 80NSSC19K0952. We thank P. F. Bernath, Mission Scientist of the Atmospheric Chemistry Experiment. ACE is supported by the Canadian Space Agency (which makes ACE data freely available).

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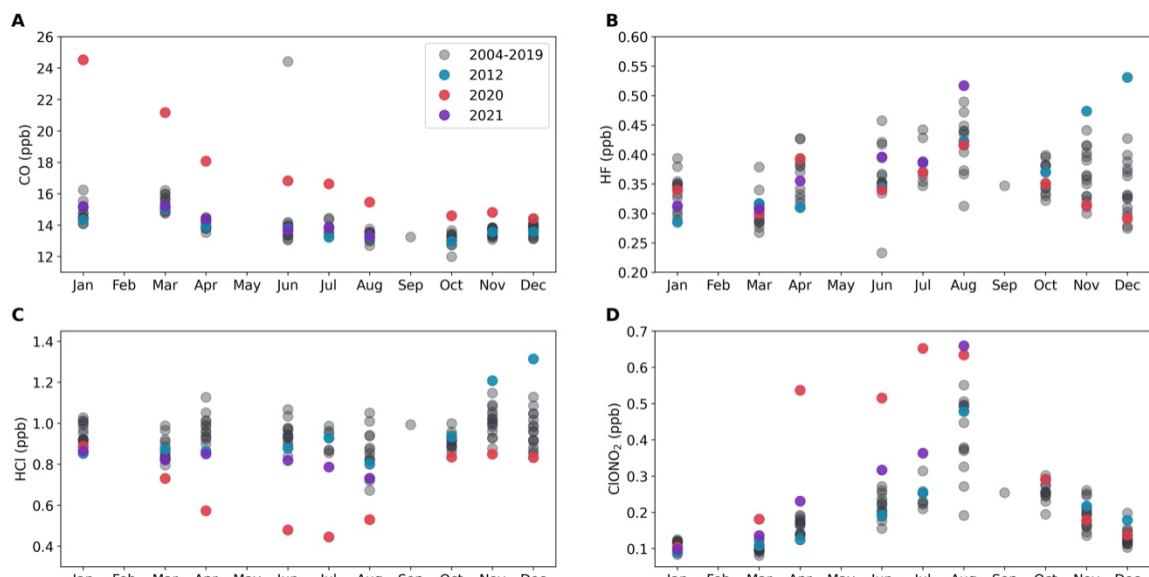


Fig. 1. The monthly mean ACE data for (A) CO, (B) HF, (C) HCl, and (D) ClONO₂ at 18.5 km averaged over 40 – 55 °S. Red dots are from 2020, purple dots are from 2021, blue dots are from 2012 (used as a reference year in this study), and gray dots are from 2004 – 2019 (excluding 2012). 40 – 55 °S is split into 3 equally spaced latitude bins and months with at least 5 samples (at least 1 sample per latitude bin) are considered in the averaging processes.

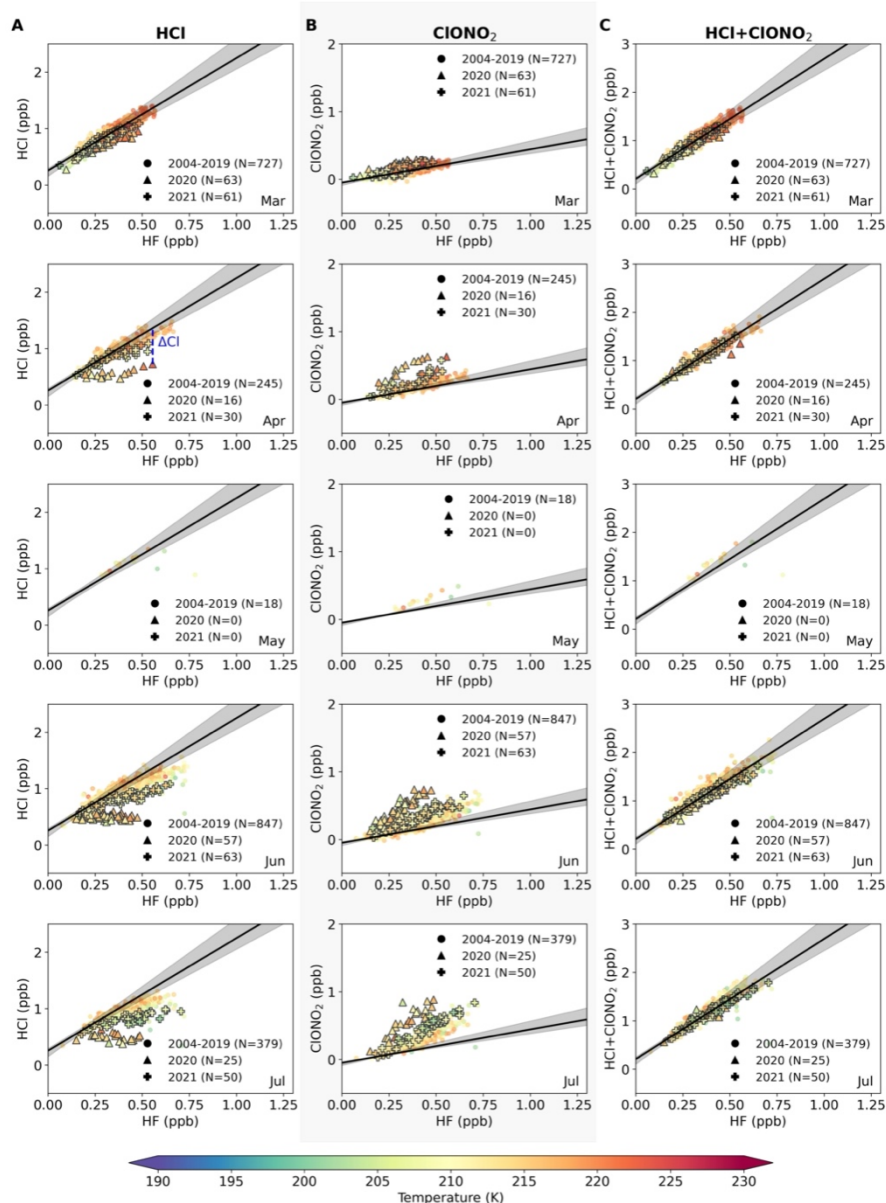


Fig. 2. Tracer-tracer correlation between HF (x-axis) and (A) HCl, (B) ClONO₂, and (C) 474 HCl+ClONO₂ (y-axes), color-coded by temperature. Each dot represents a single measurement at 18.5 km over 40 – 55 °S. Dots in 2020 and 2021 are highlighted with triangles and crosses, 476 respectively (with gray edges). Each subpanel shows a different month from March to July, labeled at the bottom right corner. The number of data plotted in each month is shown in the legend. The 478 thick black lines represent the “no-chemistry” baseline, from the linear fit over March 2004 – 2019 479 data points. The shaded regions indicate a conservative full range of baseline variability bounded 480 by the maximum and minimum baselines constructed by data in individual years from 2004 to 2019. 481 A demonstration of how ΔCl (e.g. in Fig. 4) is calculated is shown here as the vertical blue dashed 482 line in the April panel for HCl, representing the change in Cl due to chemical processes.

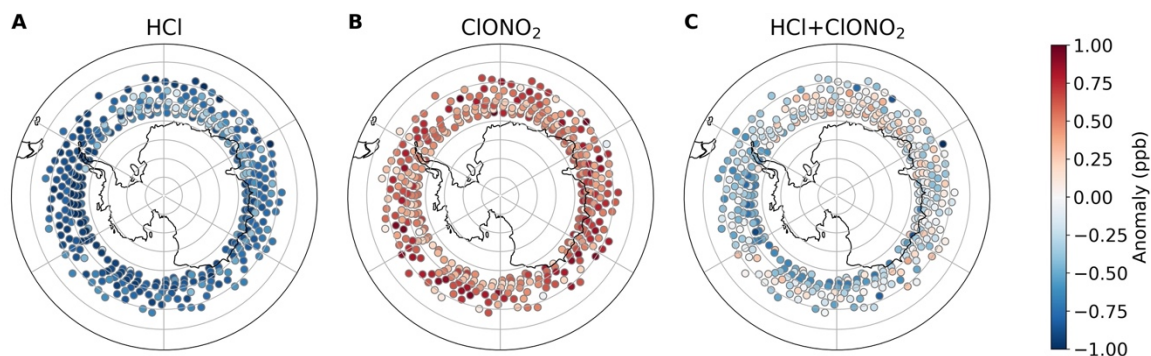


Fig. 3. Monthly anomalies for (A) HCl, (B) ClONO₂, and (C) HCl+ClONO₂ in May 2020 compared to the May climatology in 2004-2019. The maps show a latitudinal range between 50 °S and 90 °S since ACE measurements in May are mainly between 58 – 68 °S. To prevent from biasing the anomalies by latitudinal variations, the climatological mean is constructed at every 5-degree latitude bin. Therefore, the May anomalies presented here are calculated from four latitude bins from the climatology (50 – 55, 55 – 60, 60 – 65 and 65 – 70 °S).

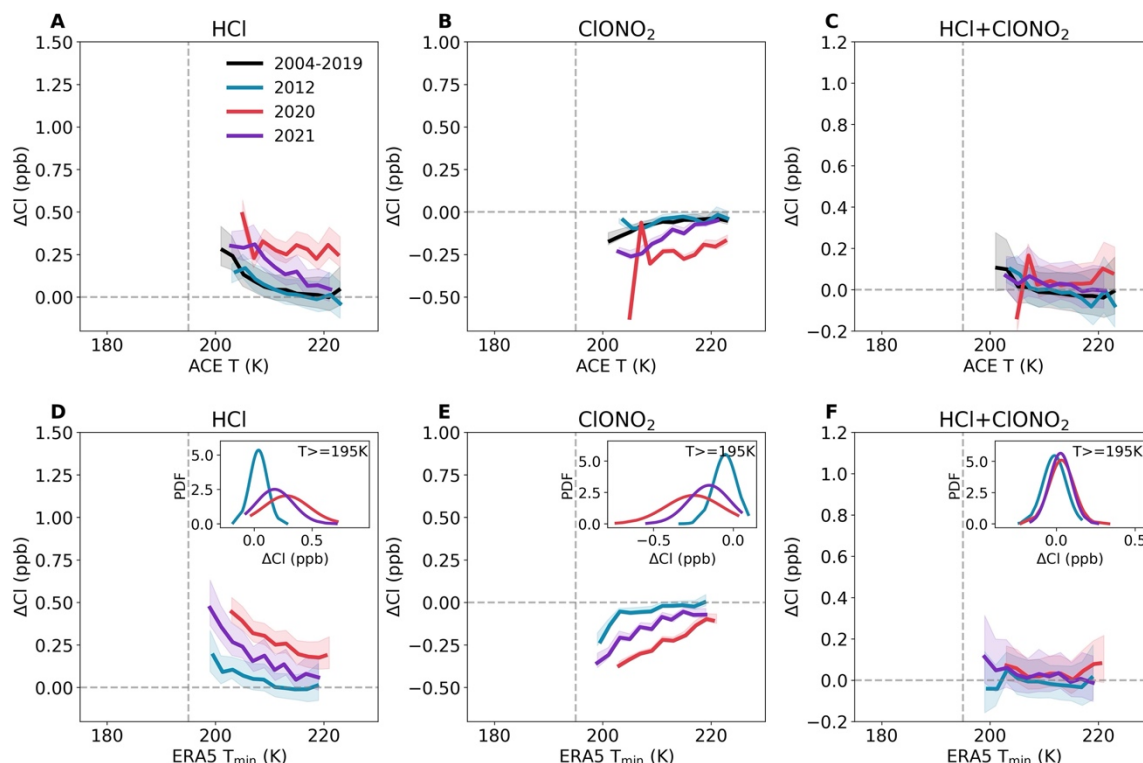


Fig. 4. Cl activation as a function of temperature at mid-latitudes (40 – 55 °S) for March-July at 18.5 km. Each panel shows the amount of Cl activation on the y-axes (deviation from the “no-493 chemistry” baseline in Fig. 2) as a function of temperature (x-axis) for (A, D) HCl, (B, E) ClONO₂, and (C, F) HCl+ClONO₂. Panels A-C use the ACE-measured temperature at the satellite overpass, and panels D-F use the minimum temperature (T_{min}) calculated along the 5-day back trajectories for each data point for 2020, 2021, and 2012. Thick lines are the average of Cl activation at every 2 K temperature ranges (temperature bins with less than 2 samples are not considered for the 498 average). The shading areas indicate the full range of Cl departures from individual baselines using data from single years. Horizontal and vertical gray dashed lines indicate zero Cl activation and 195 K, respectively. The probability distribution functions (PDF) of Cl activation at T_{min} ≥ 195 K are shown in panels D-F for 2020, 2021, and 2012.

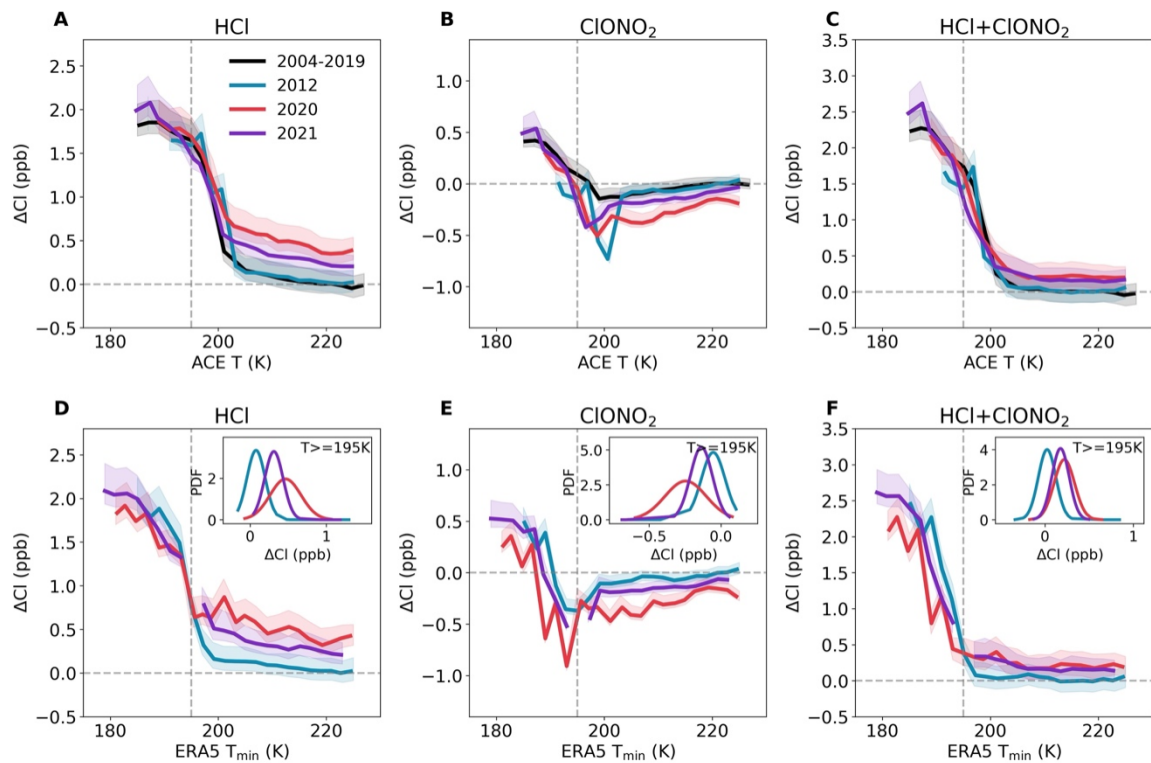


Fig. 5. Cl activation as a function of temperature in the polar vortex region (65 – 90 °S), as in Fig. 4 for mid-latitudes. Panels A-C use the ACE-measured temperature at the satellite overpass, and panels D-F use the minimum temperature ($T_{\min}$) calculated along the 5-day back trajectories for each data point for 2020, 2021, and 2012.

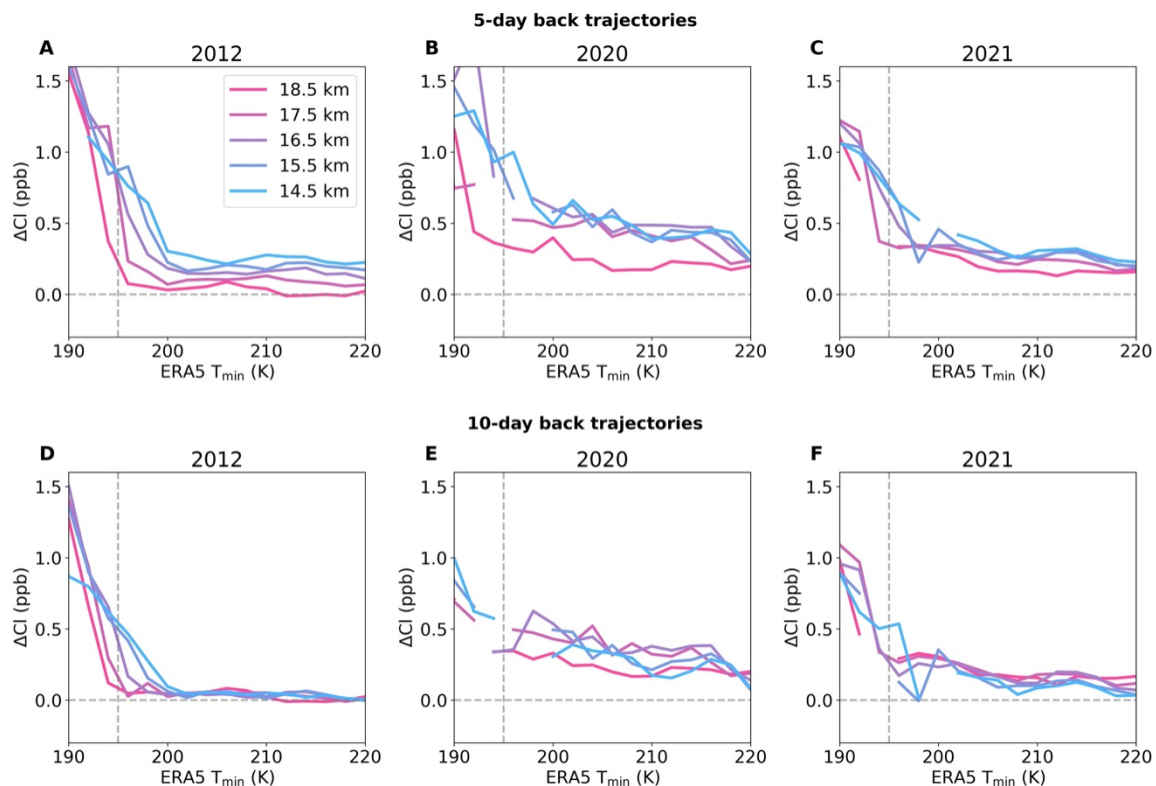


Fig. 6. The altitude-dependent CI activation in the polar vortex region (65 – 90 °S) for (A, D) 2012, (B, E) 2020, and (C, F) 2021. X-axis shows the minimum temperature calculated along the 5-day back trajectories (panels A-C) and 10-day back (panels D-F), and the y-axis shows the CI activation from the sum of HCl and ClONO₂. Only the CI activation calculated from baselines using all available data from 2004 to 2019 is shown here. Each line represents a different altitude range from 14.5 km to 18.5 km. The panels are zoomed in for 190 – 220 K to focus on the onset temperature for CI activation on PSCs.

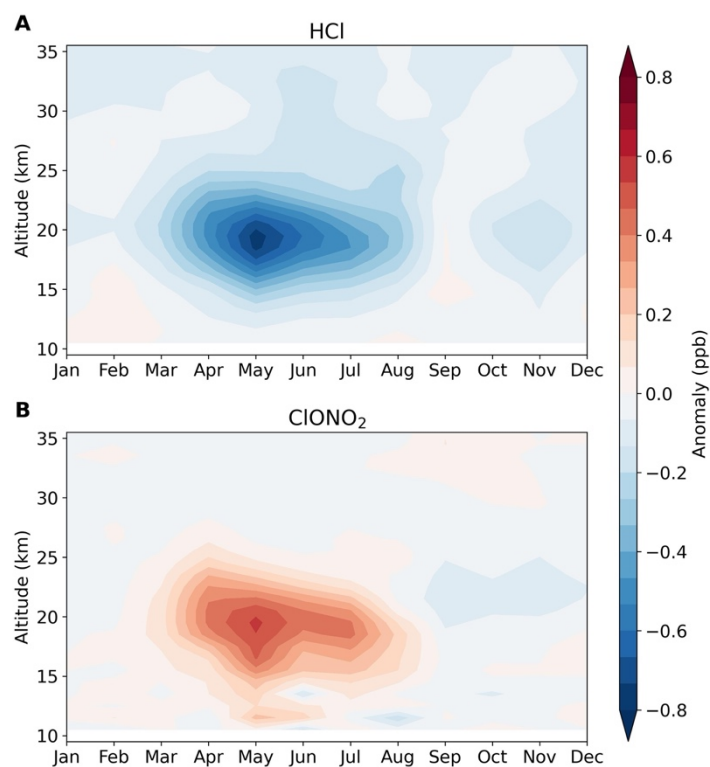


Fig. S1. Monthly anomalies of (A) HCl and (B) ClONO₂ in 2020 compared to the 2004 – 2019 climatology, as a function of the month (x-axis) and altitude (y-axis) over 40 – 60 °S.

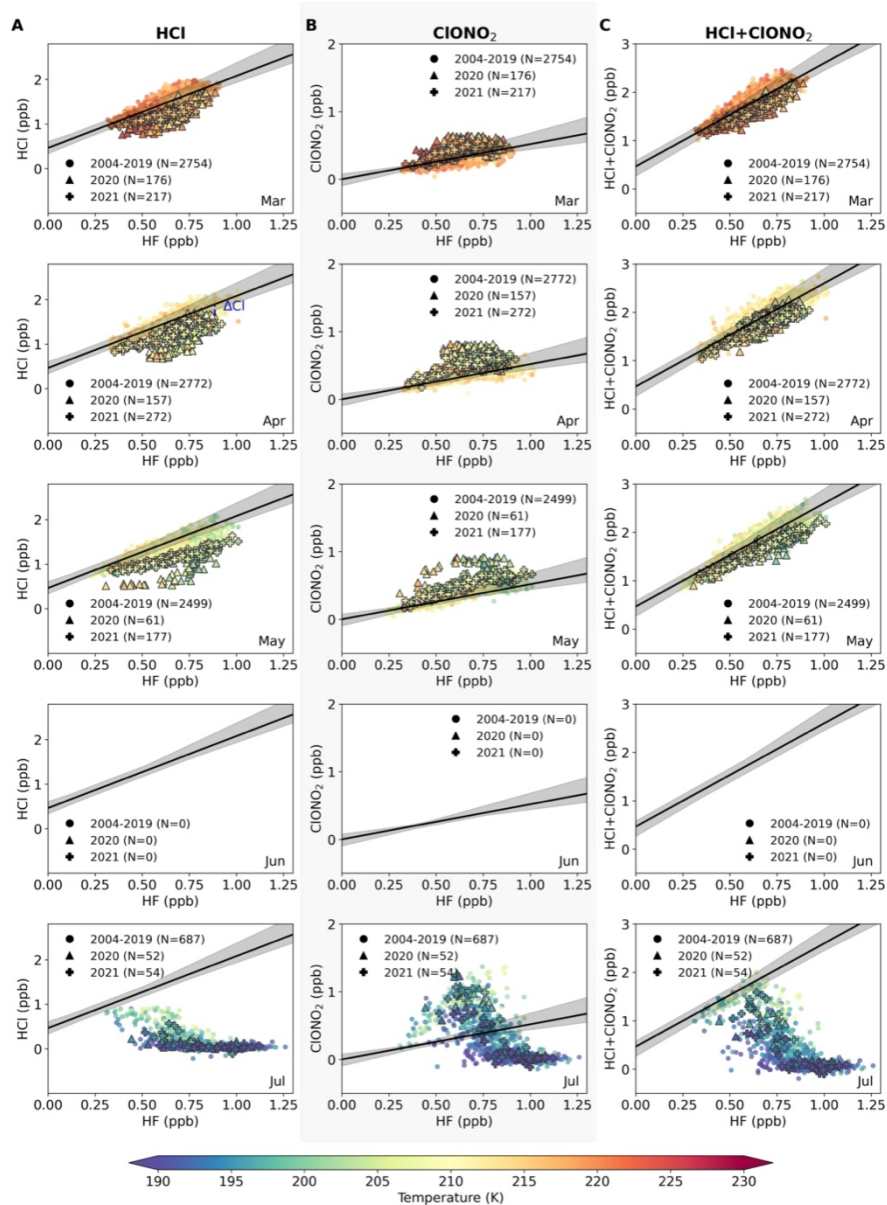


Fig. S2. Tracer-tracer correlation in the polar vortex region (65 – 90 °S), as in Fig. 2 for mid-latitudes. There is no data in June at this latitude range.

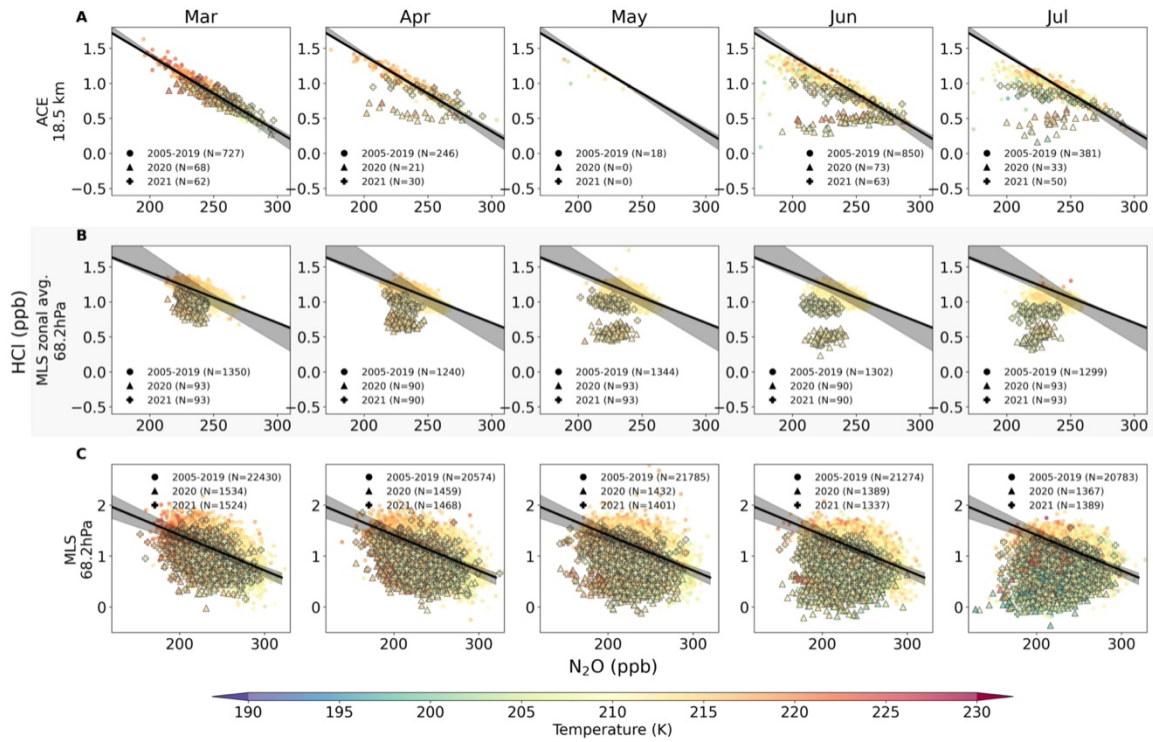


Fig. S3. Tracer-tracer correlation between N_2O (x-axis) and HCl (y-axis) in the mid-latitude (40 – 55 °S), similar to Fig. 2, but comparing ACE and MLS measurements in each row. Top row (panel A) shows results from ACE individual measurements at 18.5 km. Middle row (panel B) shows results from MLS zonally averaged data at 68.2 hPa. Bottom row (panel C) shows results from MLS individual measurements at 68.2 hPa.

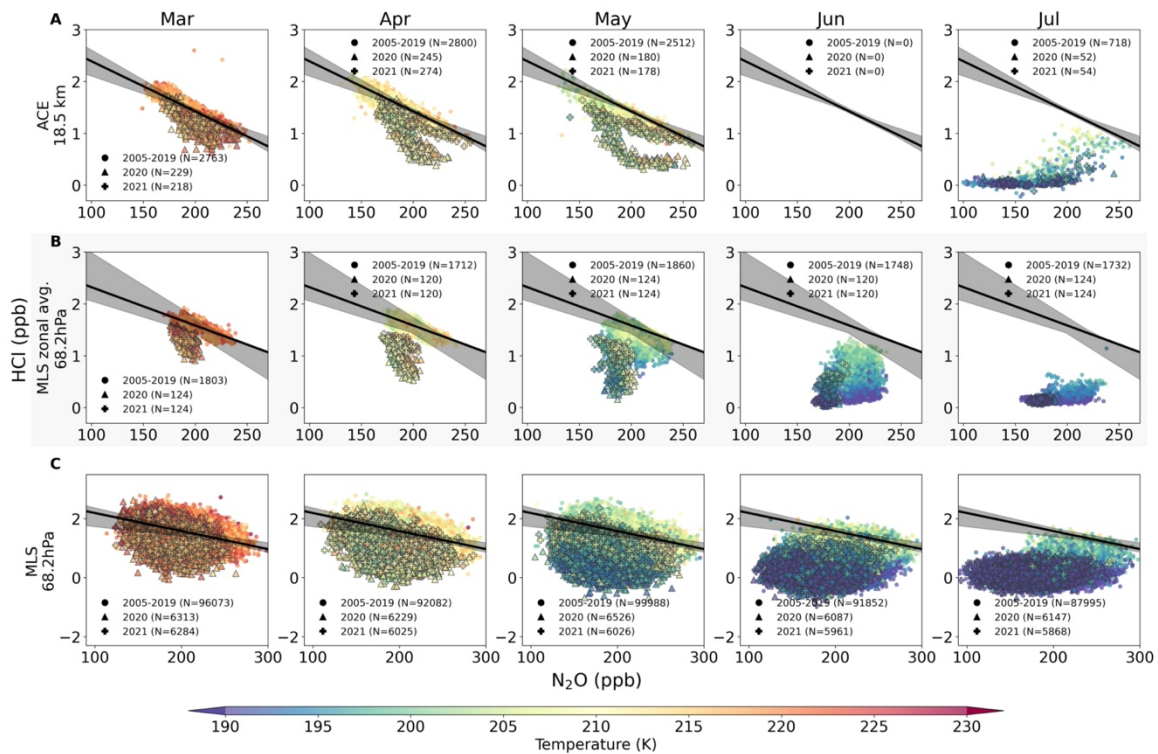
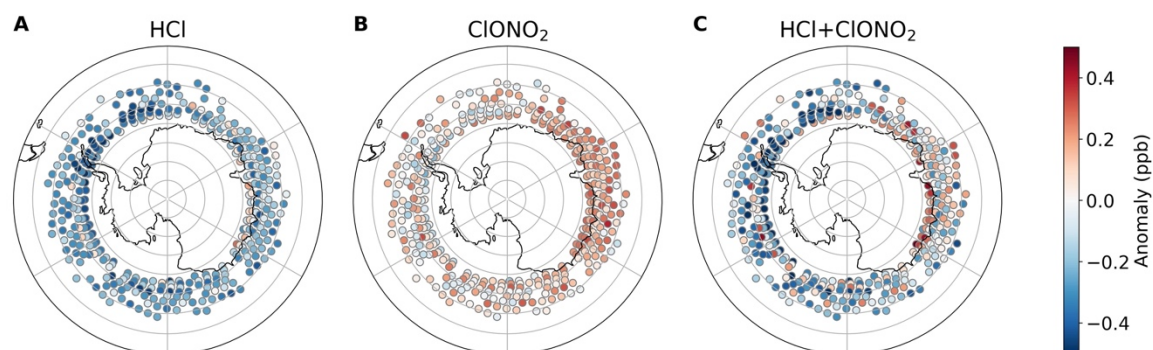


Fig. S4. Tracer-tracer correlation between N_2O (x-axis) and HCl (y-axis) in the polar vortex region (65 – 90 °S), as in Fig. S3 for mid-latitudes.

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Fig. S5. Similar to Fig. 3, but for 2021. Note that the colorbar here shows a smaller range because the magnitude of the Cly anomalies are smaller in 2021.

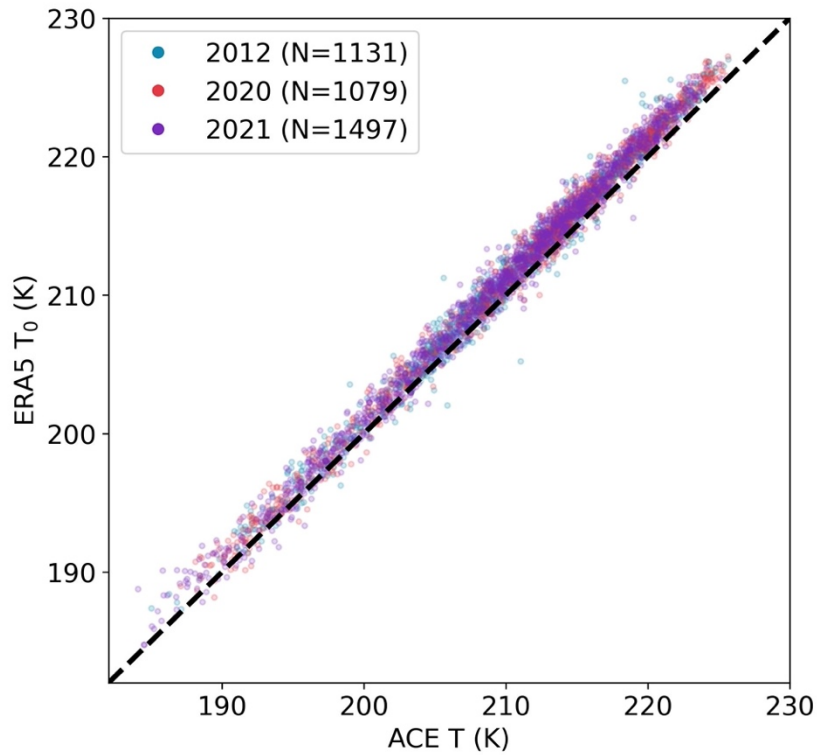


Fig. S6. Sanity check on ACE and ERA5 temperature at 18.5 km. X-axis shows the ACE-observed temperature (ACE T), and the y-axis shows the ERA5 temperature at the closest rounded location and time with ACE satellite overpass (ERA5 T_0) for individual data points in 2020 (red), 2021 (purple), and 2012 (blue) over the full latitude range we use in this study (40 – 90 °S). The black dotted line indicates the 1-1 ratio. The total coefficient of determination R^2 value for ACE T and ERA5 T_0 (concatenating all three years) is 0.97, with a mean bias of 1.1 K.

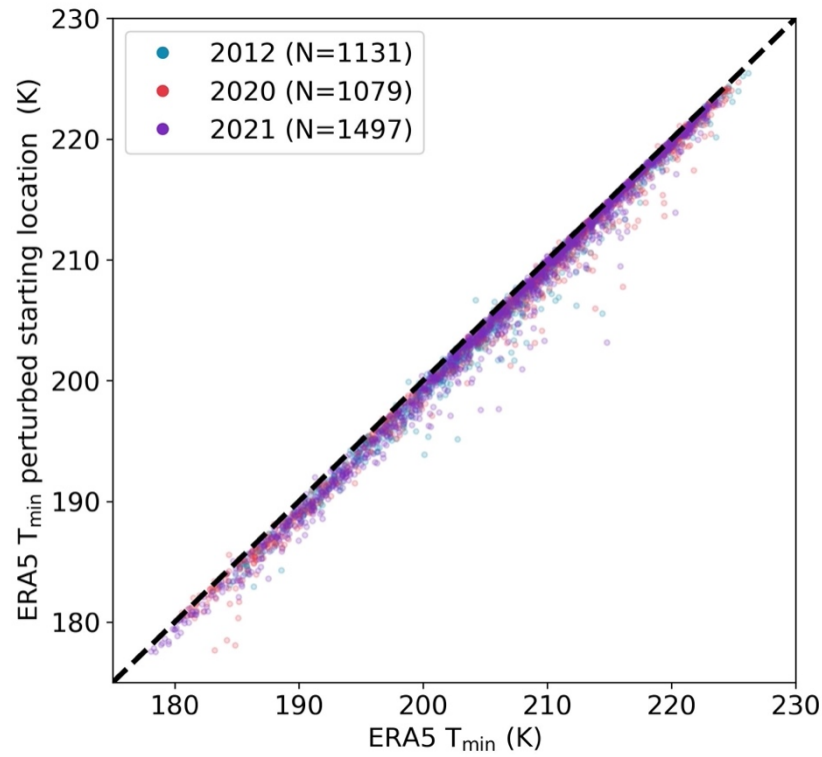


Fig. S7. Sensitivity test for the back trajectory calculation at different starting locations at 18.5 km. X-axis shows the minimum temperature from the 5-day back trajectory starting at the closest latitude/longitude from ACE observation. Y-axis shows a similar 5-day minimum temperature from back trajectory calculations but for data points released at ± 1 degree latitude and longitude from the satellite overpass location. The dashed black line indicates the 1-1 ratio. With such perturbations in the starting location, $T_{\min}$ can have a mean bias at -0.8 K.

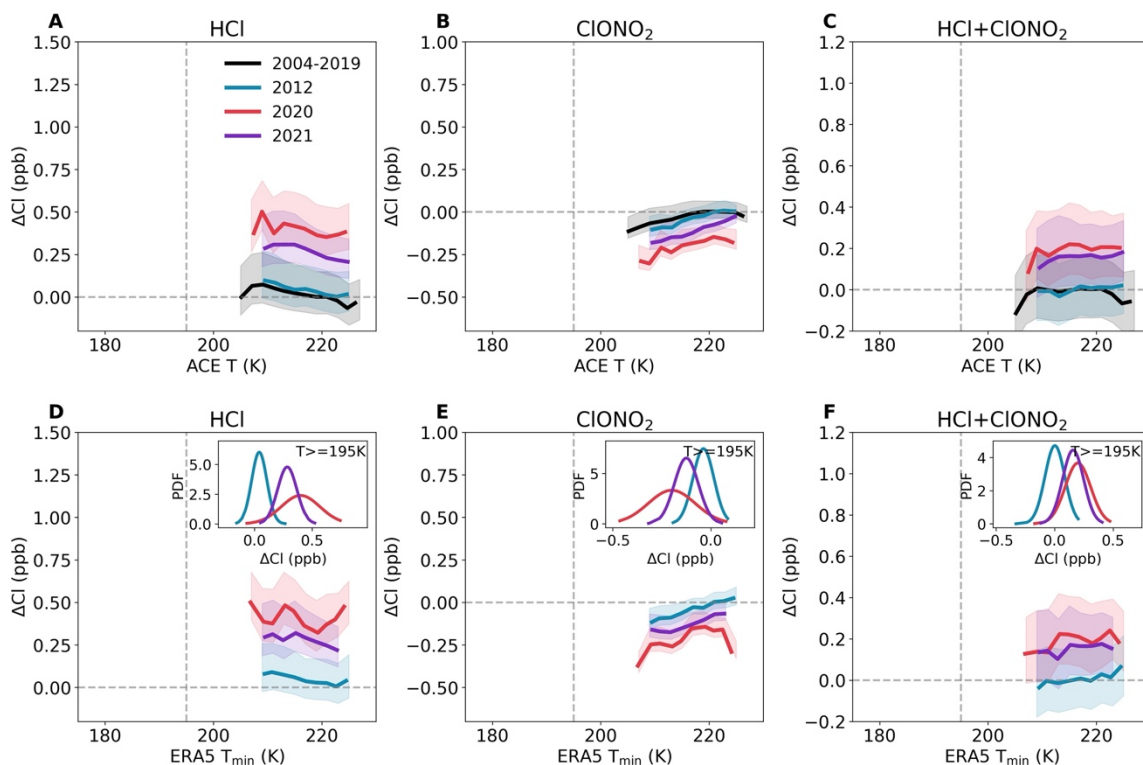


Fig. S8. Cl activation as a function of temperature at the core of the polar vortex region (70 – 90 °S). Most of the data points in Fig. 5 are over 65 – 70 °S, which might not represent the behaviors within the core of polar vortex. This figure shows data points over 70 – 90 °S, where data is only 553 available in March and April (when temperatures are well above 200 K).

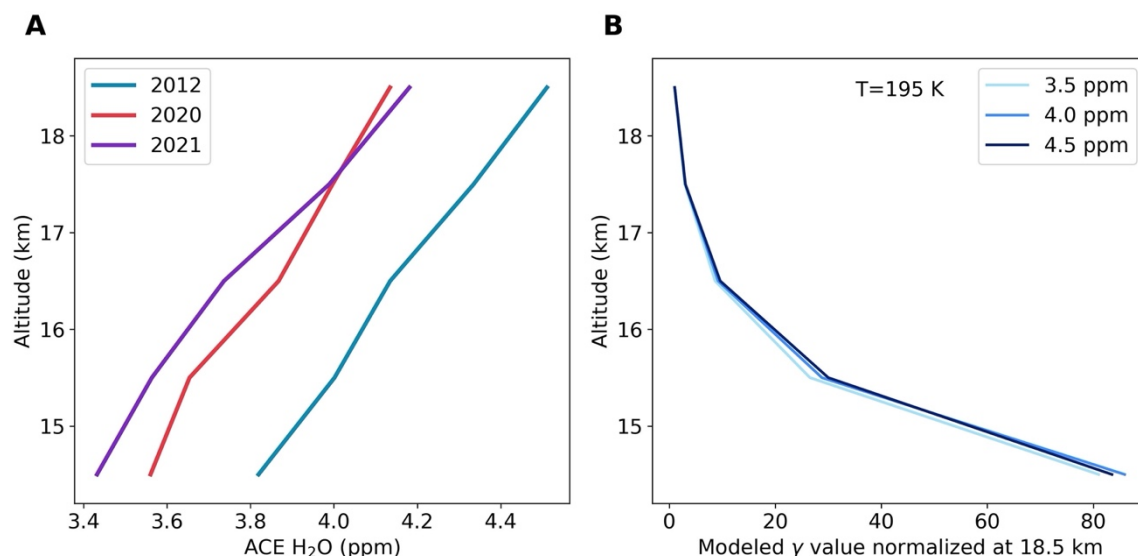


Fig. S9. (A) shows the ACE measured July H₂O in the polar vortex region (65 – 90 °S) at different altitudes from 14.5 km to 18.5 km. The spread of H₂O is around 3.5 ppm to 4.5 ppm. (B) shows the γ value (reaction efficiency of HCl+ClONO₂) calculated from a similar parameterization used in WACCM at a fixed temperature of 195 K at different altitudes. γ values are normalized as ratios compared to the reaction efficiency at 18.5 km. An adopted spread in H₂O volume mixing ratio of ±0.5 ppm from 4 ppm is shown in panel B, illustrating that water vapor mixing ratio has a small effect on the reaction efficiency, while pressure plays a dominating role for the background condition. At lower altitudes (high pressure), the efficiency of the HCl+ClONO₂ reaction is significantly enhanced compared to higher altitudes (low pressure).