Halocarbons in the Lower Stratosphere during the North American Summer Monsoon Season

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1. Introduction

Intense convection occurs in summer within the North American Monsoon Anticyclone (NAMA) circulation, with on average over 100 storms penetrating the tropopause daily. These storms can inject water vapor and other chemicals into the lower stratosphere, with possible effects on stratospheric ozone. The Dynamics and Chemistry of the Summer Stratosphere (DCOTSS) mission was designed to study this coupled dynamical and chemical system, and included deployments of the ER-2 aircraft from Salina, KS in 2021 and 2022, along with radar, satellite and sonde observations of atmospheric structure, composition, and convection. We present here measurements and analysis of organic halogen-containing compounds from DCOTSS 2021. Long-lived anthropogenic halocarbons, such as CFCs and halons, are broken down at high altitudes before descending into the lower stratosphere. Shorter-lived compounds have both anthropogenic and natural sources, and can enter the stratosphere from the tropics or via direct injection by convection at mid-latitudes. Photochemical destruction of all these compounds releases inorganic chlorine and bromine, which can lead to halogen-catalyzed ozone loss.

The DCOTSS Mission

Deep convection over the central U.S. and northern Mexico brings moist boundary layer air and trace gases into the lower stratosphere. Because aerosol growth and surface area are very sensitive to temperature and water content, injection of condensed water and water vapor in low temperature regions of the midlatitude stratosphere could cause rapid aerosol growth and increased reactivity. Inorganic chlorine reservoir species ($ClONO_2$ and HCl) can be converted to active species (Cl_2 and HOCl, which are then photolyzed to become Cl and ClO) on aerosol surfaces, and the resulting chlorine radicals could then catalytically destroy ozone. DCOTSS was developed to provide an in-depth study of this region over North America. The amount of convective overshoot above the tropopause, hydration of the lower stratosphere, and the basic chemistry of the upper troposphere and lower stratosphere in the NAMA with or without additional water vapor, were probed with coordinated aircraft, balloon, radar, and remote sensing observations, combined with a detailed analysis and modeling effort.

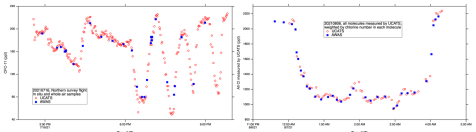
The NASA ER-2 on takeoff with the DCOTSS payload. UCATS is located in the upper Q-Bay, directly behind the cockpit. The sampling inlet for UCATS is visible on the bottom, forward of the landing gear. AWAS is mounted the "belly pod" aft of the wheel, with other instruments located in the nose, wing pods, and Q-Bay.

2. Data and methods used

This presentation is based on in situ data from the ER-2 aircraft in 2021. The UAS Chromatograph for Atmospheric Trace Species (UCATS) measures CFC-11, CFC-12, CFC-113, CCl_4, $CHCl_3$, and halon-1211, accounting for about 2/3 of organic chlorine, and the Advanced Whole Air Sampler (AWAS) measures a comprehensive suite of trace gases, including most organic chlorinated and brominated halocarbons of interest, allowing an analysis of the organic chlorine budget of the lower stratosphere at the higher time resolution of the UCATS instrument, using AWAS samples to estimate unmeasured species. We also calculate the approximate total amount of chlorine entering the stratosphere from the NOAA surface network and UCATS measurements of SF_6, an age of air tracer. From the difference between total chlorine and remaining organic chlorine, we estimate the amount of inorganic chlorine in each sample. UCATS also measures ozone; see Hintsa et al. [2021] for a detailed description and history of the instrument. We also make use of water vapor data from the Harvard Herriott Hygrometer and atmospheric data from the Meteorological Measurement System.

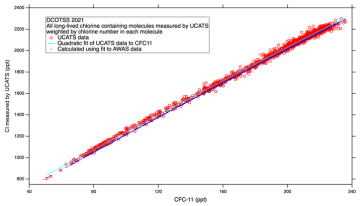
3. Analysis of organic chlorine in the stratosphere

To calculate the organic chlorine budget in the stratosphere, we divided the compounds into three groups: long-lived molecules (lifetime many years), short-lived molecules (lifetime months to a few years), and very short-lived molecules (lifetime days to weeks). Long-lived species measured by AWAS are CFC-11, CFC-12, CFC-112, CFC-112a, CFC-113, CFC-114, CFC-115, CCl_4, HCFC22, HCFC141b, HCFC142b, and halon-1211, short-lived species are $CHCl_3$, CH_2Cl_2, CH_3Cl, and CH_3CCl_3, and the very short-lived species are $CHBrCl_2$, $CHBr_2Cl$, CH_2BrCl, CH_2ClCH_2Cl, and C_2Cl_4. This accounts for almost all the organic chlorine that can enter the stratosphere from the troposphere, either by ascent through the tropical tropopause layer, or directly at mid-latitudes. Once in the stratosphere, all of these molecules are destroyed by photochemical oxidation, over their varying lifetimes, releasing inorganic chlorine that can then destroy ozone. We take advantage of fact that all of these compounds are correlated in the stratosphere, and plot them here vs. CFC-11, which is measured by both AWAS and UCATS with good precision and has a large dynamic range in DCOTSS data. The four plots above show the results of our analysis. The plot at the upper left shows the weighted sum of long-lived chlorine-containing compounds. The fit is tight and nearly linear, owing to the high precision of the measurements and the fact that the lifetimes are long with respect to both vertical and horizontal transport timescales in the stratosphere. The weighted sum of shorter-lived molecules (upper right) shows more curvature because of their shorter stratospheric lifetimes, but both are well-described by a quadratic fit to CFC-11. The very short-lived molecules (lower left) show much more scatter, because of their small concentrations and shorter lifetimes. Note the difference in scale on this plot – for lower values of CFC-11, these molecules have been completely removed. To calculate the total organic chlorine in the stratosphere (lower right), we added the long- and short-lived molecules together, plus the power-law fit to the very short-lived species, with a linear term to decrease the power law fit to zero at CFC-11=0. The quadratic fit can then be used to calculate total organic chlorine for any value of CFC-11, or any other long-lived tracer in the stratosphere. We also used an alternative approach to calculate organic chlorine by fitting each molecule not measured by UCATS to CFC-11 with AWAS data, and corrections from the NOAA surface network and other data to estimate the organic chlorine from species not measured by AWAS or UCATS, with very similar results.



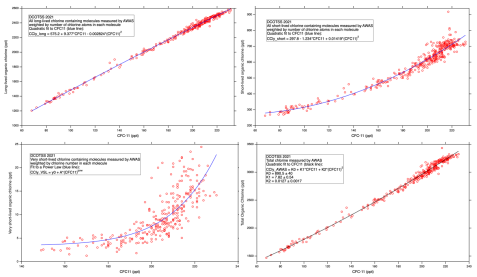
2.1 Data comparison

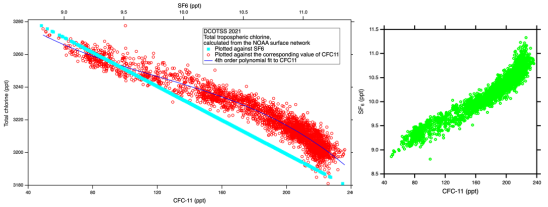
Comparison of UCATS and AWAS time series data for CFC-11 (left) and the sum of all chlorine-containing compounds measured by UCATS (CFC-11, CFC-12, CFC-113, CCl_4, $CHCl_3$, and halon-1211; right) weighted by the number of chlorine atoms in each molecule (3 for CFC-11, 2 for CFC-12, 1 for halon-1211, etc.). UCATS makes a measurement every 75 seconds, while AWAS takes up to 32 samples per flight on the ER-2. The data are not directly comparable because UCATS is essentially a 2-second "snapshot" of atmospheric composition, while the AWAS cannisters take 30-120 seconds to fill depending on altitude, but these plots indicate the excellent qualitative agreement.



2.2 Comparison of data using correlation plots

Data can also be compared by plotting against a long-lived tracer. Because long-lived tracers in the stratosphere have tight, nearly linear correlations, the data form a compact relationship. The weighted sum of all chlorine compounds measured by UCATS vs. CFC-11 is shown above, along with a quadratic fit to the data, with the corresponding fit from AWAS shown for comparison. The small difference (28 ppt for air with substantial conversion of organic to inorganic chlorine, lower left; 16 ppt for air with little or no conversion, upper right) is likely due to slightly different scales and standards or other systematic discrepancies between the two measurement systems.



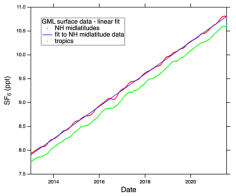


3.1 Total chlorine in the troposphere

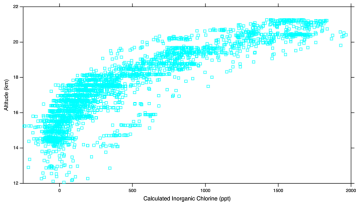
From the NOAA surface network, we calculated the total measured chlorine in the troposphere (above left), which is slowly decreasing because of the Montreal Protocol regulating long-lived halogen-containing compounds. We parameterize it in terms of SF_6, an age of air tracer (see below) measured by UCATS, as Total Cl = 3615 ppt – 38.296*SF_6, plotted above as cyan symbols. Because of the tight correlation between SF_6 and CFC-11 (above right, green), we can also plot it vs. the corresponding value of CFC-11 (red symbols), with a smoothly varying fit for reference. We then derive total inorganic chlorine:

Cly (inorganic or reactive chlorine) = Total Cl – CCly (organic chlorine)

Total chlorine is evaluated for UCATS data, allowing us to provide an estimate of total organic and total inorganic chlorine every 75 seconds along the ER-2 flight track.

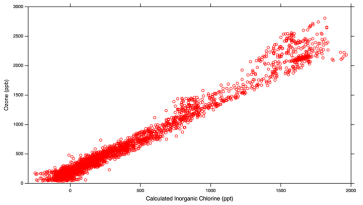


Average tropical and northern hemisphere midlatitude SF_6 data from the NOAA surface network, with a linear fit to the midlatitude data. Most emissions occur in the northern hemisphere, so mixing ratios are higher there compared to the tropics. SF_6 has an extremely long lifetime, and is growing approximately linearly, allowing it to be used as a clock in the stratosphere and in some cases the troposphere as well [Orbe et al., 2021].



3.2 Inorganic chlorine in the stratosphere

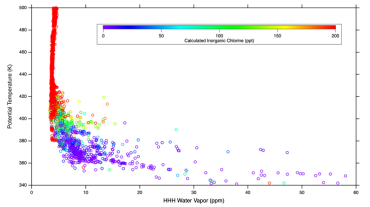
Because organic chlorine generally decreases with altitude in the stratosphere, inorganic chlorine increases from zero with altitude from the tropopause (above). Negative values of Cly reflect CFC-11 data larger than background tropospheric values and are not physical. Ozone also increases with altitude, and is roughly correlated with Cly (below).



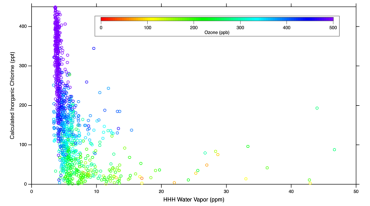
References

Hintsa, E. J., et al., UAS Chromatograph for Atmospheric Trace Species (UCATS) – a versatile instrument for trace gas measurements on airborne platforms, Atmos. Meas. Tech., 14, 6795–6819, https://doi.org/10.5194/amt-14-6795-2021, 2021.

Orbe, C., et al., Tropospheric age-of-air: Influence of SF_6 emissions on recent surface trends and model biases, J. Geophys. Res., 126, e2021JD035451, https://doi.org/10.1029/2021JD035451, 2021.



Measured water vapor (x-axis) plotted against potential temperature, showing the many instances of water vapor injections above the tropopause (~360 K) observed in DCOTSS 2021. Data are color coded by Cly. Chlorine activation could occur in air parcels with elevated water content and significant Cly (>~100 ppt), depending on temperature and aerosol loading. Near the tropopause, Cly (and ozone) are almost uniformly low, indicating the low likelihood of any significant effects on ozone there.



A different way of looking at the chlorine, water and ozone data, with Cly also acting as a surrogate for altitude. Points where interesting chemistry could occur are those with both elevated Cly and water, and are color-coded by ozone to show where there is the potential for ozone loss.

4. Summary

- We characterized the organic and inorganic chlorine budget for DCOTSS 2021.
- Comparisons with AWAS data agree well along flight tracks and for correlations between molecules measured by both instruments.
- Using slightly different methods to derive CCly and Cly gave very similar results; uncertainties are largely systematic owing to slight differences in scales and standards.
- The ER-2 aircraft intercepted a large number of plumes of tropospheric air injected into the stratosphere during DCOTSS.
- There is some overlap between elevated water vapor and significant Cly and ozone, but many air masses with injections of water vapor had low ozone and inorganic chlorine.
- Further analyses of the influence of convection can be performed with chemical modeling, and also await the results from flights in 2022.

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5. Data availability

All data shown here are publicly available from the NASA Langley Airborne Science Data Center (https://asdc.larc.nasa.gov/project/DCOTSS and https://asdc.larc.nasa.gov/project/DCOTSS/DCOTSS-Aircraft-Data_1). Data from DCOTSS 2022 will be available in 2023. DCOTSS 2022 occurred earlier in the year (May-June vs. July-August), and encountered even more frequent and intense convection.

DCOTSS
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