

Airborne measurements of cirrus-activated C₂Cl₄ depletion in the upper troposphere with evidence against Cl reactions

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[1] Airborne whole air samples collected over the western Pacific in spring, 2001 showed depletion of tetrachloroethene (C₂Cl₄) in every upper tropospheric (UT) air parcel that had interacted with large areas of cirrus less than three days upwind. The amount of C₂Cl₄ depletion showed a negative correlation with time since the interaction, consistent with the C₂Cl₄-depleted air parcels mixing with the ambient air as they moved downwind of the cirrus. Ethane and C₂Cl₄ both react relatively quickly with atomic chlorine (Cl) but ethane was not significantly depleted in these same air parcels, indicating that the C₂Cl₄ depletion cannot be attributed to Cl chemistry alone. Based on the minimum ethane depletion that can be detected by our measurements, a daytime upper limit of roughly 3×10^4 atom Cl cm⁻³ is indirectly estimated for heterogeneous chlorine activation by cirrus clouds in the UT in tropical- and mid-latitudes during spring. INDEX

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1. Introduction

[2] Heterogeneous reactions on the ice surfaces of polar stratospheric clouds are known to enhance the conversion of HCl and ClONO₂ to more reactive species such as Cl₂, thereby playing a critical role in activating Cl and augmenting stratospheric ozone depletion [see Solomon *et al.*, 1997 and references therein]. Several modeling studies

suggest that cirrus clouds are likely to similarly activate chlorine in the tropopause region, with the magnitude and duration of resulting ClO enhancement depending upon season, latitude and altitude [Borrmann *et al.*, 1996; Solomon *et al.*, 1997; Bregman *et al.*, 2002]. In support of this, ice particles in cirrus ($T = 235$ K) and aircraft condensation trails ($T = 220$ K) are reported to take up large amounts of atmospheric HCl [Thibert and Dominé, 1997], with the uptake coefficient increasing with decreasing temperature [Hynes *et al.*, 2001].

[3] Airborne studies have investigated chlorine activation by cirrus near the tropopause and in the lowermost stratosphere for various latitudes and seasons. Lelieveld *et al.* [1999] observed enhanced CO/ethane ratios over Sweden, from which they inferred mean diurnal Cl values of up to 1.0×10^4 atom cm⁻³ based on heterogeneous activation. Enhanced ClO has been observed at polar latitudes during winter (averaging 15–20 pptv; Thornton *et al.*, 2003), and at midlatitudes during spring (>90 pptv; Keim *et al.*, 1996) and winter (2.7 pptv in cirrus and up to 70 pptv near the tropopause; Borrmann *et al.*, 1997). The Thornton *et al.* and Borrmann *et al.* studies refrained from or were not able to link the ClO enhancements to chlorine activation by cirrus, and the results by Keim *et al.* were consistent with heterogeneous reactions. By contrast, Smith *et al.* [2001] suggest that midlatitude ozone loss is not controlled by chlorine activation by cirrus near the tropopause, based on a consistent absence of ClO enhancements in summer. However, this disparity among the midlatitude studies may reflect different conditions (water subsaturation in the case of Smith *et al.*) rather than conflicting results [Thornton *et al.*, 2003]. Here we use aircraft measurements of hydrocarbons and halocarbons at midlatitudes during spring, together with backward trajectories and satellite images, to indirectly investigate chemical processing by cirrus in the UT between 10–12 km. This is the first study of its kind in the UT.

2. Experimental

[4] The measurements were made during the Transport and Chemical Evolution over the Pacific (TRACE-P) experiment (February–April, 2001) [Jacob *et al.*, 2003], using airborne whole air sampling and laboratory gas chromatographic analysis with flame ionization-, electron capture-, and mass spectrometer detection [Colman *et al.*, 2001]. During 17 science flights of the NASA DC-8 aircraft, 2725 whole air samples were collected between 0–12 km, including 231 between 10–12 km. The samples were collected into individual conditioned, evacuated 2-L stain-

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Table 1. Rate Constants (cm³ molec⁻¹ s⁻¹) for the Reaction of Selected Compounds with OH (k_{OH}) and Cl (k_{Cl}) at 220 K and 250 mb for the Pressure-Dependent Reaction C₂Cl₄ + Cl

Compound	k_{OH}	k_{Cl}
CHCl ₃	$3.3 \times 10^{-14\text{a}}$	$2.0 \times 10^{-14\text{a}}$
CH ₂ Cl ₂	$3.2 \times 10^{-14\text{a}}$	$6.7 \times 10^{-14\text{a}}$
Ethane	$7.6 \times 10^{-14\text{b}}$	$5.3 \times 10^{-11\text{b}}$
C ₂ Cl ₄	$4.0 \times 10^{-14\text{a}}$	$5.8 \times 10^{-11\text{a}}$

^aDeMore *et al.* [1997].^bAtkinson [1997].

less steel canisters every 4–5 minutes during horizontal flight legs. Typical canister fill times were 1 minute, equivalent to a sampling distance of ~12 km.

[5] After each flight, the canisters were shipped to our UCI laboratory and analyzed for 78 compounds within 10 days of sampling. Ethane, C₂Cl₄, methylene chloride (CH₂Cl₂) and chloroform (CHCl₃) were used in this study. Their limits of detection (LOD) are: ethane (3 pptv); C₂Cl₄ (0.05 pptv); CH₂Cl₂ (1 pptv); CHCl₃ (0.1 pptv). The precisions are: ethane (0.5%); C₂Cl₄ and CHCl₃ (1%); CH₂Cl₂ (5%). The accuracy is 5% for ethane and CHCl₃, and 10% for C₂Cl₄ and CH₂Cl₂.

[6] The possible influence of Cl chemistry in the UT was investigated using ratios of compounds with similar rate constants for reaction with OH (k_{OH}) and quite different rate constants for reaction with Cl (k_{Cl}), specifically CH₂Cl₂/C₂Cl₄, CHCl₃/C₂Cl₄, CH₂Cl₂/ethane and CHCl₃/ethane. All four gases have similar k_{OH} values whereas C₂Cl₄ and ethane have much larger k_{Cl} values (Table 1), and an increase in these ratios may indicate recent Cl chemistry. Ethane and C₂Cl₄ have previously been used to evaluate tropospheric Cl levels [Rudolph *et al.*, 1996; Singh *et al.*, 1996; Wingenter *et al.*, 1999].

[7] The following data editing procedures ensured that any ratio increases were consistent with Cl chemistry in the UT. First, air parcels that showed stratospheric influence (O₃ > 100 ppbv and CO < 50 ppbv) were removed from further analysis. Of 14 air parcels sampled for at least 20 minutes at altitudes ≥ 10.7 km, two showed stratospheric influence. Secondly, because the ratios become less reliable at very low mixing ratios, only mixing ratios > 5 × LOD were used. Though this cutoff prevented us from using other compound pairs such as benzene/ethyne, the mixing ratios of C₂Cl₄ and ethane were always > 5 × LOD in the UT air samples (mean ± 1σ of 1.9 ± 1.3 pptv for C₂Cl₄ and 584 ± 205 pptv for ethane). Thirdly, the ratios were inspected to ensure that any enhancements were caused by depleted C₂Cl₄ or ethane (consistent with possible Cl chemistry) rather than enhanced CH₂Cl₂ or CHCl₃. In our experience C₂Cl₄ and CH₂Cl₂ emissions are often co-located, and here CHCl₃ correlated more poorly with C₂Cl₄ than did CH₂Cl₂. Fourthly, because Cl chemistry has been previously detected in the marine boundary layer (MBL), the air parcels were tested for possible deep convective influence from the MBL. Five-day backward trajectories were calculated every 5 minutes for each flight leg using a kinematic model described in Fuelberg *et al.* [1996, 2003]. Of the 12 air parcels considered here, seven had 5-day backward trajectories that remained in the UT, with no evidence for MBL influence.

[8] Backward trajectories and infrared satellite images were used to investigate the occurrence of broad cirrus regions in the upwind paths of the seven air parcels. The images were taken by the GMS 5 and GOES 10 satellites and created using McIDAS image processing, typically in 3-hour intervals. The backward trajectory locations were superimposed on a satellite image taken at the same time, and these can be viewed at www-gte.larc.nasa.gov/gte-met/gettracepucinfo.html (15–48 images per air parcel). The cirrus cloud heights were determined using colorized infrared satellite imagery, and radiosonde data were used to verify that the upper level air parcels were saturated (see below). In general, backward trajectories are uncertain to within 20% of the travel distance. This investigation looks for interactions between parcel trajectories and cirrus on a broad scale, and we do not believe that the uncertainty in their co-locations is sufficiently large to frustrate our analysis.

3. Results and Discussion

[9] Using the edited data set, CH₂Cl₂/C₂Cl₄ and CHCl₃/C₂Cl₄ were notably enhanced in the UT, particularly between 11–12 km (Figure 1 shows CH₂Cl₂/C₂Cl₄). The enhanced ratios (depleted C₂Cl₄) occurred during encounters with four separate air parcels sampled in the region 19–31°N and 129°E–160°W (Table 2). The average (±1σ) CH₂Cl₂/C₂Cl₄ and CHCl₃/C₂Cl₄ ratios from the four encounters (24 ± 8 and 9 ± 3 pptv/pptv, respectively) were ~3 times larger than those measured for 25 background UT air samples at comparable altitudes (11–12 km; Table 2). By contrast, the average ratios of CH₂Cl₂/ethane and CHCl₃/ethane in the same four air parcels (25 ± 4 and 10 ± 2 pptv/ppbv, respectively) were not significantly different from the background ratios at 11–12 km, though we note that values for individual “depleted C₂Cl₄” and “undepleted C₂Cl₄” flights sometimes differed. Because C₂Cl₄ and ethane have similar k_{OH} and k_{Cl} values at UT

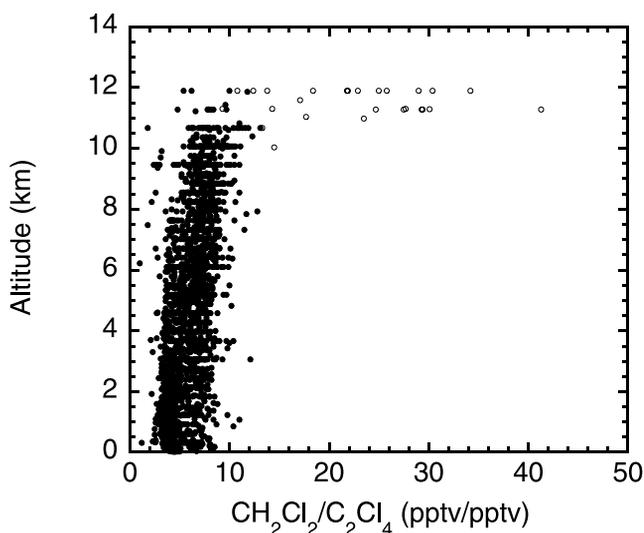


Figure 1. Altitude profile of CH₂Cl₂/C₂Cl₄ for air samples that passed the data editing procedures outlined in the text. Open circles are from the four air parcels that showed depleted C₂Cl₄.

Table 2. Details of Seven UT Air Parcels That Were Inspected for Possible Influence From Cl Activation by Cirrus

DC-8 Flight	Sampling Date (UTC)	Sampling Interval (UTC)	Main Sampling Alt. (km)	<i>n</i>	CH ₂ Cl ₂ /C ₂ Cl ₄ (pptv/pptv)	CHCl ₃ /C ₂ Cl ₄ (pptv/pppv)	CH ₂ Cl ₂ /Ethane (pptv/ppbv)	CHCl ₃ /Ethane (pptv/ppbv)	Time since cirrus (days)	Duration of interaction (hours)
<i>Depleted C₂Cl₄</i>										
D4	Feb.26–27	23:40–0:49	11.9	9	25 ± 6	10 ± 4	27 ± 3	12 ± 2	1.2–1.9	18
D9	Mar.11	6:30–6:51	11.9	4	18 ± 5	6 ± 2	24 ± 3	8 ± 1	1.8–3.2	36
D16	Mar.30	1:08–1:53	11.0–11.3	9	22 ± 8	8 ± 3	25 ± 5	9 ± 2	1.4–2.3	21
D18	Apr.4	6:28–7:00	11.3	5	32 ± 9	11 ± 3	24 ± 2	9 ± 1	0.8–1.4	15
<i>UT Background</i>										
D3–20	Feb.28–Apr.9	n/a	11–12	25	9 ± 3	3 ± 1	30 ± 6	11 ± 4	n/a	n/a
<i>Undepleted C₂Cl₄</i>										
D5	Feb.27–28	23:41–0:05	10.4–10.7	4	10 ± 1	4 ± 1	35 ± 1	15 ± 1	-none-	-none-
D6	Mar.4	5:44–6:10	10.7	5	11 ± 1	6 ± 1	22 ± 2	12 ± 2	-none-	-none-
D13	Mar.21	1:37–2:24	10.7	9	8 ± 1	3 ± 1	36 ± 2	14 ± 1	2.7–3.1	11

Uncertainty estimates represent $\pm 1\sigma$; n = number of samples; none = no cirrus interaction for at least 5 days upwind.

temperatures and pressures (Table 1), the failure of ethane to corroborate the C₂Cl₄ findings indicates that Cl chemistry alone does not explain the observed C₂Cl₄ depletion.

[10] To understand the cause of the C₂Cl₄ depletion, all seven air parcels were tested for upwind interactions with cirrus. Interestingly, all four air parcels that showed elevated CH₂Cl₂/C₂Cl₄ and CHCl₃/C₂Cl₄ also had major interactions with cirrus (lasting 15–36 hours) 1–3 days upwind (Table 2). The cirrus were located over eastern Asia and the western Pacific (5–40°N and 90°E–160°W; see website) and were associated with frontal activity for the D4 and D18 air parcels and with tropical convection for D9 and D16. Using D4 as an example, the backward trajectory heights (8–13 km or 150–300 mb) overlap the estimated cirrus height (10–13 km or 225–240 K). At these temperatures the clouds are expected to be mostly ice with little supercooled water. Hygistor measurements from a Shanghai radiosonde sounding the day before sampling are near saturation from 5–11 km (200–500 mb), providing consistent evidence that the upper level air was humid and is expected to contain cirrus. All four air parcels showed similar evidence for interaction between the trajectories and cirrus.

[11] Of the three UT air parcels that do not show depleted C₂Cl₄, two do not interact with cirrus for at least 5 days upwind (Table 2). By contrast, the D13 air parcel shows an 11-hour interaction with cirrus between 2.7–3.1 days upwind, even though C₂Cl₄ was not depleted. This behavior was investigated by plotting the CH₂Cl₂/C₂Cl₄ ratio (normalized to the change of CH₂Cl₂/C₂Cl₄ with altitude in background air) against time since the upwind cirrus interaction (Figure 2a). Bearing in mind that only four data points are available in Figure 2a, the magnitude of C₂Cl₄ depletion shows a negative correlation with time ($r^2 = 0.86$ for an exponential fit), which is consistent with the C₂Cl₄-depleted air parcels mixing with the ambient air as they move downwind of the cirrus. Taking the ratio uncertainty into account, the normalized CH₂Cl₂/C₂Cl₄ ratio crosses the background value of 1 within the characteristic 3–5 day mixing time for an air parcel in the UT [R. Newell, pers. comm., 2002]. That is, the D13 air parcel is likely to have almost completely mixed with the ambient air by the time it was sampled, consistent with the observed lack of C₂Cl₄ depletion.

[12] Unlike CH₂Cl₂/C₂Cl₄, the ratio of CH₂Cl₂/ethane shows no correlation with time since the upwind cirrus interaction (Figure 2b). The depletion of C₂Cl₄ but not ethane following encounters with cirrus indicates a primary depletion mechanism other than reaction with Cl. We rule out reaction with bromine (Br) based on a very slow C₂Cl₄ + Br rate constant (5×10^{-15} at 220 K; Ramacher et al., 2001) and an estimated upper limit Br range of 0.5–2 pptv. Tetrachloroethene has a much lower vapour pressure than ethane, and in snow doping experiments at Summit, Greenland we have found that addition of equal amounts of C₂Cl₄ and ethane leads to a 10–100 fold greater amount of ethane downstream as a result of preferential C₂Cl₄ adsorption onto

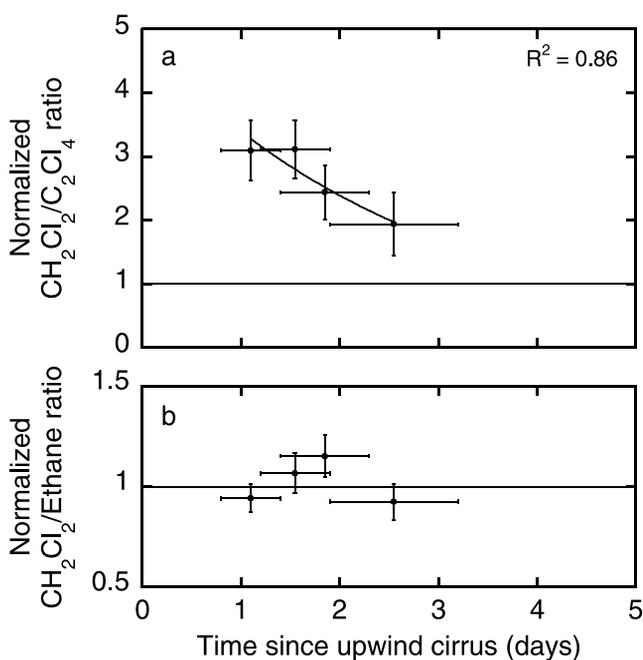


Figure 2. Time since cirrus interaction versus the normalized ratio of (a) CH₂Cl₂/C₂Cl₄ and (b) CH₂Cl₂/ethane for the four UT air parcels that showed depleted C₂Cl₄. The horizontal range shows the duration of the cirrus interaction, and the vertical error bars show propagated uncertainty based on the standard deviation of the mean.

the snow. While recognizing that the snow results may not extrapolate to ice surfaces, it is possible that C₂Cl₄ is preferentially adsorbed onto the cirrus particles, then becomes depleted via an addition reaction across its double bond, surface photolysis, or sedimentation. However the exact cause of the C₂Cl₄ depletion is unknown.

[13] The ClO values presented in Section 1 can be used to estimate roughly the extent that ethane would be depleted under such conditions. (Of the dozens of compounds that we measure, ethane is one of our most precise measurements: precision = 3 pptv at UT mixing ratios.) In the UT under TRACE-P conditions (265 mb; 223 K; O₃ = 50 ppbv; CO = 120 ppbv; SZA = 30°), we modeled a ClO/Cl ratio of roughly 330 for NO = 50 pptv and 170 for NO = 100 pptv. During TRACE-P, NO_x levels over the western Pacific were generally <100 pptv, and background values at all altitudes were ~25 pptv [Talbot *et al.*, 2003]. Choosing a ClO/Cl ratio of 300 (NO ~ 50 pptv) yields roughly 0.01 and 0.03 pptv Cl, respectively, for 2.7 and 10 pptv ClO. By comparison, background Cl levels in the northern hemisphere free troposphere are estimated to be <10³ atom cm⁻³ (<0.0002 pptv Cl at 250 mb) [Rudolph *et al.*, 1996]. Using $\ln([\text{ethane}]/[\text{ethane}]_0) = -k_{\text{Cl}} [\text{Cl}] t$ (where t is the duration of interaction with cirrus, and the background UT value [ethane]₀ was ~610 pptv during TRACE-P), 0.01 pptv Cl would cause ethane to be depleted by 65 pptv for $t = 12$ hours. Such an ethane depletion is well within our measurement capability but was not observed during TRACE-P, suggesting that Cl levels of 0.01 pptv (ClO levels of 2.7 pptv) were not present.

[14] An upper limit for Cl can be indirectly calculated based on the minimum detectable ethane depletion. The natural variability of ethane in a typical 20-minute UT flight leg is 5 pptv (1σ), and we estimate that 40 pptv (which would be diluted to roughly 30 pptv after 1 day of downwind travel; see Figure 2a) is the minimum ethane depletion that we could confidently detect in the UT. A 40 pptv ethane depletion requires 3 × 10⁴ atom Cl cm⁻³ (0.005 pptv Cl) for 12 hours of photochemical processing in the UT, and 1.5 × 10⁴ atom Cl cm⁻³ (0.002 pptv) for 1 day. Therefore, if it occurs, the maximum Cl activation by UT cirrus in tropical- and mid-latitudes during spring is likely within an order of magnitude of background tropospheric Cl levels, and is not expected to exceed 3 × 10⁴ atom Cl cm⁻³. The limited Cl activation by UT cirrus is consistent with laboratory studies by Hynes *et al.* [2002], who found that HCl uptake onto ice is inhibited by HNO₃ at $T > 210$ K.

4. Conclusions

[15] Airborne C₂Cl₄ and ethane measurements were used to indirectly investigate the possibility of heterogeneous chlorine activation by UT cirrus. Of seven UT air parcels that had not been recently influenced by the stratosphere or lower troposphere, four had 15–36 hour interactions with cirrus between 1–3 days upwind. Tetrachloroethene was depleted in each of these air parcels, and the magnitude of the depletion was negatively correlated with time since the interaction. A lack of significant ethane depletion in these air parcels rules out the possibility that Cl is the primary cause of the C₂Cl₄ depletion. We tentatively speculate that C₂Cl₄ was preferentially adsorbed onto the

clouds, followed by chemical processing at the ice surface and/or sedimentation.

[16] Ethane is abundant in the UT and it is one of our most precise measurements. We used a minimum detectable ethane depletion of 40 pptv to indirectly estimate an upper-limit Cl abundance of 3 × 10⁴ atom Cl cm⁻³ (0.005 pptv Cl) in the vicinity of UT cirrus in tropical- and mid-latitudes during spring. Assuming a ClO/Cl ratio of 300 in the springtime UT, this corresponds to an upper limit of 1.5 pptv ClO. This value lies in the low range of modeled ClO enhancements of 1–100 pptv for chlorine activation by cirrus in cold conditions (near and above the tropopause), and suggests that cirrus in relatively warmer conditions (in the UT) play a much more limited role in midlatitude chlorine activation during spring.

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