# Ozone Destruction in Continental Stratus Clouds: Experimental Evidence for Heterogeneous Chemistry

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## Introduction

There is considerable interest in studying tropospheric ozone because of its role as a greenhouse gas and as a key element in tropospheric chemistry. Heterogeneous chemistry involving reactions with aerosols and cloud droplets can affect $O_3$ in a number of ways. The results of model studies show that aqueous phase chemistry is shown to decrease ozone concentrations significantly in the troposphere (Jacob 1986, 1997; Lelieveld and Crutzen 1990; Liang and Jacob 1997; and Matthijsenetal et al. 1997). Reichardt et al. (1996) and Sassen et al. (1998a) found pronounced $O_3$ minima at high altitudes in the presence of cirrus clouds and suggested that these minima were due to heterogeneous chemistry. But no evidence in lower level clouds has been previously reported (Jacob 1997). In this paper, evidence for the negative correlation between ozone concentration and liquid water content (LWC) in a widespread continental stratus cloud system is reported for the first time. Detailed analysis of extensive in situ data will show the magnitude of the effect of heterogeneous chemistry on $O_3$ concentration.

## Effects of Clouds on Tropospheric Ozone: Theory

Clouds have two main effects on tropospheric ozone: radiative cloud and aqueous-phase chemistry. The chemistry of the atmosphere is driven by solar radiation, which dissociates certain molecules into reactive atoms or free radicals. Weele and Duynkerke (1993) have shown that the actinic flux above the clouds is always enhanced relative to the clear-sky values, and the actinic flux below the clouds is usually reduced. In a homogeneous cloud, the actinic flux changes almost linearly with height in the clouds. Matthijsen et al.'s (1997) model results of the radiative cloud effect show that a reduction of $O_3$ concentrations compared to clear-sky runs under virtually all circumstances.

Besides the radiative effect of clouds, a series of aqueous-phase reactions will disturb the gas-phase reactions. The $HO_2$ radical is scavenged efficiently by cloud droplets as a result of acid-base dissociation of $HO_2$(aq) ($pk_a$=4.7). A large fraction of dissolved $HO_2$ (dependent on the PH) dissociates into $H^+$ and $O_2^-$.

$$HO_2(g) = HQ_2(aq), \quad (1)$$

$$HO_2(aq) = H^+ + O_2^-, \quad (2)$$

followed by electron transfer between $HO_2$(aq) and $O_2^-$:

$$HO_2 + O_2^- \xrightarrow{H_2O} H_2O_2 + O_2 + OH^-, \quad (3)$$

and reaction of $O_2^-$ with $O_3$(aq)

$$O_2^- + O_3 \xrightarrow{H_2O} 2O_2 + OH + OH^-. \quad (4)$$

The depletion of $HO_2$(g) in clouds suppresses the gas phase reaction [Eq. (5)], which provides the major source of $O_3$ in the troposphere:

$$HO_2 + NO \longrightarrow OH + NO_2, \quad (5)$$

$$NO_2 + hv \xrightarrow{O_2} NO + O_3. \quad (6)$$

Model calculation by Jacob (1986) indicated that $HO_2$(g) concentrations in a cloud of PH4 are depleted by 70% relative to clear sky because of reactors (1)-(3), and $HO_2$(g) decreases almost linearly with an increase in LWC.

So the destruction of $O_3$ in clouds finally is given by:

$$\Delta O_3 \propto \Delta HO_2 \propto \text{LWC}. \quad (7)$$

# Experimental Data

This case study is based on aircraft operations collected during the April 1994 Remote Cloud Sensing Intensive Observation Period (RCS IOP) at the Atmospheric Radiation Measurement (ARM) Cloud and Radiation Testbed (CART) site near Lamont, Oklahoma. The in situ $O_3$ monitor in the University of North Dakota Citation aircraft was a Scintrix Chemiluminescent (CL) analyzer used with eosin. The CL device with eosin is effective for measuring ambient ozone at a high-response frequency (up to 7 Hz) and a detection limit of 0.2 ppb ozone. Other atmospheric species, including water vapor, produce no interference. Intercomparisons with an ultraviolet (UV) absorption ozone analyzer show that rain and high humidity do not change the instrument response (Ray et al. 1986). The CL $O_3$ analyzer used in this experiment was not calibrated on a daily basis, and so its absolute accuracy is uncertain due to the effects of relatively small drifts between calibrations. Nonetheless, because relative changes in $O_3$ concentration on any given flight should be reasonably accurate (M. R. Poellot, personal communication), this data can appropriately be used to analyze the effects of clouds on ozone. The LWC profiles here were measured by the forward-scattering spectrometer probe (FSSP).

The stratus clouds studied on the afternoon of 30 April 1994 were associated with a widespread springtime cold-air outbreak over the central United States. A detailed remote sensing and in situ case study of this cloud has been reported by Sassen et al. (1998b). Figure 1 shows the profiles of LWC and ozone for each aircraft profile. To eliminate high-frequency changes in LWC, these profiles are averaged over 30 m in the vertical direction. From Figure 1, we can see that the stratus are mainly distributed between 1.1 km and 1.7 km above mean sea level (MSL), LWC extends up to 0.6 $gm^{-3}$, and the vertical distribution of LWC is variable with time as the stratus cloud system evolved. The ozone concentration correspondingly shows a large change for each profile. These changes in LWC and $O_3$ provide the necessary conditions to examine the effect of water clouds on ozone.

Figure 2 shows a series of plots of ozone concentration versus LWC for each vertical profile. It is obvious that the

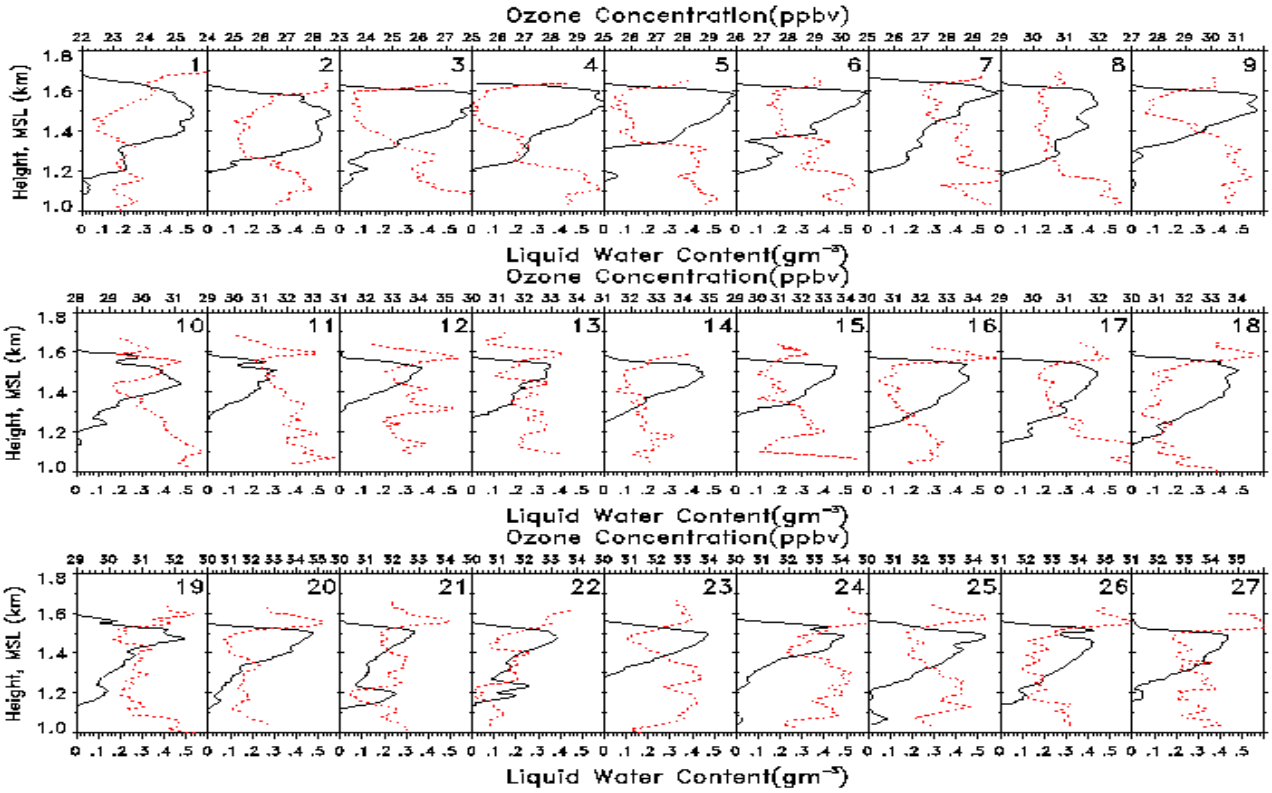


**Figure 1**. Vertical profiles of LWC (solid) and ozone concentration in parts per billion by volume (dashed) on 30 April 1994 corresponding to the first 27 aircraft profiles. (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/wangz-98.pdf*.)

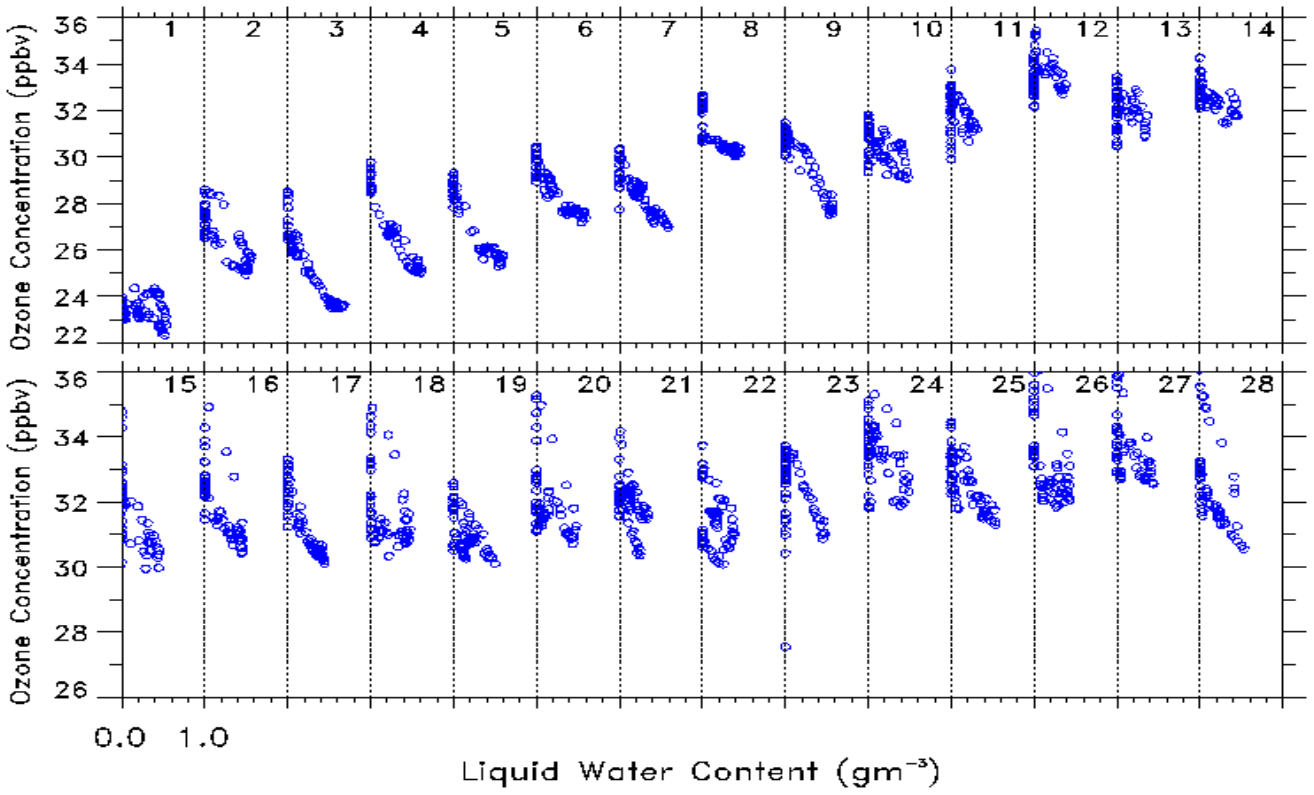


**Figure 2**. Scatter plots of ozone concentration versus LWC for each profile. (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/wangz-98.pdf*.)

ozone concentration is negatively correlated to LWC in the cloud for the majority of profiles. In the following analysis, we attribute this correlation mostly to the effects of aqueous phase chemistry. Figure 3 is a scatter plot of relative ozone change (related to the average ozone concentration outside the cloud) with LWC. The curve fitted to this data (solid line, see figure caption), clearly shows that the ozone change is negatively correlated to the LWC in the cloud.

# Data Analysis

By starting with the conservation relation of $O_3$ for an air parcel, $dO_3/dt=Q_{O3}$, a general parcel $O_3$ budget equation can be written (Lenschow et al. 1981) as

$$\frac{\partial O_3}{\partial t} + u\frac{\partial O_3}{\partial x} + w\frac{\partial O_3}{\partial z} = Q_{O_3} \qquad (8)$$

where $Q_{O3}$ represents the mean internal sources and sinks of $O_3$, z is height, and u and w represent horizontal and vertical wind speed. This assumes an elastic continuity, horizontal homogeneity of flux terms, and a coordinate system oriented along the direction of the mean wind u.

If we can neglect the effect of clouds on the horizontal and vertical transfer, and assume that the pseudo-steady-state of chemistry reactions is achieved here, we can express the vertical ozone distribution as follows:

$$O_3(z) = \beta_1 + \beta_2 z + \beta_3 LWC(z) + \beta_4 \int_z^{top} \sigma_{cl} dz, \qquad (9)$$

where $\beta_1$, $\beta_2$, $\beta_3$, and $\beta_4$ are constants for each profile, and $\sigma_{cl}$ is the extinction coefficient of the cloud. $\beta_1+\beta_2 z$ represents the ozone profile in the well mixed cloudless boundary layer, $\beta_3 LWC(z)$ represents the effect of aqueous-phase chemistry, and the last term represents the effect of radiation.

Based on the above linear diagnostic model, the regression method of multifactors can be employed to determine the coefficients in the model. Using only the data from within

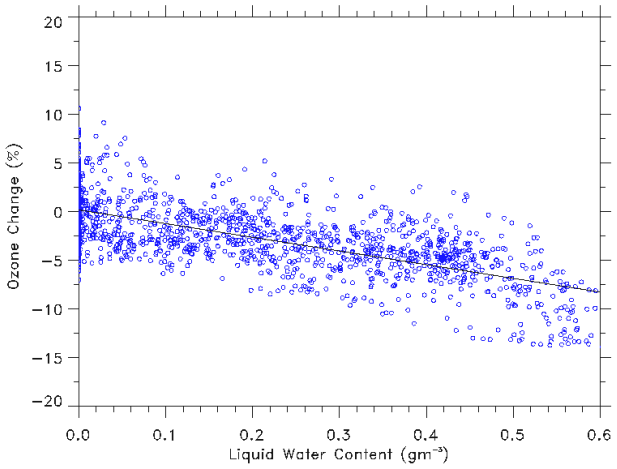


**Figure 3**. Scatter plot of ozone change (relative to the average ozone concentration above and below the cloud) with LWC. The solid line provides a fit to the data points, as given by $O_3$=0.15-14.0×LWC. (For a color version of this figure, please see *http://www.arm.gov/docs/documents/technical/conf_9803/wangz-98.pdf*.)

the stratus cloud to calculate the model coefficients, values of $\beta_3$ and the correlation coefficient are given in Table 1 for each profile. The student t statistic for the null hypothesis of $\beta_s = 0$ is shown in the brackets. It can be seen from the table that most of the correlation coefficients of regression are above 80%, meaning that the model explains most of the ozone changes observed in the stratus cloud layer.

**Table 1.** Regression analysis results of $\beta_3$ and the correlation coefficient R. The student t statistics of $\beta_3$ are shown in the parentheses.

| n | $\beta_3$ | R | N | $\beta_3$ | R |
|---|---|---|---|---|---|
| 1 | -2.53(-8.6) | .74 | 15 | -2.10( -2.2) | .73 |
| 2 | -4.98(-21.5) | .96 | 16 | -9.41(-15.9) | .92 |
| 3 | -4.88(-14.3) | .95 | 17 | -4.29(-15.0) | .92 |
| 4 | -5.89(-21.3) | .96 | 18 | -7.31(-13.7) | .92 |
| 5 | -3.80( -5.9) | .83 | 19 | -3.66( -9.9) | .73 |
| 6 | -3.85( -9.4) | .87 | 20 | -8.13(-17.4) | .90 |
| 7 | -4.39( -9.5) | .90 | 21 | -7.35(-19.8) | .94 |
| 8 | -1.57( -9.0) | .81 | 22 | -5.61( -9.6) | .82 |
| 9 | -5.30(-12.4) | .95 | 23 | -13.36(-15.2) | .99 |
| 10 | -1.05( -2.4) | .70 | 24 | -6.48(-10.5) | .86 |
| 11 | -2.73( -4.5) | .89 | 25 | -4.91(-11.8) | .80 |
| 12 | -5.67( -6.8) | .67 | 26 | -7.00( -8.9) | .83 |
| 13 | -4.57( -3.8) | .42 | 27 | -6.86(-14.6) | .88 |
| 14 | -2.68( -6.8) | .73 | 28 | -8.60(17.9) | .91 |

The favorable student t statistic of $\beta_3$ suggests that $\beta_3$ is significantly different from zero. All $\beta_3$ values are negative, supporting the results of theoretical studies that liquid water clouds reduce the ozone concentration due to aqueous phase chemistry. The average value of $\beta_3$ for R larger than 0.8 is -6.08 ppbv/gm$^{-3}$, and the standard error is 2.59. In our measurements, the average LWC in the clouds is about 0.3 gm$^{-3}$, so the average ozone reduction is about 1.8 ppbv, compared to the average ozone concentration of 31 ppbv outside of the cloud layer. Then, the average reduction in $O_3$ is about 6%. If this result is related to a 24-hour average under conditions similar to model studies (which use an alternating pattern of 2-hour cloudy periods followed by 12-hour cloud-free periods), then the daily average ozone reduction is about 1%. This result is clearly consistent with recent theoretical results (Liang and Jacob 1997; Matthijsen et al. 1997).

# Conclusions

Based on in situ data derived from an intensively studied cloud event from the Southern Great Plains (SGP) CART site, we have found a strong negative correlation between ozone concentration and LWC. Based on the conservation of ozone, a diagnostic model has been constructed to interpret the field data. In this model, we have added the effects of clouds to an assumed cloud-free profile. The results of regression analysis show that aqueous phase chemistry contributes the most to the negative correlation. The average depletion rate of heterogeneous chemistry was estimated to be about -6.08 ppbv/gm$^{-3}$ with a standard error of 2.59. We suggest that this rate is appropriate for use in climate models to parameterize the effect of aqueous phase chemistry on ozone. This finding supports recent model results.

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# Other Publications in Progress

Jacob, D., 1997: Heterogeneous chemistry and tropospheric ozone. *NARSTO critical review paper*. *Atmos. Env.*, submitted.