

UV Dosage Levels in Summer: Increased Risk of Ozone Loss from Convectively Injected Water Vapor

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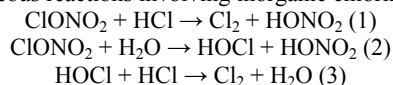
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The observed presence of water vapor convectively injected deep into the stratosphere over the US fundamentally changes the catalytic chlorine/bromine free radical chemistry of the lower stratosphere by shifting total available inorganic chlorine into the catalytically active free radical form, ClO. This chemical shift markedly affects total ozone loss rates and makes the catalytic system extraordinarily sensitive to convective injection into the mid-latitude lower stratosphere in summer. Were the intensity and frequency of convective injection to increase as a result of climate forcing by the continued addition of CO₂ and CH₄ to the atmosphere, increased risk of ozone loss and associated increases in UV dosage would follow.

The occurrence, evolution and cause of dramatic stratospheric ozone losses over the Antarctic in winter/early spring have been documented for three decades (1–9). Large ozone losses over the Arctic in NH winter/early spring (10–12) also have been reported and analyzed, with the largest ozone loss ever recorded over the Arctic occurring in 2011, rivaling losses observed over the Antarctic (13). Here we present a chain of evidence that addresses the probability of increased ozone loss over mid-latitudes of the northern hemisphere (NH) arising from a series of observations of the convective injection of water vapor into the stratosphere over the US in summer.

Large ozone losses that occur over the polar regions result directly from heterogeneous reactions involving inorganic chlorine:



These reactions serve primarily to transform inorganic chlorine (principally HCl and ClONO₂ that constitute ~ 97% of available inorganic chlorine) into the rapidly photolyzed intermediates Cl₂ and HOCl, followed by reaction of the product Cl atoms with ozone to form the primary catalytically active chlorine radical, ClO. This shift of inorganic chlorine to free radical form (“chlorine activation”) then establishes, under conditions of solar illumination, a photochemical steady state between ClO, ClOOCl, ClONO₂ and HCl.

Of key concern [(14, 15) and citations therein] is the temperature at which the above triad of heterogeneous reactions begins to become important. Examination of conditions in the Arctic lower stratosphere coupled with emerging results from laboratory experiments have shown that the dominant pathway for chlorine activation appears to be on cold sulfate-water aerosols (14–18). Thus it is both temperature and water vapor in combination with simple binary sulfate-water aerosols that primarily determine the kinetics for rapid chlorine activation.

Figure 1A summarizes the relationship defining the threshold for rapid activation of chlorine as a function of the combination of temperature, water vapor mixing ratio, and aerosol reactive surface area for a solar zenith angle (45°) representative of mid-latitude summer conditions. The threshold for activation is defined as the point at which net

chlorine activation exceeds a 10% conversion of inorganic chlorine to free radical form in the initial diurnal cycle following convective injection of water vapor. The rate of chlorine activation is calculated using the complete kinetic model for the triad of heterogeneous reactions (Eqs. 1 to 3) using the formulation of Shi *et al.* (14), as well as the relevant photochemical reaction kinetics discussed subsequently. As the water vapor concentration increases, so too does the threshold temperature for chlorine activation. As sulfate aerosol surface area increases, the temperature necessary for chlorine activation increases further. For example, at a commonly observed, unperturbed, stratospheric water vapor mixing ratio of 5 parts per million and aerosol surface area of 2 μm²/cm³, the threshold temperature for activation is ~198 K. But at a water vapor mixing ratio of 12 ppmv and aerosol surface area of 2 μm²/cm³, the threshold temperature increases by ~5 K, substantially increasing the probability of heterogene-

ous chlorine activation, because temperatures in the lower stratosphere over the mid-latitude northern hemisphere in summer frequently lie in the range 200–205 K.

Because the binary sulfate-water aerosols are ubiquitous in the lower stratosphere, if the necessary temperature and water conditions are met, then heterogeneous conversion of inorganic chlorine to free radical form can occur anywhere, not just in the polar regions. While the Arctic lower stratosphere is marginally colder than the mid-latitude lower stratosphere over the US in summer, what matters is the combination of water vapor concentration and temperature.

The in situ observations of H₂O obtained from both the high altitude NASA ER-2 and WB-57 aircraft extending over a number of recent missions are summarized in Fig. 1B. The data shown were retrieved during flights originally selected to observe the outflow from typical convective storms over the US in summer. What proved surprising is the remarkable altitude to which large concentrations of water vapor are observed to penetrate. The convective injection of water into the stratosphere was also observed with surprising frequency, occurring in approximately 50% of the summertime flights over the US. The convective origin of this water vapor is established by simultaneous in situ observations of H₂O and the HDO isotopologue (19, 20), the concentration of which differentiates between direct convective injection and other pathways linking the troposphere and stratosphere (19, 21–23). The observed presence of water vapor enhancements reaching and occasionally exceeding 12 ppmv at temperatures in the vicinity of 200 K in the altitude region between 15 and 20 km, as displayed in Fig. 1B, has significant consequences.

The initiation of fundamental changes in the photochemistry of the lower stratosphere in summer is captured in Fig. 1C, that superimposes on the threshold plot for chlorine activation over the range of 2–10 μm²/cm³ for reactive surface area, the observed in situ H₂O mixing ratios and temperatures at 90 ± 10 mb pressure. It is clear that, at observed water vapor concentrations and temperatures, the threshold for chlorine activation converting inorganic chlorine to free radical form is routinely crossed in the summertime. The result is that ClO can become a major component of the available inorganic chlorine budget within regions of

high water vapor. Convective injection of water vapor to heights reported here can occur in storm systems that are ~50 km across, with smaller domains of high altitude injection imbedded within them at their origin (24). The elevated concentrations of water can spread to 100 km or more in horizontal extent within a few days (19, 25), and remain at the elevated levels reported here over a period of days. This phenomenon has been analyzed by Newman *et al.* (26) using high altitude (70–100 mb) observations of rocket plume dispersion that defines the rate of horizontal spreading from a point source. Additionally, the circular flow pattern of air in the lower stratosphere over the US resulting from the North American summer monsoon provides the potential for repeated convective injection events into the summer lower stratosphere over the US.

In order to address the photochemical catalytic free radical chemistry that controls the loss rate of ozone in the lower stratosphere, we use extensive observations of the free radical photochemistry under unperturbed conditions (i.e., in the absence of convectively injected H₂O) in the mid-latitude lower stratosphere developed over nearly a decade of simultaneous in situ observations of OH, HO₂, ClO, BrO, NO, NO₂, HCl, H₂O, O₃, and the important tracers CO₂, N₂O, and CH₄ [e.g., Wennberg *et al.* (27)]. We also draw heavily on studies that followed under an array of perturbed conditions in the vicinity of and within the Arctic vortex during conditions before, during and after rapid ozone loss (28–32) that included measurements of ClONO₂ and ClOOCl in addition to the species listed above. These analyses provide strict tests for the completeness of the photochemical reaction sets used to calculate the concentrations of the important species, as well as the reaction rate constants, and photodissociation cross sections. We then add the heterogeneous reactions on cold binary sulfate-water aerosols using the latest JPL evaluation (33) to the network of reactions for unperturbed conditions. Our calculations are formulated to investigate the impact of heterogeneous processing of inorganic chlorine based on observed water vapor concentrations. For simplicity, the volume element in the calculations presented here is fixed at a selected pressure altitude and temperature; daylight is represented by a fixed solar zenith angle of 45°. The model incorporates the standard reactions necessary to provide a comprehensive treatment of the evolution of NO_y, Cl_y, Br_y, and HO_x species that includes 62 photochemical reactions and 31 molecular species.

We present the results by displaying the evolution of the key species with time by contrasting the mixing ratios of HCl, ClONO₂, Cl₂, NO₂, NO, ClOOCl, and ClO with time for two conditions:

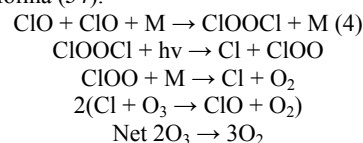
In Fig. 2A we track the evolution with time for summertime, mid-latitude conditions over four 14-hour segments of daylight with three intervening 10-hour periods of darkness for conditions of 90 mb pressure, a temperature of 200 K, a water vapor mixing ratio of 5 ppmv, and a typical reactive surface area of 2 μm²/cm³. As Fig. 2A demonstrates, under these conditions, the key inorganic chlorine species HCl and ClONO₂ are unaffected by the heterogeneous reactions on cold sulfate-water aerosols – nor are the NO, NO₂ and ClO concentrations affected under these unperturbed conditions in the lower stratosphere. The concentrations and ratios of HCl to ClONO₂ and NO to NO₂ match in situ observations under these conditions, as do the concentrations of the other 27 species in the calculation, including the catalytic free radicals.

In Fig. 2B we hold all conditions the same as in Fig. 2A, except we increase the mixing ratio of H₂O to that observed repeatedly in regions influenced by convective injection: 12 ppmv. The impact of crossing the threshold for chlorine activation is clear, even on the time scale of just four days exposure to solar illumination. The observed conditions of H₂O and temperature displayed in Fig. 1C result in the response of the key species displayed in Fig. 2B. Figure 2C shows the case for 18 ppmv water that represents a reasonable estimate of the initial water vapor mixing ratio following convective injection, as the region of enhanced water vapor in Fig. 1C mixed horizontally over 2.5 days prior to being intercepted by the aircraft. The contrast between 5 ppmv (the unperturbed case) and the cases for 12 ppmv and 18 ppmv highlights the sensitivity of the reaction system to injected water vapor.

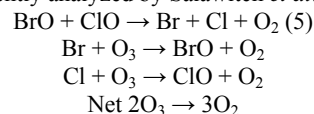
turbed case) and the cases for 12 ppmv and 18 ppmv highlights the sensitivity of the reaction system to injected water vapor.

We can summarize the sequence of events following injection of water vapor. In the first diurnal period the heterogeneous reactions on cold sulfate-water aerosols begin to rapidly convert HCl to ClONO₂ by first producing Cl₂ and HOCl. The Cl₂ and HOCl photodissociate quickly to Cl atoms, which then react with O₃ producing ClO. The ClO thus produced reacts with NO₂ to produce ClONO₂, effectively shifting available inorganic chlorine from HCl to ClONO₂. Simultaneously, the reaction of ClONO₂ with HCl in effect converts NO₂ to HONO₂. Because NO and NO₂ interconvert on the time scale of minutes, the removal of NO₂ draws down the concentration of NO in unison. As NO₂ is diminished, ClO begins to increase because its conversion to ClONO₂ begins to slow. With the termination of sunlight in the first diurnal period, Cl₂ begins to build up rapidly, fed by the heterogeneous reactions but without removal by photodissociation. The heterogeneous reactions continue to remove HCl and ClONO₂ forming Cl₂, HOCl, and HONO₂ in the dark. With sunrise on the second day, a rapid increase in ClO occurs as a result of Cl₂ photolysis followed by reaction of Cl with O₃. The rate of increase of ClO and ClOOCl depends upon the concentration of water vapor as the contrast between Fig. 2, B and C, makes clear. With the reinitiation of sunlight on the third day, the pattern of highly amplified ClO and ClOOCl in steady state with ClONO₂ repeats, in combination with slow production of HCl from the reaction of Cl with CH₄ and of ClO with OH.

The impact on ozone loss rates for the perturbed cases displayed in Fig. 2, B and C, evolves rapidly over the same time scale. During the first diurnal period, control of the catalytic destruction rate of ozone shifts to a combination of (a) the ClO dimer catalytic cycle introduced by Molina and Molina (34):



and (b) the bromine-controlled catalytic cycle introduced by McElroy *et al.* (3) and subsequently analyzed by Salawitch *et al.* (35):



As a result, the catalytic loss of ozone can increase by two orders of magnitude over that for the unperturbed case within the horizontal and vertical extent of the region of injected water vapor.

Figure 2D contrasts the fractional removal of ozone as a function of time following convective injection of water for the case of 12 ppmv and 18 ppmv water compared to the unperturbed case. For the case of 12 ppmv water, approximately 13% of the ozone is lost after four sunlight periods and the loss rate of ozone is approximately 4% per day in the following few diurnal periods. For the 18 ppmv case, approximately 21% of the ozone is lost after four sunlight periods, with a loss rate of approximately 6% per day in the following few diurnal periods. Therefore, the catalytic destruction of ozone within the domain of high water vapor concentration has taken full control of the ozone loss rate and dominates the local photochemical production rate (and the rate of transport-controlled replenishment of ozone) by two orders of magnitude. Once inorganic chlorine has been activated to free radical form, several days are required for the reformation of HCl and ClONO₂ after the water vapor concentration has dropped below about 8 ppmv. However, because the kinetics of heterogeneous chlorine activation also depends on temperature, and water vapor radiatively cools the lower stratosphere, ozone loss rates can persist. As a result, ozone continues to decrease within the affected region so, for example, after 7 diurnal peri-

ods at 12 ppmv water, approximately 25% of the ozone has been removed; the corresponding amount for 18 ppmv is 35% removal.

As exemplified by the in situ observations presented in Fig. 1B, there is a growing realization that convective moistening occurs in the lower stratosphere over the central United States during the summer (19, 36–38). Two instances of elevated ClO at mid-latitudes have been reported. The first by Keim *et al.* 1996 (39) and the second by Thornton *et al.* 2007 (40), both in the tropopause region under conditions of elevated H₂O. There is also growing recognition of the potential link between the forcing of climate by increasing concentrations of CO₂, CH₄ and other infrared active gasses and convective injection of water over the US (41, 42). Again, what is remarkable is the depth to which these convective events penetrate into the stratosphere coupled with the steep gradients of increasing (a) inorganic chlorine, (b) free radical concentrations and (c) ozone concentrations with altitude into which this water is injected. The altitude interval between 15 and 20 km that is affected by this convective injection contains approximately 20% of the ozone column in the summertime over the US.

Noteworthy is the fact that as a result of the separation of NASA airborne missions into either (a) a chemistry/ozone-loss focus or (b) a climate/dynamics/radiation focus, the in situ free radical instruments for OH, HO₂, NO₂, ClO, BrO, ClONO₂, and ClOOCl have never been deployed into regions of convectively injected water vapor over mid-latitudes of the northern hemisphere and so these measurements are lacking.

There are a number of important considerations associated with the issue of convective injection of water vapor inducing chlorine activation and catalytic removal of ozone over mid-latitudes of the NH in summer. First is the fact that a remarkably dry stratosphere characterizes the current climate state. However, the paleorecord holds evidence that the stratosphere, under conditions of high CO₂ concentrations, was characterized by significantly higher water vapor concentrations than is the case today (43, 44). If currently increasing concentrations of CO₂, CH₄ and other infrared active gasses force the stratospheric system to a state of increasing water vapor concentrations, the impact on ozone is of significant concern given the concentrations of chlorine and bromine in the stratosphere today.

Second, the loss of ice from the Arctic Ocean opens the possibility for significant increases in CO₂ and CH₄ release from melt zones in the Arctic. A release of just 0.5% per year of the carbon tied up in the soils of Siberia and Northern Alaska alone will double the carbon added to the atmosphere each year from the combustion of fossil fuels world-wide (45). This release of carbon from clathrates and permafrost will accelerate the forcing of the climate that is potentially linked to the intensity and frequency of convective injection of water into the stratosphere.

Third, engineering the climate by the addition of sulfates to increase reflective aerosol concentrations and thereby reduce climate forcing by reflecting sunlight back to space (46, 47) would significantly increase reactive surface area which would accelerate the processing of chlorine to free radical form (Fig. 1, A and C), thereby decreasing ozone concentrations. In the same vein, the convective injection of water vapor into the stratosphere increases the sensitivity of ozone loss to volcanic injection of sulfates into a stratosphere with current loading of chlorine and bromine. Evidence for this was presented for the eruption, in 1991, of Mt. Pinatubo by Salawitch *et al.* (35).

Fourth, from the perspective of human health, a primary concern is that decreasing ozone concentrations, particularly in summer over populated areas, results in increased UV dosage levels. Sustained increases in UV dosage levels are in turn associated with the increased incidence of skin cancer (48, 49), which is currently 1 million new cases a year in the US (49).

Lastly we emphasize that, because chlorine activation depends exponentially on water vapor and temperature, and in turn that the forcing

of climate may well control the convective injection of water into the lower stratosphere, the idea that ozone “recovery” is in sight because we have controlled CFC and halon release is a potentially significant misjudgment.

We have focused in this paper on conditions in the summer lower stratosphere over the US because that is the region for which we have direct experimental evidence of deep convective injection. Similar conditions may hold elsewhere, for example over the Tibetan plateau, north of the Asian Monsoon.

The point is not that we know exactly when ozone will begin to decrease over the mid-latitude NH in summer if convective injection of water continues or increases, but rather that (1) the photochemical system controlling the concentration of ozone in the stratosphere is extraordinarily sensitive to the convective injection of water vapor that occurs over populated areas in summer, (2) the response of ozone to chlorine dimer and chlorine/bromine catalytic cycles is extremely sensitive to the altitude of penetration of convective injection, and (3) were the intensity and frequency of these convective events to increase irreversibly as a result of climate forcing by the continued addition of CO₂ and CH₄ to the atmosphere, decreases in ozone and associated increases in UV dosage would also be irreversible.

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Fig. 1. The lines of evidence leading to the conclusion that observed combinations of high water vapor concentrations and low temperatures over the US lead to the conversion or activation of inorganic chlorine to free radical form on cold sulfate-water aerosols. **(A)** The regime of water vapor and temperature for the triad of heterogeneous reactions responsible for rapid chlorine activation under sunlight conditions in the mid-latitude lower stratosphere is identified for two aerosol surface areas. **(B)** Observations of water vapor in the summertime over the US show numerous occurrences in the range of 10 to 18 ppmv reaching pressure altitudes deep into the stratosphere. As described in the text, invariably, regions high in water vapor are found to be high in the isotopologue HDO demonstrating that the high water vapor concentrations result from direct convective injection. **(C)** Observations of convectively injected water vapor mixing ratios and temperatures at 90 ± 10 mb superimposed on a plot of the threshold conditions for chlorine activation at $SA = 2$ and $10 \mu\text{m}^2/\text{cm}^3$.

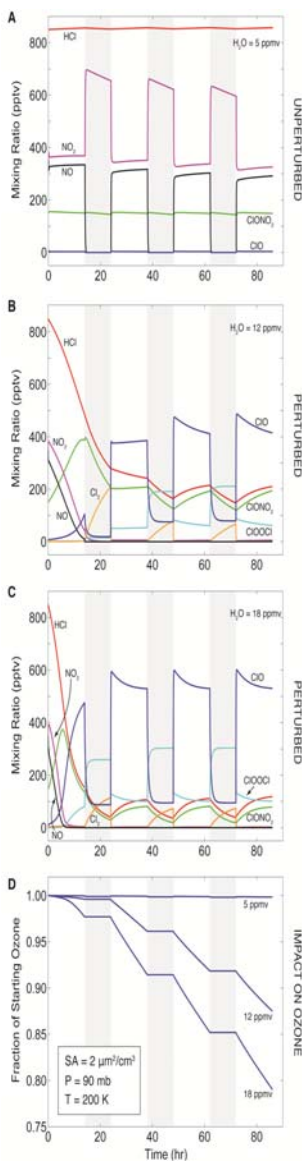
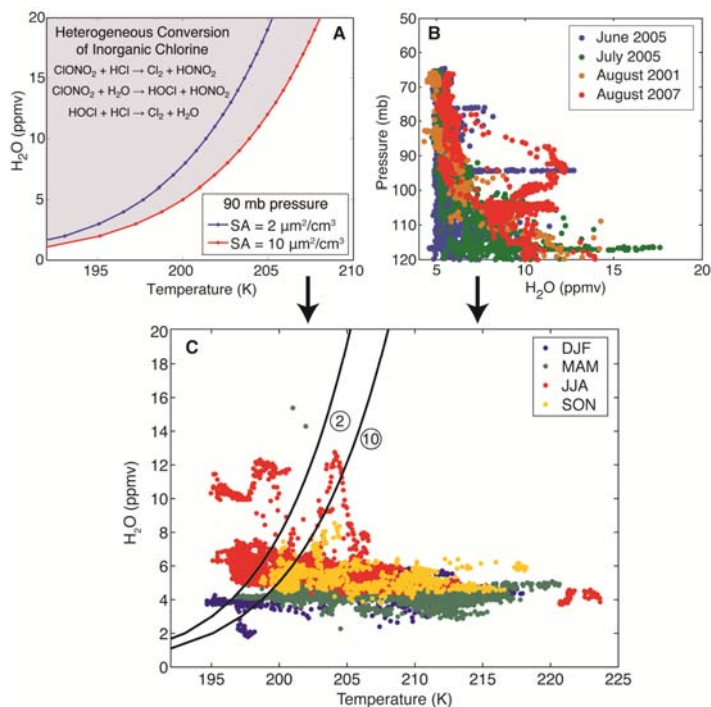


Fig. 2. The impact of convectively injected water vapor into the NH mid-latitude stratosphere in summer is summarized in three stages. **(A)** Calculation of the time dependence of HCl, ClONO₂, ClOOCl, NO, NO₂, Cl₂, and ClO under unperturbed conditions in the summertime lower stratosphere (90 mb pressure) for which 5 ppmv H₂O, 200 K, and $2 \mu\text{m}^2/\text{cm}^3$ are appropriate. **(B)** Time evolution of the same species over the four diurnal periods following convective injection of water vapor to 12 ppmv. **(C)** Time evolution of the same species but with a water vapor mixing ratio of 18 ppmv following convective injection. **(D)** Loss of ozone over the four diurnal periods for 5 ppmv, 12 ppmv and 18 ppmv of water vapor. Daytime calculations are run at a solar zenith angle of 45°; regions shaded in gray represent darkness.