The Nonlinear Response of Stratospheric Ozone to NO_x and ClO_x Perturbations

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Abstract. A mathematical analysis of the stratospheric photochemical system (gas phase reactions only) shows the existence of potential catastrophe mechanisms which could produce a dramatic reduction in the ozone concentration near 25 km altitude. The conditions leading to such catastrophe correspond to a relatively modest (i.e., factor 2–2.5) increase in the stratospheric source of reactive nitrogen (NO_x). For a tenfold increase in the source of reactive chlorine (ClO_x), the ozone system exhibits a large amplitude oscillatory behavior with a period of several tens of years. Transport processes could, however, damp these dramatic changes resulting from the nonlinear nature of the stratospheric chemical system.

1. Introduction

Mathematical models as well as field observations have demonstrated that stratospheric ozone depletion is caused by the release in the atmosphere of industrially manufactured halo-carbons including long-lived chlorofluorocarbons (CFCs). Except in polar regions, where dramatic ozone depletion has been observed (i.e., the Antarctic ozone hole), the magnitude of the ozone decrease at mid-latitudes has remained limited to a few percent. Over the last 15 years, several studies have revealed that, under certain circumstances, atmospheric chemical systems could exhibit multiple equilibrium solutions, catastrophic transitions between stable states or even periodic oscillations [*Prather et al.*, 1979; *Fox et al.*, 1982, *White and Dietz*, 1984; *Kasting and Ackerman*, 1985; *Stewart*, 1993; *Yang and Brasseur*, 1994; *Hess and Madronich*, 1997; *Montecinos and Felmer*, 1999]. In the present paper, we show that for enhanced injections of nitrogen and/or chlorine in the atmosphere, stratospheric ozone at mid-latitudes could be dramatically depleted through a catastro-phic transition towards new stable states. These new states correspond to a quasi-disappearance of ozone or are characterized by low frequency (high amplitude) periodic time variations in the chemical composition of the stratosphere.

2. The Model

To address this question, we consider a zero-dimensional diurnally varying box model with a simplified chemical scheme (Table 1a and b) that accounts for the most important chemical and photochemical processes affecting ozone in the

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middle and upper stratosphere [*Brasseur and Solomon*, 1984; *DeMore et al.*, 1997]. In addition to the stable atmospheric constituents (N_2, O_2, H_2O), the scheme includes 18 species belonging to the oxygen, hydrogen, nitrogen, chlorine, and carbon families, and 43 chemical and photochemical (gas phase) reactions. The effects of bromine (which are small above 20 km altitude) are neglected. We solve the chemical equations at 40°N on March 15 for conditions representative of 25 km (i.e., in the vicinity of the maximum ozone density), and 40 km altitude. At 40 km, ozone is in photochemical equilibrium, while at 25 km its concentration is affected by photochemistry and transport. By limiting the present calculation to 2 specific points of the atmosphere, the purpose of the study is not to produce a realistic simulation of stratospheric chemistry, but to highlight the existence of complex mechanisms that could potentially lead to catastrophic transitions in the ozone concentration. In the present study, we examine the behavior of the photochemical system and deliberately ignore the influence of atmospheric

Table 1a. Chemical reactions used in the box model

Reaction	Reaction Rate* ($cm^3 s^{-1}$) at 220K (25 km)	Reaction Rate* ($cm^3 s^{-1}$) at 250 K (40 km)
1. $O+O_2+M \rightarrow O_3+M$	1.0(-15)	7.6 (-17)
2 $O+O_3 \rightarrow 2O_2$	6.86(-16)	2.11 (-15)
3a. $O(^1D)+N_2 \rightarrow O+N_2$	2.97(-11)	2.79 (-11)
3b. $O(^1D)+O_2 \rightarrow O+O_2$	4.40(-11)	4.23 (-11)
4. $H_2O+O(^1D) \rightarrow 2OH$	2.2(-10)	2.2 (-10)
5. $OH+O_3 \rightarrow O_2+HO_2$	2.23(-14)	3.73 (-14)
6. $HO_2+O_3 \rightarrow 2O_2+OH$	1.13(-15)	1.49 (-15)
7. $HO_2+HO_2 \rightarrow H_2O_2+O_2$	3.52(-12)	2.54 (-12)
8. $OH+H_2O_2 \rightarrow H_2O+HO_2$	1.4(-12)	1.53 (-12)
9. $OH+HO_2 \rightarrow H_2O+O_2$	1.5(-10)	1.3 (-10)
10 $HO_2+O \rightarrow O_2+OH$	7.4(-11)	6.68 (-11)
11 $NO+O_3 \rightarrow NO_2+O_2$	3.45(-15)	7.40 (-15)
12 $NO_2+O \rightarrow NO+O_2$	1.12(-11)	1.05 (-11)
13 $NO_2+O_3 \rightarrow NO_3+O_2$	1.75(-18)	6.65 (-18)
14 $NO_2+NO_3+M \rightarrow N_2O_5+M$	9.5(-13)	2.1 (-13)
15 $N_2O_5+M \rightarrow NO_2+NO_3+M$	6.83(-8)	8.6 (-6)
16 $NO_2+OH+M \rightarrow HNO_3+M$	4.16(-12)	3.4 (-13)
17 $HNO_3+OH \rightarrow NO_3+H_2O$	2.88(-13)	2.11 (-13)
18 $NO+HO_2 \rightarrow NO_2+OH$	1.09(-11)	9.5 (-12)
19 $Cl+O_3 \rightarrow ClO+O_2$	8.9(-12)	1.03 (-11)
20 $ClO+O \rightarrow Cl+O_2$	4.1(-11)	3.97 (-11)
21 $Cl+HO_2 \rightarrow O_2+HCl$	3.9(-11)	3.55 (-11)
22 $Cl+CH_4 \rightarrow HCl+CO+HO_2+H_2O$	1.9(-14)	4.07 (-14)
23 $ClO+NO \rightarrow Cl+NO_2$	2.4(-11)	2.04 (-11)
24 $ClO+NO_2+M \rightarrow ClONO_2+M$	4.2(-13)	2.6 (-14)
25 $ClO+HO_2 \rightarrow HOCl+O_2$	1.2(-11)	7.89 (-12)
26 $HCl+OH \rightarrow H_2O+Cl$	5.3(-13)	6.4 (-13)
27 $HOCl+OH \rightarrow H_2O+ClO$	3.1(-13)	4.06 (-13)
28 $OH+CH_4 \rightarrow 2H_2O+CO+HO_2$	7.68(-16)	2.02 (-15)
29 $O(^1D)+CH_4 \rightarrow CO+2H_2O$	1.4(-10)	1.4 (-10)
30 $CO+OH \rightarrow HO_2+CO_2$	1.5(-13)	1.5 (-13)

*For three-body reactions, equivalent second-order rate constants are calculated for air density of
8.21(17) cm^{-3} at 25 km and 6.5(16) cm^{-3} at 40 km·

Table 1b. Photolysis reactions used in the box model

Reaction	Photolysis Frequency* (s^{-1}) at 25 km	Photolysis Frequency (s^{-1}) at 40 km
1. $O_2+h\nu \rightarrow O+O$	2.5(-12)	3.0(-10)
2. $O_3+h\nu \rightarrow O_2+O(^1D)$	6.0(-05)	1.5(-03)
3. $O_3+h\nu \rightarrow O_2+O$	5.4(-04)	7.0(-04)
4. $H_2O_2+h\nu \rightarrow 2OH$	1.01(-05)	3.9(-05)
5a. $NO_3+h\nu \rightarrow NO_2+O$	1.56(-01)	1.56(-01)
5b. $NO_3+h\nu \rightarrow NO+O_2$	2.01(-02)	2.01(-02)
6. $NO_2+h\nu \rightarrow NO+O$	1.2(-02)	1.3(-02)
7. $N_2O_5+h\nu \rightarrow NO_2+NO_3$	2.8(-05)	1.15(-04)
8. $HNO_3+h\nu \rightarrow OH+NO_2$	1.9(-06)	5.0(-05)
9a. $ClONO_2+h\nu \rightarrow NO_3+Cl$	5.45(-05)	2.7(-04)
9b. $ClONO_2+h\nu \rightarrow NO_2+ClO$	6.05(-06)	3.0(-05)
10. $HOCl+h\nu \rightarrow OH+Cl$	4.05(-04)	5.50(-04)

*Daytime values on March 15, at 40°N

dynamics. The solution of the numerically "stiff" nonlinear first-order differential equations is obtained using the Gear algorithm [*Gear*, 1969] with the computer codes provided by Hindemarsh [*Hindmarsh*, 1992]. Convergence of the solution to equilibrium conditions is assumed to be satisfied when the 4 first digits of the calculated concentrations for all chemical species remains unchanged for at least 100 years of the model integration. The local sources of reactive nitrogen and chlorine (denoted S_N and S_{Cl}) are assumed to be provided by the photo-oxidation of nitrous oxide (N_2O) and the photolysis of chlorofluorocarbons (CFCs), respectively, but could also result from direct sources such as the in situ injection of NO_x from high-altitude aircraft or from nuclear tests in the atmosphere. S_N and S_{Cl} will be referred to as control parameters of the system since the sensitivity of the species concentration to the strength of these two parameters will be investigated. The compensating loss of nitrogen and chlorine by transport and eventually by wet scavenging of nitric acid (HNO_3) and hydrogen chlorine (HCl) is represented by first-order losses with rate constants of 1×10^{-8} s^{-1} and 3×10^{-8} s^{-1}, respectively. A loss rate of 1×10^{-8} s^{-1} for carbon monoxide (CO) is balanced by a source (upward transport from the troposphere) of methane (CH_4) of 1800 cm^{-3} s^{-1}. The model is integrated to convergence for successive fixed values of S_N and S_{Cl}. All photochemical states presented below are the averages between the daytime and nighttime solutions.

3. The Chemical System at 25 km

The concentrations at 25 km altitude and 40°N provided by the model are in reasonable agreement with currently observed values when the control parameters are chosen to be $S_N = 42$ cm^{-3} s^{-1} and $S_{Cl} = 20$ cm^{-3} s^{-1}. In this case, the calculated ozone concentration is 4.9×10^{12} cm^{-3} in good agreement with other model values [*Fox et al.*, 1982; *Wang et al.*, 1992]. The mixing ratio of NO_x (=NO + NO_2) is 2.4 ppbv; it is 45 pptv in the case of ClO_x (=Cl + ClO), 0.81 ppbv in the case of HCl and 0.78 ppbv in the case of $ClONO_2$. This situation will be referred to as the current state and the corresponding magnitudes of the control parameters S_N and S_{Cl} as the current parameter values. In order to simplify our analysis and focus on the impact of reactive nitrogen and chlorine on ozone, the behavior of the chemical system is studied for varying values of S_N and S_{Cl}, while the source term for methane S_{CH_4} and the pseudo first-order loss coefficients for HNO_3, HCl and CO remain at their current value.

3.1. Response to increasing NO_x source

As shown in Figure 1, if the source of reactive nitrogen S_N increases while S_{Cl} remains at the current value of 20 cm^{-3} s^{-1}, the concentration of ozone decreases gradually along an equilibrium branch from 5.1×10^{12} cm^{-3} for $S_N = 30$ cm^{-3} s^{-1} to 1.3×10^{12} cm^{-3} for $S_N = 96$ cm^{-3} s^{-1}. Under this equilibrium state, an increase in S_N of 50% leads to a reduction in the ozone density of only 10%. For S_N greater than 92 cm^{-3} s^{-1}, however, a second stable equilibrium branch is found: the [92, 96 cm^{-3} s^{-1}] domain is characterized by multi-equilibrium solutions. A catastrophic transition from the first branch (on which the current state resides) to the second branch occurs when S_N reaches 96 cm^{-3} s^{-1}, leading to an abrupt reduction in the ozone concentration by about 2 orders of magnitude and dramatic changes in the concentration of other chemical compounds (enhanced NO_x and reduced HO_x and ClO_x densities). This abrupt behavior results from the titration of OH and HO_2 by NO_2 (which becomes effective when the NO_x concentration reaches a given threshold) and hence from the slower conversion of NO_x molecules to HNO_3. As a result, the NO_x density is substantially enhanced, leading to large catalytic ozone depletion [*Yang and Brasseur*, 1994]. At the same time, the faster conversion of ClO into $ClONO_2$ by NO_2 reduces the concentration of reactive chlorine (Cl and ClO). The photochemical lifetime of methane, which is 30 years at 25 km for background conditions increases to approximately 3000 years when S_N becomes larger than the transition point near 96 cm^{-3} s^{-1} since, beyond the transition, the loss rate of methane (e. g., by OH and $O(^1D)$) is reduced by a factor 100. Note that if, for values of S_N larger than the transition point, the model is integrated with the background concentrations as initial values, the
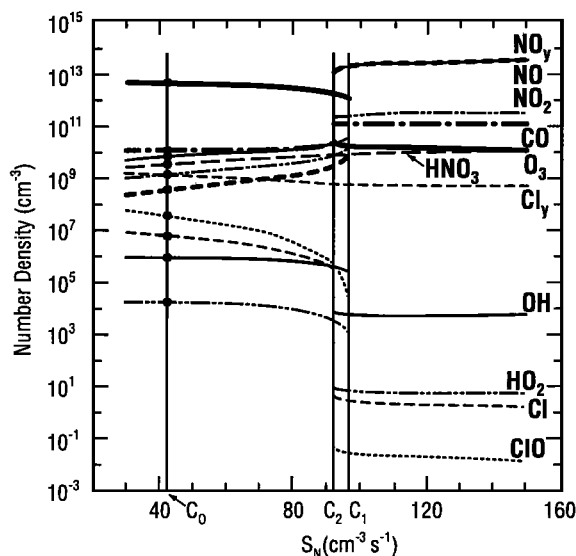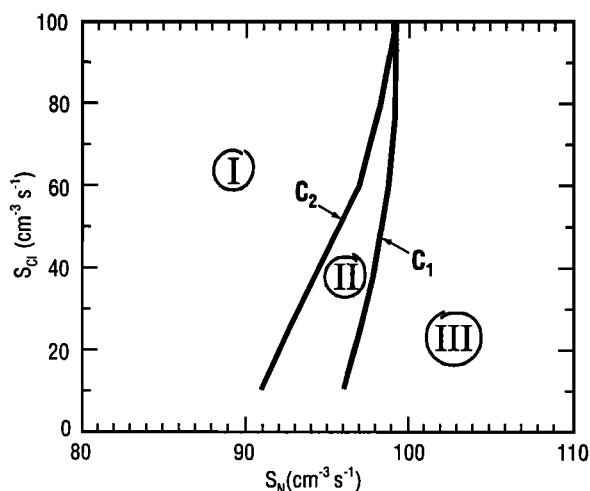

Figure 1. Number density of several important chemical species in the stratosphere (25 km altitude, 40°N latitude, 15 March) calculated as a function of the external source parameter S_N (cm^{-3} s^{-1}) of nitrogen compounds (for a source S_{Cl} of chlorine of 20 cm^{-3} s^{-1} representing current conditions). $C_0 = 42$ cm^{-3} s^{-1} represents the value of S_N corresponding to current conditions, while $C_1 = 96$ cm^{-3} s^{-1} and $C_2 = 92$ cm^{-3} s^{-1} are the critical parameter values leading to catastrophic transitions from the first to the second branch of the solution, and from the second to the first branch, respectively. The [C_1, C_2] domain is characterized by multi-equilibrium solutions.

integration time required to reach convergence of the solution is as long as 10^5 years. For a state of ozone located on the lower branch of the solution (high values of S_N), a reduction in the source of reactive nitrogen leads to a slow increase in the ozone concentration followed by an abrupt jump to the upper branch of the solution as S_N reaches the other threshold of 92 cm^{-3} s^{-1}. This hysteresis effect is common to many catastrophe phenomena.
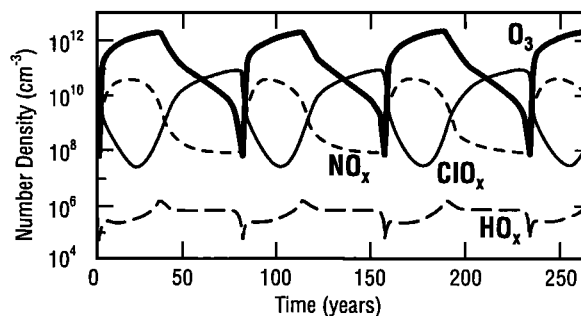
The distribution of these equilibrium solutions in parameter space $P(S_{Cl}, S_N)$ is represented in Figure 2, which shows that the parameter range can be divided into three domains separated by curves C_1 and C_2. Domains noted I and III correspond to the single equilibrium regions, while domain II represents the multi-equilibrium region. If a solution point crosses curve C_1 from its left or curve C_2 from its right, catastrophic transitions occur. Note that theory shows that at least one unstable equilibrium solution should exist in domain II [*Joseph*, 1976], so that domain II should represent a "cusp" [*Zeeman*, 1976].

3.2. Response to increasing ClO_x source

If the nitrogen source parameter S_N is kept at its current value of 42 cm^{-3} s^{-1} and the chorine source term S_{Cl} varies, for example, from 10 to 270 cm^{-3} s^{-1}, a first stable equilibrium solution is found for S_{Cl} smaller than 248 cm^{-3} s^{-1} (stationary attractor). In this case, a ten-fold increase in S_{Cl} leads to an ozone reduction of approximately 11%. As S_{Cl} reaches a value near 248 cm^{-3} s^{-1}, a supercritical Hopf bifurcation takes place, and for S_{Cl} exceeding this value, the original equilibrium solution looses stability and a new stable periodic solution appears (periodic attractor) with an amplitude increasing as a function of S_{Cl}. For example, if $S_{Cl} = 260$ cm^{-3} s^{-1}, the period of the solution is about 50 years and its amplitude represents only 3 percent of the mean concentration value (not shown). For $S_{Cl} = 250$ cm^{-3} s^{-1}, the amplitude is only 0.01 percent. In addition, for S_{Cl} becoming larger than 228 cm^{-3} s^{-1}, a second solution branch exists and corresponds to a large-amplitude periodic behavior of the solution. For example, for $S_{Cl} = 255$ cm^{-3} s^{-1}, the calculated ozone

Figure 3. Periodic evolution of the concentration of ozone and other chemical compounds obtained for external source parameters $S_{Cl} = 255$ cm^{-3} s^{-1} and $S_N = 40$ cm^{-3} s^{-1}. The period of the oscillation is approximately 80 years.

concentration found on this second branch oscillates by several orders of magnitude with a period of approximately 80 years. In this case, the stratosphere continuously alternates from a NO_x-dominated to a ClO_x-dominated ozone destruction regime (Figure 3). During the part of the periodic cycle characterized by an increase in the ClO concentration, the abundance of NO_x decreases (titration of NO_2 by ClO) and, as ClO reaches high densities, the concentration of ozone and of OH and HO_2 decreases abruptly (in response to the high efficiency of the chlorine driven catalytic ozone-destroying cycle). At the same time, the conversion of NO_x to its stable reservoirs (e.g., HNO_3) becomes very slow and hence the abundance of NO_x increases rapidly with a corresponding decrease in ClO_x (titration of ClO by NO_2) and a sharp increase in the ozone and OH densities. At that time, the conversion of NO_x into HNO_3 becomes effective again, leading to a decrease in the NO_x density in favor of ClO_x. Over a period, the concentration of ozone varies by about 4 orders of magnitude. The coexistence of the small and large amplitude oscillations in the region where $S_{Cl} = 248$-265 cm^{-3} s^{-1} corresponds to the phenomenon referred to as birythmicity (Epstein and Pojman, 1998). A schematic representation of the dependency of the ozone concentration on parameter S_{Cl} with the coexistence of multiple stable solutions is shown in Figure 4a. It is interesting to note (see Fig. 4b) that for $S_{Cl} = 265$ cm^{-3} s^{-1}, the trajectory of the small amplitude periodic solution (first branch) becomes increasingly attracted by the solution that corresponds to the large amplitude oscillation (second branch).

4. The Chemical System at 40 km

When the calculation is repeated at 40 km altitude, the values of the control parameters S_N and S_{Cl} that match the current concentration values are $S_N = 0.6$ cm^{-3} s^{-1} and $S_{Cl} = 1.5$ cm^{-3} s^{-1}, respectively. If the source of active chlorine S_{Cl} remains equal to 1.5 cm^{-3} s^{-1} and the source of active nitrogen is increased from its current value, a catastrophic transition (not shown) is found for S_N reaching 9.1 cm^{-3} s^{-1}. This transition is characterized by a reduction in the ozone density from 3×10^{10} cm^{-3} ($S_N = 9.0$ cm^{-3} s^{-1}) to 4.7×10^9 cm^{-3} ($S_N = 9.4$ cm^{-3} s^{-1}).

If the source of chlorine S_{Cl} is increased while the source of nitrogen S_N remains at its current value, the response of the photochemical system is considerably simpler at 40 km than at 25 km (no bifurcation, no periodic solution). A large variation in the calculated concentrations is found when

Figure 2. Representation of the different equilibrium solutions in the parameter space $P(S_N, S_{Cl})$ for the following values of the control parameters: $0 < S_N < 180$ cm^{-3} s^{-1} and $0 < S_{Cl} < 120$ cm^{-3} s^{-1}. Domains I and III correspond to single equilibrium solutions while domain II corresponds to multi-equilibrium solutions. Curves C_1 and C_2 correspond to catastrophic transitions
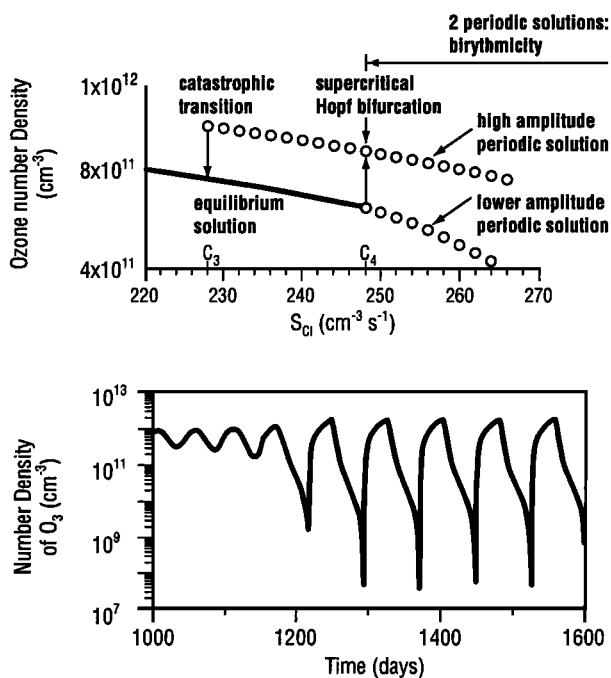
Figure 4 a: Schematic representation of the dependency of the ozone concentration on control parameter S_{Cl} with the coexistence of multiple stable solutions ($S_N = 42$ cm^{-3} s^{-1}). The solid line represents the equilibrium solution branch, and the open circle curves the periodic solutions. Parameter value C_3 corresponds to a catastrophic transition from the large amplitude periodic solution to the equilibrium solution, while parameter C_4 corresponds to a supercritical Hopf bifurcation on the equilibrium branch. **b:** Time evolution of the ozone concentration as a function of time for $S_{Cl} = 265$ cm^{-3} s^{-1} and $S_N = 42$ cm^{-3} s^{-1} with the trajectory of the small amplitude solution being attracted by the large amplitude solution.

parameter S_{Cl} increases from 19.5 to 22.0 cm^{-3} s^{-1}. This gradient structure corresponds to the degeneration of a Hopf bifurcation.

5. Conclusions

In conclusion, the nonlinear nature of the chemical system in the stratosphere can potentially generate catastrophic changes in the chemical composition of the atmosphere (specifically in the concentration of ozone) for specific threshold values of the stratospheric sources of reactive nitrogen and chlorine. When analyzing the solutions provided at 25 km altitude by a box model that accounts for the most important gas-phase chemical processes in the stratosphere at mid-latitudes, a transition from current to much lower (factor of 100) ozone abundance is predicted for only a doubling of the reactive nitrogen source (assuming that the chlorine source remains at its present level). A catastrophic transition also occurs for a 10-fold increase in the stratospheric chlorine source. At 40 km altitude, the photochemical system appears to be simpler and the amplitude of the catastrophic transition smaller. One should note that such dramatic changes are obtained without considering any (nonlinear) heterogeneous chemical mechanisms, which are involved in polar ozone depletion below 25 km (e.g., the Antarctic ozone hole). Finally, it should be emphasized that the quantitative behavior of the chemical system depends directly on the adopted chemical scheme and the location (altitude, latitude) for which

the calculation is performed. The present model study only illustrates the possible behavior of the "ozone system" at 2 given points in the stratosphere. In addition, the role of transport processes which is significant in the lower stratosphere and the existence of strong coupling between chemistry, radiation and dynamics should be taken into account and could modify substantially the quantitative and even the qualitative responses obtained when considering only a pure photochemical system. Bifurcations and limit cycles may still be found, but for different parameter values than those found in the present study. For example, for local NO_x sources (such as NO_x emissions by high altitude aircraft), transport should become a dominant factor. Current models addressing the specific issue of aircraft pollution do not predict catastrophic ozone changes. Finally, if rather than integrating the model for different fixed values of the control parameters, a time-dependent, increasing NO_x source had been applied, the very slow response in methane would quite possibly have wiped out the bifurcation and allowed ozone to adjust more slowly from high to lower concentration values.

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