

As before,  $\mathbf{v}_0$  is yours to choose.

To finish the story, note that in each of the three cases, there are solutions  $\begin{pmatrix} x(t) \\ y(t) \end{pmatrix}$  that do not approach  $\mathbf{0}$  as time increases when the conditions in (7) are violated. [You have to choose  $x(0)$  and  $y(0)$  correctly in (6) for this to happen. Actually, this happens for the generic choice—you have to choose  $x(0)$  and  $y(0)$  in a very special way in order for it not to happen.] When the conditions in (7) hold, then *all* solutions will approach  $\mathbf{0}$  as time increases.

## 8.6 Lessons

Here are some key points to take from this chapter:

- Learn the condition for the stability of the equilibrium point to (1).
- Remember the definition of the matrix in (3), and remember the definition of its trace and determinant. Then learn the criteria in (5) for stability.

## READINGS FOR CHAPTER 8

### READING 8.1

#### *Better Protection of the Ozone Layer*

**Commentary:** The purpose of this article is only to point out that even the very simple Equation (1) in Chapter 8 has its applications. In this case, the applications are to the equations for the production of chlorine in the stratosphere. In particular, the first two lines of Equation (1) in this article constitute a two-component differential equation that is exactly of the form of Equation (1) in Chapter 8. Indeed, setting  $x = B_T$  and  $y = B_S$ , the constants  $(a, b, c, d)$  in Equation (1) of Chapter 8 are given by the constants in Equation (1) of this article by the following rule:  $a = -1/L_T - f/\tau_1$ ,  $b = 1/\tau_1$ ,  $c = -1/L_S - 1/\tau_1$ , and  $d = f/\tau_1$ . Notice that the article's equations (2a, b) give an exact solution for certain starting values for  $B_T(0)$  and  $B_S(0)$ . Compare with Equation (9) in Section 8.5 of this chapter.

---

#### *Better Protection of the Ozone Layer*

*Nature*, **367** (1994) 505–508.

Malcolm K. W. Ko, Michael J. Prather, Nien-Dak Sze

**How can we extend the Montreal Protocol to other ozone-depleting chemicals, such as fuel from the Space Shuttle and pharmaceuticals, when the life cycles of these compounds and the scales of the**

**industries are different?**

International agreements have been enacted to protect the ozone layer by regulating the release of chlorine- and bromine-bearing chemicals such as

---

Author affiliations: Malcolm K. W. Ko and Nien-Dak Sze: Atmospheric and Environmental Research Inc., Cambridge, Massachusetts. Michael J. Prather: Department of Earth System Science, University of California, Irvine.

the chlorofluorocarbons and the halons. One of the criteria by which such chemicals are assessed and regulated is the ozone depletion potential (ODP) [1-5]. But because more and more chemicals are turning out to be ozone-depleting, we believe that a more refined approach is needed for effective and equitable control. Here, we address ways to extend international agreements to include other contemporary ozone-depleting chemicals whose applications and life cycles are very different from synthetic halocarbons used in the industries already singled out for concern, such as refrigeration, insulation and fire-fighting applications.

During the past decade, an international regime has emerged for limiting the consumption of chemicals believed to carry chlorine (Cl) and bromine (Br) into the upper atmosphere (stratosphere) (see box). The Convention on the Protection of the Ozone Layer (Vienna, 1985) was followed in 1987 by the Montreal Protocol, subsequently amended in 1990 (London amendment) and in 1992 (Copenhagen amendment). The governments that have signed these treaties are committed to phase out the production and consumption of CFCs (chlorofluorocarbons) and halons (brominated hydrocarbons), and to limit the production of their substitutes (for example hydrochlorofluorocarbons, HCFCs) in the expectation that the stratospheric concentration of chlorine and bromine can thereby be reduced. Ultimately, the goal is to reverse the observed downward trend of global ozone, and to limit the possible consequential damage to the biosphere from increased ultraviolet radiation. The adherence of governments to these agreements, which have the status in international law of formal treaties, is mirrored in national legislation such as the US Clean Air Act (1992).

The evolving protocols have given precedence to controlling synthetic CFCs and halons used in applications such as electronic and metal cleaning, foam blowing and refrigeration (CFCs); and fire extinguishers (halons). These chemicals are released in the lower atmosphere (the troposphere), but are sufficiently long-lived that they can be transported to the stratosphere where most of them are broken down by ultraviolet radiation, producing highly reactive Cl and Br radicals that are chiefly responsible for the catalytic destruction of stratospheric ozone. Because the timescale of mixing in the troposphere is less than the residence time of these halocarbons, the effect on ozone (as measured by the ODP) does

not depend exactly on where, when and how they are released.

But there are other more direct and effective means by which chlorine can enter the stratosphere. These include solid-fuel rocket motors in the Space Shuttle launches, which deposit chlorine directly in the stratosphere. Prudence, as well as consistency, requires that these sources should also be evaluated under the same criteria (for example, ODPs) to determine their contributions, if any, to ozone depletion. Before the Copenhagen meeting, the scientific community was asked to quantify the impact of other atmospheric emissions such as solid rocket motors [6], stratospheric aircraft [7] and use of methyl bromide ( $\text{CH}_3\text{Br}$ ) [8] in agricultural activities. But no ODPs were calculated for solid rocket motors and stratospheric aircraft. Based on the findings on  $\text{CH}_3\text{Br}$ , a freeze on its production beginning in 1995 was adopted in the Copenhagen amendment.

What follows is a demonstration that some potential ozone-depleting substances have life cycles that differ qualitatively as well as quantitatively from the chemicals now controlled by the agreements. We discuss what factors should be considered when developing a strategy for control of compounds whose applications and life cycles are very different from the CFCs. Specifically, we look for ways to ensure that the resulting strategy is practical (can it be applied easily?), effective (does it omit chemicals whose net impact may be comparable to individual HCFCs or CFCs?), and equitable (does it ban or impose excessive penalty on uses that have relatively small effects on the ozone layer?). We will use three examples to illustrate these points: chlorine deposited by the solid-fuel rockets from the Space Shuttle launches;  $\text{CH}_3\text{Br}$  used in soil fumigation; and brominated compounds in pharmaceutical use.

### Ozone depletion potentials

First defined for CFCs a decade ago, the ODP is an index measuring the time-integrated ozone depletion caused by specific quantity of a chemical relative to that caused by the same quantity of the chlorofluorocarbon CFC-11 (the fully substituted methane  $\text{CFCl}_3$ ). The definition presumes the chemical is ultimately released into the atmosphere. Policy makers and industry representatives have since asked scientists to extend and calculate ODPs for HCFCs [2] and the halons [3, 5]. To-

### Chronology of ozone-protection agreements

The Vienna Convention for the Protection of the Ozone Layer was agreed March 1985 and entered into force in September 1988. It was set up with the intention of preventing any further damage to the ozone layer by "recognising the possibility that world-wide emissions and use of fully halogenated chlorofluorocarbons (CFCs) and other chlorine-containing substances can significantly deplete and otherwise modify the ozone layer, leading to potentially adverse effects on human health, crops, marine life, materials and climate, and recognising at the same time the need to further assess possible modifications and their potentially adverse effects."

It was also agreed that negotiations would continue on the development of a protocol to control equitably global production, emissions and use of CFCs. From this, the Montreal Protocol, an international agreement to phase out ozone-depleting substances, was agreed in 1987.

- 1987. Montreal Protocol on Substances that Deplete the Ozone Layer. It was agreed that global action was needed to phase out CFCs and halons.
- 1989. First meeting of the parties to the Protocol in Helsinki. Declaration adopted calling for CFCs and halons to be phased out by 2000.
- 1990. Second meeting of the parties of the Protocol in London. Agreement to phase out CFCs, halons and carbon tetrachloride by 2000 and methyl chloroform by 2005. Financial mechanism set up to assist developing countries.
- 1991. New European regulation 594/91 came into force. CFCs to be phased out within the European Communities by 1997.

Second meeting of the parties to the Vienna Convention and third meeting of the parties to the Montreal Protocol.

- 1992. Fourth meeting of the parties to the Montreal Protocol in Copenhagen. Parties agreed to bring forward phase-out dates for CFCs, carbon tetrachloride and methyl chloroform to 1996; halons to be phased out by 1994. Controls agreed for methyl bromide and HCFCs.
- 1993. Fifth meeting of the parties to the Montreal Protocol. It was agreed that there would be no essential uses for halons in 1994. Multilateral fund replenished.

Third meeting of the parties to the Vienna Convention.

Source: UK Department of the Environment.

tal chlorine loading of the atmosphere [9] has also been used to assess the global ozone loss caused by these chemicals, either separately or in combination for specific emission predictions. The amount of chlorine in the stratosphere not still tied up in the parent halocarbon is defined as the stratospheric chlorine loading [10]. To understand the relation between ODP and chlorine loading, it is necessary to examine the life cycles of the halocarbons.

The life cycles of the halocarbons are illustrated in the figure. These halocarbons are, in general, relatively long-lived and thus well mixed in the troposphere. They cycle between the troposphere and stratosphere where a portion of the compound is dissociated during repeated excursions into the stratosphere and the troposphere. The Cl and Br atoms formed in the stratosphere participate in catalytic cycles removing ozone until, on average after

3 years, they are transported back, to the troposphere. The Cl and Br atoms in the troposphere, either produced *in situ* by degradation of the halocarbons or transported from the stratosphere, are assumed to be removed quickly by rain out or surface deposition. For CFCs, almost all the chlorine atoms are produced in the stratosphere. The HCFCs react with hydroxyl radicals (OH) and thus are destroyed readily (on a timescale of a few years to decades) in the troposphere. As a result, they contribute less to the stratosphere chlorine loading on a per-molecule-emitted basis.

Numerical simulations using photochemical models indicate that the time-integrated stratospheric chlorine loading is a good proxy for cumulative ozone loss [9,10]. We have used a simple two-box model (with tropospheric and stratospheric compartments) to calculate, as a function

of time after release, the amounts of chlorine still tied up in the undissociated halocarbons in the troposphere ( $B_T$ ) and stratosphere ( $B_S$ ), as well as the quantity of free chlorine in the stratosphere ( $C$ , stratospheric chlorine loading). The differential equations describing the evolution over time of the three reservoirs are

$$\begin{aligned} \frac{dB_T}{dt} &= -\frac{B_T}{L_T} - \frac{B_T f - B_S}{\tau_t} \\ \frac{dB_S}{dt} &= -\frac{B_S}{L_S} - \frac{B_S - B_T f}{\tau_t} \\ \frac{dC}{dt} &= -\frac{C}{\tau_t} + \frac{B_S}{L_S} \end{aligned} \quad (1)$$

where  $L_T$  and  $L_S$  are the tropospheric and stratospheric lifetimes for chemical loss of the halocarbons and  $\tau_t$  is the turnover time for replacing stratospheric air by tropospheric air. In calculating the exchange flux, the tropospheric burden is scaled by a factor  $f = 0.15/0.85$  (assuming here that 15% of the atmospheric mass is in the stratosphere) so that the flux is proportional to difference in the mixing ratios. We select  $\tau_t = 3$  yr, consistent with Holton's [11] derivation of 2.5 yr for the turnover of air above 100 mbar. Based on two-dimensional model results [12], we select  $L_T = 1,000$  yr and  $L_S = 5$  yr for CFC-11.

Assuming  $B_T(0) = 1$  kg chlorine in the form of CFC-11,  $B_S(0) = C_{F-11}(0) = 0$ , the burdens (in kg chlorine) for year  $t$  are

$$B_T = 0.930 \exp[-t/46.5] + 0.070 \exp[-t/1.75] \quad (2a)$$

$$B_S(t) = 0.107(\exp[-t/46.5] - \exp[-t/1.75]) \quad (2b)$$

$$C_{F-11}(t) = 0.068 \exp[-t/46.5] + 0.090 \exp[-t/1.75] - 0.158 \exp[-t/3] \quad (2c)$$

The integrated chlorine loading (p.p.t.v.-year) for emission of 1 kton ( $1 \times 10^6$  kg) of CFC-11 is obtained by integrating equation (2c) and multiplying by 0.81.

$$IC_{F-11}(t) = 2.33(1 + 0.16 \exp[-t/3] - 1.11 \exp[-t/46.5] - 0.05 \exp[-t/1.75]) \text{p.p.t.v.-year} \quad (3)$$

The ODP of a compound  $X$  can be approximated as the ratio  $IC_X(t)/IC_{F-11}(t)$ , where  $IC_X(t)$  is the integrated chlorine loading due to 1 kiloton release of  $X$  calculated using appropriate  $L_T$  and  $L_S$ . The steady state ODP corresponds to the ratio in the limit as  $t \rightarrow \infty$ .

### Regulating halocarbons

The Protocol to date has focused on limiting the production of halocarbons used in traditional applications. The list of products containing controlled species (annex D of the Protocol) specifies automobile and truck air-conditioning units; domestic and commercial refrigeration equipment; aerosol products (except medical aerosols); portable fire extinguishers; insulation boards, panels and pipe covers and pre-polymers. The list of controlled species (annexes A-C) is mainly limited to synthetic fluorochlorocarbons or bromocarbons with no known natural sources.

Although the Protocol recognizes the ODP as a measure of the environmental danger, the lists of controlled species in the annex are not grouped by ODP values. Rather, the species were classified according to chemical type, by use and by when they were included in the Protocol. However, the ODP values are used explicitly in the following way. Instead of imposing production limits on an individual chemical, the control is applied to groups of chemicals. Within each group, the production of each chemical can be traded after appropriate weighting by its ODP value. The Protocol states that "each Party shall, for each group of substances ... determine its calculated levels of Production by (i) multiplying its annual production of each controlled substance by the ozone depleting potential specified ...; (ii) adding together, for each such Group, the resulting figures." Under the Copenhagen amendment, the annual production limit on the transition substances (HCFCs) are specified as the 1989 production plus 3.1% of the ODP weighted annual production of the CFCs in the same year.

Although it is not explicitly stated, a reading of the protocols and the US Clean Air Act suggests that their formulations are based on considerations of both ODP and chlorine loading from the current emission rates. There is agreement to phase out production of the CFCs (annex A group I and annex B group I) and  $CCl_4$  (annex B group II) by 1996; and halons (annex A group II) by this year. These compounds all have ODPs of about 0.5 or larger.