Volume 2, Number 1, 2018, 147–157

Yokohama Publishers ISSN 2189-1664 Online Journal C Copyright 2018

NONLINEAR DYNAMICAL SYSTEM AND DATA ANALYSIS FOR PREDICTION OF OZONE LEVEL

XINYU BAO, SHENG-YA FENG*, YUNCAN LI, AND ZHIJIE YUAN

ABSTRACT. In this paper, we mathematically study the Ozone level around Antarctic regions. In the first part of this paper, we propose a nonlinear dynamical model to characterize the Ozone depletion based on the chemical mechanism. In the second part, we carry out data analysis and predict the stratospheric ozone levels over the next half a century. Moreover, this research provides reasonable and mild analysis for the changing size of Ozone Holes.

1. INTRODUCTION

In this introduction, we reach back several significant concerns with respect to Ozone level of the planet. A nice exposition on this topic could be found in [5] and the references therein. Nowadays, updated technical development and economic growth of the world during the last century have caused severed environmental problems. We acknowledge that though these technological advances may contribute to human comfort, they also would threaten the environment by means of ozone depletion and global warming [3, 7].

Ozone depletion and global warming turn out to environmentally affect the future development of the industrial economy. The actions on the industry to reduce ozone depletion and global warming become more and more frequent. As a variant of oxygen, the ozone molecule having three atoms of oxygen. Ozone is a poisonous gas could cause death if heavily inhaled. Ozone layer is about 11 km above the earth surface, surrounding the earth's stratosphere. This protecting layer keeps life on the earth away from the harmful ultraviolet radiation for thousands of years [2].

The dangerous ultraviolet B (UV-B) radiation are effectively screened by Ozone layer (moderate UV-A is allowed through while UV-C is captured by oxygen). Ozone layer blocks off harmful UV-B radiation to avoid serious loss to the environment and life on earth. The excessive UV-A and UV-B radiation could cause eye damage, reducing rates of plant growth, imbalance of ecosystems, and accelerating risk of disease [13].

Human activity seldom threatened the depletion of ozone layer before 1970s. Ozone depleting and greenhouse gas halocarbons are primarily caused by industrialization [13]. Halocarbons, mostly man-made gases, consist of both carbon and at

²⁰¹⁰ Mathematics Subject Classification. Primary: 37J55; Secondary: 37M05.

Key words and phrases. Dynamical system, ozone depletion, global warming, data analysis, polynomial fitting.

^{*} The corresponding author.

This research is supported in part by the National Natural Science Foundation of China (Grant No. 11426109 and No. 11501203), the China Postdoctoral Science Foundation (Grant No. 2016M600278), as well as the Shanghai Innovative Training Program (Grant No. S13048).

least one of the halogens, inculding fluorine, chlorine, iodine, and bromine. They were first synthesized in 1928, and extensively used for industrial production such as propellants in aerosol cans, soft and hard foams, refrigeration and air conditioning, and cleaning solvents [2]. These products mainly include chlorofluorocarbons (CFCs), hydro-chlorofluorocarbons (HCFCs) and hydro-fluorocarbons (HFCs).

Used as refrigerants, solvents and blowing agents, CFCs and HCFCs have stable structures to attack the ozone layer. After escaping into the atmosphere, they break their chemical bonds to release chlorine with the help of intense UV-C radiation, reducing it to oxygen molecule. Chlorine acts as a catalyst to go on repeating the process without any permanent changes.

It was discovered that one chlorine atom could destroy 100,000 ozone molecules. The higher the chlorine contains, the longer it acts on the ozone layer. Comparing to HCFC, CFCs have larger content of chlorine and longer potential for ozone depletion. The efficacy of ozone destruction is often measured by Ozone depletion potential (ODP). It is reported that nearly 70% of ozone depleting chemicals in the atmosphere were contributed by CFCs [14]. The inventors would never foresee the harmful effects produced by refrigerants on the ozone layer. High stability is a double-edged sword between ozone protection and human demands [6].

The other major environmental concern is global warming. Some of these greenhouse gasses consist of CFCs, HCFCs, CO_2 , methane (CH_4) and nitrous oxide (N_2O) . Different gasses absorb and trap discriminating amounts of infrared. According to Ko et al. [8, 9], insulating blanket of the atmosphere adjusts the temperature built-up by the trapping heat energy. Global warming allows life to exist in all its variety [11]. The absorbed amount of radiant energy is measured by Global Warming Potential (GWP). A more appropriate measure to global warming is based on Total Equivalent Warming Impact (TEWI). The developed and developing nations phased out CFCs in year 1996 and 2010 respectively. Some hydro-chlorofluorocarbons (HCFCs) are temporary alternatives to CFCs and they are to be phased out respectively by year 2020 and 2030 in developed and developing countries, as their ODPs and GWPs are in high levels although less than those of CFCs [10, 4].

The aim of this paper is to set up a mathematical model based on the chemical mechanism of Ozone depletion. In section 2, some basic notions are concisely exposed for understanding the chemical mechanism. After introducing notations and assumptions, we analyze the reaction process of Ozone and set up a nonlinear dynamical system in section 3. In section 4 and section 5, we carry out data analysis and predict the stratospheric ozone levels around Antarctic regions. As a conclusion in section 6, we make final remarks of this paper.

2. Preliminaries

In order to indicate the origin of Ozone Depletion problem, we concisely introduce several basic notions. 2.1. Ozone Basics. Ozone is a gas made up of three oxygen atoms (O_3) . Ninety percent of the ozone in the atmosphere sits in the stratosphere, the layer of atmosphere between about 10 and 50 kilometers' altitude. The ozone in the stratosphere is commonly known as the ozone layer. The natural level of ozone in the stratosphere is a result of a balance between sunlight that creates ozone and chemical reactions that destroy it. Ozone is created when O_2 is split apart by sunlight into single oxygen atoms. Single oxygen atoms can re-join to make O_2 , or they can join with O_2 molecules to make ozone (O_3) . Ozone is destroyed when it reacts with molecules containing nitrogen, hydrogen, chlorine, or bromine (halogen). Some of the ozonedepleting gases occur naturally, and some are due to anthropogenic emissions. The remaining ozone is in the lower region of the atmosphere, which is commonly called the troposphere.

2.2. Stratospheric "good" Ozone and Tropospheric "bad" Ozone. Ozone in the stratosphere provides a shield to protect life on Earth. It absorbs most of the ultraviolet radiation from the Sun. Ozone screens all of the most energetic, UV-C radiation, and most of the UV-B radiation. Ozone only screens about half of the UV-A radiation. Excessive UV-B and UV-A radiation can cause sunburn and can lead to eye damage. Nevertheless, direct contact with ozone is harmful to both plants and animals. Ozone reacts strongly with other molecules, while high levels of ozone are toxic to living systems. And near-surface ozone is also a key component of photochemical "smog", a familiar problem in the atmosphere of many cities around the world.

2.3. **Polar Vortex.** The chemistry of the Antarctic polar vortex has created severe ozone depletion. The nitric acid in polar stratospheric clouds reacts with chlorofluorocarbons to form chlorine, which catalyzes the photochemical destruction of ozone. Chlorine concentrations build up during the polar winter, and the consequent ozone destruction is greatest when the sunlight returns in spring. These clouds can only form at temperatures below about minus 80 degrees Celsius. Since there is greater air exchange between the Arctic and the mid-latitudes, ozone depletion at the north pole is much less severe than at the south. Accordingly, the seasonal reduction of ozone levels over the Arctic is usually characterized as an "ozone dent", whereas the more severe ozone depletion over the Antarctic is considered as "ozone hole".

3. Nonlinear dynamical system

In this section, we establish a nonlinear dynamical model according to the chemical mechanism of Ozone depletion.

3.1. Terms, Definitions and Symbols. We first introduce some frequently used notations in Table 1.

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Meaning
Stratospheric ozone level around Antarctic regions
Chloride ion level around Antarctic regions
Chlorate ion level around Antarctic regions
Natural decomposition rate of $CF_x Cl_y$
Rate of O_3 returning back to the stratosphere
Ozone depletion potential

TABLE 1. Terms, Definitions and Symbols

3.2. Assumptions. Moreover, our model would be based on the following assumptions.

- There are enough stratospheric ozone around Antarctic regions.
- Each ionized Chloride ion can react with ozone.
- Assume all the ozone-depleting gases that will be generated over the next 50 years stay in the atmosphere, because their longevity is above 50 years.

3.3. The Foundation of Model. The Antarctic ozone hole is an area of the Antarctic stratosphere in which the recent ozone levels have dropped to as low as 33 percent of their values before 1975. The ozone hole occurs during the Antarctic spring, from September to early December, as strong westerly winds start to circulate around the continent and create an atmospheric container. Within this polar vortex, over 50 percent of the lower stratospheric ozone is destroyed during the Antarctic spring. And the primary cause of ozone depletion is the presence of chlorine-containing source gases (primarily CFCs and related halocarbons). In the presence of UV light, these gases dissociate, releasing chlorine atoms, which then go on to catalyze ozone destruction.

3.3.1. The Basic Chemical Equations. The primary chemical equations follow that [15]

$$CF_xCl_y + h\nu \longrightarrow CF_xCl_{y-1} + Cl \bullet$$
$$Cl \bullet + O_3 \longrightarrow ClO + O_2$$
$$ClO + O_3 \longrightarrow Cl \bullet + 2O_2$$

3.3.2. The Chapman Cycle. The stratosphere is in a constant cycle with oxygen molecules and their interaction with ultraviolet rays. This process is considered as a cycle because of its constant conversion between different molecules of oxygen. The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the Chapman cycle [12].

(1) An oxygen molecule is photolyzed by solar radiation, creating two oxygen radicals:

$$O_2 + h\nu \longrightarrow 2O \bullet$$

(2) Oxygen radicals then react with molecular oxygen to produce ozone:

$$O \bullet + O_2 \longrightarrow O_3$$

(3) Ozone then reacts with an additional oxygen radical to form molecular oxygen:

$$O_3 + O \bullet \longrightarrow 2O_2$$

(4) Ozone can also be recycled into molecular oxygen by reacting with a photon:

$$O_3 + h\nu_{(240-310 \text{ nm})} \longrightarrow O_2 + O_3$$

Remark 1. It is important to keep in mind that ozone is constantly being created and destroyed by the Chapman cycle and that these reactions are natural processes, which have been taking place for millions of years. Because of this, the thickness the ozone layer at any particular time can vary greatly. It is also important to know that O_2 is constantly being introduced into the atmosphere through photosynthesis, so the ozone layer has the capability of regenerating itself.

3.4. **Dynamical Model.** Based on the chemical equations listed above, we then generate our dynamical model

$$\begin{cases} \dot{y_1} = \beta y_1 - (1+\alpha)y_2 - y_3\\ \dot{y_2} = y_1 - (1+\alpha)y_2 + y_3\\ \dot{y_3} = (1+\alpha)y_2 - y_3 \end{cases},$$

where $y_1 = y_1(t)$ denotes stratospheric ozone level around Antarctic regions, $y_2 = y_2(t)$ denotes Chloride ion level around Antarctic regions, $y_3 = y_3(t)$ denotes Chlorate ion level around Antarctic regions. And $\alpha = \alpha(t, y_1, y_2, y_3)$ is the natural decomposition rate of CF_xCl_y , which is determined by the volume of decomposed CF_xCl_y , while $\beta = \beta(t, y_1, y_2, y_3)$ represents the rate of O_3 returning back to the stratosphere.

Code	Longevity(yrs)	ODP	GWP
CFC-11	60	1	3400
CFC-12	120	1	7100
CFC-113	90	0.8	4500
CFC-114	200	0.7	7000
CFC-115	400	0.4	7000
HFC-134a	16	0	1200
$\mathrm{HFC}\text{-}152\mathrm{a}$	2	0	150

TABLE 2. Terms, Definitions and Symbols

3.5. Simplified Version. Since most of the CF_xCl_y in the natural world decomposes in the troposphere before reaching the stratosphere, only a few of them will decompose in the stratosphere to produce chloride ion. Generally, the value of α is sufficiently small and it will not affect the stratospheric ozone level. Therefore, we can ignore the influence of factor α in the reaction. Thus, we simplify the nonlinear system as follows,

$$\begin{cases} \dot{y}_1 = \beta y_1 - y_2 - y_3 \\ \dot{y}_2 = y_1 - y_2 + y_3 \\ \dot{y}_3 = y_2 - y_3 \end{cases}.$$

4. Data Analysis

In this section, we start to analyze primary chemicals to simulate and predict the stratospheric ozone levels around Antarctic regions. For this purpose, we here adopt a straight forward way.

4.1. Simulation of CFC Level. Using CFC-11 as a demonstration, we utilized the CFC-11 level around Antarctic regions from year 2006 to year 2016 (after the signing of the Montreal Protocol), and we implemented Cubic Spline Interpolation using MATLAB to generate a polynomial indicating the CFC-11 level, and then we calculated the chloride level in CFC-11 by its proportion. Finally, we multiplied the chloride level in CFC-11 by the rate of chloride being ionized out of CFC-11 by UV rays (winter and summer), to obtain the chloride electron volume polynomial $y_1(t)$. Similarly, we generated the volume polynomials of the chemicals in Table 2.

Using CFC-11 as benchmark, we calculated the chemicals' multiple comparing to CFC-11, and then multiplied it by their respective ODPs to obtain their relative ozone-depleting volumes. The figures below show the polynomial of CFC-11 level and CFC-12 level, their ODPs are both 1.



FIGURE 1. The polynomial of CFC-11 level



FIGURE 2. The polynomial of CFC-12 level



FIGURE 3. Ozone depleted by CFC-11

4.2. Solution and Result. We let the initial value of y_2 and y_3 be zero, and simulate the ozone level. We yield the ozone level with CFC-11 and CFC-12 effect as well as their respective influences, which are illustrated in the following figures.



FIGURE 5. Ozone depleted by CFC-11 and CFC-12

4.3. Analysis of the Result. As shown in the above figures, the ozone level over the next 50 years will first decrease in first 30 years, and then return back to a normal level in the next 20 years. We believe that the delay is partially caused by greenhouse gases.

5. Polynomial fitting

In this section, we implement Polynomial fitting simply by means of the Ozone Hole size data to analyze the Ozone Holes size changing over the years.

5.1. **Data Cleaning.** We obtain the raw data of Ozone Hole size from NASA databases. And then we filter out the maximum data from year 1979 to year 2016. And we calculate yearly data to do the fitting. Figure 6 shows the curve that we have obtained.

The solid line is the fitting curve, the point is the original data.

We then use monthly data from year 1980, year 1999, and year 2013 to do the fitting. Figure 7 shows the result.

The black solid line represents the 1980 ozone hole size curve, "*" represents the raw data for the year; the red double-dash line represents the fitting curve of the ozone hole size in 2013, and " \circ " represents the original data of the year ; Blue

245.679 L 2010



FIGURE 6. Ozone Hole size fitting curve using maximum yearly data



FIGURE 7. Ozone Hole size fitting curve using monthly data

dotted line represents the 1999 ozone hole size of the fitting curve, "+" represents the year of the original data.

5.2. Analysis of the Result. From the curve in Figure 6, we see that the hole in the ozone layer began to expand dramatically in 1979, and even reached a maximum of nearly 30 million square kilometers. It began to slow down only around 2000, and fluctuated in the following years, with a slight decrease. And it can be seen from the Figure 7 that the size of the hole in the ozone layer above Antarctic regions will change with the seasons, reaching the maximum around September each year, which coincides with the spring of the southern hemisphere. And every year in September, also happens to be the ozone layer density minimum season. In addition, it can be intuitively discovered that in 1980 the ozone layer was almost empty, and 20 years later, 1999 was also one of the few years with the lowest density of the ozone layer, and the size of the ozone hole in that year exceeded 20 million square kilometers. And more than 10 years after the situation in 2013 is improved.

6. Further discussion

In the light of the simulation model by J. Austin and N. Butchart [1], a more comprehensive model shall be under consideration which includes temperature, atmospheric circulation, oceanic circulation, greenhouse forcing and other factors. The relationship between the Southern Hemisphere (SH) circulation and ozone depletion would be a key point to explore. Moreover, one would utilize and combine other models to investigate ozone depletion, such as Atmospheric modeling, Forecast models, Radiative transfer models, Chemical box models, Chemical transport models, General circulation models, Coupled chemical-dynamical models, etc. A systematic mathematical study on the nonlinear dynamical model proposed in this paper would appear in the near future.

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Manuscript received February 5 2018 revised April 5 2018

X. BAO

School of business, East China University of Science and Technology, Shanghai 200237, P.R. China *E-mail address:* tenag_hirmb@hotmail.com

S.-Y. Feng

Department of Mathematics, East China University of Science and Technology, Shanghai 200237, P.R. China

School of Mathematical Sciences and Key Lab of Mathematics for Nonlinear Science, Fudan University, Shanghai 200433, P.R. China

E-mail address: s.y.feng@ecust.edu.cn

Y. Li

School of information science and engineering, East China University of Science and Technology, Shanghai 200237, P.R. China

 $E\text{-}mail\ address:\ \texttt{m15216692767@163.com}$

Z. Yuan

School of information science and engineering, East China University of Science and Technology, Shanghai 200237, P.R. China

E-mail address: m13816214450@163.com