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Review Article

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Confinement of ozone hole mainly in the Antarctic stratosphere to protect the living kingdom on the earth: chemistry behind this Nature's unique gift

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Abstract: Man-made activities can release the ozone depleting substances (ODSs) like chlorofluorocarbons (CFCs) and other halocarbons stable in atmosphere and ultimately, they migrate to the stratosphere where they can destroy the ozone layer through the XO_x catalytic cycle (X = Cl, Br). The active forms in this catalytic cycle are X and XO that can be arrested in the inactive forms like $XONO_2$ (halogen nitrate, an additive compound of two odd electron molecules XO and NO_2) and HX (produced in the reaction of X with CH_4) in the stratosphere to prevent the ozone depletion cycle. The catalytically active forms from these inactive species can be regenerated in the reactions on heterogeneous solid surface like polar stratospheric cloud (specially Type II PSC formed at about −85 °C). Formation of such PSC in the stratosphere is only possible in the supercooled stable Antarctic vortex produced in the prolonged winter. In fact, formation of such PSC in the stratosphere is not possible in the other regions of the earth and not even in the Arctic pole where no stable Arctic vortex is generally formed in the winter. Thus nature confines the ozone depletion reactions mainly in the stratosphere of Antarctica pole which is practically inhabited.

Keywords: Antarctic ozone hole; Chapman ozone cycle; chlorofluorocarbons (CFCs); polar stratospheric cloud (PSC); stratosphere; UV radiation.

1 Introduction and background

The present topic has been discussed in class rooms and different forums and it has been accepted enthusiastically, specially by the students. It has been able to create a scientific awareness among the students in the present hot environmental issue. In open discussions, different questions have been raised from different levels of the students to penetrate into the subject. Some questions in deeper levels in connection with the photochemistry of ozone cycle were received from the top level students. This article has been prepared based on the students' feedback and to answer all these questions received from different batches of the students on the present topic. The representative questions raised in the discussions are:

•What is the importance of ozone layer? •How is it formed, and where is it in the atmosphere? •What do we mean by '**good ozone**' and '**bad ozone**'? •What is **Chapman ozone cycle**? •What do we mean by UV-A, UV-B and

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UV-C radiations? •What are the untoward effects of UV-radiation exposure to us? •How does ozone arrest the UV radiation? •What are the longest (threshold) wavelengths of radiation for photodissociation of O_2 and O_3? •How can we calculate the threshold wavelengths for photodissociation of O_2 and O_3 from the thermochemical data of bond dissociation energy? •From the bond dissociation energy (BDE) values, photodissociation of O_2 (BDE = 495 kJ mol^{-1} equivalent to 242 nm) requires the UV radiation while photodissociation of O_3 (BDE = 106 kJ mol^{-1} equivalent to 1123 nm) requires the IR-radiation, but both of them require UV radiation for their photodissociation. How can we rationalize these observations? •Why do their energetics of photodissociation differ? •What is the **spin conservation principle** in photodissociation of O_2 and O_3? •What is **Hartley band** in stratospheric photochemistry of ozone? What is its importance in ozone cycle? •What do we mean by **Herzberg continuum** in stratospheric photochemistry of oxygen? What is its importance in Chapmann ozone cycle? •What is the spin forbidden **Chappuis band** leading to the photodissociation of ozone in the visible range of light? What is its importance in atmospheric chemistry? •What are the main routes of photodissociation of ozone through the **spin allowed channels**? How can you calculate the threshold wavelengths for these spin allowed photodissociations from the bond energy values? •How is ozone measured in the atmosphere? •What is the basic principle behind the spectrophotometric measurement of atmospheric ozone concentration? •What is the unit of ozone concentration measurement? •What are the possible catalytic cycles to deplete ozone? •What are the ozone depleting substances (ODSs)? •How do emissions of halogen source gases lead to stratospheric ozone depletion? •What are the sources of stratospheric halogen? •Is there any natural activity besides the man made activities to release halogen into the atmosphere? •Why are the ozone depleting catalytic cycles called the **null cycles**? •Why is the Br-BrO catalytic cycle more efficient than the Cl–ClO catalytic cycle in depleting ozone? **•Why is the ozone hole created mainly over the Antarctica though the ozone-depleting substances are present throughout the stratosphere**? •Is there any ozone depletion in the Arctic ozone layer? **•Is there any possibility of formation of ozone hole in the non-polar regions**? •What is **Montreal Protocol**? •What is the success of Montreal Protocol in reducing the ozone-depleting substances in the atmosphere? •What is **ozone depletion potential** (ODP)? •What are the **greener substitutes of CFCs**? •Why are the ODP values of AFCs (*i.e.* HCFCs and HFCs) less? •Is ozone a greenhouse gas? •What is the contribution of CFCs in global warming? •Is there any relation between ozone chemistry and global warming? •How is ozone expected to change the global climate in the coming decades?

The purpose of this mini tutorial review is to answer the frequently asked questions by the students on the present topic. **It is expected that this self explanatory review article will act as a teacher to satisfy the inquisitiveness of the students**. The article answers **some questions on energetics of atmospheric photochemistry of oxygen and ozone and these are not available in common books on environmental chemistry**. The author has successfully used this review material several times in class rooms and the students are satisfied and benefited. In fact, the author believes from his long term experience that this tutorial review will immensely help in chemistry education on this particular hot topic throughout the globe.

2 Ozone layer and its importance

Ozone in the ground level atmosphere is harmful but beneficial in the stratosphere to us. This is why, ground level ozone is called '**bad ozone**' while stratospheric ozone is called '**good ozone**'. Ozone produced near the ground from the automobile pollution in presence of sunlight can react with the hydrocarbons and volatile organics to produce the photochemical smog and toxic substances to cause a number of respiratory problems (Das & Das, 2012). Ozone is itself also a human health irritant. However, ozone produced in the stratosphere can protect us from the UV radiation which is divided into three bands in terms of wavelength: **UV-A** (315–400 nm), **UV-B** (280–315 nm) and **UV-C** (<280 nm). The absorption of highest energy UV-C (λ < 280 nm) by stratospheric O_3 and O_2 prevents almost completely the reaching of UV-C to the earth surface. In fact, both O_3 and O_2 can jointly prevent the UV-C radiation but UV-B (λ = 280–315 nm) radiation can only interact with O_3 (Baird & Cann, 2005; Das & Das, 2012). If there is any depletion of ozone in the stratosphere, transmission of UV-C can still be prevented strongly by atmospheric O_2, but the transmission of UV-B radiation to the earth surface increases. This is why, the amount of transmission of UV-B radiation sensitively depends on the ozone concentration in the stratosphere and the biological system experiences the harmful effects mainly from the UV-B radiation under the ozone depleted condition in stratosphere (de Gruijl et al., 2003; Rowland, 2006).

As stated above, ozone (O_3) gas present in the upper atmosphere (*i.e.* stratosphere) protects the earth from the incoming solar ultraviolet (mainly UV-B) radiation which may damage the biological system through sunburn (erythema) and destruction of DNA, protein and other biomolecules (Madronich & de Gruijl, 1993; Taylor, 1990). Increased exposure of human being to the UV-B radiation raises the risks of skin cancer and eye cataracts, and it may also suppress the immune system. UV-B exposure also can damage the plant life including the agricultural crops, and aquatic ecosystems. The pollution in the upper atmosphere can destroy ozone to create the ozone holes allowing the harmful UV radiation (mainly UV-B, 280–315 nm) to reach the earth (Cicerone, 1987, 1994; Douglass et al., 2014; Farman et al., 1985; Solomon et al., 1986; Solomon 2019).

The highest energy (*i.e.* shortest wavelength range) UV radiation (*i.e.* UV-C) is highly dangerous to biosphere and materials but fortunately, completely arrested by atmosphere. The lowest energy (*i.e.* the longest wavelength range) UV radiation (*i.e.* UV-A) is transmitted through the atmosphere to the earth surface and it can cause premature ageing of the skin. The intermediate energy UV radiation (*i.e.* UV-B) is mostly blocked by the stratospheric ozone layer. Consequently, most of the UV rays that come in contact with us are UV-A with a small amount of UV-B.

Discovery of the Antarctic ozone hole by Farman et al. in 1985 revolutionized the understanding of atmospheric science and it led to the development of successful global environmental policies. In 1995, Paul Crutzen, Mario Molina and F. Sherwood Rowland were awarded Noble Prize for their contribution to understand different aspects of ozone depletion. **Dobson unit** (DU) is used to measure the thickness of ozone layer. 1 DU = 0.001 cm thickness of pure ozone layer having density the same at 1 atm pressure and 0 °C (Das & Das, 2012). At the temperate latitudes (region between the tropics and the polar circles), amount of ozone is about 350 DU. In reality, the relative concentration of O_3 never exceeds 10 ppm but it is sufficient to prevent UV-B (Das & Das, 2012). Thus, the term ozone-screen appears better than the term ozone layer.

Atmospheric ozone concentration is measured by the instruments based on the absorption of UV light by ozone that absorbs the radiations with the wavelengths in the range 200 nm–315 nm (**Hartley band**, discussed later) with the maximum absorption at about 255 nm. Both the land-based permanent and mobile flight-based systems operating from the balloons, aircrafts and satellites are available to conduct the measurement of ozone concentrations. Total ozone mapping spectrometer (TOMS), a satellite-based ozone monitoring system, conducts the ozone concentration measurement around the world.

Anthropogenic activities may perturb the natural ozone cycle (Chapman cycle) to deplete the ozone layer to threaten the living kingdom on the earth but nature confines such ozone depletion mainly in the Antarctic stratospheric region (Farman et al., 1985; Rowland, 2006; Solomon, 1999, 2019) which is practically an inhibited region. These are produced there only in the spring time. Thus practically no threatening effect appears on the living kingdom from the man-made activity induced ozone hole creation confined in the Antarctic polar region. Thus article explains how the nature performs this unique task in saving the living kingdom.

3 Ozone cycle in stratosphere

Ozone cycle in stratosphere is maintained by the formation of ozone from oxygen and destruction of ozone to oxygen by using the UV radiation (Baird & Cann, 2005; Das & Das, 2012; Sodhi, 2000).

Ozone formation reactions in ozone cycle: The earth is effectively screened from the extremely high energy UV radiation (λ < 242 nm *i.e.*, UV–C) by O_2 as follows.

$$O_2 + h\nu\ (<242\,\text{nm}) \xrightarrow{k_1} O + O;\ O_2 + O + M \xrightarrow{k_2} O_3 + M^*\ (\text{excited})$$

The first reaction (*i.e.* photodissociation of oxygen molecule) is an endothermic process ($\Delta H^\circ = +495\ \text{kJ mol}^{-1}$ which is the bond dissociation energy [BDE] of O_2) while the second reaction (ozone formation) is an exothermic process.

The ozone molecule produced in the above three body reaction remains in an excited state and it comes to the ground state by transmitting its extra energy to the neutral body M (*e.g.* molecules like N_2, O_2 or any other atom) which remains chemically unchanged. Thus the neutral body M is required to carry off the excess energy released in the above exothermic reaction. The reaction involving the neutral body (M) as shown above is commonly described as **'three body reaction'**. Such three body reactions are quite important in atmospheric chemistry. The net reaction is:

$$3O_2 + h\nu + M \rightarrow 2O_3 + M^*$$

Thus the ozone produced can absorb the radiation of relatively longer wavelength (240–320 nm) (*i.e.* middle UV radiation of moderately high energy, *i.e.* UV–B) in the following process.

$$O_3 + h\nu\,(240 - 320\,\text{nm}) \xrightarrow{k_3} O_2 + O$$

In the above reaction, the products (*i.e.* atomic and molecular oxygen) remain in the first excited singlet states, *i.e.* O_2 ($^1\Delta_g$) and O ($^1D_2$) and it is an endothermic process ($\Delta H° = +386$ kJ mol^{-1}) for which wavelength of the incident radiation must be less than 309 nm as calculated from the bond energy data (illustrated later).

Here it is worth noting that bond dissociation energy of O_3 (singlet ground state) producing the products in ground state (*i.e.* atomic and molecular oxygen in the triplet states; O_2 ($X^3\sum_g{}^-$) and O ($^3P_2$)) is 106 kJ mol^{-1} that corresponds to the wavelength 1123 nm (infra-red region). According to the **spin conservation principle**, both the products (*i.e.* atomic and molecular oxygen) must remain in the ground (triplet) or excited (singlet) states as the reactant ozone remains in a singlet ground state. In the case of dissociation of oxygen molecule, triplet states are the ground states for both reactant and products. This forbidden reaction is partially allowed due to spin–orbit coupling mechanism discussed later and in fact, this partially allowed reaction having a **fairly high absorption cross-section (σ)** is the most important reaction for ozone formation in the stratosphere. The rate constant of a photochemical reaction depends on the absorption cross-section (σ) measuring the ability to absorb the incident radiation by the molecule under consideration and it depends on the wavelength. For the ozone molecule, at $\lambda = 1123$ nm producing the products in the ground (triplet) states, **the absorption cross-section (σ) is very small** and the corresponding rate constant approaches to almost zero (Vanloon & Duffy, 2011). However, absorption cross-section (σ) of the reaction increases with the decrease of the incident wavelength. Here it is worth mentioning that ozone absorbs weakly in the visible range (**Chappuis bands**) and dissociates to produce the products into the ground triplet states (Sindhu, 2010). By considering the products to remain in the first excited states, *i.e.* O_2 ($a^1\Delta_g$) and O ($^1D_2$) having the excitation energies 90 and 190 kJ mol^{-1} respectively, the $\Delta H°$ of the reaction becomes:

$$\begin{aligned}\Delta H° &= \text{ground state bond dissociation energy (BDE) of } O_3\\ &\quad + \text{excitation energy of the products from their ground triplet states to first excited singlet states}\\ &= +(106 + 90 + 190)\,\text{kJ mol}^{-1} = 386\,\text{kJ mol}^{-1} \text{ that corresponds to the wavelength 309 nm.}\end{aligned}$$

In fact, in the UV-region between 315 and 200 nm (Hartley continuum), ozone absorbs strongly with a maximum absorbance at about 255 nm (Sindhu, 2010). The above discussion clearly indicates the difference in energetics of photodissociation of O_2 and O_3.

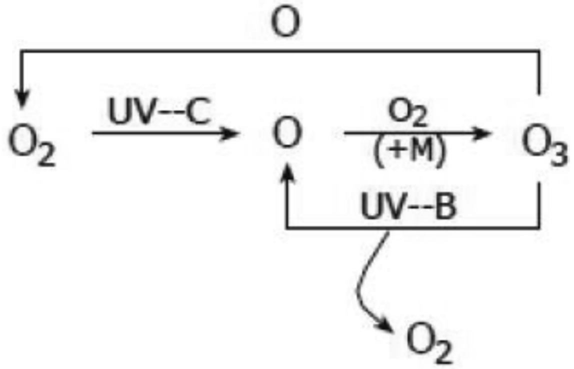
Ozone depletion reactions in ozone cycle: O_3 can combine with O produced in the above reaction to generate O_2.

$$O_3 + O \xrightarrow{k_4} 2O_2$$

Without any external disturbance, the ozone cycle operates through the k_1, k_2, k_3 and k_4 paths. At equilibrium, the rate of O_3 formation = rate of O_3 depletion,

$$\text{i.e. } k_2[O][O_2][M] = k_3[O_3] + k_4[O][O_3]$$

At equilibrium, $[O_2]/[O_3] = 10^{25}$ (on the earth surface), and the ratio is 3×10^5 at an altitude of 30 km, where O_3-concentration is maximum. The above mentioned ozone formation and depletion reactions maintain the steady state concentration of ozone to constitute the **Chapman cycle** as shown below (Chapman, 1930).



Chapman Cycle

4 Energetics of photodissociation of O_2 and O_3 in Chapman ozone cycle

The UV photodissociation of oxygen molecule is the primary step in the formation of ozone (O_3). It can occur in three different wavelength regions (Alexander et al., 2003): the **Herzberg continuum** ~242–200 nm, the **Schumann–Runge bands** ~200–176 nm, and the **Schumann–Runge continuum** ~176–130 nm. At the threshold wavelength (242 nm), the Herzberg continuum arises from the following forbidden photodissociation path that plays the most crucial role in natural ozone cycle in stratosphere. The following photodissociation occurs through the Herzberg transition-I to the **weakly bound state** $O_2(A^3\Sigma_u{}^+)$ favouring easy dissociation into two triplet ($^3P_2$, ground state) oxygen atoms (Das & Das, 2014, 2021).

$$O_2\left(X^3\Sigma_g^-\right) \xrightarrow{h\nu\ (\lambda=200\,\text{nm})} O_2\left(A^3\Sigma_u^+\right) \xrightarrow{\text{Dissociation}} 2O\left(^3P_2\right)$$

$$i.e.\ O_2\left(X^3\Sigma_g^-\right) + h\nu \rightarrow O\left(^3P_2\right) + \left(^3P_2\right), \left(i.e.\ \text{triplet} \rightarrow \text{triplet} + \text{triplet}, \Delta H^\circ = +495\,\text{kJ mol}^{-1}\right)$$

It may be noted that the above symmetry forbidden Herzberg transition (−⟶ + transition) leading to the above photodissociation borrows some intensity from the allowed transitions, mainly through spin–orbit (SO) coupling interactions between the ground and excited states (Alexander et al., 2003). Because of this fact, absorption cross-section (σ) in Herzberg transition is fairly high and photodissociation of O_2 in Herzberg continuum (200–242 nm) is the major source of O-atom for O_3 formation in the stratosphere.

$$O\left(^3P_2\right) + O_2\left(X^3\Sigma_g^-\right) + M \xrightarrow{\text{three body reaction}} O_3 + M^*; M = N_2, O_2$$

The ground state bond dissociation energy of O_2 (*i.e.* 495 kJ mol^{-1}) is the required energy for the endothermic photodissociation reaction of triplet diatomic oxygen molecule to produce two triplet atomic oxygen atoms. By considering the energy expression of a photon ($E = h\nu$), the longest (*i.e.* threshold value) wavelength of light that can dissociate O_2 in the above reaction can be calculated as follows:

$$E = h\nu, \text{or}\, E = hc/\lambda\ (\text{since}\, c = \text{velocity of light} = \nu\lambda, \nu = \text{frequency and}\, \lambda$$
$$= \text{wavelength of the radiation) and}\, \lambda = hc/E.$$

In the above equation, the product hc can be evaluated on a molar basis and assuming one molecule to absorb one photon, we can write:

$$\lambda = Nhc/E \text{ where } E \text{ in J mol}^{-1}, N = \text{Avogadro number}$$

By using the standard values: $N = 6.022 \times 10^{23}$ mol^{-1}, h (Planck constant) = 6.626×10^{-34} J s and $c = 2.998 \times 10^{8}$ m s^{-1}, we get for photodissociation of O_2 (triplet in ground state) producing two triplet oxygen atoms in the ground state.

$$\begin{aligned}\lambda\ (\text{threshold value}) &= 6.022 \times 10^{23}\ \text{mol}^{-1} \times 6.626 \times 10^{-34}\ \text{J s} \times 2.998 \times 10^{8}\ \text{m s}^{-1} \times 10^{9}\ \text{nm m}^{-1} / 495 \times 10^{3}\ \text{J mol}^{-1} \\ &\approx 242\ \text{nm}\end{aligned}$$

It shows that for the photodissociation of O_2 molecule, the wavelength of the incident radiation must be less than 242 nm (*i.e.* UV-C). The following spin and symmetry allowed photodissociation of O_2 involving the excited state $B^3\Sigma_u^-$ occurs at $\lambda < 176$ nm (threshold value for Schumann–Runge continuum) and it possesses the much higher absorption cross section (σ) (Baird & Cann, 2005; Sindhu, 2010).

$$O_2\left(X^3\Sigma_g^-\right) \xrightarrow{h\nu\ (\lambda < 176\,\text{nm})} O_2\left(B^3\Sigma_u^-\right) \xrightarrow{\textit{Dissociation}} O\left({}^3P_2\right) + O\left({}^1D_2\right).$$

$$\textit{i.e.}\ O_2\left({}^3\Sigma_g^-\right) + h\nu \rightarrow O\left({}^3P_2\right) + O\left({}^1D_2\right),\ (\textit{i.e.}\ \text{triplet} \rightarrow \text{triplet} + \text{singlet})$$

Photodissociation of O_2 at λ (threshold value) > 242 nm (energy below the Herzberg continuum) is not possible. The threshold value of λ for Schumann-Runge continuum is 176 nm. It may be noted that the Herzberg and Schumann-Runge continua generate directly the **dissociative excited electronic state**, yielding the $O(^3P_2) + O(^3P_2)$ and $O(^3P_2) + O(^1D_2)$ products, respectively. Photodissociation of O_2 in Herzberg continuum (200–242 nm) is primarily responsible for O_3 formation in the stratosphere.

$$O_2\left({}^3\Sigma_g^-\right) + h\nu \rightarrow O\left({}^3P_2\right) + O\left({}^3P_2\right);\ O\left({}^3P_2\right) + O_2\left({}^3\Sigma_g^-\right)(+\text{M}) \rightarrow O_3$$

Theoretically ozone can photodissociate through the following **two spin conserved channels** (Han et al., 2020; Vanloon & Duffy, 2011):

(i) O_3 (singlet) + $h\nu \rightarrow O_2$ ($^3\sum_g^-$, triplet) + O ($^3P_2$, triplet), ($\Delta H° = +106$ kJ mol^{-1}, ground state bond dissociation energy of O_3)

$$\begin{aligned}\lambda\,(\text{threshold value}) &= 6.022 \times 10^{23}\text{mol}^{-1} \times 6.626 \times 10^{-34}\,\text{J s} \times 2.998 \times 10^{8}\,\text{m s}^{-1} \times 10^{9}\,\text{n mm}^{-1/106} \times 10^{3}\,\text{J mol}^{-1} \\ &\approx 1123\,\text{nm (very low absorption cross} - \text{section}\,(\sigma))\end{aligned}$$

(ii) O_3 (singlet) → O_2 ($^1\Delta_g$, singlet) + O (^{1}D, singlet), ($\Delta H° = +386$ kJ mol^{-1}, calculated value as already discussed)

$$\begin{aligned}\lambda\,(\text{threshold value}) &= 6.022 \times 10^{23}\text{mol}^{-1} \times 6.626 \times 10^{-34}\text{J s} \times 2.998 \times 10^{8}\text{ms}^{-1} \times 10^{9}\,\text{n mm}^{-1/-386} \times 10^{3}\,\text{J mol}^{-1} \\ &\approx 309\,\text{nm (fairly high absorption cross} - \text{section}\,(\sigma))\end{aligned}$$

In stratosphere, ozone absorbs strongly in the UV-region between 315 and 200 nm (**Hartley band**), with a maximum absorbance at about 255 nm and dissociates producing the molecular oxygen and atomic oxygen in the excited singlet states as shown in reaction (ii). Absorption cross-section (σ) for the reaction (i) is very small but it increases with the decrease of incident wavelength. In the visible range, it weakly absorbs with the absorption maximum at about 600 nm (**Chappuis band**) and dissociates producing the products in the ground states (*i.e.* triplet states) in troposphere (Sindhu, 2010).

In summary, in stratosphere, to maintain the ozone cycle, the Hartley band (~315–200 nm) for absorption by ozone and its dissociation and Herzberg continuum (~242–200 nm) for absorption by oxygen and its dissociation are mainly important to maintain the Chapman ozone cycle.

5 Possible ozone depletion pathways in stratosphere leading to ozone hole formation

Theoretically there are three possible routes to deplete the ozone layer involving the NO_x (nitrogen oxide), ClO_x (chlorine oxide) and OH radical (Das & Das, 2012; Sodhi, 2000; Vanloon & Duffy, 2011). Presence of ClO_x and NO_x in the stratosphere is due to the man-made activities (Das & Das, 2012; Farman et al., 1985).

Ozone depletion by NO_x: The principal source of NO_x is from supersonic transports (SST) of the concorde type (Das & Das, 2012; Sodhi, 2000; Vanloon & Duffy, 2011). These are produced when air containing O_2 and N_2 passes through the high temperature of the jet engine.

$$N_2 + O_2 \rightarrow 2NO, \text{ (in jet engine)}$$

$$NO + O_3 \rightarrow NO_2 + O_2; NO_2 + O \rightarrow NO + O_2$$

It may be noted that liquid NO_2 is used as an oxidant for the rocket fuel N_2H_4. This NO–NO_2 catalytic system (called NO_x cycle) can effectively remove O_3 in stratosphere.

In biological nitrogen cycle, bacterial denitrification of nitrogenous residues in soil and ocean releases N_2O to some extent. This denitrification process mainly releases nitrogen in the form of N_2 to the atmosphere. The small amount of N_2O released to the atmosphere in the denitrification process plays a crucial role in controlling the stratospheric ozone level. N_2O is not chemically much reactive and it is not also significantly removed from the atmosphere by rainfall. Thus N_2O molecules can survive for decades in atmosphere and these are ultimately transported to stratosphere where they participate in the following reactions by using the UV radiation.

$$N_2O + h\nu \rightarrow N_2 + O; N_2O + h\nu \rightarrow NO + N;$$

$$N_2O + O \rightarrow 2NO; NO + O_3 \rightarrow NO_2 + O_2;$$

$$NO_2 + O \rightarrow NO + O_2$$

It may be noted that this biological source is a minor contributor to the NO_x cycle. The overall NO_x catalysed O_3 depletion reaction is:

$$O_3 + O \xrightarrow{NOx} NO_x \ 2O_2$$

Ozone depletion by ClO_x (Drdla & Müller, 2012; Engel et al. 2018; Kerr, 1987; Molina & Rowland, 1974; Molina et al. 1987; Sander et al. 1989): ClO_x catalysed O_3 depletion is mainly important to create the ozone holes. ClO_x is generated from chlorofluorocarbons (CFCs) (*e.g.* freon-11, $CFCl_3$; freon-12, CF_2Cl_2) widely used as propellants in aerosol spray cans and as refrigerants.

$F_3CCl + h\nu\,(190\ - 220\,\text{nm}) \rightarrow F_3C^{\bullet} + Cl; CF_2Cl_2 + h\nu \rightarrow {}^{\bullet}CF_2Cl + Cl$

The CFCs are extremely inert and have very long residence time (*ca.* 70–100 years) in atmosphere (Baird & Cann, 2005; Das & Das, 2012; Sodhi, 2000). Because of their chemical inertness, they are not broken in atmosphere. So they ultimately make their way to stratosphere where they are photochemically broken in presence of UV-flux to release the free Cl atoms.

The free radical Cl subsequently participates in the following reactions to deplete O_3.

$$Cl + O_3 \rightarrow ClO + O_2; ClO + ClO + M \rightarrow (ClO)_2 + M^*$$

$$(ClO)_2 + h\nu \rightarrow Cl + ClOO^{\bullet}; ClOO^{\bullet} + M \rightarrow Cl + O_2 + M^*$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$\text{i.e.,}\ 2O_3 + h\nu \xrightarrow{ClO_x} 3O_2$$

Inactivation of chlorine occurs through the following reactions to prevent ozone depletion.

$$ClO + NO_2 \rightarrow ClONO_2\ (\textbf{chlorine nitrate});$$

$$CH_4 + Cl \rightarrow {}^{\bullet}CH_3 + HCl$$

Relative importance of the ClO_x and NO_x catalytic cycles to deplete ozone: It is established that the ClO_x cycle is more efficient than the NO_x cycle to destroy the ozone layer. It has been estimated that one chlorine atom can destroy about one million ozone molecules. This efficiency arises from its regeneration in the reaction sequence shown above. It has been found that NO_x can remove the active ClO species which is the key player in the ozone depletion reaction. Both NO_2 and ClO are the odd electron species and they can combine as follows.

$$ClO^{\bullet}+{}^{\bullet}NO_2 \rightarrow ClONO_2\,(\text{chlorine nitrate})$$

Here it is worth mentioning that the BrO_x cycle is more efficient than the ClO_x cycle in ozone depletion because the inactive forms (*i.e.* HBr and $BrONO_2$) in the BrO_x cycle are relatively less stable compared to those of the ClO_x cycle and they are more readily photochemically decomposed to generate the active forms (*i.e.* Br and BrO) (Das & Das, 2012). The X-removal reaction to inactivate the catalytic cycle is also much slower for Br, *i.e.* the reaction $CH_4 + Br \rightarrow {}^{\bullet}CH_3 + HBr$, is relatively much slower than the reaction, $CH_4 + Cl \rightarrow {}^{\bullet}CH_3 + HCl$. It is mainly due to the weaker H–Br bond (*cf.* BDE in kJ mol^{-1}: 428 for H–Cl bond and 362 for H–Br bond). It indicates that formation of the catalytically inactive HX form is much slower in the BrO_x cycle. Thus stratospheric Br is more harmful in the ozone depletion reaction. The important sources of Br are the use of CH_3Br as a fumigant insecticide and bromine containing hydrocarbons (halons, *e.g.* halon-1211 $CBrClF_2$; halon-1301 $CBrF_3$; halon-2402 $CBrF_2$–$CBrF_2$) as the fire extinguishers. These being transported into the stratosphere undergo photolysis to generate the Br radical.

Based on the above argument, for the different halogens, the effectiveness to deplete ozone increases in the sequence: F < Cl < Br < I. Iodo-copounds are not present in the atmosphere. Fluoro-compounds having the C–F bonds as in CFCs and its greener substitutes (AFCs discussed later) are not important in the ozone depletion reaction because the C–F bond dissociation energy (484 kJ mol^{-1}) is much higher than the other halo-carbon bonds (*cf.* 338 kJ mol^{-1} for C–Cl bond). It makes the photodissociation of the C–F bond very difficult. Besides this, F-atom (if at all produced) is rapidly converted into its inactive form HF having a strong covalent bond (565 kJ mol^{-1} for H–F bond) and HF is not easily photolysed.

Null cycle: Interconversion between the reactive species X and XO can catalyse the photochemical decomposition of O_3. In this process, there is no net removal of the O-atom from the X–XO cycle. Thus the null cycles interconvert the reactive species but do not react with ozone. Such catalysing cycles (*i.e.* ClO_x cycle and NO_x cycle) are called the null cycles (null meaning doing nothing) (Vanloon & Duffy, 2011).

$$O_3 + h\nu \xrightarrow{NO-NO_2} O_2 + O$$

$$O_3 + h\nu \xrightarrow{Cl-ClO} O_2 + O$$

Ozone depletion by OH radical: Ozone depletion may also occur by the hydroxyl radicals present in the stratosphere in the following routes.

$$HO^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2;\ O_3 + h\nu \rightarrow O_2 + O;$$

$$HO_2^{\bullet} + O \rightarrow HO^{\bullet} + O_2;\ HO^{\bullet} + O \rightarrow H + O_2;$$

$$H + O_3 \rightarrow HO^{\bullet} + O_2;\ HO_2^{\bullet} + O_3 + h\nu \rightarrow HO^{\bullet} + 2O_2$$

The hydroxyl radicals (${}^{\bullet}OH$) and hydroperoxy radicals ($HO_2^{\bullet}$) are only generated when plenty of water vapours is present in the stratosphere. But the condition does not normally prevail. Thus in reality, ozone destruction by this path is not of much importance. It may be mentioned that water vapour present in the aircraft exhaust (specially by supersonic transports, SSTs) may be a weak source of the hydroxyl radicals (${}^{\bullet}OH$) in stratosphere.

$$O + H_2O \rightarrow 2\,{}^{\bullet}OH$$

6 Ozone depletion mainly in the stratosphere over the Antarctica during spring (September – October): ozone depletion relatively less significant in the Arctic region

It has been noted that ClO_x is primarily responsible for ozone depletion in stratosphere (Drdla & Müller, 2012; Engel et al. 2018; Kerr, 1987; Molina & Rowland, 1974; Molina et al. 1987; Sander et al. 1989; Solomon et al. 1984, 1986). Theoretically, the ozone depletion process mediated by ClO_x can go on all over the stratosphere. In reality, the ozone holes have been noticed mainly in the stratosphere over the Antarctica during spring. In other parts of the stratosphere, there are two key reactions, which can remove the active species ClO and Cl which are mainly responsible for ozone depletion (Baird & Cann, 2005).

$$ClO^{\bullet} + {}^{\bullet}NO_2 \rightarrow ClONO_2\,(\text{chlorine nitrate});\; CH_4 + Cl \rightarrow {}^{\bullet}CH_3 + HCl$$

Removal of ClO (by NO_2) through the formation of chlorine nitrate and removal of Cl (by CH_4) through the formation of HCl can prevent the chain mechanism to deplete O_3. In fact, most of the atmospheric chlorine remains in these inactive forms. Subsequently, under some restricted conditions (discussed later), from these nonreactive forms, the active forms may be regenerated to participate in the ozone depletion reactions. The HCl molecules produced in presence of CH_4 (*ca.* 15% of the total CH_4 released at the earth surface ultimately diffuse into the stratosphere) diffuse down the troposphere and then these are removed through rainfall. Consequently, the possibility to regenerate Cl atoms in the stratosphere from HCl is minimised.

In the Antarctica region, during winter the sun sets for six months and darkness prevails over the polar cap. It becomes very cold. The rapid cooling sets up a polar vortex (*i.e.* tight whirlpool of winds) that encircles the pole. This polar vortex is quite stable and it can isolate the air within itself. Thus, the air present within the polar vortex remains isolated from the sun and warmer air of the temperate areas. This stable structure of polar vortex remains throughout the winter and it starts to breakdown with the return of sunlight in the month of September (*i.e.* spring). The breaking continues and completes in the month of November (*i.e.* summer). In the isolated Antarctic vortex, the core becomes cold enough to produce the Polar Stratospheric Clouds (PSCs). In the Antarctic vortex, there are two types of PSCs (Das & Das, 2012; Drdla & Müller, 2012; Hamill & Toon 1991; Solomon, 1999; Tritscher et al., 2021; WMO, 2018). These are:

Type-1 PSC: solidified $HNO_3{\cdot}3H_2O$ (nitric acid trihydrate, NAT), formed at about −77 °C (Voigt et al., 2005) and **Type-II PSC**: ice (H_2O), formed at about −85 °C. These solid PSCs (specially Type-II) provide the heterogeneous surfaces to allow the following reactions.

$$ClONO_2\ (\text{chlorine nitrate}) + H_2O\ (\mathbf{PSC, Type-II}) \rightarrow HOCl + HNO_3;$$

$$ClONO_2 + HCl\ (\textbf{dissolved in solid ice}) \rightarrow Cl_2 + HNO_3$$

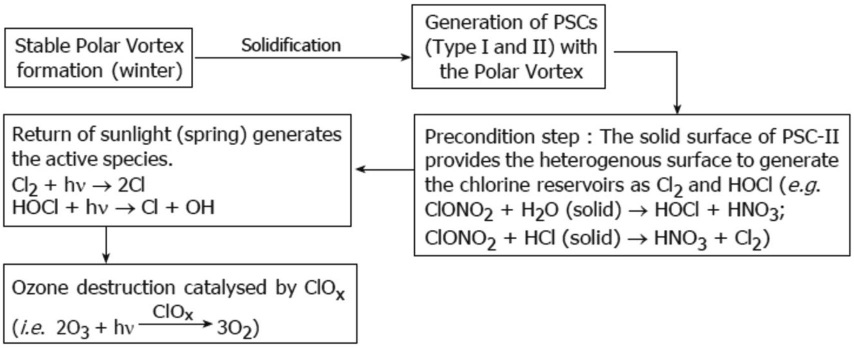
The above two reactions can only occur on the heterogeneous surface of PSC (Type-II). Thus the produced species HOCl and Cl_2 even on mild condition can regenerate the active Cl atoms through photolysis to allow the ozone depletion process. In spring (Sept. – Oct.), sun begins to shine over the Antarctic skies. Then HOCl and Cl_2 are easily photolysed by sunlight to generate the active Cl atoms required to deplete O_3.

$$HOCl + h\nu \rightarrow Cl + {}^{\bullet}OH\,;\; Cl_2 + h\nu \rightarrow 2Cl$$

In the Antarctica region (which is surrounded by the oceans), the temperature may fall up to −90 °C to allow the formation of both types of PSC. On the other hand, in the Arctic region (which is in contact with the habited land masses), the temperature may fall up to −80 °C to allow the formation of only PSC Type-I; and in this region, PSC Type-II (which is required to carry out the ozone depletion reactions) is rarely observed (Solomon et al., 2007, 2014). Besides this, the Arctic vortex is not much stable and its duration is also very short. With the break of Arctic vortex, air from the non-polar regions reaches the arctic zone. This air brings NO_x (scavenger of active forms of ClOx cycle), and fresh ozone. Thus, ozone depleted (if at all), is replenished immediately. In fact, because of the absence of PSC Type-II and stable polar vortex in the arctic region, ozone depletion does not occur in the Arctic region to any significant extent (Solomon et al., 2007, 2014). Here it is worth mentioning that in 2011 (Kuttippurath et al. 2012; Manney et al. 2011) and 2020 (Dameris et al., 2021; Feng et al., 2021; Grooß and Müller, 2021; Lawrence et al. 2020; Wohltmann et al. 2020), the Arctic stratospheric temperatures were exceptionally low to favour the formation of stable and strong Arctic stratospheric polar vortex in winter and PSC within this polar vortex and consequently, it led to the huge ozone depletion in the Arctic stratosphere.

7 Sequence of steps leading to ozone depletion in the Antarctic stratosphere

It is illustrated in Scheme 1.



Scheme 1: Schematic representation of the sequence of steps leading to ozone depletion in the Antarctica pole.

8 Possibility of ozone depletion in the non-polar regions

In the non-polar regions, OH radical and Cl radical can jointly destroy the ozone to some extent. It has been already explained that ozone depletion by OH radical is not important and ozone depletion by Cl radical is not also important in the non-polar regions because of the reasons discussed below (Das & Das, 2012; Sodhi, 2000).

Release of Cl atom (which is the key player in ozone depletion) from $ClONO_2$ occurs on the heterogeneous surfaces. In the polar region, the PSCs provide the required heterogeneous surface. Outside the polar region, the Cl atom releasing reactions are less important in the stratosphere because of the absence of heterogeneous solid surface. However, the surface of **sulphate aerosols** in the stratosphere can allow the said heterogeneous reactions which in turn allow the ozone depletion reactions (Das & Das, 2012; Das & Das, 2016; Tolbert, 1994). Thus, with the increase of sulphate aerosol concentration in the stratosphere, the possibility of ozone depletion increases in the non-polar regions. It may be noted that after the massive volcanoes in 1991 (Mt. Pinatubo in the Philippines), the ozone depletion occurred to a significant extent throughout the globe (Brasseur & Granier, 1992; Das & Das, 2012, 2016; Hansen et al. 1992; Kerr, 1993). In fact, the massive volcanic eruptions injected a huge amount of sulphur (mainly as SO_2) in the atmosphere (Das & Das, 2012, 2016). Thus the ejected sulphur was ultimately converted into the sulphate aerosols that were subsequently distributed throughout the globe in the stratospheric level. These sulphate aerosols acted as the heterogeneous reaction sites for the release of ozone depleting Cl atoms.

9 Ozone depleting substances (ODSs) – chlorofluorocarbons (CFCs), hydrochloro-fluorocarbons (HCFCs) and halons

All these ozone depleting substances can be classified in terms of ozone-depleting potential (ODP) (*cf.* Tables 1 and 2) (Das & Das, 2012; Sodhi, 2000; Vanloon & Duffy, 2011). ODP gives the measure of long-term impact of a particular chemical on atmospheric ozone and it is measured with respect to that of the standard, CFC-11. These substances are discussed below.

Chlorofluorocarbons (CFCs) and other halocarbons: CFCs are called freons. Because of their unique properties like chemical stability, inert character, nontoxicity, noninflammability, these are widely used for refrigeration, aerosol production, air conditioning, plastic foam production (as a foam blowing agent in making polystyrene foam), cleaning purpose, etc. These are also used as solvents and in preparing inhalers. Besides the

Table 1: Comparison of the ozone depletion potentials (ODPs) of CFCs and AFCs.

Commercial name	Formula	ODP value (relative)
Chlorofluorocarbones (CFCs)		
CFC – 11	CCl_3F	1.0
CFC – 12	CCl_2F_2	1.0
CFC – 113	$CCl_3–CF_3$	0.8
CFC – 114	$CClF_2–CClF_2$	1.0
CFC – 115	$CClF_2–CF_3$	0.6
Alternative fluorocarbones (ACFs) as green replacements		
Hydrochlorofluorocarbones (HCFCs)		
HCFC – 22	$CHClF_2$	0.05
HCFC – 123	$CHCl_2–CF_3$	0.02
HCFC – 124	$CHClF–CF_3$	0.02
HCFC – 141b	$CH_3–CCl_2F$	0.11
HCFC – 142b	$CH_3–CClF_2$	0.06
Hydrofluorocarbones (HFCs)		
HFC – 22	CH_2F_2	0
HFC – 125	$CHF_2–CF_3$	0
HFC – 134a	$CH_2F–CF_3$	0
HFC – 152a	$CH_3–CHF_2$	0

Table 2: Comparison of the ozone depletion potentials of halons and other chlorocarbons.

Commercial name	Formula	ODP value (relative)
Halons		
Halon – 1211	$CBrClF_2$	3.0
Halon – 1301	$CBrF_3$	10.0
Halon – 2402	$CBrF_2–CBrF_2$	6.0
Others		
	CCl_4	1.1
	$CH_3–CCl_3$	0.1

CFCs, other halocarbons like halons (bromine containing hydrocarbons used as the fire extinguishers), methyl bromide (used as a fumigant insecticide) and chlorinated hydrocarbon solvents (*e.g.* carbon tetrachloride, trichloroethane, etc.) are also industrially used for many purposes (Das & Das, 2012). Among these, CFCs are the major sources of stratospheric chlorine. Because of their tremendous ozone depleting power, now restrictions have been imposed to curtail down their use. In 1987, this framework led to the **Montreal Protocol**, an international treaty, designed to control the production and consumption of CFCs and other ODSs. As a result of the Montreal Protocol and its amendments and adjustments in subsequent years, attentions have been concentrated to the development of “ozone-friendly” substitutes to replace CFCs, and chlorine levels in the stratosphere have been slowly declining since about the year 2000 (Kuttippurath et al. 2018; Montzka et al., 1999; WMO, 2018). Here it is worth mentioning that the day, 16th September, the Montreal Protocol was accepted, is now celebrated as the International Day for the Preservation of the Ozone Layer.

Because of the tremendous chemical inertness of CFCs, they can survive in atmosphere year after year (up to 100 years) without any transformation. Ultimately they reach stratosphere where they can initiate the ozone depletion process. Here it should be mentioned that the CFCs are also the potential greenhouse gases to cause global warming. Besides the man made activities releasing CFCs as the source of chlorine in the stratosphere, the natural activities (like interaction of chloride ion with the decomposing vegetation in oceans) also release methyl chloride (CH_3Cl) and only a part of this released methyl chloride is destroyed in troposphere and the remaining portion is ultimately transported into the stratosphere. Similarly, methyl bromide is also released from the natural activities (Baird & Cann, 2005).

Alternative fluorocarbons (AFCs): The ODP values of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are less compared to those of CFCs (Table 1). The HCFCs and HFCs are jointly called AFCs (Baird & Cann, 2005; Das & Das, 2012). Some examples are: HCFC-22 ($CHClF_2$), HCFC-142 (CH_3CClF_2), HCFC-123 ($CHCl_2CF_3$), etc. For such compounds, OH-radical present in the troposphere preferably attacks the C–H bond rather than on the C–Cl bond. Thus their lifetime in atmosphere is much shorter than that of CFCs having no C–H bond. In AFCs, the presence of stronger C–X bonds (*cf.* C–F bond energy: 484 kJ mol^{-1}) weakens the C–H bonds and these are easily destroyed in troposphere. In fact, before reaching the stratosphere, a large fraction of the AFCs is destroyed, and only a small part of the AFCs can reach the stratosphere, where photolysis can generate the Cl atoms (that is the key player of ozone depletion). In this way, the possibility of generation of Cl radical in the stratosphere is relatively reduced. It may be noted that CFCs and other hydrocarbons as the foam blowing agents are now replaced by carbon dioxide as a greener blowing agent (Das & Das, 2012).

In terms of the ODP values, the chlorine free HFCs are the better alternatives as their ODP values are zero. But because of their greenhouse properties, there is a serious objection against the HCFs. The ODP values of HCFCs are quite small and their greenhouse potentials are also quite low. This is why, the HCFCs are the best alternatives. But their production cost is much higher. Moreover, their environmental degradation may produce the toxic and harmful compounds like (hydrofluoric acid), CF_3CO_2H (trifluoroacetic acid). Thus, they may produce environmental problems in other ways.

From the standpoint of ozone depletion and greenhouse potential values, CFCs should be first replaced by AFCs having low ODP and greenhouse potentials, and then AFCs should be substituted by the compounds having zero greenhouse potential and zero ozone depletion potential. Such compounds, *i.e.* perfectly green replacements, are not yet known. Scientists should search for such compounds that can economically substitute CFCs.

10 Global warming and atmospheric ozone chemistry

Ozone itself is a greenhouse gas absorbing the earth radiated infra-red (IR) radiation (absorption maxima: 5.75 μm and 9.6 μm) (Das & Das, 2012). Thus ozone hole formation in the polar region may lead to cooling and it was noticed so in the Antarctica in the late 20th century due to the formation of ozone hole in the stratosphere of Antarctica. In this connection, the role of the ozone depleting CFCs is of worth mentioning. CFCs are the potential greenhouse gases absorbing IR-radiation in the **atmospheric window** 8–12 μm which is transparent to the other IR-absorbing species such as CO_2 and water vapour. In terms of heat trapping capacity, the greenhouse gases can be placed in the order: $CFC >> N_2O >> CH_4 > CO_2$ and the approximate ratio is: 19,000:200: 25:1 (Das & Das, 2012). It indicates that CFC is about 19,000 more powerful than CO_2 per molecule in terms of atmospheric heat trapping capacity or radiative forcing power. Thus, if the usage of CFCs is not restricted as per the Montreal recommendations, it will seal the atmospheric window to increase the earth's temperature further. Thus atmospheric chemistry of ozone and its perturbation by the man made or natural activities like volcanic eruption have an important role to control the global climate.

11 The Asian brown cloud and atmospheric brown cloud

The **Asian Brown Cloud (ABC)** known also as the '**Indian Ocean Brown Cloud**' is an extensive layer of toxic air pollution that covers parts of the northern Indian Ocean, the Indian subcontinent, Bangladesh, China, Pakistan, and parts of South Asia (Srinivasan & Gadgil, 2002). The cloud appears as a giant brown stain hanging in the atmosphere over the said area every year between December and March, the time when there is little or no rain to wash the pollutants out of the air. The term **atmospheric brown cloud** is used for a more generic context as it is a global issue and it occurs in many other parts of the world like in parts of Europe, North America, southern Africa and the Amazone basin (Manahan, 2010). In fact, atmospheric brown cloud is related to the photochemical smog which is a regional problem to affect the large urban areas as in Los Angeles Basin but atmospheric brown cloud (defined by United Nations Environment Programme in 2008) refers to the smog as a larger air pollution problem. The brown cloud (approximately 3 km thick) contains various types of noxious air pollutants including ozone and greenhouse gases, particles of black carbon, soot, fly ash and other particles. The brown cloud is created from the combustion of fossil fuels, biomass and agricultural wastes, and industrial processes with incomplete burning of fossil fuels.

12 Conclusions

In fact, discovery of the Antarctic ozone hole in 1985 by Farman et al. established the fact that chlorofluorocarbons (CFCs) (often used in aerosol cans and as refrigerants) and other halocarbons like halons (used as fire extinguishers) and methyl bromide (used as fumigant insecticide), etc. were responsible for the unanticipated observation. This discovery revolutionized the atmospheric science and created a dramatic change in understanding the atmospheric chemistry and led to the global changes in the environmental policies. Now it is understood that the ozone depleting substances (ODSs) can destroy the ozone layer mainly in the Antarctic stratosphere in spring. The important catalytic XO_x cycle (X = Cl, Br) to deplete the stratospheric ozone requires a heterogeneous solid surface like Type-II PSC (polar stratospheric cloud) formed at about −85 °C. In the earth, the geographical position of Antarctic pole can only provide the required conditions by producing the Type-II PSC to carry out the XO_x catalysed ozone depletion reactions. Thus nature protects the earth from the threatening effect of ozone depletion by confining this untoward phenomenon in the Antarctic zone which is practically inhibited. It may be noted that recommendations of the Montreal protocol have curtailed down the industrial use of the potential ODSs. In fact, CFC-based products are banned in many countries like the United States, Norway, Sweden, Canada and many other countries of Europe. The Kigali Amendment to the Montreal protocol has recommended to reduce the production and consumption of HFCs (powerful greenhouse gases that contribute to climate change).

This mini tutorial review is written from the author's experience in class rooms. This material has been utilized by the author several times in teaching the present hot environmental issue. Based on the questions asked by the students and feedback from them, this self explanatory review article has been prepared to act itself as a teacher for chemistry education on this topic.

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