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0521020956 - The Effects of UV Radiation in the Marine Environment
Edited by Stephen de Mora, Serge Demers and Maria Vernet
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Enhanced UV radiation – a new problem for the marine environment

Robert F. Whitehead, Stephen J. de Mora* and Serge Demers

1.1 Introduction

UV irradiance at the earth's surface is intimately related to stratospheric ozone. This gas tends to be concentrated in the lower stratosphere (hence the notion of an ozone layer) and is primarily responsible for the absorption of solar UV radiation (UVR). UVR has been recognised for many years (e.g. Worrest, Dyke & Thomson, 1978; Worrest *et al*., 1981; Calkins, 1982) as a potential stress for organisms in a variety of environments and as a factor in biogeochemical cycling (Zepp, Callaghan & Erickson, 1995). The trend in recent years of an intensifying, but periodic, anthropogenic-induced decline in stratospheric ozone concentrations with concurrent enhanced UV-B radiation is quite alarming. Altered solar radiation regimes can potentially upset established balances in marine ecosystems and thus presents a new problem. Most attention has been given to the 'ozone hole' over Antarctica that has been recorded annually since the 1980s. However, recent observations have confirmed measurable ozone losses over other regions, including the development of an Arctic ozone hole. The major factor responsible for the destruction of the ozone layer is anthropogenic emissions of chlorofluorocarbons (CFCs). These gases, having no natural sources, are non-toxic and inert in the troposphere, but are photolysed in the stratosphere, thereby releasing reactive chlorine atoms that catalytically destroy ozone. Other anthropogenic contributions to ozone depletion may include global changes in land use and the increased emission of nitrogen dioxide as a result of fertiliser applications (Bouwman, 1998). Paradoxically, the anthropogenic emissions of greenhouse gases that tend to cause a temperature increase at the earth's surface also produce a decrease in stratospheric temperatures. This decrease in stratospheric temperatures leads to enhanced formation of polar stratospheric clouds and may serve to increase ozone

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loss in polar regions (Salawitch, 1998; Shindell, Rind & Lonergan, 1998).

The understanding of the atmospheric chemistry involved in ozone depletion has greatly expanded since the link to CFCs was first proposed in 1974 (Molina & Rowland, 1974). A worldwide network of ozone observation stations has documented continuing ozone reductions over many areas of the globe. The effects have been especially pronounced in the Antarctic region, where an ozone hole, characterised by the depletion of 60% or more of the ozone, opens up each spring over an area that is now slightly larger than the size of Canada (Smith *et al.*, 1992). In the Arctic and into the North Temperate Zone, the ozone layer diminished by 15% to 20% during the 1991–2 winter[1]. The increases in atmospheric carbon dioxide anticipated over the next 50 years should lead to stratospheric cooling, thereby accelerating the destruction of stratospheric ozone and perhaps leading to an Arctic ozone hole as severe as that over Antarctica (Austin, Butchart & Shine, 1992). The latest Environmental Canada (Wardle *et al.*, 1997) report indicates ozone loss over the Arctic of up to 45% during the spring of 1997 in response to atmospheric conditions that may be indicative of changes due to stratospheric cooling (Mühler *et al.*, 1997; Wardle *et al.*, 1997). The magnitude of ozone destruction is predicted to increase over the next century despite international efforts to reduce the usage and emission of CFCs in accordance with the Montreal Protocol (Shindell *et al.*, 1998).

Regardless of the cause, the decrease in stratospheric ozone concentrations provokes an increase of UV-B radiation in the wavelength range 280 to 320 nm (Crutzen, 1992; Smith *et al.*, 1992; Kerr & McElroy, 1993). For example, an annual increase in UV-B of up to 35% has been observed in Canada for the winter–spring period during 1989–93 (Kerr & McElroy, 1993). The UV-B wave band represents less that 0.8 % of the total energy reaching the surface of the earth but is responsible for almost half of the photochemical effects in the aquatic and marine environments. Although not widely recognised due to a lack of field measurements, biologically effective levels of solar UVR penetrate water columns to significant depths: at least 30 m for UV-B (280–320 nm) and 60 m for UV-A (320–400 nm) (Smith & Baker, 1979; Holm-Hansen, Lubin & Helbing, 1993). Even in highly productive lakes and coastal regions, UVR can penetrate to at least 20 m (Kirk, 1994b; Scully & Lean, 1994) and this penetration increases as stratospheric ozone declines (Smith *et al.*, 1992).

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[1] A number of articles on Arctic ozone and atmospheric chemistry can be found in *Science* (1993) **261**.

The environmental impact of this rise in solar UV-B has recently become a source of much concern and speculation in public as well as scientific literature.

Solar UV-B radiation is known to have a wide range of harmful effects, generally manifested as reduced productivity, on freshwater and marine organisms, including bacterioplankton and phytoplankton (Vincent & Roy, 1993; Cullen & Neale, 1994; Booth *et al*., 1997). Analogous studies on zooplankton and on the early life history stages of fishes indicate that exposure to relatively low levels of UV-B also deleteriously affects these groups (Holm-Hansen *et al*., 1993). All plant, animal and microbial groups appear to be susceptible to UV-B, but to a highly variable extent that depends on the individual species and its environment (Vincent & Roy, 1993). In addition, UV-B may have significant effects on community structure that are not apparent through studies based on individual species or trophic levels (e.g. Bothwell, Sherbot & Pollock, 1994; Vernet *et al*., 1994).

This chapter provides an introduction to some fundamental aspects of the behaviour of solar radiation in the atmosphere and water column. The fate of photons is also considered in respect of basic photochemistry and photobiology. The introduction is intended to form a basis for the understanding of the relationships amongst anthropogenic-related changes in the atmosphere, changes in solar radiation and the new problems they present to marine ecosystems. Subsequent chapters elucidate effects on specific biological structures and organisms, trophic-level interactions, photochemical reactions and biogeochemical cycling.

1.2 The solar spectrum and the nature of light

The effect of solar radiation on chemical and biological processes in the marine environment depends on both intensity and spectral distribution. There is significant natural variability in the factors that attenuate solar radiation and UV-B in both the atmosphere and the ocean. At the edge of the earth's atmosphere, the solar energy reaching a surface perpendicular to the radial direction from the sun is approximately 1394 W m^{-2} and has a spectrum characterised as UV (UV-C 200–280 nm, UV-B 280–320 nm, UV-A 320–400 nm), photosynthetically available radiation (PAR 400–700 nm) and infrared (IR $>$ 700 nm) (Figure 1.1). The energy characteristic of each wavelength is determined by the relationship:

$$E = hc/\lambda \tag{1.1}$$

where E is the energy in joules, h is the Planck constant, c is the speed of light, and λ is the wavelength in metres. When dealing with biological and chemical systems, the most commonly used unit is the mole photon (also called an Einstein) which contains N photons (where N is Avogadro's number $= 6.023 \times 10^{23}$). The radiant energy of 1 mole photon is defined by:

$$E_{(\text{mole photon})} = Nhc/\lambda = 1.19629 \times 10^8\ \text{J}/\lambda \tag{1.2}$$

Thus, the energy of a mole photon varies inversely with wavelength (Figure 1.2). For example, the energy of 1 mole photon of 300 nm light is 398 kJ. In contrast, the energy of 1 mole photon of 700 nm light is only 171 kJ. The large increase in energy with decreasing wavelength has important chemical and biological implications when one is considering systems under changing solar spectral distributions.

1.3 Attenuation of solar energy

1.3.1 Attenuation in the atmosphere

In general terms, the relative solar spectral distribution outside the

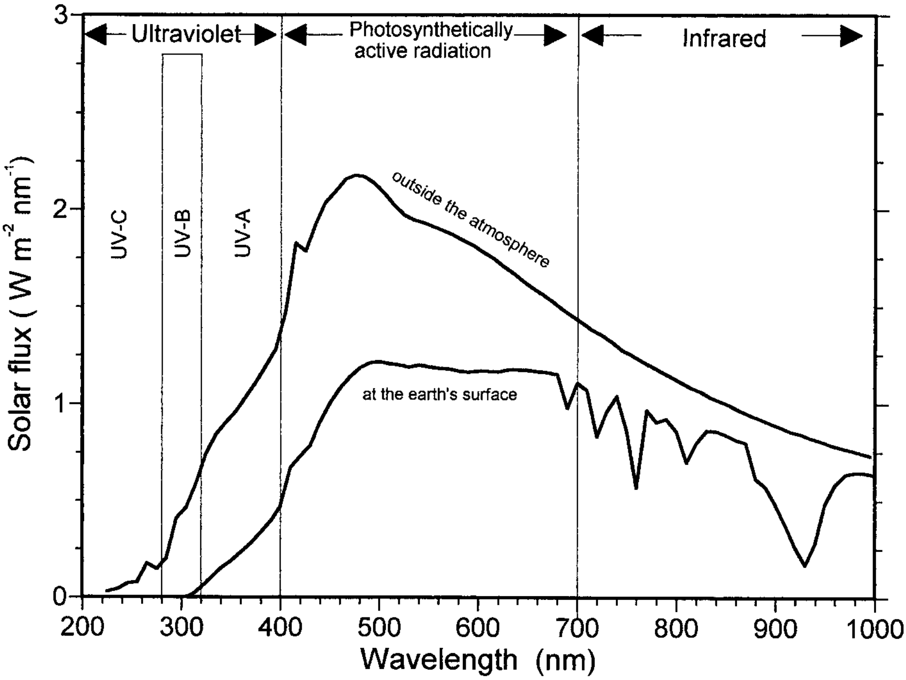

Figure 1.1. General characteristics of solar radiation outside the atmosphere and at the earth's surface.

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Excerpt
More information

atmosphere comprises 51% in the IR region, 41% in the visible (PAR) region and 8% in the UV region (Figure 1.3). Passing through the atmosphere, the radiation is subject to scattering and absorption which reduces its intensity by ~35% before it reaches the earth's surface. As a result, the spectral distribution at the earth's surface differs from that experienced at the edge of the atmosphere and is a combination of direct and diffuse radiation. The amount of scattering and absorption is a function of the atmospheric composition (gases and particles) and the pathlength of the photons through the atmosphere. Thus, given a uniform atmospheric composition the spectral distribution and intensity would still vary as a function of solar zenith angle (i.e. time of day, season and latitude). A typical solar spectral distribution for a low latitude (30° N) site on a sunny day with the sun at zenith is composed of about 43% IR, 52% PAR and 5% UV radiation. For the same location with a zenith angle of 60° or 79°, the distribution changes to about 45% IR, 52% PAR and 3% UV radiation or 53% IR, 46% PAR and 1% UV, respectively (Figure 1.3). The reason for the larger relative reduction at the UV end of the spectrum

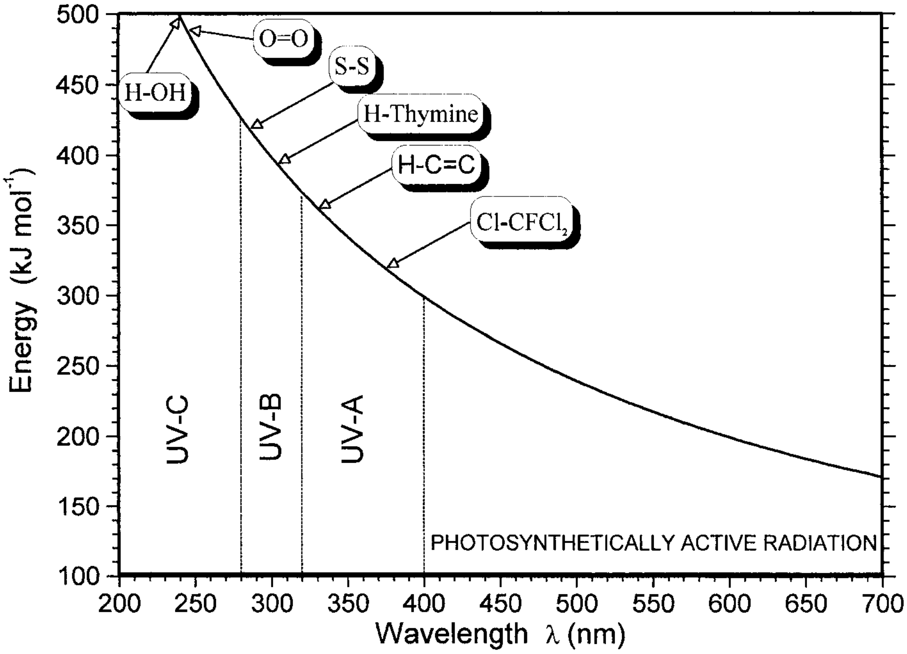

Figure 1.2. The inverse relationship between energy per mole and wavelength of solar radiation. Bond dissociation energies of some important biomolecular bonds are indicated by the location of the arrows on the curve.

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with increasing atmospheric pathlength is two-fold:

1. *Enhancement of scattering*: Scattering in the atmosphere is inversely proportional to the fourth power of the wavelength and is therefore more effective in the UV region. Scattering may redirect a photon's path away from the earth such that it is lost back to space or may enhance the probability of absorption due to longer pathlengths.
2. *Enhancement of absorption*: UV radiation <320 nm is strongly absorbed by ozone and to some extent by oxygen (Figure 1.4). Longer pathlengths effectively increase the total ozone encountered by a photon and thereby enhances the probability of absorption.

1.3.1.1 Absorbance of UV and the ozone cycle

The strong reduction in UVR (<320 nm) reaching ground level (Figure 1.1) is due primarily to absorption by ozone and oxygen. Although ozone is a trace gas in the atmosphere (maximum concentration ~8 parts per

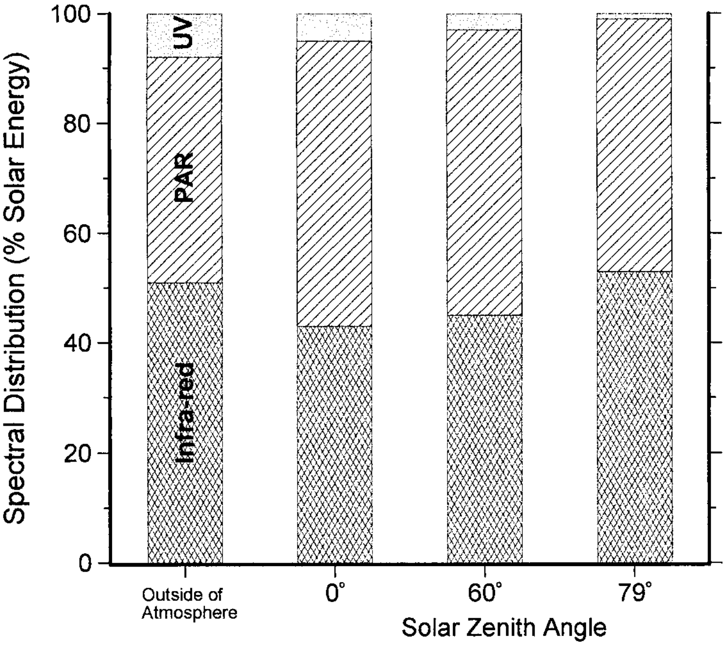

Figure 1.3. Spectral distributions of wavelength regions as a percentage of total solar radiation. Bars represent solar radiation outside the atmosphere and at the earth's surface (30° N) for three solar zenith angles. Atmospheric attenuation causes the largest relative reduction at the UV end of the spectrum.

million by volume (ppmv) at ~35 km altitude), the attenuation of UV by ozone is orders of magnitude higher than that of oxygen. The absorption of UV with enough energy to break the O═O bond ($\Delta H = 494\,\mathrm{kJ\,mol^{-1}}$ requires $\lambda < 240\,\mathrm{nm}$) is the first step in the production of ozone (O_3):

$$O_2 + h\nu(\lambda < 240\,\mathrm{nm}) \rightarrow O + O \qquad [1.1]$$

where ν is the wave frequency.

The O atoms released may then react with O_2 to form O_3:

$$2(O + O_2 + M \rightarrow O_3 + M) \qquad [1.2]$$

where M is a collision chaperone that absorbs excess energy but is itself unreactive. Net ozone production is $3\,O_2 \rightarrow 2\,O_3$. Ozone can be destroyed by direct photolysis:

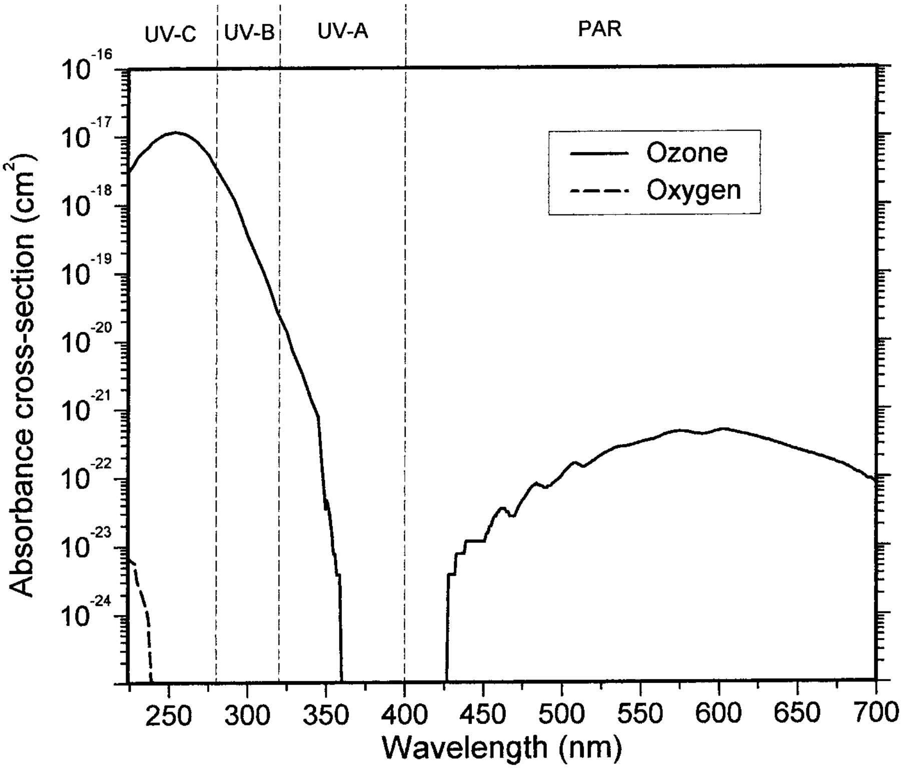

Figure 1.4. Spectral characteristics of the absorbance cross-sections of oxygen (O_2) and ozone (O_3) at 298 K. Whereas wavelengths in the UV-C and UV-B regions are strongly absorbed by O_3, UV-A and PAR are little affected. (Data from Inn & Tanaka, 1953; Molina & Molina, 1986.)

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$$O_3 + h\nu(\lambda < 410\,\text{nm}) \rightarrow O + O_2 \qquad [1.3]$$

or by recombination with O:

$$O_3 + O \rightarrow 2\,O_2 \qquad [1.4]$$

Net ozone destruction is thus $2\,O_3 \rightarrow 3\,O_2$.
However, at all times the concentration of oxygen far exceeds that of ozone and the recombination reaction is slower than production. If pure oxygen reactions were the only mechanism for ozone production and destruction, the ozone layer would be approximately twice as thick as is currently observed. Thus, other destruction reactions are necessary to explain natural ozone levels.

The rate of recombination is greatly enhanced by catalytic cycles of the general form involving a free radical, X:

$$O_3 + X \rightarrow XO + O_2 \qquad [1.5]$$
$$O + XO \rightarrow O_2 + X \qquad [1.6]$$

or

$$O_3 + XO \rightarrow 2\,O_2 + X \qquad [1.7]$$

where X may be NO, HO, Cl, I or Br. The X species are regenerated in this sequence and may be involved in as many as 100 000 ozone-destroying cycles before being sequestered into less active reservoir species by slower reactions such as:

$$HO + NO_2 \rightarrow HNO_3 \qquad [1.8]$$
$$XO + NO_2 \rightarrow XONO_2 \qquad [1.9]$$

Stratospheric ozone levels are therefore maintained by a dynamic balance between photochemical production and destruction. Intuitively, one might expect to find the highest stratospheric ozone levels at low latitudes and high altitudes where solar irradiance is strongest. However, ozone levels are highest in the middle stratosphere over high latitudes and not the upper stratosphere above the equator. In fact, ozone levels above the equator are relatively constant at about 260 DU[2] whereas ozone levels above high latitudes in the northern hemisphere may reach 450 DU. The pattern is a result of the redistribution of high altitude ozone-rich air from the tropics to lower altitudes in the polar regions (Figure 1.5).

[2] 100 Dobson units, DU, are equivalent to an ozone layer 1 mm thick at 0 °C and 1 atm pressure.

The natural O_3 cycle can be perturbed by interactions with anthropogenic compounds, most notably CFCs (WMO, 1995). CFCs were first produced in the 1930s and were heralded as non-toxic, non-flammable compounds with a wide variety of uses as refrigerants, propellants for aerosol cans, cleaning compounds for electronic parts and blowing agents for foam manufacturing. Over the 50 years since the introduction of CFCs, their concentrations in the atmosphere, in general, have shown a steady increase, with a corresponding decrease in stratospheric ozone (Figure 1.6). Mario Molina and F. Sherwood Rowland first proposed their role in the destruction of atmospheric ozone in 1974. They shared the 1995 Nobel Prize for Chemistry with Paul Crutzen for their work in this field. The ozone hole over Antarctica was first reported in 1985 and led to work that has firmly established the link between CFCs and ozone depletion.

CFCs are quite stable and inert in the troposphere. They have long residence times in the atmosphere and are mixed into the stratosphere, attaining notable concentrations. Once in the stratosphere, CFCs are exposed to UV radiation of sufficient energy to break the carbon–chlorine bonds. The released chlorine can then attack O_3 in the following reaction sequence:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad [1.10]$$

$$ClO + ClO \rightarrow Cl_2O_2 \qquad [1.11]$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO \qquad [1.12]$$

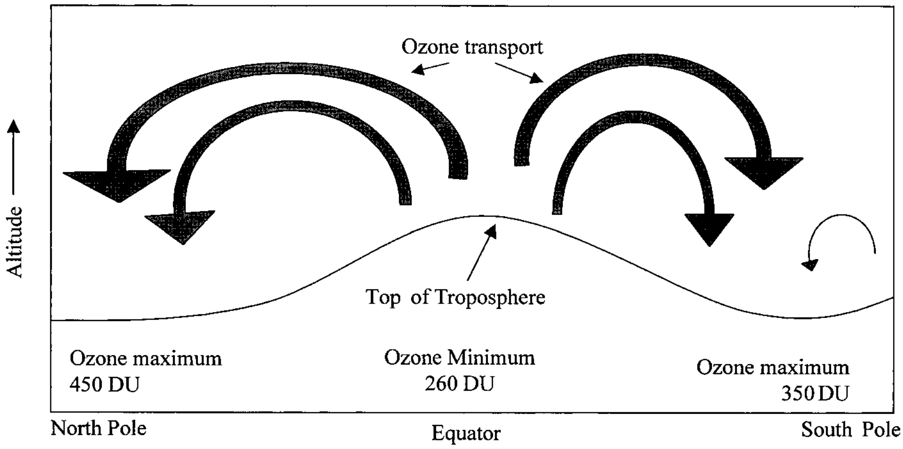

Figure 1.5. Generalised atmospheric redistribution of O_3 without the influence of O_3 depletion. Highest O_3 production occurs over the equator and tropics, but atmospheric circulation transports the O_3 produced there towards the poles, giving rise to an O_3 maximum at higher latitudes. (Adapted from Stolarski, 1988.)

$$ClOO + O \rightarrow ClO + O_2 \qquad [1.13]$$
$$2 \times (Cl + O_3 \rightarrow ClO + O_2) \qquad [1.14]$$

giving a net destruction of $2\,O_3 \rightarrow 3\,O_2$.

These gas phase reactions can occur anywhere in the stratosphere, however, the rates are not sufficiently fast to explain the large ozone hole that has been observed in the spring over Antarctica since the early 1980s. In the gas phase reactions, reactive chlorine species (Cl, ClO) can be removed from the ozone destruction cycle and transformed into non-reactive reservoir chlorine compounds (HOCl, $ClONO_2$) by reactions [1.8] and [1.9]. A rapid conversion of reservoir chlorine into reactive chlorine is necessary to explain the ozone hole over Antarctica. The mechanism for this rapid conversion is heterogeneous (gas–solid) reactions catalysed on the surface of polar stratospheric clouds (PSCs). PSCs are composed largely of condensed nitric acid, which also reduce atmospheric NO_2 concentrations. Low NO_2 concentrations extend the life of reactive chlorine species by reducing the importance of reaction [1.9] in the gas

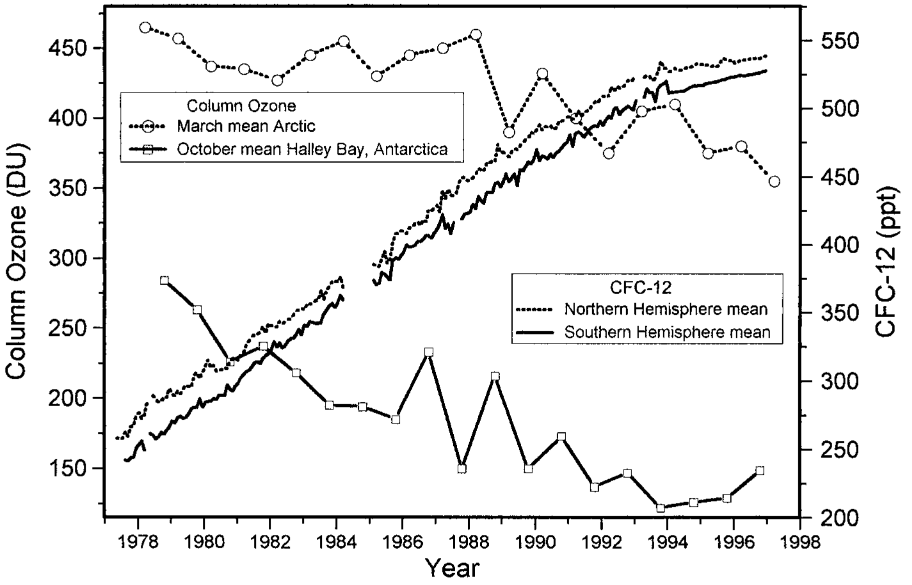

Figure 1.6. Comparison of the decrease in springtime stratospheric ozone over the Arctic and the Antarctic with the build-up of chlorofluorocarbon (CFC)12 in the northern and southern hemispheres. Natural atmospheric chlorine concentrations are relatively constant (≅ 0.6 p.p.b.v.) whereas anthropogenic sources have steadily increased since the introduction of CFCs. ppt, parts per trillion. (CFC data from Elkins, NOAA; Antarctic ozone from British Antarctic Survey; Arctic ozone from Environment Canada.)