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# Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2004

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## Abstract

The complexity of the linkages between ozone depletion, UV-B radiation and climate change has become more apparent.



## Keywords

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# Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2004

United Nations Environment Programme, Environmental Effects Assessment Panel[1]

## Introduction

The measures needed for the protection of the Earth's ozone layer are decided regularly by the Parties to the Montreal Protocol, now consisting of 188 countries. The Parties are advised on knowledge relevant to this task by three panels of experts: the Scientific, Environmental Effects, and Technology and Economic Assessment Panels. These panels produce an assessment every four years. The Environmental Effects Assessments are also published in the scientific literature; the latest report was published as a series of papers in Photochemical & Photobiological Sciences, 2003, **2,** 1-72. In the intermediate years, the panels keep the Parties informed on new developments. The following Progress Report is the 2004 update by the Environmental Effects Assessment Panel and follows that for 2003 (Photochemical & Photobiological Sciences, 2004, **3,** 1-6).

Since the first assessments in 1989, the complexity of the linkages between ozone depletion, UV-B radiation (Fig. 1) and climate change has become more apparent. This makes it even clearer than before that we are dealing with long-term developments, which can be complicated by large year to year variability.

**Figs. 1,2 HERE underneath each other: see** Photochemical & Photobiological Sciences, 2004, **3,** 1-6 for layout

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## Ozone and UV changes

- **The Montreal Protocol is working, but detection of stratospheric ozone recovery remains difficult.** Concentrations of ozone-depleting gases in the atmosphere show a downward trend, which is now discernable in the lower stratosphere. Some evidence has been presented (e.g.,[1]) to indicate a slow-down of the depletion rate of stratospheric ozone, which is more clear-cut in the southern hemisphere, as expected from previous studies.[2] The detection of a turnaround in total ozone would be difficult due to the natural inter-annual variation in several contributing factors[3, 4] (also see Figure 2). This variability in ozone may be much larger than has been assumed based on the measurements over the past 25 years.[5, 6] Monitoring over several more years would be required before any increase in ozone attributable to the measures of the Montreal Protocol can be unambiguously identified.

- **Impacts of climate change on ozone depletion have been further explored, but there is not yet a consensus on whether the overall effect will be to delay or accelerate ozone recovery**. Some processes would result in slowing of ozone recovery,[7, 8] while others would result in an acceleration.[9] Future changes in methyl bromide and methyl chloride emissions resulting from climate change may also be important. Although the majority of methyl bromide is from natural sources, and declines in its concentrations have been reported,[10, 11] its future role in ozone depletion cannot yet be discounted. For example, methyl bromide emissions from rice paddies may increase appreciably with global warming.[12] Finally, the finding that the ozone-depleted air exported from polar latitudes comprises a significant portion of ozone losses at mid-latitudes (e.g., [13-15]) may also have negative implications for future ozone recovery at mid-latitudes. This is important, since further cooling of the polar stratosphere, which is conducive to rapid ozone loss, is expected as a consequence of global climate change.

- **Changes in ozone and UV radiation can potentially influence climate**. Observational data and a new modelling study have both suggested that decreases in stratospheric ozone in Antarctica have led to climatic changes both in the stratosphere and at the Earth’s surface. These changes in ozone have led to increased westerly winds at latitudes 50 to 60ºS. This in turn has resulted in a surface cooling in Antarctica and a warming at high latitudes outside the Antarctic continent.[16] Climate change can also be mediated through UV-induced changes[17] in dimethyl sulphide (DMS), a substance emitted from phytoplankton that can modify the reflectivity of the atmosphere, as discussed further in the section on Aquatic Ecosystems, below.

- **Aerosols and trace gases emitted near the surface of the Earth have large impacts on UV radiation.** New evidence has shown that in urban areas, aerosols and air-pollutants such as ozone and nitrogen dioxide can significantly attenuate solar UV (e.g., [18, 19]). The types of the aerosols and their optical properties are also important.[20] Recent studies have shown that aerosols and trace gases from biomass burning can penetrate into the stratosphere,[21] and consequently affect its chemistry. Increases in UV-B and UV-A solar radiation observed during the last two decades in Germany and Greece[22, 23] cannot be explained by changes in ozone amounts alone, and it is necessary to include diminishing influences from other factors such as pollution at these sites.[24, 25]

- **There have been further improvements in the dissemination of UV information to the public.** The UV Index (UVI), a measure of sunburning UV, is gaining wider acceptance. The routine forecasts to the public have been evaluated at some sites, and have been found to be sufficiently accurate.[26] Methods for converting older UV-B data (and other weightings of UV) to UVI have been published.[27] Progress has also been made to improve extended range forecasts of total ozone (and therefore UV-B radiation) over seasonal time scales.[28, 29]

## Health

- **Distinct pathways, possibly involving UV radiation, in development of melanomas occurring on the skin (cutaneous melanoma: CM) have been confirmed**. Mutations in multiple copies of a particular gene (BRAF) were common in melanomas occurring on skin exposed to intermittent sunlight such as on the trunk.[30] In contrast, there was an almost complete absence of BRAF mutations in melanomas on chronically sun-damaged skin [30] or in UV-protected mucosal sites such as those of the oral cavity.[31] The concept of different pathways leading to melanoma is strengthened by a case-case comparative study of patients in Queensland, Australia, which showed that melanomas on the trunk may arise by melanocyte proliferation and occur in people with high mole counts, while melanomas of the same histological type occurring on the head and neck may arise as a result of chronic sun exposure and occur in people with high solar keratoses counts.[32]

- **The incidence of, and mortality rates from, CM continue to increase. In Eastern and Southern Europe, the rates of CM are still rising sharply, while in Western and Northern Europe, the rise is becoming more gradual**. Although the exact reason for these observations is unknown, one possibility is that incidence is approaching its peak in the West and North but not in the East and South.[33]

- **It is becoming increasingly clear that it is intermittent high dose exposure to UV that increases the risk of basal cell carcinoma (BCC)**. Recent work found that such high dose exposure, i.e., sunburns received early in life, are a major risk factor for BCC.[34]

- **Regular but limited sun exposures are inferred to be adequate for maintaining appropriate vitamin D levels**. Vitamin D is found in food and dietary supplements, but in most people is mainly produced from UV-B irradiation of pro-vitamin D in the skin. One recommendation is for people living at mid-latitudes to aim for 10-15 minutes per day in the sun when the weather allows.[35] However, a proportion of the population, even in areas of intense solar exposure, e.g., Queensland, Australia, show deficient vitamin D levels.[36] Whether an increase in terrestrial UV would be beneficial to such individuals is questionable, particularly if their vitamin D deficiency results from an extreme indoor-living pattern.

- **In contrast to earlier conclusions, the results of recent epidemiologic studies support a relationship between nuclear cataract (an opacity of the centre of the lens) and exposure to sunlight**. One study showed that the severity of nuclear cataract increased with UV-B exposure and that lifetime cumulative UV-B exposure and, in particular, exposure after the teenage years correlated with the presence of nuclear opacities in females.[37] Another report indicated that the association was strongest for sun exposure occurring between the ages of 20 and 29 years.[38] Supporting evidence for such a difference in age susceptibility is provided by an animal study in which the same dose of UV radiation induced more severe cataracts in young than in older animals.[39]

- **UV-absorbing soft contact lenses protect the lens and cornea of the eye against UV radiation from any direction.** Recent studies[40, 41] have confirmed that such lenses provide better protection than some sunglasses, which may not adequately shield the lens and cornea of the eye from lateral and reflected UV.

- **The safety testing of substitutes for CFCs now in use, or proposed for use, continues to indicate very low toxicity.** However, in at least one industrial setting, the switch from CFC 11 to a recommended substitute (HCFC 123) was associated with abnormal liver function tests in workers, indicating that it is important to monitor work practices in order to ensure continued safety.[42].

## Terrestrial ecosystems

- **Recent reports confirm that UV-B may alter biochemical compounds in plants resulting in changed herbivory (consumption of plant tissues by insects and other animals).** Reports continue to show both positive and negative effects of UV-B on herbivores in both crop and non-agricultural plants. For example, reductions in herbivory were recently reported in UV-B-exposed southern beech trees[43] and plants of wild tobacco[44], whereas increases in herbivore numbers were reported for UV-B-exposed willows.[45] However, the latter result did not lead to increased herbivory *per se*. A review of numerous reports concluded that herbivory is generally reduced by UV-B and it was also suggested that enhanced UV-B may influence the predators of insect herbivores.[46]

- **New studies further probe the genetic basis of plant response to UV-B radiation.** Internal plant signals, including gene activation, triggered by various environmental stresses overlap at several levels in the pathways. Recent studies have found commonalities in the responses induced by UV-B and other stress factors, including wounding and herbivory.[44, 47, 48] This convergence in internal plant signals and response may contribute to an explanation of the interactions between solar UV-B and herbivory highlighted above. A recent study has identified suites of genes that are regulated by low UV-B levels through mechanisms that are independent of known photoreceptors.[49] There is also evidence that UV-B activates unique plant signalling pathways.[48] In other work, the genetic basis of UV-B tolerance in rice has been reported to involve several different genes and the location of these putative genes is being determined.[50, 51] Another study has shown that plant growth inhibition by UV-B is better explained by DNA damage than by simple oxidative injury.[52]

- **Biological spectral weighting functions (action spectra; sensitivity to different UV wavelengths) for stimulation of some secondary compounds differ from those for plant growth**. Two recent reports indicate that weighting functions for production of UV-B-absorbing pigments decline more abruptly with increasing wavelength than do those for plant growth and morphological changes.[53, 54] Thus, increasing UV-B resulting from ozone reduction needs to be evaluated differently for these responses and perhaps for induction of a variety of plant secondary compounds that might mediate important ecological responses.

- **Synergistic interactions between UV-B and some other environmental factors can occur, although simple additive responses are found for many plant responses.** In agreement with past results, enhanced concentrations of $CO_2$ supplied to cotton did not show any interaction with UV-B radiation[55] and did not ameliorate any UV-B effects.[56] For secondary compounds, however, other investigators saw synergistic effects between UV-B and other environmental stress factors. Drought and UV-B interacted synergistically to produce substantial increases in flavonol glycosides in drought-stressed plants.[57] Under ambient UV-B, high temperatures induced accumulation of some secondary metabolites in a lichen species, but under enhanced UV-B the high-temperature-induced accumulation of these compounds was suppressed.[58] A new field study on Rhododendron reported that UV-B increased cold-hardiness.[59] Although ambient UV-B did not significantly affect growth of ryegrass, it was reported to decrease the rate of evolution of herbicide resistance in populations of this grass.[60] Thus, the genetic structure of the population of grasses can be altered by a combination of herbicides and ambient UV-B. Development of herbicide and pesticide resistance is a common problem when such chemicals are applied at high frequency and concentration. In this study, UV-B appeared to decrease the development of plant resistance.

- **Although recent field experiments tend to confirm earlier findings that an impairment of plant productivity is seldom seen in realistic UV-B supplementation experiments, some exceptions have been observed.** Photosynthesis and productivity were not affected by supplemental UV-B in three recent studies of non-agricultural plants.[61-63] For soybean, Chimphango et al.[64] reported no impairment of plant productivity due to UV-B supplementation in the varieties they studied; whereas Feng et al.[65] and Zu et al.[66] reported significant inhibition of growth and physiological function in some varieties in their field experiments.

## Aquatic ecosystems

- **With ozone-related increase in UV radiation, organisms that can produce or make use of photoprotective mechanisms appear favoured for survival.** UV screening in phytoplankton and zooplankton is mediated by protective pigments (phlorotannins, melanin, mycosporine-like amino acids (MAAs), scytonemin, and carotenoids). *De novo* synthesis of proteins and lipids also allows the organisms to tolerate UV-B stress. Phlorotannins appear to play multiple roles in brown algae, including the production of water soluble UV-screening compounds, forming natural UV-protected areas along coastal shores.[67, 68] Enzymes and quenchers are involved in attenuating the effects of reactive oxygen species (ROS) induced by UV-B.[69] In the natural habitat, UVR radiation can act as a trigger for the induction of photoprotective mechanisms against high solar irradiance.[70] It is not yet known whether the selection of organisms with different photoprotection will influence species composition of aquatic ecosystems.

- **New long-term studies show interactions between effects of UV-B radiation and other environmental stressors in aquatic communities**. Results show that long-term effects of UV-B may become manifested only in combination with other stressors.[71, 72] The interactive effects of multiple stressors on aquatic systems (including UV radiation, climate change, temperature, precipitation, eutrophication, food web alterations, pH, toxic metals, and oil contamination) often show enhanced damage to the system. Results suggest that the ability to predict effects depends upon understanding the interactions among multiple environmental variables, imposing limits on inferences made from single-factor experiments.[73] Cyanobacteria play a central role in polar ecosystems by contributing significantly to the nitrogen economy. Continuing ozone depletion, which affects these organisms, raises serious concerns about the already nutrient-impoverished plant communities in the Arctic.[74] Climate change can alter responses to UV through temperature-mediated effects in aquatic ecosystems, and these effects can be species-specific and are dependent on repair ability.[75]

- **Recent research continues to show that solar UV-B in conjunction with other stress factors can have detrimental effects on consumers in both marine and freshwater ecosystems**. During the Antarctic Spring, larval and juvenile forms of krill are almost always found near the surface along the ice edge, even in daylight, where they are damaged by UV-B exposure. Adverse UV-B effects on krill would be significant because of the ecological importance of the species within the Antarctic marine ecosystem. Other marine studies demonstrated that UV exposure causes mortality in Atlantic cod eggs.[76] Shark ocular systems acclimate to increased exposure to UV-B radiation by increasing UV blocking pigment in their corneal tissue.[77] Recent studies confirmed that exposure of sea urchin embryos to UV-B radiation causes a decrease in survival; a result of both direct and indirect effects.[78] In a freshwater system, a direct relationship was found between UV-B irradiance and sublethal, stressful behavioural effects in juvenile rainbow trout, although a response to UV-A could not be ruled out.[79] In addition, exposure of northern pike larvae to UV-B radiation caused DNA damage and mortality.[80] Many studies have suggested that a wide range of causes can explain amphibian declines (e.g., [81]). These causes include enhanced UV-B radiation, habitat destruction, disease, parasites, introduced exotic species, environmental contaminants and global climate change. With regards to UV-B as a causal agent, there are also reports showing that most amphibian habitats are protected from harmful levels of UV-B radiation by dissolved organic compounds (e.g., [82]).

- **Preliminary work shows a correlation between global biomass productivity in the oceans and total ozone concentration.** Biomass was assayed from ocean colour (SeaWiFS) data for the period of September 1997 to December 2003.[83] Total column ozone values were taken from the Total Ozone Mapping Spectrometer (TOMS) onboard the Earth Probe satellite.[84] In most years a small but significant reduction can be seen in the biomass of the Southern Hemisphere during the time of the Antarctic ozone hole. Satellite data of both surface solar ultraviolet radiation and chlorophyll over two decades show that increases in biologically significant ultraviolet radiation started occurring over the Southern Ocean even before the ozone “hole” was discovered.[85]

## Biogeochemical cycles

- **UV-B can enhance the biological availability and reactivity of metals in aquatic environments.** UV-B can enhance the toxicity and reactivity of metals in aquatic environments. Although essential as trace nutrients, most metals are toxic above a certain concentration threshold. In sunlit surface waters and in clouds, metals such as iron and copper usually exist in forms that are not biologically available. UV-B can alter the chemical speciation of these metals to produce forms that are available to aquatic microorganisms. In the case of iron and copper, these alterations involve UV-induced reduction of iron(III) [86, 87] and copper(II) complexes.[88] Iron and copper also can affect aquatic carbon cycling by catalyzing UV-induced oxidation of organic matter. Mercury cycling also is affected by UV exposure in aquatic ecosystems. For example, elemental mercury in brackish water is oxidized by UV to form mercuric species [89] that are precursors to toxic methyl mercury that can adversely affect human health through biomagnification in aquatic food webs.

- **Climate-related changes in continental hydrology can alter the transport of UV-absorbing substances from land to the ocean.** In Arctic systems boreal wetlands are the major source of dissolved organic matter (DOM) in streams, rivers, lakes and the coastal ocean. The coloured part of dissolved organic matter (CDOM) controls the penetration of UV into these Arctic waters. Changes in temperature and precipitation affect the concentration and discharge of DOM from boreal wetlands [90] and UV-B induces the degradation of CDOM at high latitudes.[91] Degradation of terrestrially-derived DOM in the Arctic Ocean limits its movement into the deep ocean.[92]

- **Marine sulphur emissions depend on interactions between climate-sensitive surface turbulence, UV transmission and nitrate concentrations in the surface ocean.** Oceanic emissions of dimethyl sulphide (DMS) produce particulates (i.e., sulphate aerosols) that directly and indirectly (via clouds) have a cooling effect on the marine atmosphere. New studies show that DMS concentrations can be enhanced by changes in its production during summer months in high UV, low nutrient waters such as the Sargasso Sea.[17, 93] The build-up of DMS in nitrate-rich Antarctic Ocean waters is limited by its UV-induced photooxidation.[94] These results indicate that the effects of enhanced UV-B on DMS emissions are complex and can vary from one ocean region to another.

- **Remote sensing techniques facilitate the global high resolution analysis of aquatic UV impacts on marine biogeochemical cycles**. Relationships have been developed between remotely sensed ocean colour and UV attenuation in coastal regions of the ocean. The relationships were applied to determine changes in UV penetration into the Mid-Atlantic and South-Atlantic Bight near the eastern coast of the U.S.A.[95]

- **Soil disturbance (e.g., ploughing) affects UV-B-mediated alterations in carbon utilization that occur in soil microbial communities.** Microbial communities in the rhizosphere (the soil around root systems) are necessary for plant nutrient supply. New results in upland grasslands indicate that enhanced UV-B exposure altered carbon utilization by microbial rhizosphere communities in soils disturbed to a depth of 5 cm. No changes were observed in undisturbed grasslands or unirradiated controls The changes observed in the disturbed soils were likely mediated by UV-B effects on root exudation and/or changes in litter quality.[63]

- **Methyl halide emissions from terrestrial plants are enhanced by increased temperatures.** Many terrestrial plants are known to be sources of methyl bromide and other methyl halides but little is known about the effects of environmental conditions on the emissions. A recent study indicates that emissions of methyl bromide and other methyl halides from rice plants increase with increasing air temperature.[12] Recent observations indicate that atmospheric methyl bromide concentrations are decreasing at a rate of 2.5 – 3.0 % per year.[96] However, assuming that emissions of methyl bromide generally respond positively to increased temperature, future global warming may change the current rate of decline of methyl bromide concentrations in the atmosphere.

## Air Quality

- **Confidence in models of the impact of ozone change on the oxidation capacity of the atmosphere has improved**. These refinements imply that stratospheric ozone changes have had less impact on ground level OH production than originally thought. Photolysis of ozone is a key process where ozone depletion could significantly have an impact on the oxidizing capacity of the troposphere. There is now much greater confidence in the quantification of the UV driven OH radical production.[97] This has resulted in very good agreement between chemical and spectroradiometric measurements of the photolysis rate.[98] Measurements in the lower atmosphere of UV radiation and chemical composition, including OH, now normally agree with chemical models to within measurement accuracy.[99, 100]

- **An analysis of surface-level ozone observations in Antarctica suggests that there has been a significant change in the chemistry of the boundary layer of the atmosphere in this region as a result of stratospheric ozone depletion**. Measurements of surface ozone (1975 – 2001) show a recent (since 1990) increase in the number of days when the daily ozone concentrations were greater in October – December than in June and July.[101] This is consistent with more UV reaching the earth's surface during the ozone hole, and is predicted to cause a 43% enhancement in the production of nitrogen oxides from the ice in November. Thus, the Antarctic boundary layer is estimated to be more highly oxidizing now than before the development of the ozone hole. The ecological consequences of this have not been studied.

- **The tropospheric concentration of HFC-134a, the main known anthropogenic source of trifluoroacetic acid, is increasing rapidly**. The increase is in agreement with the known usage and atmospheric loss processes. Observations in both hemispheres (Mace Head, Ireland and Cape Grim, Tasmania) between 1998 and 2002 show the concentration of HFC-134a increasing rapidly (3 picomole/mole/year).[102] The good agreement between observations and known sources and sinks gives great confidence in predictions of the environmental build-up of trifluoroacetic acid. As HFC-134a is a potent greenhouse gas, this increasing concentration has implications for climate change.[103]

- **The mechanisms of the atmospheric breakdown of hydrochlorofluorocarbons (HCFCs) have been further characterized, with some chemical intermediates more likely to be removed by clouds**. Studies on the atmospheric oxidation of the intermediate fluorinated aldehydes show that the atmospheric lifetime of these species with respect to OH oxidation is relatively long (around 18 days)[104], indicating that they are not likely to form the perfluorocarboxylic acids (PFCAs), such as trifluoroacetic acid (TFA). It is likely that these aldehydes are dissolved in cloud water and react/washout there. This mechanism may also be an additional source of $C_8$ (longer chain) PFCAs, which have low relevance to ozone depletion but have been observed to biomagnify in mammals and birds, where they may have harmful effects.[105]

- **Risks to humans and the environment from substances, such as trifluoroacetic acid and chlorodifluoroacetic acid, produced by atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are still considered minimal**. Recent studies have not identified additional environmental hazards from current environmental loadings in fresh water.[106, 107] Although the amounts of these compounds are expected to continue to increase in the future because of climate change and continued use of HCFCs and HFCs, risks for freshwater organisms and humans are judged minimal. Trifluoroacetic acid in oceans is present at concentrations of 200 ng/L and appears to have pre-industrial origins.[108] Risks to saltwater organisms are likely to be minimal as potential inputs to the oceans represent a very small proportion of the total amount already present.

## Materials

- **Several mechanistic studies on the degradation of conventionally stabilized polyethylenes by solar UV wavelengths contribute to better understanding of the photodamaging process.** Conventional light stabilizers (HALS) and carbon fillers provide synergistic photostabilization of polyethylenes exposed to solar UV wavelengths.[109] The presence of calcium carbonate filler in polyethylenes was reported to significantly lower the rate of photodamage on exposure to solar UV radiation. Where the polyethylenes were exposed to UV radiation while under mechanical stress, the rate of degradation was reported to increase linearly with stress.[110] In agricultural and building application, plastic materials are routinely subjected to stress. These findings suggest potential refinements in the estimation of outdoor lifetimes for these materials.

- **Natural polymers including wood, hair and wool are readily discoloured by solar UV-B radiation**. Semi-quantitative data on the discoloration of commercially important tropical hardwoods exposed to solar radiation[111] showed that the characteristics of wood extractives determined their susceptibility to light-induced discoloration. Studies on human hair confirm the particular damaging role of solar UV-B wavelengths; the discoloration due to the UV- B component in sunlight can be 2-5 times as high as for the combined UV-A and visible radiation in sunlight.[112] Studies on dyed wool showed that UV-induced fading occurs faster with natural dyes compared to synthetic dyes.[113]

- **New techniques aid the detection of early stages of UV-induced degradation of polymers and refinements in modelling of photodamage to materials are being developed**. New analytical techniques (positron-based)[114] are being developed to supplement the exiting approaches to characterize the early stage in photodegradation of complex substrates, such as organic coatings. Recent advances in quantifying the irradiance dependence of photodamage [115] have facilitated the development of better models to estimate UV-induced damage to materials.

- **Photodegradation studies on polycarbonates used in glazing have further clarified the mechanism of damage**. Chemical analysis of the degradation products as a function of depth in polycarbonates exposed to UV radiation revealed protective surface hardening due to crosslinking of the polymer.[116] A photoresistant copolymer grade of polycarbonate that can be used as a photoprotective surface layer on films and moulded pieces has been developed recently.[117] These findings could help in the development of polycarbonates that are more resistant to photodamage by solar UV radiation.

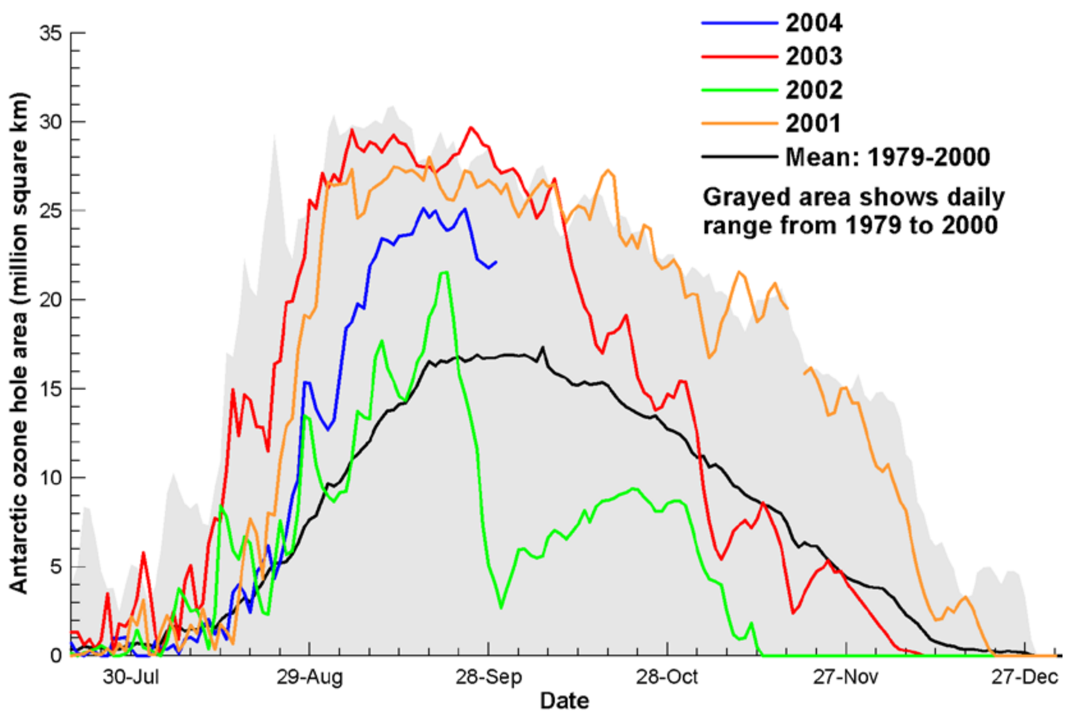


**Fig. 1** The Antarctic ozone hole area (area with $O_3$ < 220 DU) for 2001, 2002, 2003, and 2004 to date, compared with a 1979–2000 climatology. These calculations are based on the NIWA assimilated total column ozone database.

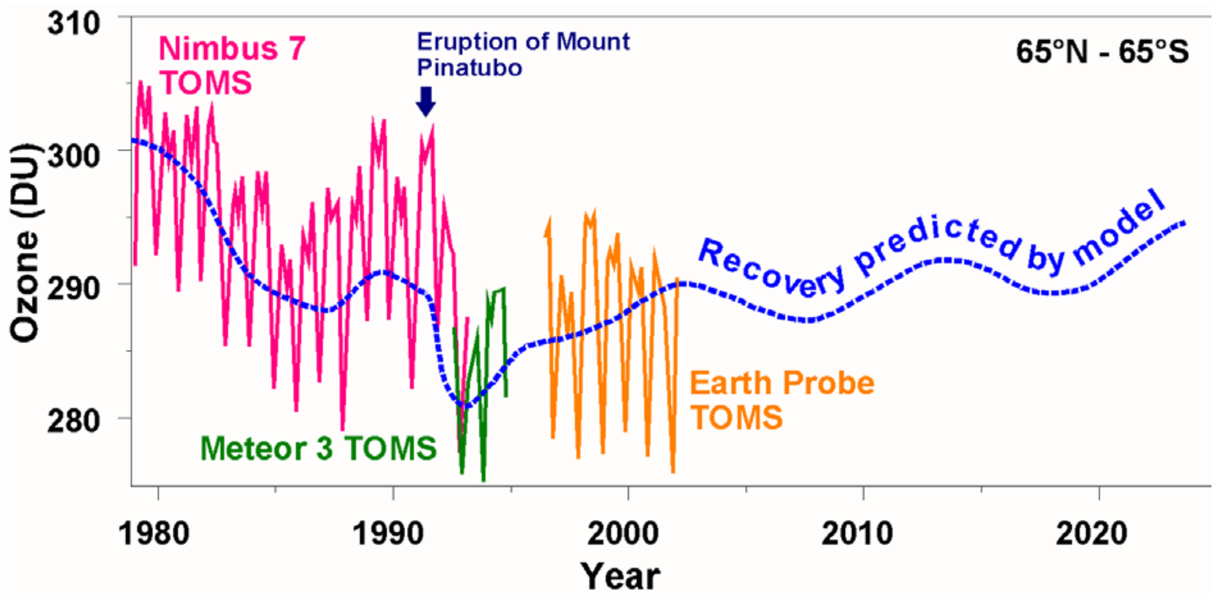


**Fig. 2**. Detection of a turnaround for ozone is difficult. The plot shows monthly averaged ozone amounts measured with satellite instruments over the past 25 years, and compares these with annual means calculated with the NASA Goddard 2D model, which is just one of several such models available. The effects of the Pinatubo volcanic eruption, the solar cycle, the annual and inter-annual cycles (e.g., from the Quasi Biennial Oscillation) are evident. These contribute to the difficulty in unambiguously detecting the recovery of ozone from the presently available data. Redrawn from Bhartia et al.[4]

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