

Madronich, S., Bernhard, G.H., Neale, P.J., Heikkilä, A., Andersen, M.P. Sulbæk, Andrady, A.L., Aucamp, P.J., Bais, A.F., Banaszak, A.T., Barnes, P.J., Bornman, J.F., Bruckman, L.S., Busquets, R., Chiodo, G., Häder, D-P., Hanson, M.L., Hylander, S., Jansen, M.A.K., Lingham, G., Lucas, R.M., Calderon, R. Mackenzie, Olsen, C., Ossola, R., Pandey, K.K., Petropavlovskikh, I., Revell, L.E., Rhodes, L.E., Robinson, S.A., Robson, Matthew ORCID: <https://orcid.org/0000-0002-8631-796X> , Rose, K.C., Schikowski, T., Solomon, K.R., Sulzberger, B., Wallington, T.J., Wang, Q-W., Wängberg, S-Å., White, C.C., Wilson, S.R., Zhu, L. and Neale, R.E. (2024) Continuing benefits of the Montreal Protocol and protection of the stratospheric ozone layer for human health and the environment. *Photochemical & Photobiological Sciences*, 23 (6). pp. 1087-1115.

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# Continuing benefits of the Montreal Protocol and protection of the stratospheric ozone layer for human health and the environment

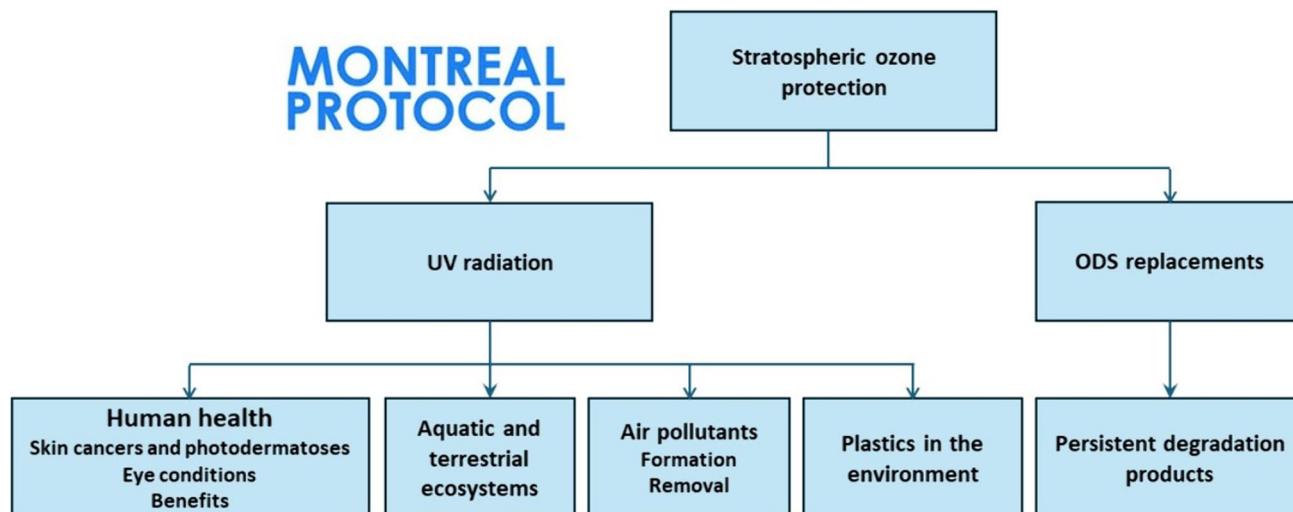
S. Madronich · G. H. Bernhard · P. J. Neale · A. Heikkilä · M. P. Sulbæk Andersen · A. L. Andradý, et al. *[full author details at the end of the article]*

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## Abstract

The protection of Earth's stratospheric ozone ( $O_3$ ) is an ongoing process under the auspices of the universally ratified Montreal Protocol and its Amendments and adjustments. A critical part of this process is the assessment of the environmental issues related to changes in  $O_3$ . The United Nations Environment Programme's Environmental Effects Assessment Panel provides annual scientific evaluations of some of the key issues arising in the recent collective knowledge base. This current update includes a comprehensive assessment of the incidence rates of skin cancer, cataract and other skin and eye diseases observed worldwide; the effects of UV radiation on tropospheric oxidants, and air and water quality; trends in breakdown products of fluorinated chemicals and recent information of their toxicity; and recent technological innovations of building materials for greater resistance to UV radiation. These issues span a wide range of topics, including both harmful and beneficial effects of exposure to UV radiation, and complex interactions with climate change. While the Montreal Protocol has succeeded in preventing large reductions in stratospheric  $O_3$ , future changes may occur due to a number of natural and anthropogenic factors. Thus, frequent assessments of potential environmental impacts are essential to ensure that policies remain based on the best available scientific knowledge.

## Graphical abstract



## 1 Introduction

The Earth's stratospheric ozone ( $O_3$ ) layer regulates the amount of ultraviolet (UV) radiation reaching the lower atmosphere and surface. Some human-made substances can destroy  $O_3$  (ozone-depleting substances, ODSs) if emitted into the atmosphere, and therefore a phase-out of their production was agreed internationally under the 1987 Montreal Protocol. The Montreal Protocol and subsequent Amendments and adjustments have limited mid-latitude  $O_3$  depletion to a few percent, and atmospheric concentrations of ODSs are expected to return to pre-1980 values by the middle of this century. However, larger changes in stratospheric  $O_3$  could occur for several other reasons under different possible future scenarios. Scenarios with large greenhouse gas emissions predict increases in stratospheric  $O_3$ , e.g., climate-dependent super-recovery with  $O_3$  values exceeding those of 1980. Other scenarios could entail further depletion, e.g., in response to attempts to modify solar radiation reaching the Earth's surface by injecting sulfur into the stratosphere [1].

Full implementation of the Montreal Protocol critically relies on regular scientific evaluations of the state of the ozone layer, UV radiation, and the associated effects of UV radiation on human health and ecosystems. Comprehensive Quadrennial Assessments reflect this evolving knowledge and constitute the scientific basis for any Amendments and adjustments to the Montreal Protocol; i.e., the recent assessments of ozone science [1] and effects on related environmental effects [2] (see also [3–11]). Annual updates assess information emerging from rapidly evolving fields and newly recognised interactions.

One important outcome of this ongoing assessment process is a move away from the notion that exposure to UV radiation is harmful in every aspect and should always be minimised. Like temperature and humidity, UV radiation is an environmental variable that increases the chemical reactivity of irradiated substances, whether these be biological tissues, materials, or atmospheric contaminants. Harmful effects—including the induction of skin cancer (Sect. 2) and cataracts (Sect. 3), formation of local photochemical smog (Sect. 5), and degradation of materials (Sect. 7) must be viewed alongside potentially beneficial effects such as production of vitamin D (Sect. 4), disinfection of surface waters, and regional/global destruction of air pollutants (also in Sect. 5). Furthermore, the phase-out of ODSs has helped to avoid additional global warming (Sect. 1.2). However, some of the chemicals used as replacements can degrade to compounds that are persistent in the environment (e.g., trifluoroacetic acid, TFA), requiring ongoing assessment of potential risks (Sect. 6).

### 1.1 The Montreal Protocol and global warming

Ozone-depleting substances controlled by the Montreal Protocol are also potent greenhouse gases (GHGs). The global warming potentials (GWPs) of ODSs are far greater than those of carbon dioxide ( $CO_2$ ), e.g., Table A-5 of [1]. Hence, the increase of ODSs in the atmosphere since their invention in the 1920s and 1930s has contributed substantially to global warming. In our 2022 Quadrennial Assessment [2, 5], we concluded that, as of 2019, the phase-out of ODSs prompted by the Montreal Protocol may have avoided warming by 0.5–1.0 °C in mid-latitude regions of the continents,

and by more than 1.0 °C in the Arctic. A new study by Sigmond et al. [12] generally confirmed these earlier estimates and concluded that ODSs were responsible for 30% of global and 37% of Arctic warming between 1955 and 2005. Taking into account all GHGs (including ODSs) plus the cooling effect from the rise of anthropogenic aerosols over this period, the modelled global mean surface air temperature (GSAT) increased by 0.95 °C between 1995 and 2005, in good agreement with observations. The warming attributed to CO<sub>2</sub> and ODSs alone was calculated as 0.63 and 0.38 °C, respectively.

In our 2022 assessment [5], we also concluded that the uncertainty in estimating changes in GSAT from changes in ODSs is large because the depletion of stratospheric ozone caused by ODSs has a cooling effect that is not well understood [5]. New calculations by Sigmond et al. [12] using a single model confirmed that the indirect impact of ODSs on GSAT via stratospheric ozone depletion is negligible due to the relatively small radiative forcing of stratospheric ozone. While some uncertainties remain, this study adds to the emerging evidence that ODSs have played a substantial role in historical warming. By phasing out the production and consumption of ODSs, the Montreal Protocol will also play a crucial role in mitigating future climate change, including reduction of the loss of polar sea ice. Several studies find that the phase-out of ODSs will delay the appearance of an ice-free Arctic summer (defined as the first year with September sea ice extent smaller than 1 million km<sup>2</sup>), by between 15 and even 40 years, depending on the model used [13, 14].

## 1.2 Extremes of the UV index

Measurements from satellites suggest that the highest UV Index on Earth is about 25 and occurs at high altitudes within the tropics of the Southern Hemisphere, such as the Altiplano Region of Peru and Bolivia [15]. Recent measurements by Cordero et al. [16] using a spectroradiometer that meets the quality standards of the Network for the Detection of Atmospheric Composition Change [17] have now confirmed this value. On 22 January 2020, measurements of the UV Index performed at the Altiplano of the Atacama Desert in Chile peaked at 25.8, which can be considered the world's highest value ever registered by a high-quality instrument. The observation occurred during partial cloudy skies when the sun was visible and clouds in the vicinity of the sun reflected additional radiation toward the instrument. This “cloud enhancement” is a well-documented effect [18]. In this particular instance, the UV Index was increased by about 30% beyond the value of 20 that would have been expected for clear skies.

These high values of the UV Index would have been greatly surpassed if the Montreal Protocol had not been implemented. According to model calculations [19], the clear-sky UV Index observed at noon during summer at mid-latitudes and the tropics would have been as high as 40 by the end of the twenty-first century in the absence of the Montreal Protocol, even before considering additional enhancements by clouds.

## 2 Exposure to ultraviolet radiation and the skin

Exposing the skin to UV radiation is the primary cause of skin cancer and can also lead to inflammatory skin conditions known as photodermatoses. The incidence of these conditions, particularly skin cancer, is influenced by the intensity of ambient UV radiation to which a population is exposed, so maintaining the integrity of the ozone layer is vital to avoid large increases in these medical conditions. While it is thus important to monitor trends in skin cancer, it is difficult to disentangle the effects of changes in ozone and sun exposure behaviour that have changed dramatically over the past century.

### 2.1 Skin cancers: malignant melanoma

#### 2.1.1 Incidence

New population-based reports on trends in the incidence of invasive melanoma in high-risk populations, including those in Canada [20], the Netherlands [21], Lithuania [22], Minnesota (United States) [23] and some Australian states [24, 25], generally report rising incidence over the past 2–3 decades. A concerning trend of rising incidence among children and adolescents was reported for Finland, with an average annual increase of 5.6% per year from 1990 to 2014 [26]. An increase in incidence of invasive melanoma was also reported for countries where the population is at lower inherent risk due to a high proportion of the population having darker skin types, including Columbia (2006–2015) [27], Brazil (1980–2019) [28], Jordan (2000–2016) [29], and South Korea (2008–2016) [30]. In contrast, incidence was stable in the state of South Australia between 1997 and 2016 [24], and in Hungary between 2013 and 2017 [31]. The cause of the increasing incidence, particularly in children and people who are at lower inherent risk, needs to be determined, but is likely to be driven by changes in behaviour and/or diagnostic practices rather than to any changes in ambient UV radiation.

### 2.1.2 Overdiagnosis as a potential contributor to increases in melanoma incidence

Melanomas that are confined to the epidermis (the top layer of the skin) at diagnosis are called melanoma in situ. Once they have invaded into the dermis they are called invasive melanomas. It is not clear how often in situ melanomas become invasive, or how long this takes. However, there is concern that a high proportion of melanomas in situ is indicative of overdiagnosis; i.e., diagnosis of a lesion that if left undetected would not have caused harm within a person's lifetime. Potential drivers of the overdiagnosis of in situ and thin melanomas include increased awareness and attendances for skin examinations, higher rates of diagnostic biopsies and a lowering of diagnostic thresholds [32].

An analysis of long-term incidence trends (1982–2018) for in situ and invasive melanomas in three predominantly white populations with high, medium, and low melanoma rates (Queensland (Australia), United States, and Scotland, respectively) reported a much faster increase in the incidence of melanoma in situ compared to invasive melanoma in all three populations; this difference was most marked in Queensland, Australia, where opportunistic screening practices are common [33]. In the United States, the incidence of melanoma in situ is rising in all areas, whereas the incidence of invasive melanoma is stabilizing in metropolitan regions but increasing in nonmetropolitan and rural populations [34]. These trends are consistent with a pattern of overdiagnosis.

At the height of the COVID-19 pandemic, fewer notifications of skin cancers to cancer registries were reported worldwide [35–37]. There may be a rebound from the observed trend of a reduction in incidence in the period immediately following the pandemic, and some have suggested that delayed melanoma diagnoses may influence future mortality rates [38].

### 2.1.3 Mortality

Mortality rates due to skin cancer reflect both incidence and survival, so mortality rates were historically highest in regions of high incidence. The past decade has seen dramatic improvements in treatment and survival for patients with localised or metastatic disease with the use of targeted and immunotherapies, which has resulted in significant reductions in melanoma mortality over the past decade.

Analysis of recent trends in melanoma mortality in the United States showed recent stabilisation in mortality rates. Rates increased between 1975 and 1988 at a rate of 1.7% per year, stabilised between 1988 and 2013, and then decreased at a rate of 6.3% per year to 2017 [39]. Stabilising or declining mortality rates were also reported for Canada [20],

Columbia [27] and the Australian state of New South Wales for all age groups under 60 years [25].

Other country-specific reports of long-term trends (e.g., decadal) in melanoma mortality generally show overall increases in mortality in recent decades, including for Italy [40], Poland [41] and Lithuania [22]. A study of trends in melanoma mortality in 28 European countries (25 member states and Norway, Russia and Switzerland) covering 6 decades (1960–2020) reported diverging trends according to age. For men and women aged 45–74 years the age-standardised melanoma mortality rate decreased in 15 countries and increased in 7. For those aged 75 years and older, mortality increased for men in all 28 countries, and for women in all except Hungary and Portugal [42]. The mortality rate was consistently higher among men compared with women and was highest in the Nordic countries. Geographic differences in mortality rates in the future will likely reflect heterogeneity in the timing of introduction and uptake of advanced new treatments across countries.

## 2.2 Skin cancers: keratinocyte cancers

### 2.2.1 Incidence

Recent reports confirm that the incidence of keratinocyte cancers continues to increase, driven largely by increases in older age groups who were not exposed to sun protection messages until later in life. The incidence of squamous cutaneous carcinoma (SCC) increased between 1990 and 2020 in the Netherlands, Scotland and Germany (Saarland/Schleswig–Holstein) at a rate of between 2.4 and 5.7% per year, with the greatest increase seen among people aged 60 years or older [43]. The incidence of basal cell carcinoma (BCC) in Sweden increased between 2004 and 2017 at an average annual rate of 2.1% per year for women and 1.4% per year for men [44]. Increases of a similar magnitude were reported for both BCC and SCC in England (2013–2019) [45] and Wales (2000–2018) [46]. Tasmania, the most southerly state of Australia, is the only state to record incidence of BCC and SCC in its registry. Incidence in Tasmania increased between 1985 and 2018 at a rate of 3% per year for BCC and 4% per year for SCC [47], and a history of multiple primary diagnoses over a 5-year follow-up period was common (ca. 30% of people had more than one skin cancer diagnosed) [48]. A trend of increasing incidence of keratinocyte cancers (BCC and SCC combined) has been reported for lower-risk countries including Jordan [29], Hong Kong [49], and South Korea [30]. Studies using the Global Burden of Diseases (GBD) database (covering 33 countries) reported that Australia and the United States had the highest incidence of both BCC and SCC in the period 2015–2017 [50], and estimated that the number of new cases of keratinocyte cancer worldwide will increase by at least

1.5 times between 2020 and 2044 [51]. It is likely that in the absence of the Montreal Protocol there would have been a larger increase in the incidence of keratinocyte cancers in some countries.

### 2.2.2 Mortality

As in the case of melanoma, keratinocyte cancer mortality rates are highest in regions of high incidence. A recent analysis of the GBD database reported that Australia had the highest mortality rate for both men and women [51]. Overall, the age-standardised mortality rate for keratinocyte cancers increased significantly between 1990 and 2019 at a rate of 0.4% per year; however, decreasing mortality was seen in some countries including Spain, Finland and Switzerland [51]. The age-standardised mortality rate for cutaneous SCC increased slightly at an average annual rate of between 1.4 and 3.2% in Germany and Scotland between 1990 and 2020, but was stable or declining in the Netherlands [43]. The number of deaths globally attributable to keratinocyte cancer in 2019 was estimated to be 56,054 [51].

## 2.3 Drug photosensitivity and skin cancer

Several oral medications are photosensitisers capable of causing inflammatory skin reactions upon exposure to UV radiation [52], with recent attention focusing on their additional potential to increase the risk of skin cancer. Mechanisms underlying this may include oxidative damage to DNA and impaired repair of DNA damage. Recent changes to warning labels for the diuretic hydrochlorothiazide from the FDA [53] and European Medicines Agency [54] also note a possible increase in skin cancer risk. However, the evidence remains uncertain due to issues in study design and evidence of publication bias. Given the frequency with which these drugs are used, further understanding of the risks posed is important.

## 2.4 Non-cancerous skin conditions

Photodermatoses are inflammatory skin conditions induced or aggravated by exposure to solar radiation. Their action spectrum depends upon, although can vary within, the specific photodermatosis. UV-A (315–400 nm) radiation, the predominant waveband in many of the conditions, together with UV-B (280–315 nm) and visible radiation are contributing to or are the main provoking waveband in some conditions. A recent systematic review and meta-analysis reported the global pooled estimated prevalence of polymorphic light eruption was 10% (95% CI 6–15%) (15 research studies,  $n = 19,287$ ) [55]. There is a dearth of prevalence studies in photodermatoses other than polymorphic light eruption, and few population-based studies (random selection of people to

be representative of the population) using doctor-diagnosed case definitions, highlighting the need for data collection, at the global level, to better understand the burden of disease they pose.

A recent study reported a prevalence of photodermatoses (based on dermatological examination) of 65% in children <18 years in six population centres exposed to mine tailings and located at over 2500 m above sea level in Peru ( $n = 594$ ) [56]. The most frequent condition (49%) was actinic prurigo, which causes severe itching and painful inflammation of sun-exposed skin, followed by scarring. Living in a region with altitude >3500 m above sea level, compared with living in a different region at 2500–3500 m above sea level, was independently associated with the risk of photodermatoses/dermatoses overall [adjusted odds ratio (aOR) = 2.76; CI 95% 1.57–4.64]. A possible explanation for the association with altitude is the higher ambient UV radiation at higher altitudes, although there could be other differences between regions.

## 3 The effects of exposing the eyes to UV radiation

The eyes are directly exposed to environmental UV radiation and are susceptible to its effects. The majority of UV radiation is absorbed as it passes through the cornea and lens, with very little reaching the posterior segment of the eye. Therefore, the harmful effects of UV radiation are generally realised in the anterior portion of the eye as cataract, pterygium, photokeratitis and cancers of the ocular surface, but there is some debate around the role of environmental UV radiation in intraocular melanoma.

### 3.1 Prevalence of cataract

Globally, cataract is the leading cause of blindness and the second leading cause of moderate to severe visual impairment in adults [57]. Cataracts are predominantly an age-related condition, being rare or uncommon under the age of 50 [58], with cumulative exposure to UV radiation playing an important role. Greater exposure to UV radiation appears to contribute to the development primarily of cortical and posterior subcapsular cataracts [59].

A systematic review and meta-analysis of studies from China (2001–2019) estimated that cataracts affect 27% of adults aged 50 years and older (ranging from 8% in 50–59 year olds; 25% in 60–69 year olds; 52% in 70–79 year olds and 78% in the 80+ age group) [60], while a recent epidemiological study of Chinese adults aged 65 years and older living in suburban Shanghai (not included in the meta-analysis) found that the prevalence of cataract overall was 57%, and prevalence of visually



significant cataract was 33% [61]. Studies re-analysing data from the GBD study have found that the age-standardised prevalence of visual impairment due to cataract has increased slightly over time from 1150 cases per 100,000 population in 1990 to 1210 per 100,000 population in 2019, although the direction of change has differed across countries. For example, there was a 20% decrease in southern sub-Saharan Africa (from 1080 per 100,000 to 860 per 100,000) but a 14% increase in East Asia (from 850 per 100,000 to 970 per 100,000). Lower-income countries remain disproportionately affected, with age-adjusted prevalence per 100,000 of 2500 in countries with a low sociodemographic index (SDI) compared to 780 in high SDI countries [58, 62, 63].

The burden of cataract in terms of disability-adjusted life years (DALYs) remains high. Analyses of the GBD data show both the number and rate of DALYs attributable to cataract have been increasing since 1990, but this trend was stable or reversed for age-standardised DALY rates, indicating these increases are largely driven by increases in the total and ageing population [62–64]. In an Iranian study investigating the burden of conditions attributable to exposure to solar UV radiation, cataract was the largest cause of DALYs, accounting for 46% of all DALYs attributable to exposure to UV radiation (i.e., 15.9 DALYs per 100,000 population [64]).

### 3.2 The burden of pterygium

Pterygium is a common eye condition associated with exposure to UV radiation that infrequently leads to loss of vision but still places a high burden on healthcare systems. A study of over 12,000 adults aged 40 years and older in India found the prevalence of pterygium to be 20% in a Southern coastal area and between 9 and 11% in a Northern inland area [65]. This difference could be driven by either, or both, latitudinal differences in ambient UV radiation and increases in ocular exposure to UV radiation associated with reflective environmental surfaces, such as the ocean [66]. Pterygium accounts for only 0.5% of all DALYs attributable to solar UV radiation in Iran (0.02 DALYs per 100,000 population). Despite this, pterygium still places a significant burden on health care systems. In a nationwide retrospective study of all hospital admissions in China there were over 300,000 pterygium excisions in the year 2019, accounting for 7.8% of all inpatients admitted for ophthalmology services [67].

### 3.3 Ocular tumours

Superficial tissues of the eye can develop tumours, including ocular surface squamous neoplasia (OSSN) affecting

the cornea and/or the conjunctiva, and rarely, conjunctival melanoma. Tissues deeper in the eye can also develop tumours, including: uveal melanoma affecting the iris, choroid, or ciliary body, intraocular lymphoma, retinoblastoma, and hemangioma. Several studies have highlighted the possible, but limited, coexistence of pterygia and OSSN with 0.3, 0.6, and 3.6% of excised pterygia specimens found to contain OSSN upon histopathology in Canada, the United Kingdom and the United States of America (Texas), respectively [68–70]. This indicates both that pterygia are not necessarily benign and that some proportion of OSSN is likely to have similar risk factors (e.g., excessive UV radiation exposure) to those of pterygium. OSSN remains an uncommon condition, with previous reports indicating higher incidence in the southern hemisphere (2.8 per 100,000 in Brisbane, Australia) compared to the northern hemisphere (0.05 per 100,000 in the United Kingdom) [71]. A recent study from the Waikato region of northern New Zealand estimated the annual incidence of OSSN in 2020 to be 3.7 per 100,000 [71], comparable to the previously reported annual incidence in this region from 2010 to 2019 of 2.1 per 100,000.

Uveal melanoma is the most common intraocular tumour, primarily found in Caucasian populations. Uveal melanoma has a high tendency to metastasize, particularly to the liver; the 5-year relative survival of 80–85% has not changed over the last three decades [72, 73]. Unlike cutaneous melanoma, the role of UV radiation in the aetiology of uveal melanoma is debated [72]. Despite sharing similar risk factors, including light skin phenotype and genetic predisposition, there are distinct epidemiological differences including in age of onset, gender distribution, and trends over time and location. The analyses of nationwide cancer registries from Canada [74] and Australia [73] identified uveal melanoma incidence of 6.4 and 7.6 cases per million population, respectively. A meta-analysis and systematic review estimated annual uveal melanoma incidence to be 5.7 and 7.3 cases per million population in North America (predominantly the United States) and Europe, respectively [75]. The incidence of uveal melanoma in South Korea and Japan was lower at ca. 0.5 cases per million population per year [75].

Different locations report very different trends over time. For example, incidence of uveal melanoma increased between 2005 and 2017 in Canada but decreased over this same period in Australia. Similarly, incidence decreased in North America between 1970 and 2015 but was stable in Europe between 1950 and 2015 [75].

## 4 Benefits of sun exposure

Exposure to solar radiation confers a number of benefits, with the specific wavelength underpinning the effect often still undefined. Exposure to UV-B radiation initiates the synthesis of vitamin D in the skin, which may have wide-ranging effects on health in addition to musculoskeletal health. Both UV-B and UV-A irradiation also modulate the immune system through interactions with other chromophores in the skin. Exposure to non-UV wavelengths may also have health benefits, including through effects on circadian rhythms and melatonin production. Disentangling the mechanism underpinning associations between measures of sun exposure and health outcomes is challenging but vitally important. If the primary mechanism by which sun exposure promotes health benefits is via vitamin D, a reasonable public health message would be to avoid the sun and meet vitamin D requirements through supplementation. However, if exposure to UV radiation has other benefits this would not be the complete answer. Research is ongoing but this issue is not yet resolved.

### 4.1 Sun exposure and mental health

There is consistent evidence that higher sun exposure (various self-reported measures) plays a role in improved mental health, including for generalised anxiety disorder [76], depression [77, 78], and self-reported stress [79, 80]. One study found evidence of an association between sunlight exposure and self-reported perceived stress only in physically active individuals [80] and a systematic review similarly found that moderate physical activity, along with exposure to sunlight and green space was optimal for mental health [81]. However, most studies are cross-sectional so reverse causality cannot be excluded, with longitudinal studies showing somewhat inconsistent results.

### 4.2 Sun exposure and physical health

#### 4.2.1 Metabolic disorders

Exposure of the skin to UV-B radiation leads to higher circulating levels of the appetite stimulant ghrelin and enhanced lipid and steroid metabolism in males, but not females [82]. That is, the skin is acting as a dermato-endocrine organ, sensitive to UV radiation. A large study in China found that the increased risk of obesity associated with higher levels of ambient air pollution (PM<sub>2.5</sub>, particulate matter smaller than 2.5  $\mu\text{m}$ ) was particularly strong in the group with the lowest sun exposure. Higher lifetime and recent sun exposure were associated with lower mean

intima-media thickness of the carotid artery, a subclinical marker of cardiovascular disease in middle-aged women [83], supporting a beneficial effect of sun exposure on cardiovascular disease.

#### 4.2.2 Kidney disease

In data from the UK biobank, longer time spent outdoors ( $\geq 4$  h compared to  $< 2$  h) at baseline in people without prior acute kidney injury was associated with lower risk of new-onset acute renal failure over a median of 12 years of follow-up in older adults (mean age 56.4 years) [84].

#### 4.2.3 Myopia

Myopia (short-sightedness) continues to be a large-scale health problem in many countries. A recent study of over 700,000 children and adolescents in southern China found that ca. 85% of final-year school students have myopia [85]. A randomised controlled trial has confirmed that interventions to increase children's exposure to sunlight through spending time outdoors decrease the risk of myopia [86]. Observational analysis of data from wrist-mounted light meters worn for the 2nd year of the trial showed a dose-dependent decrease in myopia incidence and increasing progression with increasing time spent outdoors and increasing luminance. Compared to participants spending  $< 90$  min outdoors per day on average, participants who averaged 3–4 h outside per day had half the risk of incident myopia (17.3 vs. 8.3%, respectively) and almost half the amount of myopia progression [86]. It is likely that the beneficial effect of solar radiation on myopia occurs through exposure of the retina to higher levels of visible light, and that UV radiation does not play a direct role in this association [87]. However, by avoiding increases in UV radiation, the Montreal Protocol may have facilitated time outdoors in many locations, avoiding larger increases in the incidence of myopia.

### 4.3 Health effects of vitamin D

Exposing the skin to the sun produces vitamin D, and evidence is continuing to emerge indicating an important role for vitamin D in health in addition to the established benefits for musculoskeletal health. The wavelengths that produce vitamin D are the same as those that are most harmful to the skin, so balancing the harms and benefits of sun exposure is challenging. However, by protecting the ozone layer the Montreal Protocol has avoided large increases in the intensity of UV radiation that would have increased the difficulty in finding this balance.



### 4.3.1 Vitamin D and diseases related to autoimmunity

The observation that the active form of vitamin D beneficially modulates the systemic immune response is borne out by a Mendelian randomisation (MR) study nested within the large-scale UK Biobank [88]. Higher genetically predicted 25(OH)D concentration was associated with reduced risk of autoimmune diseases driven by auto-inflammatory processes (primarily psoriasis, ulcerative colitis and Crohn's disease) but not those driven by auto-immunity processes (primarily rheumatoid arthritis, Graves' disease (hyperthyroidism), coeliac diseases and polymyalgia rheumatica). For specific disease outcomes, there were protective associations with psoriasis and systemic lupus erythematosus, although for the latter, the case numbers were small. Randomised controlled trials have demonstrated a beneficial effect of vitamin D supplementation, when analysing all autoimmune diseases, not separated according to underlying pathological processes, but dominated in case numbers by autoimmune thyroid disease [89].

Higher sun exposure appears to be associated with a lower risk of developing multiple sclerosis (MS) and with less severe disease, but only in people living at latitudes greater than 40°, whereas there is no significant association for those living at lower latitudes [90]. The mechanism underpinning the association with MS is not entirely clear. Vitamin D supplementation does not appear to reduce MS risk [91] or risk of relapse [92]. However, Mendelian randomisation (MR) studies indicate an inverse association between genetically predicted 25-hydroxy vitamin D concentration and risk of MS [93, 94], suggesting that vitamin D production is likely to be at least partly responsible for the link between sun exposure, latitude, and MS.

### 4.3.2 Vitamin D and musculoskeletal health outcomes

It has been hypothesised that exposure to air pollution could increase the risk of fracture by reducing UV-B-induced synthesis of vitamin D. A study based on the UK Biobank cohort found that participants living in places in the highest air pollution quintile had a 15% increased risk of fracture (95% CI 9–22%), and that 5% of this increased risk was mediated by 25(OH)D concentration [95].

A large ( $n = 21,310$ ) Australian randomised placebo-controlled 5-year trial of vitamin D supplementation in older adults (the D-Health Trial) did not find any overall beneficial effect on fracture [96]. However, an effect emerged ca. 3 years after randomisation, and the hazard ratio at 5 years was 0.83 (95% CI 0.69–0.99). These findings are somewhat inconsistent with those of another similar 5-year trial in the United States, which found no effect [97], but due to the use of self-report to capture fracture outcomes it is possible that the results of the United States trial are biased.

### 4.3.3 Vitamin D and cardiovascular disease

Vitamin D has effects on several physiological processes that suggest a potential beneficial effect on cardiovascular disease. Observational studies have consistently shown that low 25(OH)D concentration is associated with increased risk of cardiovascular disease, and MR studies suggest that this association may be causal [98]. The D-Health Trial also found some evidence that 5 years of vitamin D supplementation may reduce the risk of major cardiovascular events, particularly in people taking medications to treat high cholesterol or other cardiovascular conditions at baseline [99]. It is possible that these were chance findings but they nevertheless support the notion that vitamin D has effects beyond musculoskeletal health.

### 4.3.4 Prevalence of vitamin D deficiency

Many studies have been published over the past year showing high prevalence of vitamin D deficiency [defined as  $25(\text{OH})\text{D} < 50 \text{ nmol L}^{-1}$ ] in a wide range of populations across much of the world. However, many of these studies have methodological issues so may not give reliable estimates of the prevalence of vitamin D deficiency in the relevant populations. Issues include the use of study samples that are not representative of the relevant population (e.g., convenience samples such as blood samples collected during routine clinical care, where there may have been a clinical indication for vitamin D testing), non-standardised 25(OH)D assays where data on precision, accuracy or both are not provided, and not reporting the season of blood draw. For example, in a meta-analysis of the prevalence of vitamin D deficiency in pregnant women in Indonesia, studies that used an ELISA assay ( $n = 4$ ) returned a lower prevalence of vitamin D deficiency of 52% compared to all assays combined (63%) [100]. In another meta-analysis, more recent studies reported lower prevalence of vitamin D deficiency than older studies [101], possibly relating to assay issues or greater awareness of the need for sun exposure and/or supplementation to maintain optimal vitamin D status.

Several studies note the high prevalence of vitamin D deficiency in infants, children and adolescents in the WHO Eastern Mediterranean [102–105] and South East Asian regions (see Table 1). This is likely attributable to the use of covering clothing and sun avoidance in these regions. A study from Bahrain found that 29% of the children aged 10–19 years reported no sun exposure, 30% reported sun exposure at least once per week, and 41% reported daily sun exposure [102]. In addition, 4.4% of these children wore clothing that covered their whole body including the face, 4.1% of their whole body except the face, 58% of their whole body, except the face and hands, and 33% wore clothing

**Table 1** Prevalence of vitamin D deficiency (VDD) in recent studies

Location	Population	N	Assay used	Definition of VDD (nmol L <sup>-1</sup> )	Prevalence
<i>MIDDLE EAST</i>					
Saudi Arabia <sup>a</sup>	Infants and children <2 years old admitted to hospital for any acute condition	484	Diasorin chemiluminescence immunoassay (Liaison)	<50	25%
Kabul <sup>b</sup>	Children and adolescents aged 1 month to 18 years old who attended acute medical care	4008	Chemiluminescence immunoassay (Biomerieux, mini VIDAS, Paris, France)	<75 <25 <50 <75	71% 37% 66% 84%
Bahrain <sup>c</sup>	Children and adolescents 10–19 years old selected from five health centres in different regions	383	Abbott Architect chemiluminescence immunoassay	<50	92%
Al Ain, UAE <sup>e</sup>	Adult (18+ years) female immigrants from Arab and South Asian countries	550	Diasorin radioimmunoassay	<50	Boys: 96% Girls: 88% Arab 87% South Asian 83%
Iran <sup>d</sup>	Healthy Iranians, all ages	87 studies	Multiple	<50	Adults (18+ years) Men: 39% Women: 51% Pregnant women: 69% Infants: 3%–86%
Birjand, Iran <sup>e</sup>	Elderly (60+ years)	1325	Beckman ELISA	<50 <75	28% 49%
<i>ASIA</i>					
India <sup>f</sup>	Indian Comprehensive National Nutrition Survey 2016–2018	11,041 13,482 13,065	Direct competitive chemiluminescent immunoassay (Advia Centaur XP, Siemens)	<30	1–4 years: 14% 5–9 years: 18% 10–15 years: 24% 63%
India <sup>g</sup>	Children aged 5–18 years old	2500	LC-MS/MS (standardised) on dried blood spots	≤50	Overall: 56%
Karachi, Pakistan <sup>h</sup>	Individuals referred from the outpatients department, mean age 38 years	26,750	Roche Cobas e411 electro-chemiluminescence immunoassay	<50	≤5 years old: 47% 6–12 years old: 65% 13–18 years old: 71% 19–50 years old: 59% >50 years old: 45%
Sunsari and Morang districts, Nepal <sup>i</sup>	18–65 years	324	Chemiluminescence immunoassay	<50	56%
Indonesia <sup>a</sup>	Children ≤19 years old—meta-analysis	5870, 7 studies	Multiple	<75	33%
Indonesia <sup>j</sup>	Pregnant women—meta-analysis	830, 6 studies	Multiple	<50	63%
<i>SOUTH AMERICA</i>					
South America <sup>e</sup>	Adults 18+ years: meta-analysis	223,778, 79 studies	Multiple	<50	35% 10°N to 10°S: 22% 11°S to 30°S: 30% 31°S to 50°S: 50%

Table 1 (continued)

Location	Population	N	Assay used	Definition of VDD (nmol L <sup>-1</sup> )	Prevalence
Brazil <sup>l</sup>	Healthy adults	1004	Chemiluminescence assay (Roche Diagnostics), DEQAS-certified	<50	Overall: 15% Salvador (13S): 12% Sao Paulo (24S): 21%
Brazil <sup>m</sup>	Children <5 years old; Brazilian National Survey on Child Nutrition	8145	Chemiluminescent immunoassay	<50	Curitiba (49S): 13% Overall: 4% 6–23 months: 2% 24–59 months: 5% South: 8% Southeast: 7% North: 1% Northeast: 1% Winter: 7% Spring: 7% Summer: 1%
AFRICA					
Cape Town, South Africa <sup>n</sup>	children, median age 9.3 years, from a disadvantaged mainly black area	1825	LC-MS/MS assay, DEQAS certified	<50	7.60%

<sup>a</sup>[104]; <sup>b</sup>[103]; <sup>c</sup>[102]; <sup>d</sup>[105]; <sup>e</sup>[110]; <sup>f</sup>[111]; <sup>g</sup>[112]; <sup>h</sup>[113]; <sup>i</sup>[108]; <sup>j</sup>[100]; <sup>k</sup>[101]; <sup>l</sup>[114]; <sup>m</sup>[109]; <sup>n</sup>[106]

that covered their whole body except for their face, hands, and feet.

The importance of sun exposure for maintaining vitamin D adequacy, particularly in people with deeply pigmented skin, is also highlighted in two reports from Africa. In a study set in a disadvantaged area of Cape Town with a population that is predominantly black, the prevalence of vitamin D deficiency was low (see Table 1); over 90% of children spent >2 h outside during daylight hours, and most (88%) had arms, legs, face and hands exposed when outdoors [106]. Nevertheless, in a study from Ethiopia, where one child in thirteen has rickets, over half of the mothers of infants attending immunisation clinics (51%) thought that sunlight exposure may have harmful effects on infants. One-third of mothers did not have ‘good practice’ of infant sunlight exposure, defined as 30 min per week starting from 6 weeks of age [107]. This highlights the importance of tailoring sun exposure messages to the population—most of these infants would be at very low risk of sun-induced skin cancers, but at very high risk of the effects of vitamin D deficiency. However, the mothers had absorbed a message that ‘the sun is harmful’.

The relationship with time of day for sun exposure for optimal vitamin D status is sometimes unexpected. In the Sunsari and Morang districts of eastern Nepal (26°N), adults (18–65 years) who had their sun exposure between 06:00 and 09:00 were more likely to be vitamin D sufficient compared to those having sun exposure later in the day—the latter used umbrellas to shade themselves from the sun, stayed in the shade and used transport rather than walking to shelter themselves from the hot sun [108].

A strong latitudinal gradient of increasing prevalence of vitamin D deficiency with more southerly latitude was noted in a meta-analysis of 79 studies from South America [101]. A similar latitude gradient, despite much lower prevalence, was observed in the Brazilian National Survey on Child Nutrition [109] (see Table 1). It is important to note, however, that the differences may not be entirely due to differences in exposure to UV radiation, with differences in other factors such as body mass index and use of dietary supplements potentially also contributing.

## 5 Effects of UV radiation on air and water quality

### 5.1 Tropospheric ozone

#### 5.1.1 Impacts of tropospheric ozone on human health

Tropospheric ozone (O<sub>3</sub>) is a toxic gas generated when mixtures of some common air pollutants, e.g., nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs), are exposed

to solar UV radiation. Tropospheric O<sub>3</sub> can affect human health by impairing respiratory and cardiovascular function [115, 116]. New evidence suggests that exposure to concentrations of tropospheric O<sub>3</sub> even below the current US Environmental Protection Agency’s National Ambient Air Quality Standard may have adverse effects on lung function, especially of children [117]. A nationwide study from China showed that long-term exposure to O<sub>3</sub> contributes to elevated risks of cardiovascular mortality, particularly from ischemic heart disease [118]. Both studies point to the large sensitivity of populations to changes in tropospheric O<sub>3</sub>. UV-B radiation has a central but complex role in the formation of tropospheric O<sub>3</sub>. As discussed in detail in the 2022 Quadrennial Assessment [8], tropospheric O<sub>3</sub> depends on UV-B radiation for its formation in urban settings (high NO<sub>x</sub>), and for its removal in more remote areas (low NO<sub>x</sub>). This fact presents additional challenges in evaluating the net effects over large populated geographic areas.

#### 5.1.2 Future trends in tropospheric ozone

Future trends in tropospheric O<sub>3</sub> will depend not only on levels of UV-B radiation, which are affected by stratospheric O<sub>3</sub>, but also on emissions of precursor pollutants including NO<sub>x</sub>, carbon monoxide (CO), methane (CH<sub>4</sub>) and other volatile organic compounds (VOCs). These emissions will depend on the future socioeconomic factors. Recent modeling studies using future scenarios from two shared socioeconomic pathways (SSPs), the middle-of-the-road (SSP2-4.5) and fossil-fuelled (SSP5-8.5) scenarios, examined the evolution of tropospheric ozone from 2020 to 2100 [119]. The SSP2-4.5 scenario shows a slight increase (<1 Dobson Unit, DU) in tropospheric ozone until 2030, followed by a decline due to decreasing emissions of NO<sub>x</sub> and CO. The SSP5-8.5 scenario shows increasing tropospheric O<sub>3</sub> for the next half century, with a predicted decline beginning in 2060 when concentrations of NO<sub>x</sub> and CO are expected to decline. Compared to 2020, the peak tropospheric O<sub>3</sub> in 2060 for the SSP5-8.5 scenario is ca. 10–20% (ca. 5 DU) above current values.

#### 5.1.3 Changes in transport of stratospheric ozone to the troposphere

Stratospheric ozone (O<sub>3</sub>) contributes a substantial fraction of the O<sub>3</sub> in the troposphere, about 26% globally according to some estimates [120], through stratosphere–troposphere exchange. Changes in stratospheric O<sub>3</sub> could play an important role in changes in concentrations of O<sub>3</sub> at ground level in the future. Ozone transport into the troposphere due to stratosphere–troposphere exchange has been estimated to increase globally by 4.7% per decade during the twenty-first century, with a third of this due to the increase

in stratospheric O<sub>3</sub> resulting from the phase-out of ODSs [121]. The remainder of the change in O<sub>3</sub> transport is due to climate-change induced variations in the Brewer–Dobson circulation. Quantifying the processes that transport O<sub>3</sub> from the stratosphere to the troposphere is a challenge, as it is not well documented by observations. Models produce a wide range of estimates of the magnitude of this transport (e.g., 28–481 Tg O<sub>3</sub> year<sup>-1</sup> [122]). Using observations of the vertical distribution of other trace gases gives an estimate of 400 ± 60 Tg year<sup>-1</sup> [123] for 2010. An analysis of satellite measurements of O<sub>3</sub> and meteorological reanalysis models (atmospheric circulation models constrained by observations) has predicted a net transport of 347 ± 12 Tg O<sub>3</sub> year<sup>-1</sup> ([124]) into the troposphere. Quantification of the factors that control amounts of O<sub>3</sub> in the lower stratosphere remains a significant challenge [125].

## 5.2 UV radiation and the self-cleaning capacity of the troposphere

### 5.2.1 Trends in the UV-induced self-cleaning capacity of the atmosphere

A beneficial effect of UV-B radiation is the generation of hydroxyl radicals (OH) via the photolysis of tropospheric O<sub>3</sub> by UV-B radiation. Hydroxyl radicals play a key role in the degradation of tropospheric pollutants. A recent modelling study [126] found that the tropospheric air-mass-weighted concentration of OH has increased by ca. 5% globally from 1980 to 2014. This compares reasonably well with earlier studies that estimated an 8% increase between 1980 and 2010 [127]. Changes in emissions of NO<sub>x</sub> (a source of OH) and methane (CH<sub>4</sub>, a sink of OH) dominated the modelled global trend in OH, while emissions of CO from natural sources and meteorology were also important for regional trends in concentrations of OH. Emissions of CO from biomass burning were responsible for the occurrence of a region with low OH concentrations over the Indian Ocean in April (based on a measurement-constrained model over 2005–2018), with interannual variability driven by the El Niño Southern Oscillation [128].

### 5.2.2 UV photolysis of particulate nitrate and the global tropospheric oxidising capacity

The UV-driven photolysis of gas-phase nitrate (HNO<sub>3</sub>) is an important source of NO<sub>x</sub> and OH radicals in remote regions [129], but this process is rather slow due to the small UV absorption cross section of gaseous HNO<sub>3</sub>. Accumulating evidence indicates that the absorption cross-section of HNO<sub>3</sub> increases when this molecule is bound to a particle, resulting in more rapid production of NO<sub>x</sub> and nitrous acid (HONO), which rapidly photolyzes to yield OH and further

NO [130–132]. Observations of HONO above the tropical Atlantic Ocean [133] could only be explained by enhanced photolysis of particle-bound nitrate, with enhancement factors (relative to gas phase photolysis) ranging from 1 to 1000, depending on environmental and chemical conditions. In a modelling study of the contiguous United States, inclusion of nitrate photolysis (with enhancement factors limited between 10 and 100) led to an increase of the background (free tropospheric) vertical NO<sub>2</sub> column of 12% on an annual basis and 25% during springtime [134, 135], bringing it into better agreement with satellite-based observations. Thus, UV photolysis of nitrate may be playing a role in both continental and marine NO<sub>x</sub> budgets, with implications for the global oxidising capacity of the troposphere. Sensitivity to future changes in UV-B radiation (e.g., due to changes in stratospheric ozone) depends on spectral dependence of these enhancements, which remain largely unknown for nitrate bound to various aerosols. By comparison, photolysis coefficients for gaseous HNO<sub>3</sub> and aqueous nitrate are estimated to increase by 0.8 and 0.6%, respectively, for every 1% decrease in stratospheric ozone [136].

### 5.2.3 UV-induced production of OH and other reactive oxygen species in the condensed phase

In the troposphere, UV-induced transformation of pollutants also takes place in the condensed phase. For example, modelling indicated that ca. 25% of the oxidation of SO<sub>2</sub> emitted from a mid-tropospheric volcanic plume occurred in the tropospheric aqueous phase [137]. Furthermore, laboratory experiments found that the rate of oxidation of SO<sub>2</sub> to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was ca 19-fold faster in aqueous microdroplets than in the aqueous bulk phase [138]. As in the gas-phase, the major oxidants in the atmospheric condensed phase are OH and other reactive oxygen species (ROS, e.g., peroxides). A potentially important pathway producing ROS in cloud and fog droplets is the UV-induced redox cycling of iron compounds [138]. Iron-containing aerosols have also been shown to catalyse the transformation of organic aerosols from biomass burning into UV-absorbing secondary organic aerosols (SOA) [139]. SOA can then act as photosensitisers for the production of singlet oxygen (<sup>1</sup>O<sub>2</sub>), a highly reactive oxygen species [140], and are 4 times more efficient in producing this ROS than the aerosols directly emitted from biomass burning.

In addition to producing ROS, UV irradiation of iron-containing particles can have important consequences for ocean productivity. There are various sources of iron emitted to the troposphere, including biomass burning and desert dust [141]. The particulate iron released from these sources is transformed into more soluble and bioavailable iron via UV-induced redox cycling, before being deposited to the oceans. Model calculations using the socioeconomic

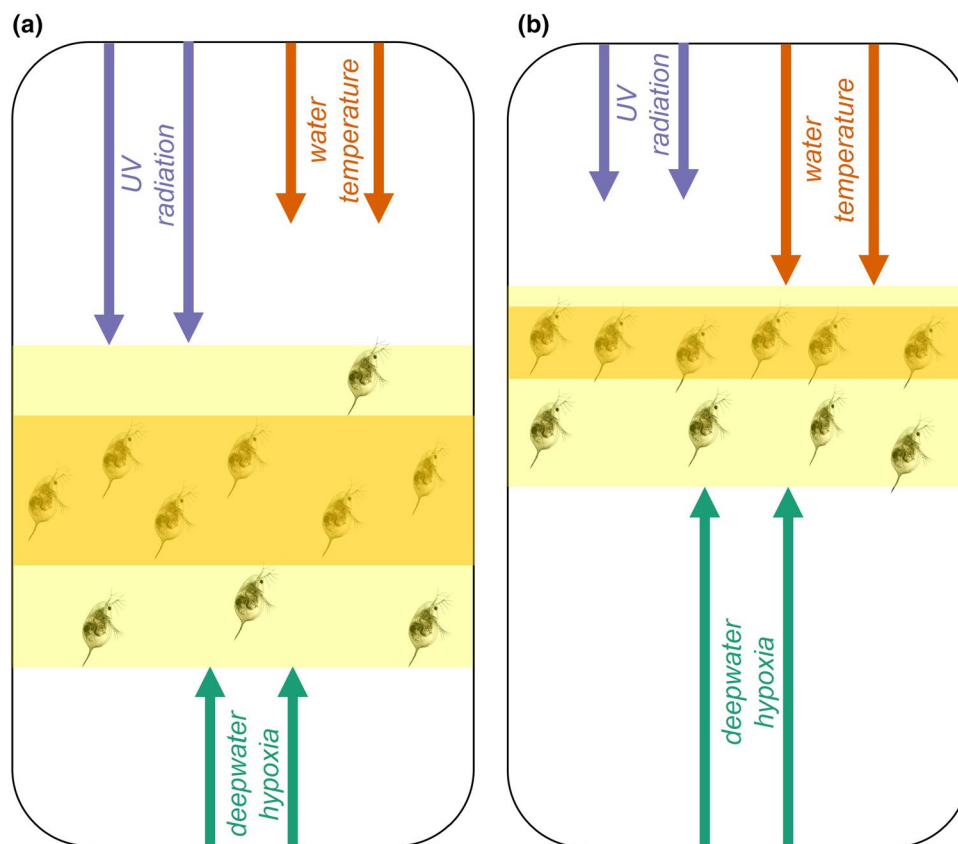


pathway SSP4.5 predict an increase in the deposition of bioavailable iron to the Southern Ocean between 63 and 95% between now and 2100, mainly driven by fires [141]. Tang et al. [142] observed an exceptional phytoplankton bloom in the Southern Ocean from December 2019 to March 2020 as a consequence of the 2019–2020 Australian wildfires. Hence the UV-induced redox cycling of iron in cloud and fog droplets can affect the environment by increasing the oxidation capacity of the troposphere and enhancing the bioavailability of iron to phytoplankton.

### 5.3 Climate change and exposure of aquatic organisms to UV radiation

Climate change is altering exposure of aquatic organisms to UV radiation in multiple ways, and this is especially important for plankton that are confined to the upper (warmer)

part of lakes and oceans. For example, shallowing of the surface mixed layer increases exposure, whereas deepening of mixed layers and browning reduce exposure [9]. Browning is the darkening of surface waters due to increased inputs of coloured dissolved organic matter. A recent study proposes a conceptual model on how the combination of global warming and browning shifts the habitable depth range of zooplankton, key organisms in the aquatic food web of lakes [143]. The upper depth of suitable habitat in clear lakes is determined by the vertical penetration of UV radiation (Fig. 1a), which can affect some zooplankton that are sensitive to UV irradiation. With the ongoing browning of inland waters, there is a reduction in penetration of UV radiation that could allow these zooplankton to spread to shallower waters (Fig. 1b). However, they now face an increased threat from climate warming, which makes these shallow waters too warm, i.e., above the maximum thermal



**Fig. 1** Conceptual diagram of the three abiotic variables that can define the boundaries of vertical suitable habitat for *Daphnia*, a species of freshwater zooplankton that is 1–5 mm in size. Abiotic constraints include UV radiation in the surface waters (purple), warm temperatures in the surface waters (orange), and lack of oxygen (hypoxia) at depth (green). The vertical span between these three limiting variables constitutes the theoretically suitable habitat (light yellow) for this species, based on these abiotic factors. The thermally optimal habitat is represented by dark gold bands, which may or may not fall within the suitable habitat. **a** In clear lakes, especially dur-

ing spring to early summer, UV radiation in the surface waters is of relatively greater importance in setting upper habitat boundaries compared to warm water temperature, and deep-water hypoxia is of less importance in setting the bottom boundaries. **b** In low transparency lakes, or lakes in mid- to late-summer, warm surface water temperatures have relatively greater importance than UV radiation in creating upper habitat boundaries, and deep-water hypoxia is more important in creating the lower habitat boundary. Reprinted from Pilla and Williamson [143] (colour figure online)

optimum for zooplankton. Meanwhile, the lower depth of habitability is being pushed shallower due to warming-induced depletion of deep-water oxygen (hypoxia), resulting in a vertical habitat squeeze (yellow bands in Fig. 1). Hence, the overall projection for lakes undergoing browning is that zooplankton will be less vulnerable to increases in incident UV-B radiation, yet this will have limited benefit since they will have smaller suitable habitat overall. Changes in the distribution and abundance of zooplankton can have wide reaching effects on lake ecosystems, as these millimetre size organisms are the primary diet of many fish species. On the other hand, oceans are less affected by browning, and changes in exposure to UV radiation among marine plankton are projected to be more related to other factors, such as changes in mixing depths and ice cover [9].

## 6 Trends in trifluoroacetic acid and other short-chain perfluorocarboxylic acids from the atmospheric degradation of chlorofluorocarbon replacements

Trifluoroacetic acid (TFA) is the terminal breakdown product of some fluorinated chemicals used as replacements for ODSs, including hydrofluorocarbons (HFCs), hydrofluoroethers and halogenated olefins (HFOs). Our knowledge of the formation of TFA from the atmospheric degradation of these chemicals continues to improve. Recent measured depositional fluxes of TFA are consistent, within the uncertainties, with regional estimates of formation from precursors of TFA related to the Montreal Protocol. Perfluoropropanoic acid (PFPrA) and perfluorobutanoic acid (PFBA) are other persistent breakdown products formed by some chlorofluorocarbon (CFC)-replacements and have been measured recently in the environment. The human health risks for these two compounds have been assessed and they are more toxic than TFA to mammals; however, their associated environmental risks are less well understood than those for TFA (see Sect. 6.5).

### 6.1 Update on the chemistry of precursors to TFA related to chemicals under the purview of the Montreal Protocol

Some atmospheric transformation products of CFC-replacements are precursors of TFA through hydrolysis of acyl halides, e.g.,  $\text{CF}_3\text{CFO}$ , or via secondary photochemistry of trifluoroacetaldehyde ( $\text{CF}_3\text{CHO}$ ). Currently, the fate of  $\text{CF}_3\text{CHO}$  is thought to be dominated by photolysis resulting in  $\text{CF}_3$  and  $\text{HCO}$  radicals. Reaction with OH radicals and interaction with liquid water are considered

minor sinks [8]. A recent modelling study using updated atmospheric photolysis coefficients of  $\text{CF}_3\text{CHO}$  gives a photolytic lifetime for  $\text{CF}_3\text{CHO}$  of  $13 \pm 4$  days (at 5 km altitude in the tropics) [144], which is significantly longer than the previous estimate of 2–3 days [145]. Further studies are needed to confirm these findings. However, a longer photolytic lifetime would translate into higher molar yields of TFA from  $\text{CF}_3\text{CHO}$  [146], and increase the potential importance of interaction of  $\text{CF}_3\text{CHO}$  with liquid water in the atmosphere. Furthermore, recent theoretical computations indicate that reaction with  $\text{HO}_2$  could be an important sink for  $\text{CF}_3\text{CHO}$  in the atmosphere [147]. This reaction would produce the  $\alpha$ -hydroxy trifluoroethyl peroxy radical,  $\text{CF}_3\text{CH}(\text{OH})\text{OO}$ , which may undergo further processing in the atmosphere to yield TFA. There are no reported experimental kinetic data for the reaction of  $\text{HO}_2$  with  $\text{CF}_3\text{CHO}$ , and its atmospheric importance is unclear.

### 6.2 Sources of TFA that are not under the purview of the Montreal Protocol

As noted previously [8], there are sources of TFA to the environment other than from the ODSs and replacement compounds that are under the purview of the Montreal Protocol. Natural sources were suggested in the 1990s (see discussion in [148]) but this has been questioned [149]. An extensive inventory of the use of fluorine-containing minerals in industry from the 1930s to 1999 [150] showed that these uses could not explain the amounts of TFA reported in the oceans in the late 1990s and early 2000s. This suggests that there are geogenic (natural) sources that are not yet fully understood. Other sources of TFA are waste streams from the manufacture of fluorinated compounds, and the release and breakdown of pharmaceuticals and pesticides in the environment that contain a  $-\text{CF}_3$  moiety (see [8]). The contribution to TFA from these sources remains uncertain for several reasons. Global use of pharmaceuticals is not well quantified, but a study of fluorinated pharmaceuticals in sewage sludge from Sweden [151] suggested that these contributed ca. 27% of the extractable organo-fluorine in the sludge. The global use of pesticides is also not well quantified in most countries. The most detailed information for use of pesticides with molecular structures containing one, or more,  $\text{CF}_3$ - groups is available from the United States [152]. However, because of lack of knowledge of yields of TFA under field conditions, the contribution of pesticide degradation to TFA in the environment remains uncertain (see [8]). Releases of TFA into the environment from pesticides and pharmaceuticals are expected to increase in the future because of greater use of fluorine to confer useful properties [153].

### 6.3 Environmental concentrations and estimations of fluxes of TFA from chemicals under the purview of the Montreal Protocol

Anthropogenic sources of TFA include point sources from industrial facilities, degradation of pharmaceuticals and agrochemicals, and atmospheric degradation of hydrochlorofluorocarbons (HCFCs), HFCs, and HFOs [154]. The contribution of chemicals under the purview of the Montreal Protocol to the global load of TFA is dominated by atmospheric degradation of HFC-134a ( $\text{CF}_3\text{CH}_2\text{F}$ ) and HFO-1234yf ( $\text{CH}_2=\text{CFCF}_3$ ). HFC-134a has an atmospheric lifetime of ca. 14 years and its TFA degradation product will be deposited globally. HFO-1234yf has an atmospheric lifetime of ca. 11 days and its TFA degradation product will be deposited regionally [155, 156]. The global flux of TFA in 2020 from HFC-134a and HFO-1234yf oxidation is estimated to be  $0.01\text{--}0.03 \text{ Tg year}^{-1}$  and  $0.03 \text{ Tg year}^{-1}$ , respectively. Assuming uniform deposition across the global scale this corresponds to average deposition fluxes of  $20\text{--}60 \text{ g km}^{-2} \text{ year}^{-1}$  from HFC-134a and  $60 \text{ g km}^{-2} \text{ year}^{-1}$  from HFO-1234yf. The measured deposition flux of TFA in precipitation in Arctic ice cores in 2007–2018 of ca.  $10 \text{ g km}^{-2} \text{ year}^{-1}$  is consistent with that expected for the atmospheric degradation of HFC-134a in 2020 [8, 157] after accounting for the lower average photochemical activity of OH in the Arctic [158]. The measured deposition flux of  $51 \text{ g km}^{-2} \text{ year}^{-1}$  in 2018–2019 in the catchment area of Lake Vättern, Sweden [159] is consistent with that expected from oxidation of HFC-134a and may also contain a contribution from oxidation of HFO-1234yf.

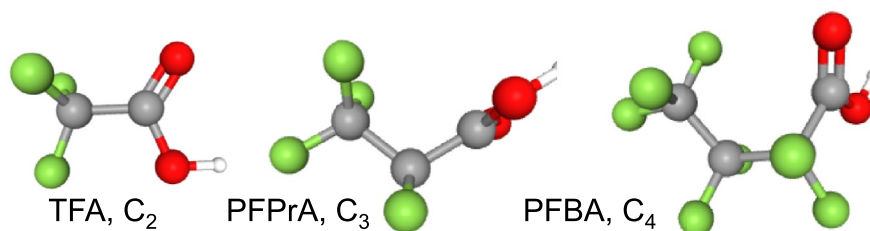
Driven by projected increases in use of HFO-1234yf, the global deposition of TFA from chemicals under the purview of the Montreal Protocol has been projected to increase to  $0.36\text{--}0.54 \text{ Tg year}^{-1}$  in 2050, and to  $0.64\text{--}1.05 \text{ Tg year}^{-1}$  in 2100 [8]. The short atmospheric lifetime of HFO-1234yf and projections of substantial increases in its future emissions are expected to result in more localised deposition of TFA from chemicals under the purview of the Montreal Protocol. It has been estimated that, for emission scenarios of HFO-1234yf in 2040 in India, China, and the Middle East, the average TFA

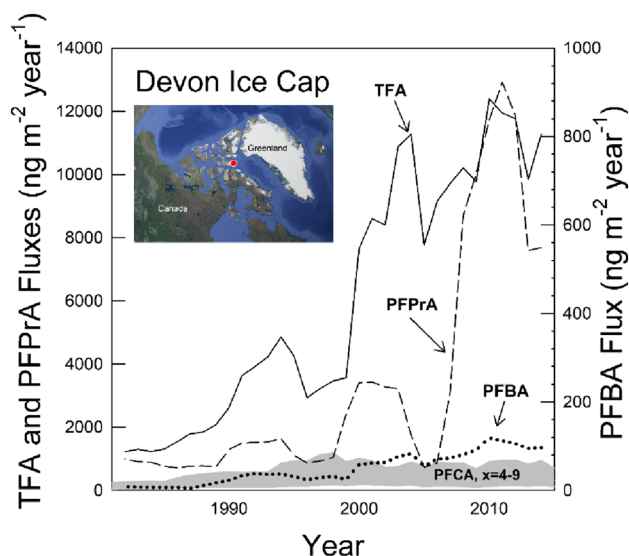
deposition fluxes would be in the range  $300\text{--}900 \text{ g km}^{-2} \text{ year}^{-1}$  [156, 160] with local fluxes higher by factors of ca. 2–4. As a result of uneven deposition, concentrations of TFA in surface waters will vary with flow rates and volumes of water. TFA will be transported via flowing water to endorheic (land-locked) lakes and the global oceans where, if evenly distributed across all oceans, the projected emissions of HFC-134a and HFO-1234yf would lead to an increase in the concentrations of TFA from a nominal value of  $200 \text{ ng L}^{-1}$  in 2000 to  $266\text{--}284 \text{ ng L}^{-1}$  in 2100 [8]. Recently TFA was detected in 95% of drinking water samples ( $n = 81$ ) in Indiana (United States) with a median concentration of  $79 \text{ ng L}^{-1}$  [161], although it is unclear if detections in drinking water stemmed from surface or groundwater. These amounts currently present *de minimis* risk to the global environment [8].

### 6.4 Short-chain PFCAs other than TFA from chemicals under the purview of the Montreal Protocol

Some replacements for CFCs and HCFCs used in foam blowing and solvent applications have short perfluorinated carbon-chains ( $\text{C}_x\text{F}_{2x-1}$ —units where  $x = 2$  or 3), meaning that short chain-length PFCAs, in addition to TFA, are likely to be found in the environment. These acids, like TFA, are recalcitrant and will accumulate in terminal basins. Perfluoropropanoic acid (PFPrA) and perfluorobutanoic acid (PFBA), three- and four-carbon analogues of TFA (Fig. 2), have significant sources, e.g., fluorotelomers, in the environment besides compounds under the purview of the Montreal Protocol. PFPrA and PFBA were first detected in Arctic ice core samples dating back to 1990 [162]. PFPrA was found in wastewater in 70% of samples collected world-wide [163] and more recently in wastewater from water-treatment plants in New Zealand [164]. Concentrations were  $12.5 \text{ ng L}^{-1}$  in influent water and  $5.5 \pm 2.1 \text{ ng L}^{-1}$  (one standard deviation, SD) in drinking water [164]. Recently, in Indiana, PFPrA was detected in 95% of drinking water samples ( $n = 81$ ) with a median concentration of  $6.9 \text{ ng L}^{-1}$  [161]. PFBA has been observed in the atmosphere over Asia [165] and has been

**Fig. 2** The structure of short-chain perfluorocarboxylic acids relevant to the Montreal Protocol. (Structures from PUBCHEM) (colour figure online)





**Fig. 3** Accumulation fluxes of trifluoroacetic acid (TFA), perfluoropropanoic acid (PFPrA) and perfluorobutanoic acid (PFBA) measured at the Devon Ice Cap [162]. The range of fluxes of long chain perfluorocarboxylic acids (PFCAs,  $C_xF_{2x+1}COOH$ ,  $x = 4-9$ ), measured at the same site, is included for comparison [168]. The inset shows a map of the Arctic with the location of Devon Ice Cap highlighted (from Google Earth, accessed 3 October 2023) (colour figure online)

detected in samples of fish, meat, and split peas from the general marketplace in Poland [166]. Mean concentrations ( $\pm$ SD) were  $3.7 \pm 1.7 \mu\text{g kg}^{-1}$  for cod;  $14 \pm 16 \mu\text{g kg}^{-1}$  for pork liver; and  $3.1 \pm 1.0 \mu\text{g kg}^{-1}$  for split peas [166]. In Indiana, PFBA was detected in 98% of drinking water samples ( $n = 81$ ) with a median concentration of  $2.4 \text{ ng L}^{-1}$  [153]. Accumulation fluxes observed in the Arctic for PFPrA and PFBA show marked increases since 2000 (Fig. 3), with the highest fluxes in the uppermost snow layers [162, 167].

Table 2 lists the estimated yields of short-chain PFCAs,  $C_xF_{2x-1}COOH$  ( $x \leq 3$ ), for selected CFC replacements. Modelling studies suggest that emissions of HCFC-225ca may be the source of the initial increase around 2000–2005 in the deposition flux of PFPrA. However, because the reported production rates of this HCFC has since declined, other sources may have become more important [162]. Based on quantum chemical calculations, PFPrA, like TFA, may form hydrogen-bonded clusters with other atmospheric molecules and thus participate in initial nucleation processes of new particle formation in the atmosphere (secondary organic aerosol formation) [169, 170]. The importance of CFC replacements as sources of short-chain PFCAs, and their impact on atmospheric processes and the environment remains uncertain.

**Table 2** Lifetimes, applications, and estimated yields of short-chain PFCAs,  $C_xF_{2x-1}COOH$  ( $x \leq 3$ ), for selected CFC replacements

		Atmospheric lifetime <sup>a</sup>	Molar yields (%) <sup>b</sup>			Use application <sup>c</sup>
			TFA	PFPrA	PFBA	
HCFC-225ca	$CF_3CF_2CHCl_2$	1.9 years	~0	100	–	Solvent
HFC-43-10mee	$CF_3CHFCHFC_2F_5$	17 years	~100	~100	–	Solvent
HFC-329p	$CF_3CF_2CF_2CHF_2$	31 years	<10	<10	<10	Impurity (no primary application)
HFC-236cb	$CF_3CF_2CH_2F$	13.4 years	~0	~100	–	Feedstock (polymers)
HFE-347mcf	$CF_3CF_2CH_2OCHF_2$	5.73 years	<10	<10	–	Foam blowing agent
HFE-365mcf3	$CF_3CF_2CH_2OCH_3$	25 days	<10	<10	–	Carrier solvent
HFE-7100	$CF_3(CF_2)_3OCH_3$	5.05 years	<10	<10	<10	Solvent
HFE-7200	$C_4F_9OC_2H_5$	0.63 years	<10	<10	<10	Solvent
HFE-7300	$C_2F_5CF(OCH_3)CF(CF_3)_2$	4.99 years	~100	–	~100	Solvent
HFE-7500	$C_3F_7CF(OC_2H_5)CF(CF_3)_2$	0.348 years	~100	–	~100	Solvent
1-ethoxy-1,1,2,2,3,3,3-heptafluoro-propane	$CF_3CF_2CF_2OCH_2CH_3$	0.728 years	<10	<10	–	n.a
HFE-54-11mecf	$CF_3CHFCF_2OCH_2CF_2CF_3$	0.95 years	~100	<10	–	Solvent
HFO-1447fz	$CH_2=CHCF_2CF_2CF_3$	33 days	<10	<10	<10	Foam blowing agent
HFO-1345zfc	$CH_2=CHCF_2CF_3$	9 days	<10	<10	–	Foam blowing agent
(E)-HFO-1438mzz	$CF_3CH=CHCF_2CF_3$	120 days	<10	<10	–	Foam blowing & heat transfer agent

<sup>a</sup>UNEP/WMO SAP [1]

<sup>b</sup>Estimated molar yields do not necessarily sum to 100% and in some cases can exceed 100%, reflecting competing reaction pathways (some of which do not form PFCAs) and the formation of more than one PFCA molecule in the degradation of some CFC replacements (e.g., HFC-43-10mee)

<sup>c</sup>Applications provided by the Technology and Economic Assessment Panel (TEAP)



## 6.5 Toxicity of TFA and other PFCAs pertinent to the Montreal Protocol

No new studies on the toxicity of TFA salts to humans or other organisms in the environment have been reported in the literature since the last Quadrennial Assessment [8], except for a paper on effects on soil processes upon exposure to TFA ([171], see below). The previous assessment of the literature on toxicity of TFA to humans and other terrestrial animals [8 and earlier papers cited therein] concluded that risks to humans are *de minimis*. This was also the conclusion of a recent independent assessment [172]. The margin of exposure is the ratio of the no-observed-adverse-effect level (NOAEL) to the exposure level and quantifies the buffer between the exposure level at which effects might be expected and the actual level of exposure. Based on a NOEL of  $10 \text{ mg kg}^{-1} \text{ day}^{-1}$  in long-term toxicity studies in rats, the margins of exposure in humans for sources of TFA in surface waters, drinking water, and food were  $6.25 \times 10^4$ ,  $4.76 \times 10^5$ , and  $4 \times 10^3$ , respectively [172]. The most recent reported concentrations in drinking water (median of  $79 \text{ ng L}^{-1}$ , maximum of  $210 \text{ ng L}^{-1}$ , see above) are less than those used by Dekant and Dekant [172] ( $630 \text{ ng L}^{-1}$ ) to estimate the risk to human health from TFA.

There is no change to the conclusion in the 2022 Quadrennial Assessment [8] of *de minimis* risk to the environment with margins of exposure of four orders of magnitude for TFA salts in oceans and in terminal endorheic basins expected for gases related to the Montreal Protocol up to 2100. Margins of exposure for organisms in flowing water are much greater, indicating *de minimis* risks. Effects in marine organisms remain the area of greatest uncertainty in terms of assessing ecological risk.

A new laboratory study characterised the response of soil structure and function over the course of six weeks after exposure to TFA in its acid form [171]. After six weeks, changes in the soil were observed. These were decreased pH, sulphate content, soil respiration (for the first three weeks only), decomposition of litter, and abundance of bacteria at concentrations  $\geq 1 \text{ mg kg}^{-1}$ . There were increases in phosphate content at concentrations of TFA  $\geq 10 \text{ mg kg}^{-1}$ . Overall, all changes from control were relatively small (typically  $<15\%$ ). There were no measured impacts on soil-aggregation, abundance of fungi, and enzyme activities at concentrations up to the greatest concentration tested ( $100 \text{ mg TFA kg}^{-1}$ ). The authors noted that the changes in pH due to the use of the acid form of TFA likely drove most of the observed differences. The study also had several additional weaknesses, including lack of a positive control for acidity, lack of confirmation of treatment concentrations, and lack of characterisation of cation exchange capacity of the soil.

There is some additional information on risks to humans of other short-chain PFCAs that are structurally similar to TFA. The US EPA evaluated the risks from exposures to PFPrA [173]. They estimated a non-cancer reference dose (RfD) of  $0.0005 \text{ mg kg}^{-1} \text{ (bw) day}^{-1}$  based on enlargement of the liver in rats exposed in long-term studies. There were insufficient data to derive a carcinogenicity endpoint for perfluoropropanoic acid. The US EPA also evaluated the risks from exposures of humans to perfluorobutanoic acid, a four-carbon analogue of TFA [174]. They estimated an overall non-cancer RfD for PFBA of  $0.001 \text{ mg kg}^{-1} \text{ day}^{-1}$ , based on effects on liver and thyroid glands in rats and foetal development in mice. Due to a lack of data, it was not possible to derive a carcinogenicity endpoint for PFBA. These RfDs should be compared to the derived no effect level (DNEL) for TFA of  $0.042 \text{ mg kg}^{-1} \text{ day}^{-1}$  from the review conducted by ECHA [175] and referred to above [172].

PFBA is reported to have low toxicity to fish and fish larvae (LC50s from  $3000\text{--}13,795 \text{ mg L}^{-1}$ ) [176–178]. LC50s for the aquatic crustaceans *Daphnia magna* and *D. pulicaria* were reported as  $>1000 \text{ mg L}^{-1}$  in 48-h exposures [179]. The effects of PFBA on the nematode (*Caenorhabditis elegans*), a commonly used test-invertebrate, were studied [180]. The no-observed-effect concentration (48 h NOEC) for lethality was  $21.4 \text{ mg L}^{-1}$ . For other endpoints such as chemotaxis, fecundity, locomotion, growth, and lifespan, the NOEC was  $2.14 \text{ mg L}^{-1}$ . Bioaccumulation was measured at three exposures ( $0.1\text{--}214 \text{ mg L}^{-1}$ ) and bioaccumulation factors were  $<1$ , suggesting no biomagnification in the food chain. Based on this small set of data, risks to aquatic and terrestrial organisms are judged to be small at this time, but there is significant uncertainty.

## 7 Exposure of materials to UV radiation

### 7.1 Replacement of legacy chemicals to decrease harmful impacts on the environment

UV radiation causes photodegradation of materials, initiating deterioration of their properties. Plastic and wood industries routinely use additives to slow down the ageing process of materials. These additives, some of which are endocrine disruptors or potential carcinogens, are released into the environment as the degradation proceeds. Their release into the environment via leaching into water bodies or migration into soil or as fragmented dust suspended into the air is of serious concern. In addition to additives, fragments of deteriorated parent macroplastics are released into the environment as meso-, micro- and nanoplastics mostly through ablation of the oxidised surface. Fragmentation of the material may enhance release of these chemicals as there is more surface exposed. The leaching rates of additives and



fragments depend on the intensity of UV radiation exposure and other weathering factors.

Legacy chemicals are being increasingly replaced with benign chemicals with less harmful impacts on the environment. The fraction of such chemicals in a plastic composition can range from less than one weight percent for UV stabilisers and biocides to over 50 weight percent with plasticisers used in PVC. Several attempts have been made to develop efficient plasticisers with reduced migration, especially for PVC applications where ca. 90% of all plasticisers are being used [181]. Overall, there is legislative and research interest in developing benign alternatives for these additives, especially to replace phthalates and polybrominated fire retardants used in relatively high weight fractions in plastic compositions.

Alternatives for legacy additive chemicals are being investigated primarily for their effectiveness as functional replacements. Bio-derived plasticisers with flame retardant functionality used in PVC represent an example of alternative additives of this kind (see, e.g., [182]). Cao et al. [183] examined samples from urban run-offs, roadside soils and ambient air in Hong Kong, and quantified five different quinones formed from antioxidants of *p*-phenylenediamine (PPD) commonly used in the rubber industry, one of which is highly toxic. Certain PPDs are critical tyre rubber additives with high-performing antidegradant (antiozonant) properties. The industry is seeking alternatives, since the use of PPDs seems to become more rigorously regulated. Toxicity and other environmental impacts of those and several other alternative additive chemicals remain to be investigated.

The use of environmentally unsustainable additives is also common in the wood industry. Alternative treatments of wood may help avoid the use of some toxic surface treatments used presently. A densification process has recently been applied [184] on Chinese fir to improve the mechanical properties of the wood. The process included partial delignification, flame-retardant modification and densification resulting in ammonium dihydrogen phosphate (ADP)-densified wood with ca. 20-fold higher tensile and flexural strength but also enhanced thermal stability and flame retardancy compared to the untreated wood. Similarly, Brohi et al. [185] experimented with a citric acid-based, non-formaldehyde flame retardant in finishing of cotton fabric. The use of citric acid and titanium dioxide with phosphoric acid as co-catalyst with pad-dry-curing resulted in effective flame retardancy.

## 7.2 Eco-friendly and UV-shielding replacement for glass and plastics in building applications

Recently developed eco-friendly and UV-shielding transparent wood products show promise as a sustainable

replacement for glass and plastics in building applications. Optically transparent wood composite (TWC) is an emerging environmentally sustainable material that has the potential to revolutionise sectors, including energy-efficient buildings, transportation, and photovoltaic devices. A novel luminescent transparent wood (LTW) prepared by pre-treatment of lignin-modified silver oak wood veneer (1 mm thick) with a low-cost commercial fabric brightener (*Ranipal*®) prior to prepolymer (epoxy) infiltration, resulted in a product with high transparency at visible wavelengths (82%) and high haze (90%), with enhanced UV-blocking properties [186]. Highly transparent TWC (transmittance 90%; haze 90%), prepared with in situ generation of TiO<sub>2</sub> nanoparticles in epoxy resin showed significantly better performance compared to traditional glass in terms of UV screening and heat shielding properties [187]. The transmittance of TiO<sub>2</sub> containing TWC was <20% in the UV band (250–400 nm) and its thermal conductivity (0.3228 W mK<sup>-1</sup>) was lower than that of glass. A photochromic transparent wood (PTW) product prepared for smart packaging applications by incorporating UV radiation/visible light switchable molecules into the delignified wood prior to pre-polymer infiltration showed a UV-shielding effect along with favourable thermal and mechanical properties and dimensional stability [188]. A facile strategy of fabrication of isotropic TWC by integrating delignified wood particles with poly(vinyl alcohol) (PVA) enables biocomposites with 62% optical transmittance [189]. The developed composite exhibited good thermal stability, low thermal conductivity (0.38–0.42 W m<sup>-1</sup> K<sup>-1</sup>) and UV-blocking properties. Incorporation of 1% lignin nanoparticles (LNs) effectively blocks all UV-C, UV-B, and UV-A radiation, suggesting LN nanocomposites with LN filler are a particularly promising candidate for UV-shielding window applications [190]. TWC can replace glass and plastic components as more sustainable building material. However, when used with PVA, the potential generation of plastic debris needs to be considered, since PVA from multiple origins is a main type of microplastic found in surface waters and urban run-off [191].

## 7.3 Production of UV-protective fabrics and the release of metal nanoparticles to the environment

Increasing use of nanotechnology in the production of UV-protective fabrics may lead to increasing release of metal (oxide) particles into the environment. Consumers are encouraged to use protective clothing as one of the measures of sun-smart behaviour. While the UV protection factor (UPF) of ordinary textile fabrics may be considered in many cases high enough to provide sufficient protection, textiles with enhanced UV shielding capabilities are increasingly entering the market. The textile industry is

constantly seeking novel methods to manufacture fabrics with high UPF. One viable approach involves augmenting the UV absorption and scattering properties of textile fibres by integrating additives or micro-/nanoparticle fillers (see, e.g., [192]). This technique has already shown promise in the design of UV protective fabrics. The effect of zinc oxide (ZnO) nanoparticles, nano-polyurethane (PU) nanocomposites, and ZnO/PU nanocomposite functionalisation on polyester fabric has been examined [193]. This treatment imparted enhanced UV protection, mechanical performance and comfort to the fabric. With 0.5% ZnO NPs, 50 g L<sup>-1</sup> nano-PU, and curing at 110 °C the UPF gained was 150, whereas the UPF of the untreated fabric was 30.

Rabiei et al. [194] investigated UV-protective properties of workwear fabrics (twill fabrics 246.67 g m<sup>-2</sup> with 70% of cotton and 30% of polyester) coated in situ with titanium dioxide (TiO<sub>2</sub>) nanoparticles. The UPF of the uncoated and coated fabrics was <4 and over 55, respectively. In addition to added UV protection, the use of nanoparticles can also impart antimicrobial or insect repellent properties. Singh and Sheikh [195] developed a functional acrylic fabric with mosquito-repellent and UV-protective properties by using a novel basic (cationic) dye. A self-cleaning, antibacterial and UV-resistant polyester fabric loaded with zinc stannate nanoparticles has also been produced [196].

Even though these approaches are being promoted as environmentally friendly, especially when they are based on one-step processes and low concentrations of non-hazardous chemicals (see, e.g., [197]), the environmental implications of these applications remain elusive. This is particularly true for textile fibres treated with nanoparticles. Those particles, whether metal or metal oxide, will inevitably be released into the environment along with the microfibrils generated from the fabric. It is, therefore, essential to consider the potential environmental impact when developing UV-protective textiles using nanotechnology.

#### 7.4 UV radiation and the formation of microfibrils and microplastics

Microfibrils are the main type of microplastic in fresh waters and in certain aquatic species. For instance, this has been demonstrated in PVC coated PET woven fabrics [198], poly(3-hydroxybutyrate) electrospun fibres loaded with zinc oxide nanoparticles [199], high-performance fibres used in firefighters' protective clothing (such as para-aramid, metaaramid, co-polymers of aramid, polybenzimidazole, and polybenzoxazole fibers) [200–202], regenerated silk fibroin [203], Mo/MoS<sub>2</sub>-Pb-PbS composite films [204], carbon fibre/epoxy composites [205], poly(lactide acid)/poly(hydroxybutyrate) (PLA/PHB) yarns/fabrics [206], and sheep wool fibres [207]. It is not yet known how UV filters and photoabsorbents such as dyes and pigments in fibres will

affect their stability/degradation under UV irradiation. Work is underway to reduce the weathering of textiles, specifically studying surface modification and finishing processes to reduce the release of microplastics and/or microfibrils. Bio-based finishes (e.g., based on chitosan and PVA combined with surface modifications) bind surface microfibrils to the structure and reduce their shedding while offering durability [208].

## 8 Conclusions

As shown throughout this update, UV radiation plays an important role in many environmental compartments. Direct exposure to UV radiation has been linked to increased incidence of skin cancer and cataracts, but also confers some health benefits, e.g., via production of vitamin D. Weathering of many materials, including plastics, is accelerated by UV irradiation. In the atmosphere, UV radiation causes the formation of photochemical smog (including ambient O<sub>3</sub> and particulate matter) in polluted regions, but also plays a key role by cleaning the atmosphere in more remote regions. Other issues not directly caused by exposure to UV radiation but nevertheless relevant, include the net transport of ozone from the stratosphere to the troposphere, and the formation of persistent chemicals (e.g., TFA) from the degradation of some compounds used to replace ODSs. The state of knowledge varies greatly, and quantification is limited. While some estimates of dose-responses for skin cancer have been made [10], the impacts of changing UV radiation on terrestrial and aquatic ecosystems, on air quality, and on the weathering of materials remain largely unquantified. Complications arise from interactions among them (e.g., air quality affecting UV transmission and vice versa) together with a changing climate. However, in most cases even their idealised isolated sensitivities to UV radiation are unknown. The future of stratospheric O<sub>3</sub> remains uncertain, with both increases and decreases falling within the range of possible scenarios considered in recent assessments [1]. Thus, more quantitative data are required for a better understanding of environmental consequences.

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## Declarations

**Conflict of interest** LER conducts collaborative research with Clinovel Pharmaceuticals Ltd and Mitsubishi Tanabe Pharma Inc. on the development of photoprotective agents. All other authors declare no conflict of interest.

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## Authors and Affiliations

S. Madronich<sup>1,2</sup> · G. H. Bernhard<sup>3</sup> · P. J. Neale<sup>4</sup> · A. Heikkilä<sup>5</sup> · M. P. Sulbæk Andersen<sup>6,7</sup> · A. L. Andradý<sup>8</sup> · P. J. Aucamp<sup>9</sup> · A. F. Bais<sup>10</sup> · A. T. Banaszak<sup>11</sup> · P. J. Barnes<sup>12</sup> · J. F. Bornman<sup>13</sup> · L. S. Bruckman<sup>14</sup> · R. Busquets<sup>15</sup> · G. Chiodo<sup>16</sup> · D.-P. Häder<sup>17</sup> · M. L. Hanson<sup>18</sup> · S. Hylander<sup>19</sup> · M. A. K. Jansen<sup>20</sup> · G. Lingham<sup>21,22</sup> · R. M. Lucas<sup>23</sup> · R. Mackenzie Calderon<sup>24,25,26</sup> · C. Olsen<sup>27</sup> · R. Ossola<sup>28</sup> · K. K. Pandey<sup>29</sup> · I. Petropavlovskikh<sup>30,31</sup> · L. E. Revell<sup>32</sup> · L. E. Rhodes<sup>33,34</sup> · S. A. Robinson<sup>35,36</sup> · T. M. Robson<sup>37,38</sup> · K. C. Rose<sup>39</sup> · T. Schikowski<sup>40</sup> · K. R. Solomon<sup>41</sup> · B. Sulzberger<sup>42</sup> · T. J. Wallington<sup>43</sup> · Q.-W. Wang<sup>44</sup> · S.-Å. Wängberg<sup>45</sup> · C. C. White<sup>46</sup> · S. R. Wilson<sup>36</sup> · L. Zhu<sup>47</sup> · R. E. Neale<sup>27,48</sup>

✉ S. Madronich  
sasha@ucar.edu

✉ R. E. Neale  
r.neale@sph.uq.edu.au

<sup>1</sup> National Center for Atmospheric Research, Boulder, CO, USA

<sup>2</sup> Natural Resource Ecology Laboratory, USDA UV-B Monitoring and Research Program, Colorado State University, Fort Collins, CO, USA

<sup>3</sup> Biospherical Instruments Inc, San Diego, CA, USA

<sup>4</sup> Smithsonian Environmental Research Center, Edgewater, MD, USA

<sup>5</sup> Finnish Meteorological Institute, Helsinki, Finland

- 6 Department of Chemistry and Biochemistry, California State University Northridge, Northridge, CA, USA
- 7 Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
- 8 Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA
- 9 Ptersa Environmental Consultants, Faerie Glen, South Africa
- 10 Laboratory of Atmospheric Physics, Department of Physics, Aristotle University, Thessaloniki, Greece
- 11 Unidad Académica de Sistemas Arrecifales, Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México, Puerto Morelos, Mexico
- 12 Department of Biological Sciences and Environment Program, Loyola University New Orleans, New Orleans, LA, USA
- 13 Food Futures Institute, Murdoch University, Perth, Australia
- 14 Department of Materials Science and Engineering, Reserve University, Cleveland, OH, USA
- 15 Chemical and Pharmaceutical Sciences, Kingston University London, Kingston Upon Thames, UK
- 16 Institute for Atmospheric and Climate Science, ETH Zürich, Zurich, Switzerland
- 17 Friedrich-Alexander University, Möhrendorf, Germany
- 18 Department of Environment and Geography, University of Manitoba, Winnipeg, MB, Canada
- 19 Centre for Ecology and Evolution in Microbial Model Systems, Linnaeus University, Kalmar, Sweden
- 20 School of Biological, Earth and Environmental Sciences, University College, Cork, Ireland
- 21 Centre For Ophthalmology and Visual Science (Incorporating Lion's Eye Institute), University of Western Australia, Perth, Australia
- 22 Centre for Eye Research Ireland, Environmental, Sustainability and Health Institute, Technological University Dublin, Dublin, Ireland
- 23 National Centre for Epidemiology and Population Health, College of Health and Medicine, Australian National University, Canberra, Australia
- 24 Cape Horn International Center, Puerto Williams, Chile
- 25 Millennium Institute Biodiversity of Antarctic and Subantarctic Ecosystems BASE, Santiago, Chile
- 26 Centro Universitario Cabo de Hornos, Universidad de Magallanes, O'Higgins 310, Puerto Williams, Chile
- 27 Population Health Program, QIMR Berghofer Medical Research Institute, Brisbane, QLD, Australia
- 28 Department of Chemistry, Colorado State University, Fort Collins, CO, USA
- 29 Indian Academy of Wood Science, Bengaluru, India
- 30 Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
- 31 NOAA Global Monitoring Laboratory, Boulder, CO, USA
- 32 School of Physical and Chemical Sciences, University of Canterbury, Christchurch, New Zealand
- 33 Faculty of Biology Medicine and Health, School of Biological Sciences, The University of Manchester, Manchester, UK
- 34 Dermatology Centre, Salford Royal Hospital, Greater Manchester, UK
- 35 Securing Antarctica's Environmental Future, University of Wollongong, Wollongong, Australia
- 36 School of Earth, Atmospheric and Life Sciences, University of Wollongong, Wollongong, Australia
- 37 UK National School of Forestry, University of Cumbria, Ambleside Campus, UK
- 38 Viikki Plant Science Centre, Faculty of Biological and Environmental Sciences, University of Helsinki, Helsinki, Finland
- 39 Department of Biological Sciences, Rensselaer Polytechnic Institute, Troy, NY, USA
- 40 IUF-Leibniz Research Institute for Environmental Medicine, Dusseldorf, Germany
- 41 School of Environmental Sciences, University of Guelph, Guelph, Canada
- 42 Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland
- 43 Center for Sustainable Systems, School for Environment and Sustainability, University of Michigan, Ann Arbor, MI, USA
- 44 Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, China
- 45 Department of Marine Sciences, University of Gothenburg, Gothenburg, Sweden
- 46 Exponent Inc, Bowie, MD, USA
- 47 State Key Lab for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China
- 48 School of Public Health, University of Queensland, Brisbane, Australia