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Montreal Protocol on Substances that Deplete the Ozone Layer United Nations Environment Programme Ozone Secretariat P.O. Box 30552 Nairobi, 00100 Kenya

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Authors: Marcel AK Jansen, Anthony L Andrady, Janet F Bornman, Pieter J Aucamp, Alkiviadis F Bais, Anastazia T Banaszak, Paul W. Barnes, Germar H Bernhard, Laura S. Bruckman, Rosa Busquets, Donat-P Häder, Mark L Hanson, Anu M Heikkilä, Samuel Hylander, Robyn M Lucas, Roy Mackenzie, Sasha Madronich, Patrick J Neale, Rachel E Neale, Catherine M Olsen, Rachele Ossola, Krishna K Pandey, Irina Petropavlovskikh, Laura E Revell, Sharon A Robinson, T Matthew Robson, Kevin C Rose, Keith R Solomon, Mads P Sulbaek Andersen, Barbara Sulzberger, Timothy J Wallington, Quing-Wei Wang, Sten-Åke Wängberg, Christopher C White, Antony R Young, Richard G Zepp, Liping Zhu

Production team: Roy Mackenzie-Calderón and Rachele Ossola (Coordinators), and Alejandro Pérez-Velásquez (Designer).

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Cover image: Stork in an exposed plastic dump site in Kampala, Uganda. Photo credit, Rosa Busquets

Highlights of the EEAP Assessment Update 2023

Solar ultraviolet radiation is a contributing factor in the environmental fate of toxic chemicals and other contaminants, with consequences that may be either beneficial or detrimental for the health of humans and the environment. This Assessment Update (2023) by the Environmental Effects Assessment Panel (EEAP) focusses on the role and significance of UV radiation and associated drivers on the breakdown of plastic waste in the environment.

Plastic is a ubiquitous pollutant. UV radiation and mechanical stress drive the degradation and fragmentation of larger plastic waste into smaller micro- and nanoplastics. The Assessment Update considers the interactive effects of UV radiation and climate change on plastic durability, weathering, longevity, and ultimately the fate of plastic debris (Figure 1).

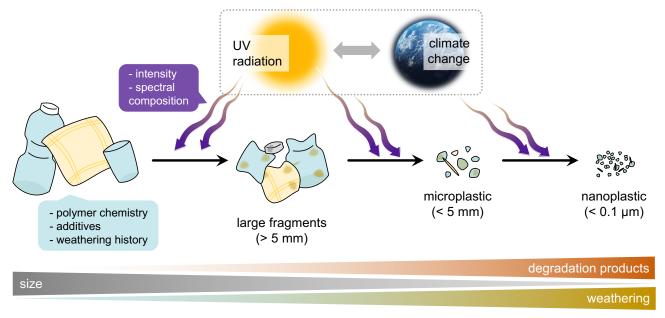


Figure 1. The role of UV radiation and other environmental factors in the formation of micro- and nanoplastics.

Relevance of the Montreal Protocol

The implementation of the Montreal Protocol and its Amendments has avoided high UV radiation at the Earth's surface, and likely decreased the rate of UV-B-driven degradation of plastics, contributing to increased durability of materials and reduced production of micro- and nanoplastic particles. Due to a lack of quantitative evaluation studies of UV-driven degradation and fragmentation in natural ecosystems, the contribution of UV radiation to the global load of environmental microplastics cannot be reliably quantified at present.

Plastic breakdown from exposure to UV-B radiation

Direct exposure of plastics to solar UV-B radiation induces free-radical photoreactions resulting in photo-oxidation of the plastic. The consequent deterioration of physical properties renders plastics weak and brittle and can result in fragmentation into micro- and nanoplastics when materials are exposed to mechanical stresses. The rate of photo-oxidation depends on properties of the plastic polymer (such as its chemical composition and the presence of specific additives). At present, major questions remain concerning the longevity of plastic waste in the environment.

Microfibres

Microfibres are the main category of microplastic particles found in the environment. Fabrics and textiles based on synthetic polymer fibres release microfibres during manufacture and use, especially during washing and drying, and this is amplified when fabrics have been exposed to solar UV-B radiation.

Climate change

Interactions between solar UV-B radiation and climate change factors, such as temperature, alter rates of plastic degradation. For example, generation of small rubber particles from tyres is increased by exposure to UV radiation as well as by heat, eroded tarmac, and impervious road surfaces.

Complete breakdown of plastic waste

Micro- and nanoplastics may undergo full mineralisation into dissolved organic matter and inorganic end-products, such as water and carbon dioxide. Direct evidence of mineralisation in the natural environment is lacking. However, there is evidence of at least partial conversion of a fraction of the plastics into water-soluble organic compounds.

Plastics in the atmosphere

Micro- and nanoplastics have been found in the atmosphere where these particles are exposed to high UV-B irradiation. The contribution of microplastics to atmospheric chemistry and physics is currently expected to be negligible, but any assessment is subject to substantial technical limitations in quantifying atmospheric plastics.

Plastics in agri-ecosytems

Soils are one of the largest depositories of plastics. Plastic mulch is a key source of plastics in soils. The use of plastic mulch in agriculture is increasing with global economic development, plastic affordability and in reducing the abiotic stresses imposed on crops by climate change. With the downward migration of plastic fragments in the soil, there is a potential risk to groundwater systems and drinking water. Further, there is early evidence that microplastics alter structure, water-holding capacity, microbial activity, and nutrient cycling in contaminated soils.

Plastics in aquatic systems

Plastics are ubiquitous in the aquatic environment. Changes in water transparency and mixing depth modify the amount of solar UV-B radiation received by plastics in the surface mixed layer. Climate change is warming aquatic ecosystems and changing wind patterns, both of which interact to determine mixing depth. Biofouling is another process that can reduce incident UV irradiation to the underlying plastic, while also increasing apparent plastic density, thereby causing fragments to sink deeper into the water column where they are exposed to less UV radiation.

Environmental health

The environmental health effects of plastic pollutants are yet to be fully understood. Elucidation of the direct biological risks associated with exposure to larger plastic debris (e.g., entanglement) and microor nanoplastic particles, requires further research. UV-induced photo-oxidation also increases the rate of leaching of additives and other chemicals into the environment. These additives are added to plastics to improve functional properties. Some legacy additives are toxic, being potential carcinogens or hormone-mimicking endocrine disruptors, which cause adverse responses at very low concentrations.

Human health

Humans are exposed to micro- and nanoplastics through ingestion, inhalation and skin contact. Micro- and nanoplastics have been found, for example, in human tissues, water and various foods. It is also of concern that the ecological, social and economic impacts of macro, micro- and nanoplastic pollution are inequitably experienced, often primarily affecting communities that are marginalised and vulnerable.

Towards a sustainable future

Plastics have been primarily designed for in-use functional performance, but rarely has end-of-life fate of these materials been a dominant consideration in their design. There is a need to design novel plastics or plastic alternatives that can be broken down into harmless substances, thus reducing accumulation of plastic debris in the environment. As part of a move towards a healthy sustainable planet, UV-B radiation and climate-mediated impacts on durability, weathering and fragmentation of plastics are key considerations in the design of such new, innovative plastics.

Marcel Jansen, Anthony Andrady, Janet F. Bornman, Paul Barnes, and Krishna Pandey

Plastics in the environment in the context of UV radiation, climate change and the Montreal Protocol

Marcel AK Jansen¹, Anthony L Andrady², Janet F Bornman³, Pieter J Aucamp⁴, Alkiviadis F Bais⁵, Anastazia T Banaszak⁶, Paul W. Barnes⁷, Germar H Bernhard⁸, Laura S. Bruckman⁹, Rosa Busquets¹⁰, Donat-P Häder¹¹, Mark L Hanson¹², Anu M Heikkilä¹³, Samuel Hylander¹⁴, Robyn M Lucas¹⁵, Roy Mackenzie^{16,17,18}, Sasha Madronich¹⁹, Patrick J Neale²⁰, Rachel E Neale^{21,22}, Catherine M Olsen^{21,23}, Rachele Ossola²⁴, Krishna K Pandey²⁵, Irina Petropavlovskikh^{26,27}, Laura E Revell²⁸, Sharon A Robinson^{29,30}, T Matthew Robson^{31,32}, Kevin C Rose³³, Keith R Solomon³⁴, Mads P Sulbaek Andersen^{35,36}, Barbara Sulzberger³⁷, Timothy J Wallington³⁸, Quing-Wei Wang³⁹, Sten-Åke Wängberg⁴⁰, Christopher C White⁴¹, Antony R Young⁴², Richard G Zepp⁴³, Liping Zhu⁴⁴

- ¹ School of Biological, Earth and Environmental Sciences, University College, Cork, Ireland
- ² Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC, USA
- ³ Food Futures Institute, Murdoch University, Perth, Australia
- ⁴ Ptersa Environmental Consultants, Pretoria, South Africa
- ⁵ Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece
- ⁶ Unidad Académica Sistemas Árrecifales, Universidad Nacional Autónoma de México, Puerto Morelos, Mexico
- ⁷ Department of Biological Sciences and Environment Program, Loyola University New Orleans, New Orleans, LA, USA
- ⁸ Biospherical Instruments, Inc., San Diego, CA, USA
- ⁹ Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH, USA
- ¹⁰ Chemical and Pharmaceutical Sciences, Kingston University London, Kingston upon Thames, UK
- ¹¹ Friedrich-Alexander University, Möhrendorf, Germany
- ¹² Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba, Canada
- ¹³ Finnish Meteorological Institute, Helsinki, Finland
- ¹⁴ Centre for Ecology and Evolution in Microbial Model Systems, Linnaeus University, Kalmar, Sweden
- ¹⁵ National Centre for Epidemiology and Population Health, College of Health and Medicine, Australian National University, Canberra, Australia
- ¹⁶ Centro Universitario Cabo de Hornos, Universidad de Magallanes, Puerto Williams, Chile
- ¹⁷ Millenium Institute Biodiversity of Antarctic and Subantarctic Ecosystems BASE, Santiago, Chile
- ¹⁸ Cape Horn International Center CHIC, Puerto Williams, Chile
- ¹⁹ UV-B Monitoring and Research Program, Colorado State University, Fort Collins, CO USA
- ²⁰ Smithsonian Environmental Research Center, Edgewater, MD, USA
- ²¹ Population Health Program, QIMR Berghofer Medical Research Institute, Brisbane, Australia
- ²² School of Public Health, University of Queensland, Brisbane, Australia
- ²³ Frazer Institute, University of Queensland, Brisbane, Australia
- ²⁴ Department of Chemistry, Colorado State University, Fort Collins, CO, USA
- ²⁵ Indian Academy of Wood Science, Bengaluru, India
- ²⁶ Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA
- ²⁷ Ozone and Water Vapor Division, NOAA ESRL Global Monitoring Laboratory, Boulder, CO, USA
- ²⁸ School of Physical and Chemical Sciences, University of Canterbury, Christchurch, New Zealand
- ²⁹ Securing Antarctica's Environmental Future, University of Wollongong, Wollongong, Australia
- ³⁰ School of Earth, Atmospheric and Life Sciences, University of Wollongong, Wollongong, Australia
- ³¹ UK National School of Forestry, University of Cumbria, Ambleside Campus, UK
- ³² Organismal & Evolutionary Ecology, Viikki Plant Science Centre, Faculty of Biological & Environmental Sciences, University of Helsinki, Finland
- 33 Department of Biological Sciences, Rensselaer Polytechnic Institute, Troy, NY, USA
- ³⁴ School of Environmental Sciences, University of Guelph, Guelph, Canada
- ³⁵ Department of Chemistry and Biochemistry, California State University Northridge, Northridge, CA, USA
- ³⁶ Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
- ³⁷ Academic Guest after retirement from Eawag: Swiss Federal Institute of Aquatic Science and Technology, Duebendorf, Switzerland
- ³⁸ Center for Sustainable Systems, School for Environment and Sustainability, University of Michigan, Ann Arbor, MLUSA
- ³⁹ Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, China
- ⁴⁰ Department of Marine Sciences, University of Gothenburg, Gothenburg, Sweden
- ⁴¹ Exponent Inc, Bowie, MD, USA
- ⁴² King's College London, London, UK
- ⁴³ ORD/CEMM, US Environmental Protection Agency, Athens, GA, USA
- ⁴⁴ State Key Lab for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai, China

1 Introduction

Solar ultraviolet radiation (UV; 290-400 nm) is a contributing factor in the environmental fate of toxic chemicals and other contaminants, with potential consequences – both beneficial and detrimental – for the health of humans and the environment. Chemical contaminants that are intentionally or accidentally released into the environment are highly diverse in their chemistry and responses to solar UV radiation. The current assessment focuses on the degradation of plastic debris in the environment, and particularly the effect of solar UV radiation and other environmental factors on the formation of micro- and nanoplastic particles.

The Montreal Protocol on Substances that Deplete the Ozone Layer (hereafter referred to as the "Montreal Protocol") has been universally ratified by all 198 member states of the United Nations and this treaty has successfully prevented large, global-scale increases in solar UV-B radiation (290-315 nm) at the Earth's surface (1). Moreover, because many ozone-depleting substances (ODS) and their replacements are potent greenhouse gases, this treaty, together with its adjustments and Amendments, has significantly reduced global warming. Furthermore, changes in stratospheric ozone also affect climate and *vice versa*.

Previous assessments by the Environmental Effects Assessment Panel (EEAP) of the United Nations Environment Programme (UNEP) have extensively reported on a range of direct and indirect interactive effects between UV radiation and contaminants and highlighted the important consequences for the environment and human health. Some examples of beneficial and detrimental effects noted were:

- 1. Solar UV radiation reacts with atmospheric gases including nitrogen oxides (NO_x) and volatile organic compounds (VOC) to create photochemical smog, including increased levels of tropospheric ozone and secondary particulate matter, with adverse effects on human health and plants (2).
- 2. UV-driven photochemical reactions in the atmosphere convert some ozone-depleting substances (ODSs) and substitutes into degradation products such as trifluoroacetic acid (TFA), which, although persistent in the environment, presents *de minimis* risk to humans and the ecosystem (2).
- 3. In the troposphere, UV radiation drives the formation of hydroxyl radicals and other reactive oxygen species (ROS) that act as atmospheric cleaning agents (2). Hydroxyl radicals also play an important role in surface waters in the transformation and breakdown of pollutants e.g., pesticides (3).
- 4. Widespread use of topical sunscreens, for protection from UV radiation, has resulted in UV-filters entering aquatic ecosystems, with potential harms for aquatic organisms (4).
- 5. UV radiation can increase the toxicity of oil pollutants to many types of aquatic organisms (4,5), but also contributes to their degradation and removal from the environment (6).
- 6. Wildfires have become more frequent and more extreme, at least partially because of climate change. They are becoming a significant source of pollutants, including aerosols, which affect human health and reduce surface UV radiation. Aerosols from wildfires may also cause depletion of stratospheric ozone (7).

Amongst the most ubiquitous of all pollutants is plastic, such that the current era has been referred to by some as the 'plasticene' (8). We define 'plastics' as a broad range of synthetic and semi-synthetic organic polymers, which can be moulded into various shapes, as well as elastomers, for example, rubbers and composite materials. Various additives, such as stabilisers, dyes, antistatic agents, flame retardants, and plasticisers are included in the plastics formulation, resulting in substantial variations in the chemical composition, and hence functional and structural properties, of plastics.

World annual plastic production was estimated at 391 million metric tonnes in 2021 (9). A substantial fraction of plastic waste generated from consumer products (especially packaging which consumes ~40% of the resins used in plastic production) ultimately ends up in the environment. Nonetheless, there are substantial uncertainties regarding the actual fate and longevity of plastic debris

in the environment. Plastic waste that is exposed to solar UV radiation will photo-oxidise and gradually degrade into microplastic (<5 mm) and nanoplastic (<0.1 µm) particles. Such particles are now ubiquitous in the environment and have been discovered in freshwater and marine systems, soils and the atmosphere across diverse geographic regions. Once released into the environment, microplastics are ingested by organisms ranging from microorganisms to humans and have been found in human blood, placental tissue, heart muscle, and urine (10-12).

Photo-oxidation and weathering are key steps in UV-induced degradation of plastic debris and determine the useful lifespan of plastic products. The resulting plastic fragments have potential ecological impacts that are closely related to the size of the plastic particles. UV-induced degradation also results in leaching of chemicals from plastic fragments, with further potential ecological impacts. The extent of UV-induced degradation of plastics in the atmosphere and terrestrial and aquatic environments depends on both the amount and spectral composition of solar UV radiation. By preventing significant increases in surface UV radiation, the Montreal Protocol and its Amendments have likely decreased the rate of UV-B-driven photodegradation of plastics, contributed to an increase in the durability of materials and reduced the production and influx of micro- and nanoplastic particles in the environment. This assessment considers the interactive effects of UV radiation and climate change on plastic distribution, weathering, longevity, and ultimately the fate of plastic debris. Findings from this assessment address a number of the United Nations Sustainable Development Goals (SDGs, https://sdgs.un.org/goals) (Table 1).

Table 1. Overview of the alignment of plastic pollution with Sustainable Development Goals.

SDG	OBJECTIVES	Risks to the SDGs from plastic pollution and effects of UV radiation
2. Zero Hunger	End hunger, achieve food security and improved nutrition and promote sustainable agriculture	UV radiation breaks down plastics commonly used in agriculture, increasing uptake by plants, humans and other animals.
3. Good health and wellbeing	Ensure healthy lives and promote well-being for all at all ages	Fragmentation of plastics into micro- and nanoparticles by UV radiation and other factors increases penetration into tissues through food, drink and inhalation. To date, potential biological effects of microplastics are still under investigation.
6. Clean water and sanitation	Ensure availability and sustainable management of water and sanitation for all	Microplastics are a growing concern in water supplies. Where disinfection by UV radiation is used, this may contribute to further microplastic formation.
9. Industry, innovation, and infrastructure	Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation	Designing and building resilent infrastructure must consider weathering effects of \boldsymbol{U} radiation on plastic materials.
11. Sustainable cities and communities	Make cities and human settlements inclusive, safe, resilient and sustainable	Efforts to increase the sustainability of cities and communities need to consider management of plastic pollution and its breakdown by UV radiation.
12. Responsible consumption and production	Ensure sustainable consumption and production patterns	Rapidly growing plastic pollution from single use, non-sustainable, weathering-resistant plastics threatens livelihoods and the environment.
13. Climate action	Take urgent action to combat climate change and its impacts	Where climate change results in reduced cloud cover, increased UV radiation at the Earth's surface together with rising temperatures will increase rates of plastic breakdown and potential release of carbon to the environment.
14. Life below water	Conserve and sustainably use the oceans, seas and marine resources for sustainable developlment	UV radiation increases entry of fragmented plastics into the aquatic food chain, contaminating food supplies.
15. Life on land	Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, halt and reverse land degradation and halt biodiversity loss	effects of the accumulation and breakdown of plastics in
17. Partnerships for the goals	Strengthen the means of implementation and revitalize the Global Partnership for Sustainable Development	

Recently, at the request of the United Nations Environment Assembly, the Executive Director of UNEP convened an Intergovernmental Negotiating Committee (INC) to develop an international legally binding agreement to end plastic pollution. This initiative will address the following: a) the global scale of plastics in the environment; b) an improved understanding of the global impact of plastic pollution, sustainable production, and consumption of plastics; c) a full life cycle approach; and d) capacity-building through scientific and technical cooperation. This UNEP EEAP assessment seeks to contribute to this international effort to mitigate the impact of plastic pollution. The current state of knowledge about stratospheric ozone and consequent UV radiation at the Earth's surface is summarised and findings are used to assess the effects of UV radiation and interacting climate change factors on plastic materials, focussing both on durability of products as well as production and dispersal of microand nano-plastic pollutants in the environment.

2 Ultraviolet radiation throughout the 21st century

An assessment on the effects of solar UV radiation on plastic pollution requires an understanding of how this part of the solar spectrum has changed over modern times. The EEAP conducts a detailed assessment of the environmental impacts of changes in stratospheric ozone and UV radiation every four years. The most recent Quadrennial Assessment (13) included a projection of the intensity of UV radiation at the Earth's surface throughout the 21st century, which was based on an earlier EEAP assessment (14) and a study by another group (15). The assessment assumed a realistic scenario of the emission of greenhouse gases (RCP 6.0, see Supplementary Information), time-invariant amounts of atmospheric aerosols, and that there is continued compliance with the Montreal Protocol. This Quadrennial Assessment concluded that erythemal ("sunburning") UV radiation will decrease by 2–5% at northern and 4–6% at southern mid-latitudes (30°–60°) between 2015 and 2090. Changes for the tropics were projected to be smaller than 1%.

There have been no new projections of changes in UV radiation on a global scale since the most recent EEAP assessment (13). However, recent studies have identified a number of factors that may affect stratospheric ozone and other factors that may affect ground-level UV radiation throughout the 21st century. These include: increasing greenhouse gas concentrations; very short-lived substances (ozone-depleting halogen-containing chemicals with a lifetime of less than six months, which are largely produced by natural processes such as emissions from macroalgae (seaweed) and phytoplankton; effects of climate change on cloud cover, aerosols, atmospheric circulation, and surface reflectivity; air pollution and tropospheric aerosols; wildfires; supersonic aircraft; potential nuclear war; potential future climate intervention (geoengineering such as stratospheric aerosol injection); and volcanic eruptions. For details on these effects see the Supplementary Information. Many of these processes do not lead to long-term changes in UV radiation reaching the Earth's surface in excess of a few percent and would be similar in magnitude to projected trends that have been published during the last ~10 years (13,14,16). However, larger changes in UV radiation could be caused by a severe breach in the adherence to the Montreal Protocol, extreme climate events, and severe wildfires, which can lead to large, localised ozone depletion events lasting several months. Likewise, reductions in air pollution can lead to large (> 40%) localised increases in UV radiation. While "colossal" volcanic eruptions that occur on millennial time scales could substantially disturb the ozone layer and Earth's climate for many years, they are not a result of human activities and are therefore typically not considered in projections of the future climate and atmospheric composition. Likewise, assessments of the effects of nuclear war are only based on scenarios, which will likely differ from the actual situation should such a war occur.

3 UV radiation and plastics: mechanisms of weathering

3.1 UV radiation-driven photo-oxidation and formation of microplastics

Pathways of UV-induced transformation of plastics have been identified (17). Direct exposure of plastics to solar UV-B radiation induces free-radical photoreactions resulting in the photo-oxidation of the plastic (Fig. 1). Exposure of a photosensitiser (e.g., dissolved organic matter (DOM)) can also result in degradation of some plastics via the production of hydroxyl radicals and other reactive oxygen species (18). The consequent deterioration of physical properties, surface erosion and discoloration, are referred

to as weathering. Exposure to UV radiation renders common plastics such as polyethylene (PE) (19,20) and polypropylene (PP) (21-24) weak and brittle. This makes them more susceptible to fragmentation under environmental mechanical stresses (19,22,23,25,26) which leads to the release of microplastics and nanoplastics into the environment (Fig. 1). Some fragmentation can also occur due to mechanical forces alone, for instance, during agricultural processes (Sect. 4.2) and in the marine environment (27-30). To counter weathering and the deterioration of mechanical properties, the practice of adding UV-protective substances to plastics is widespread, prolonging useful lifetimes of plastic products used outdoors (31).

Studies on the spectral dependence of the oxidation process indicate that solar UV-B wavelengths (290-315 nm) are far more effective in oxidising and embrittling common plastics such as PE or PP (32) as compared to UV-A (315-400 nm) or visible (400-700 nm) radiation (33,34). Numerous factors, primarily the chemical class of plastics (26), the types of additives incorporated (23,35), molecular and morphological features such as chain branching, crosslinking, and fractional crystallinity (36), and the thickness of the material (37) affect the rate at which plastics degrade and/or fragment after exposure to solar UV radiation (22,23)(Fig. 1). Common plastics oxidise more slowly in aqueous environments than in the air, likely primarily due to the lower oxygen availability in water (17). This, together with limited UV-penetration into the water column, and surface biofouling (the growth of microbial films on surfaces of plastics), allows plastics to persist for extended, but poorly quantified, periods in ocean and freshwater environments.

While the pathways of photo-oxidation of plastics are well understood (17), those of consequent fragmentation are yet to be ascertained. Notwithstanding this knowledge gap, microscale fragments of plastic are ubiquitous across water bodies, air, and soil, as well as in organisms ranging from microorganisms to humans (38). The contribution of UV radiation to the global load of environmental microplastics cannot be reliably quantified at present due to a lack of studies that have quantitatively assessed photo-oxidation and fragmentation in natural ecosystems (27,39). Nevertheless, without the Montreal Protocol the environmental load of microplastics would likely have been higher than it is now, due to long-term exposure of plastics to elevated UV-B radiation.

Photo-oxidation also causes changes in the surface properties of plastics by increasing surface roughness and hydrophilicity (40-42). The hydrophilic functional groups on the surface of microplastic generated by photo-oxidation can interact with organic pollutants via hydrogen bonding, thus having further effects on the composition of the aquatic environment. Furthermore, UV-driven photo-oxidation and fragmentation of plastics can also increase the leaching rates of additives that are present in nearly all commercially used plastics (43,44). Additives are added to plastics, to improve functional properties, and are not chemically bound to, but are dissolved in the plastic matrix. Hence, they can easily leach out from the polymer matrix, especially after fragmentation into smaller particles (45). Specifically, additives with small molecular size such as di(2-ethylhexyl)phthalate and brominated flame retardants diffuse freely (46) and become slowly desorbed into the surrounding medium. Plastics also contain a cocktail of largely unknown residual monomers, solvents, catalysts, impurities, and degradation products (47,48), all of which can leach out into the environment.

3.2 Ultraviolet radiation and microfibres

Microfibres are the main category of microplastic particles found in both the water column and in organisms living in surface water or marine environments (49-52). All fabrics and textiles based on synthetic polymer fibres release microfibres during their manufacture and use, especially during washing and drying cycles (53-57). Upon exposure to UV radiation, increased numbers of microfibres and microplastics are generated from fabrics containing poly(ethyleneterephthalate) (PET, polyester) (58,59), polyamide (PA(60)) and PP fibres (61). For example, weathering of polyester fabrics exposed to high UV radiation for 60 days (60 W/m²) generated 20-40 times more microfibres during laundering compared to control fabrics (58). UV irradiation also resulted in a four-fold increase in the number of microfibres released from protective facemasks (62). Similarly, artificial lawns and synthetic turf sports fields, which cover large surfaces exposed to solar radiation worldwide, release large amounts of microplastic fibres which, via run-off, end up in local rivers and the nearshore sea area (63).

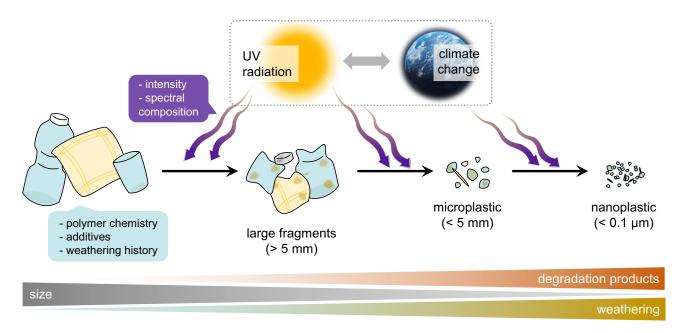


Figure 1 Conceptual diagram depicting the formation of micro- and nanoplastics under natural conditions. UV radiation and mechanical stress (not shown) drive the weathering and fragmentation of larger plastic waste into smaller fragments and other by-products (e.g., CO₂, CH₄, and leachates; not shown in the figure). The photodegradation rate depends on properties of the plastic polymer (such as its chemical composition, the presence of specific additives, and the object's weathering history) and the exposure to UV radiation, including its intensity and spectral composition. Climate change impacts photodegradation, amongst others, by modifying the intensity of UV-B radiation and increasing the ambient temperature.

As with bulk plastics, long-term exposure of fibres and fabrics to UV radiation reduces their mechanical properties, and thus durability. This has been reported for a variety of fibres and fabrics, including polyvinyl chloride (PVC)-coated PET fabrics (64), poly(3-hydroxybutyrate) electrospun fibres loaded with zinc oxide nanoparticles (65), high-performance fibres used in firefighters' protective (66-68),carbon fibre/epoxy composites (69), and poly(lactide poly(hydroxybutyrate) yarns and fabrics (70). Research is ongoing to reduce the impacts of UV-induced photo-oxidation on fabrics and textiles, particularly by introducing surface modifications. For instance, bio-based finishing of polyester fabrics using chitosan helps to strengthen the bond between fibres and matrix, which reduces the shedding of microfibre fragments during use, and improves durability of the fabric (71). The use of UV-absorbing stabilisers as coating materials in UV-sensitive fabrics can also improve durability (72,73). For instance, thermochromic materials which are often used in certain textiles and packaging, display low UV-stability but their durability significantly improves after incorporating UV-absorbers into these materials (73).

3.3 Outdoor weathering of plastic materials in a changing climate

Deterioration of plastic materials under outdoor conditions is a process driven by the interaction between solar UV radiation, and other weathering factors such as temperature. Given ongoing climate change, this is projected to change in the future (IPCC 2021). Consequently, it is expected that materials will degrade at a less predictable pace, the distribution of degradation products may also change, and harmful substances may leach into the environment at different rates.

Two examples of the importance of weathering by UV radiation and climate factors are from tyres and solar panels. The generation of small rubber particles from tyres is a process affected by exposure to UV radiation as well as heat, eroded tarmac, and impervious road surfaces (74). It is estimated to annually contribute 6 million metric tonnes of microplastics worldwide (75). Higher road surface temperatures due to climate change can also accelerate tyre degradation. Microplastics from tyre wear are prominent in urban environments, and in road run-off (74). An emerging area of concern is that these

microplastics can undergo further photothermal-oxidation and their subsequent degradation products may be toxic (76), although this issue remains largely unexplored (77-79).

As part of climate change mitigation strategies, installing of solar energy generating capacity is expected to triple between 2022 and 2027 according to the International Energy Agency (80). Thus, a thorough understanding is required of the impact of UV radiation and climate change on weathering of solar panels, and this applies particularly to plastic components such as the backsheet or outer, protective layer of solar photovoltaic cells. Solar panels retrieved from commercial sites, after operating for up to 28 years in many different climatic zones, and with different materials, displayed variable degrees of weathering of backsheets (81). Many of the PET backsheets showed microcracking and chalking, surface embrittlement and material erosion, which are generally driven by UV radiation, and which would potentially limit the functional life of the solar panel. Fluorinated plastics such as polyvinylidene difluoride, polytetrafluoroethylene-co-hexafluoropropylene-co-vinylidene fluoride, and polyvinyl fluoride display the least amount of degradation, but still show some surface erosion causing localised regions of embrittled plastics (81). Careful consideration of the choice of future backsheet materials will be essential to avoid additional release of microplastics into the environment (82), especially given the rapid increase of solar energy harvesting devices and their location in sunny (UV-exposed) locations.

3.4 Ultraviolet radiation-driven mineralisation of plastics

Degradation of plastics occurs through two basic mechanisms: (1) photo-oxidation followed by fragmentation and release of dissolved organic matter (DOM); and (2) mineralisation. Mineralisation refers to the final step in the degradation process where the plastics are being decomposed, usually oxidatively, into inorganic end-products such as water and carbon dioxide. Fragmentation, DOM release and mineralisation processes occur concurrently in the dark, but rates are enhanced, albeit to a variable extent, in plastics exposed to solar UV radiation (83). Solar UV-facilitated oxidation, and subsequent fragmentation, produces large numbers of nanoscale or very small microscale plastic fragments (20). Given their high specific area, these microplastics undergo further degradation releasing dissolved organic matter (84,85). Some of the evidence for photomineralisation of microplastics is based on accelerated laboratory studies using microplastics suspended in aqueous media and exposed to highintensity UV radiation. These studies of DOM release and mineralisation have only been conducted under a narrow range of laboratory conditions and there is much uncertainty about mineralisation rates in the natural environment. There is also uncertainty about how polymer additives (86,87), natural DOM (88), and biotic factors, which are usually excluded in laboratory studies, further modify mineralisation rates. Direct evidence of mineralisation in the natural environment is lacking. However, leaching of DOM from solar UV-exposed plastics under outdoor conditions has been reported, indicating at least the partial conversion of a fraction of the plastics into water-soluble organic compounds (89). Nevertheless, even under accelerated exposure the process is slow, and it might be speculated to be even slower in natural environments (see also Sect. 4.3).

4 Plastic pollutants in the environment

4.1 Nano- and microplastics in the atmosphere

Both micro- and nanoplastics have been found in the atmosphere (Fig. 2). Recent evidence indicates that microplastics are transported through the atmosphere to remote regions by wind (90), with different shapes (e.g., fibres *vs* fragments, (91)) being distributed to different degrees. These micro- and nanoplastics are emitted by a variety of different sources, but emission of microplastics from the ocean to the atmosphere has been the focus of recent research (92)(Fig. 2). Microplastics can be ejected from the ocean like sea spray aerosol (93,94). Stratospheric ozone depletion changes natural marine aerosol fluxes via the strength and position of the westerly jet in the Southern Ocean (95). Marine microplastic fluxes may be similarly affected, but this has not yet been examined.

Experimental data are scarce, but global chemical transport model simulations indicate that microplastics with diameters of 0.5-70 µm can be present at levels of 0.001 µg plastic per m⁻³ in the atmosphere at remote locations, compared to 0.1 µg m⁻³ in polluted environments (96). These levels

should be placed in context of the total atmospheric load of particulate matter (PM) with a diameter smaller than 2.5 μ m (PM_{2.5}) (e.g., sea salt, mineral dust, organic aerosols, sulphate, soot), which ranges in order of magnitude from 1 μ g m⁻³ in remote locations to 100 μ g m⁻³ in polluted environments (97). The mass of atmospheric aerosols with diameters less than 70 μ m (PM₇₀) is not routinely measured so no data are available. However, their mass should be substantially greater than that of PM_{2.5}. This means that, overall, microplastics are likely to comprise less than 0.1% of the overall mass of atmospheric aerosols. There is no evidence that microplastic aerosols have effects that are disproportionately large compared to other atmospheric aerosols. Consequently, and given technical limitations in quantifying atmospheric plastics, the contribution of microplastics to atmospheric chemistry and physics is currently expected to be negligible.

Few atmospheric observations exist of microplastics smaller than about 10 µm because of technical limitations (98). Smaller particles may be transported over longer distances and provide more surface area (per unit mass) for chemical and radiative processes. Recent modelling studies have examined whether microplastics in the atmosphere contribute to climate change. Assuming that microplastics are confined to the boundary layer (bottom 2 km of the atmosphere), direct microplastic-radiation interactions may have a weak cooling effect, but this is subject to large uncertainties in concentration and distribution of particles (98). Microplastics can also act as ice-condensation nuclei (ICN) and/or cloud condensation nuclei (CCN) as they undergo ageing (99). However, as stated above, their abundance is small compared with other sources of CCN and/or ICN. For example, cloud water collected near Mt. Fuji, Japan, contained only 120 plastic particles L-1, many orders of magnitude below the concentration needed to have an effect on cloud formation (100). While their CCN and ICN efficiency has not yet been assessed, given their low abundance microplastics are not expected to make a substantial contribution to radiative forcing via indirect microplastic-cloud interactions. However, further quantitative monitoring of microplastics in the atmosphere is required to confirm this interpretation.

Microplastics suspended in the atmosphere are subjected to some of the highest levels of UV radiation in their life cycles, with contributions from direct and diffuse sky radiation, as well as reflections from the surface (Fig. 2). Photons of shorter wavelengths (e.g., UV-B) are more abundant in the atmosphere than in other environments (e.g., aquatic) where microplastics are found. Hence microplastics are likely to degrade faster in the atmosphere by UV-driven processes, although data on this process are currently lacking. UV-B radiation also affects the air surrounding suspended particles, generating highly reactive hydroxyl radicals (OH) that readily oxidise micro- and nanoplastics. Shorter wavelengths, which are most sensitive to changes in stratospheric ozone, have stronger effects on UV-driven weathering of plastic than longer wavelengths (40). Although knowledge of the spectral dependence of the relevant photo-oxidation reactions is limited, changing UV radiation in the context of stratospheric ozone depletion and recovery, as well as accelerating climate change, will likely affect the lifetime of microplastics in the atmosphere.

4.2 Plastics in terrestrial environments: agroecosystems and the built environment

Plastics are found in terrestrial ecosystems because of their use in agriculture and horticulture, building and construction activities, their disposal in landfills, and as debris generated on land. Agriculture, horticulture, and forestry are major sources of microplastics in terrestrial environments (101). The use of plastics in these sectors is increasing with global economic development, plastic affordability and in countering the abiotic stresses imposed on crops by climate change (102). This section addresses the effects of UV radiation on plastics in terrestrial ecosystems with an emphasis on the generation of microplastics in agroecosystems and implications for food security and sustainable agriculture.

The United Nations Food and Agriculture Organisation (102) has estimated that agricultural usage of plastics (mainly PE and PP) is 12.5 million tonnes annually. Plastic materials are widely used as netting, irrigation pipes, seed coatings, greenhouses, growth tunnels, tree guards and shelters, and packaging (103). Agricultural plastic mulch is considered a key source of small plastics in soils (104). Mulching involves seasonal covering of soil with lightweight plastic sheets (often PE) and this practice is increasingly used to retain soil moisture and heat, and to prevent soil erosion and weed growth (105).

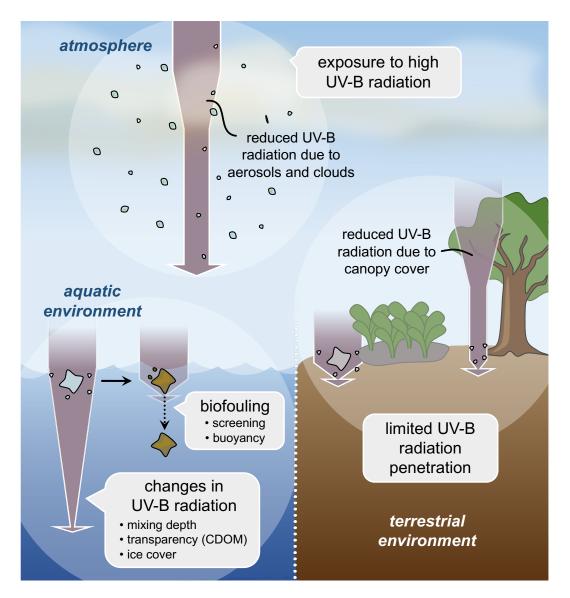


Figure 2. Effects of UV(-B) radiation on plastic litter in various environmental compartments. In the atmosphere, micro- and nanoplastics are exposed to high levels of UV-B radiation; only aerosols and clouds provide a partial UV screen. In aquatic environments, UV-B radiation penetrates only to a limited extent into the water column, leading to a gradient of UV-B varying from high exposure at the water surface to virtually zero exposure deeper in the water column and within sediments. How UV exposure varies with depth depends on various factors, including the mixed layer depth, water transparency, and the presence of surface ice. Biofouling – the growth of a biofilm on the surface of plastic debris – further limits the amount of UV-B radiation plastic fragments are exposed to both by screening radiation and by altering buoyancy (i.e., the position of plastic debris within the water column). In terrestrial environments, plastic can be exposed to high UV-B radiation at the soil surface, but UV is fully screened at depths greater than a few centimeters. Plant canopy cover can reduce further UV radiation at the soil surface. Differences in arrow length and width depict the different availability of UV radiation across the three environments; a change in arrow width indicates a decrease in UV-B availability.

With increasing frequency of droughts under climate change (106), use of mulching is expected to escalate to control water loss from agricultural soils (107,108). The disposal of plastic mulch represents a major challenge and belies its promotion as a sustainable product. If tilled and buried, it becomes a source of microplastics and leached additives in soil ecosystems (109-111). Plastic pollution is not limited to agricultural soils; substantial amounts of microplastics are present in all soils studied, including in industrial and urban environments (112).

It has been estimated that annually some 57,000-390,000 and 39,000-272,000 tonnes of microplastics are added to European and North American farmlands, respectively, making soils a larger reservoir for plastics than the oceans (113). Use of plastic mulch is associated with soil contamination of between 0.1 to 324.5 kg ha⁻¹ plastics (>5 mm), and up to 1076 ± 347 microplastic particles per kg soil (104). It is likely that breakdown of buried plastics is slow; consequently, soils accumulate plastic debris (112,114). Another key source of soil plastic pollution is sludge from wastewater treatment plants, which is applied to condition and enrich soils on agricultural land (115). Sludge can incorporate a variety of chemically different plastic particles (116). Other sources of plastic in soils include general plastic litter, tyre wear, and atmospheric deposition (117,118).

Any plastic on the soil surface, such as plastic mulch, will be exposed to solar radiation, oxygen, and ambient temperatures and becomes brittle due to UV radiation-mediated weathering (Fig. 2, 3). This makes these plastics prone to subsequent fragmentation under minimal mechanical stress (23,25). Even plastic buried ~1 mm deep in soil and exposed to UV radiation in the laboratory can generate microplastics through weathering (119). Photo-oxidation in combination with fragmentation, will increase the downward migration of plastic fragments in the soil, with particles found on soil surfaces and to depths of *ca* 100 cm. This poses a risk due to potential contamination of groundwater systems and drinking water (114)(Fig. 2). It is especially likely that smaller (< 1 µm) plastic particles will migrate downwards at a faster rate and contaminate aquifers (120). However, there are still considerable knowledge gaps in our understanding of the vertical migration of plastics through soils. For example, incorporation of plastics into soil aggregates limits vertical transport, while water infiltration and activities of soil fauna can enhance downward movement. Conversely, the roots of some plants are associated with the upward movement of plastics. Thus, a picture emerges of variable transport kinetics, and this in combination with ploughing may affect exposure to UV radiation, photo-oxidation and further fragmentation of the plastics (121)(Fig. 2, 3).

There is accumulating evidence concerning the broad spectrum of impacts of microplastics on plants, including crops, as well as other soil biota. Most studies are performed using unrealistically high concentrations of micro- and nanoplastics, and it remains to be ascertained which of the identified hazards poses a realistic risk. Nevertheless, there is now evidence that microplastics alter the structure, water-holding capacity, microbial activities, nutrient cycling, and bioavailability of other pollutants in contaminated soil, and exert phytotoxic effects in combination with other pollutants (117,122). Effects of microplastics on plant growth and development may relate to the above-mentioned changes in soil conditions (e.g., nutrient cycling and soil structure (122)), or can be due to direct effects of microplastics on plants (117,123), including interactions with abiotic factors (e.g., UV radiation and drought stress (124). Uptake of plastics by plants has been demonstrated for smaller micro- and nanoplastics (125). This process has potential consequences for food chains and food quality including human nutrition (123). However, it is possible that adherence to roots can also be exploited as part of a bioremediation strategy whereby plants are used to remove plastic particles from contaminated soils (126). Furthermore, microplastics in the soil may, under some conditions, increase the release of greenhouse gases such as carbon dioxide, methane and nitrogen dioxide (127). Overall, better-substantiated experimental data are required to fully assess effects of microplastics on plants, crops and soil ecosystems.

4.3 Nano- and microplastics in aquatic environments

Plastics are also ubiquitous in the aquatic environment. For example, a recent survey of 38 lakes and reservoirs across 23 countries found plastic debris >250 µm in size in all water bodies and sometimes at concentrations substantially higher than in ocean gyres¹ where plastics are known to accumulate at high concentrations (128,129). Most of these plastics are transported by rivers and the atmosphere into the ocean environment (90).

¹ Gyres are large scale circulation systems in the ocean forming circular patterns of currents that trap floating materials in their central regions. The main ocean gyres are in the North and South Atlantic, the North and South Pacific and in the Indian Ocean.

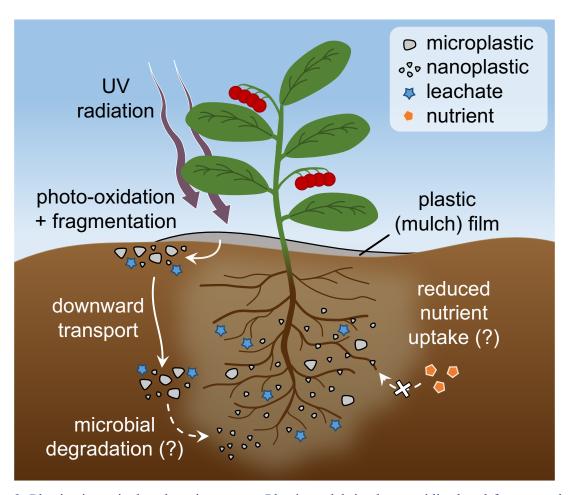


Figure 3. Plastics in agricultural environments. Plastic mulch is photo-oxidised and fragmented due to exposure to UV radiation and mechanical stressors. This process releases variously sized plastic fragments (grey) and leachates (blue stars). These degradation products are dispersed downwards into the soil, where they are not subjected to further photo-oxidation and thus tend to accumulate. The fate of buried plastics is subject to considerable uncertainties. Potentially, microbial processes can degrade plastics, contributing to its removal. Plastic fragments may also interfere with plant nutrient uptake. Full arrows indicate processes that are well established; dashed arrows show processes whose occurrence is less certain.

As in terrestrial environments, exposure of plastics to solar UV radiation in the aquatic environment is an important factor leading to fragmentation into microplastics. As described in section 3.4, the exposure of many types of plastics to UV radiation releases DOM and other products, including greenhouse gases (e.g., CO₂, CH₄) (84). Release of DOM occurs by photochemical breakdown of microplastics, a process for which UV-B radiation plays a key role in regulating the initial rate (84). One study estimated overall photodegradation rates of ~2% of carbon mass per year for floating plastics in the sub-tropical ocean with DOM release accounting for more than 50% of the carbon loss. However, this estimate cannot be generalised, since it only applies to one size of PE and PP fragments, and relies on rates extrapolated from laboratory exposures (130). The chemical composition of the plastic, particle size, and previous environmental processing all affect the amount of DOM released, with greater DOM production reported from aged plastics (89). Additionally, exposure to UV radiation accelerates the degradation rate of the remaining material by biological (microbial) processes, as shown in a study of cellulose diacetate, a common synthetic fabric polymer (131).

The DOM leached from photodegraded plastics comprises tens of thousands of compounds ranging from relatively bioavailable, low molecular weight organics to large, complex, and recalcitrant polymer fragments (132). While the formation of these breakdown products is part of the process of the ultimate removal of plastics from aquatic ecosystems, DOM may also act as a photosensitiser that further catalyses plastic degradation.

Most of the dissolved organic carbon released during photodegradation is rapidly assimilated by bacteria (89,133). Organic carbon derived from plastics may be more accessible to organisms for uptake and metabolism than natural organic carbon and foster more bacterial growth (134). However, there is concern that some leached substances may be potentially toxic to aquatic organisms. In a recent study of polyethylene bags exposed underwater to combined UV and visible radiation (in a solar simulator), no acute toxicity was reported in zebrafish from photoproducts, although RNA sequencing showed changes in gene expression associated with disrupted neuromuscular processes (135). The study also showed that the net impacts of released photoproducts likely depend on the leachate composition, as differences were noted in leachate-induced gene expression among polyethylene bags depending on the presence of additives such as titanium oxide (TiO₂). Additives reduce the photo-degradation of plastics, but this benefit should be balanced against the potential phototoxicity of the additive itself.

Studies on the spectral dependency of plastic degradation in the aquatic environment using natural or ecologically relevant laboratory exposures are still in the early phases. One contributing factor to this difference is that laboratory studies often neglect to account for biofouling that can reduce incident UV irradiation to the underlying plastic (136). Biofouling can also increase apparent plastic density, thereby allowing fragments to sink deeper in the water column where they are exposed to less UV radiation (136,137)(Fig. 2). Additional variables that impact plastic photodegradation, but are seldom investigated, are environmental history (i.e., virgin vs aged plastic; (89), and water type (i.e., seawater vs. freshwaters) (138).

Changes in water transparency and mixing depth modify the amount of solar radiation received by plastic debris in the surface mixed layer, affecting both the cumulative exposure of plastics to solar UV radiation as well as the spectrum of the radiation (Fig. 2). Climate change is warming aquatic ecosystems and changing wind patterns, both of which interact to determine mixing depth. This interaction deepens mixing in some areas (mainly marine) and leads to shallower mixing in other water bodies (mainly freshwater) (4). Exposure of microplastics to UV radiation in the Arctic Ocean will increase in the future because of sea ice loss. This effect outweighs small decreases in UV-B radiation that are projected in response to the anticipated recovery of stratospheric ozone at high latitudes (13). Both effects are expected with a warming climate (13). The Arctic cryosphere (sea ice, glaciers, and permafrost) is assumed to function as a temporal sink for microplastics, similar to that for many other pollutants that are transported there either by precipitation from the air or by currents entering the Arctic Ocean from the Pacific or Atlantic Oceans (139,140). The decade-long model by Huserbråten and colleagues (141) examined transport of buoyant microplastics into the Arctic Ocean from the major rivers in Northern Europe and Russia. It shows that over time there will be an accumulation of particles in specific regions of the Arctic Ocean. However, the ability to forecast the effects of these microplastics in the Arctic is challenged by limited data (140). There are no specific studies on photochemical transformations of microplastics in the Arctic. Nevertheless, given the key role of UV-B radiation in forming and degrading microplastics, rates of accumulation of microplastics in the Arctic will depend on many factors including long-term changes in stratospheric ozone, ice cover and other factors as discussed in section 2 and the Supplementary Information.

5 Environmental risks associated with weathered and fragmented plastics

As outlined above, UV radiation-driven weathering affects the physical properties of plastics including strength, brittleness, surface charges and colour, as well as the attached biofilm (biofouling). In turn, this can affect the rates at which organisms ingest microplastics with potential biological impacts (142). There is a need for comprehensive research into the risks associated with microplastics in the environment. Such research needs to include direct risks associated with exposure to larger plastic debris (e.g., entanglement) and micro- or nanoplastic particles, as well as indirect risks associated with exposure to pollutants adsorbed to plastic particles or leachates containing plastic breakdown products generated during photo-oxidation. The impacts of microplastic pollution on organisms are not central to this assessment, but it is noted that frameworks designed to discern relevant eco-toxicological effects are being developed (143). Currently, knowledge about the toxicity of microplastics to organisms under environmentally relevant conditions is limited, and so is our understanding of the impact of UV radiation

and climate change conditions thereupon (144). Nevertheless, concerns are justified given the ubiquitous presence of microplastics in the environment and within organisms. In accordance with the precautionary principle, protective action should be taken to reduce the risks of exposure of organisms to plastic degradation products despite scientific uncertainty (145).

5.1 Leachates from weathered plastics

Plastics typically contain multiple types of additives that improve performance and ensure their durability. Some legacy additives are toxic (146,147), being potential carcinogens or hormone-mimicking endocrine disruptors that cause adverse responses at very low concentrations (148). The fraction of the additive chemicals in a plastic composition varies from less than 1% by weight (UV stabilisers or biocides in polyolefins) to over 50% by weight (plasticisers used in PVC).

Photo-oxidation and weathering affect the rates at which additives and products of plastic degradation leach into the environment. These effects of UV radiation on leaching are associated with fragmentation caused by weathering, which increases the specific surface area of the fragmented particle. For example, photo-oxidation of polycarbonate can result in the leaching of the endocrine disruptor bisphenol A (44), while photo-oxidation of PE can enhance the leaching of another endocrine disruptor, dibutylphthalate (43). It is not yet known whether these endocrine disruptors leach to such an extent that they affect biota. Similarly, exposure of common plastics (e.g., polystyrene (PS), low-density PE, and high-density PE) to solar UV radiation resulted in increased leaching of the harmful plasticiser bis(2-ethylhexyl) phthalate (149). Organisms may be affected by leachates through ingestion of plastics or through contact with leachate present in the environment (150). In both cases, leachates containing additives can contribute to the potential toxicity of plastics (151). However, while effects of UV radiation on the generation of leachates have been reported, there is still considerable uncertainty regarding their biological effects.

An important topic of emerging concern is the weathering of tyres (in part due to exposure to UV radiation, see Sect. 3.3), and the consequences thereof for leachate release. Among the hazardous chemicals leaching from weathered tyres are p-phenylenediamines, used as antioxidants. P-phenylenediamines have been found with high frequency bound to particulate matter in air (PM_{2.5}) as well as in urban runoff, roadside soil (152), and urban surface water (79). These aromatic amines transform to toxic quinone derivatives by reaction with ozone and environmental oxidants (153). Weathering affects the composition of the leachates released from tyres. Some hazardous chemicals are not found in leachates when tyres are subjected to natural ageing, while the concentration of other leaching substances increases (78). At present the chemical composition of leachates of weathered tyres and other plastic products is subject to considerable uncertainty (78). As a consequence, potential environmental effects of leachates from weathered plastics remain largely unknown.

Chemical compounds are also leached from weathered fabrics (59,60). Composite fabrics have drawn attention as they tend to release complex chemical molecules into the environment. For instance, polyurethane coated PET-based fabrics release a large number of carbon- and nitrogen-containing substances during photodegradation (59). Per- and polyfluoroalkyl substances (PFAS) are released from water-repellent PA textile fabrics and microfibres following weathering (60). In turn, these PFAS are of concern because of their potential toxicity, persistence, and capacity to undergo long-range transport to remote regions (154).

5.2 Changes in the adsorption of pollutants to plastics due to photo-oxidation

Photo-oxidation will cause changes in the surface properties of microplastics by increasing their surface roughness and hydrophilicity (Sect. 3.1) (40-42). These surface changes will affect the adsorption of organic pollutants (41,155-157). However, it is difficult to predict whether the adsorption of various pollutants onto microplastic will increase or decrease subsequent to photo-oxidation. For metals, such as lead, the situation is more predictable; their adsorption onto photo-oxidised microplastic compared to pristine ones will increase (158). However, current data are not adequate to assess whether these adsorbed metals are bioavailable and/or cause a toxic effect.

Changes in surface properties of microplastics do not just concern the adsorption of pollutants, but also of natural organic substances. For example, UV-oxidation can enhance adsorption of humic

acids in the freshwater environment (159). As a result, photo-oxidised microplastics can become more dispersible in the water column, and exhibit altered settling rates and settling depth (160). Hence, in addition to the adsorption of pollutants, photo-oxidation of microplastics may alter the distribution of plastics in the environment. However, overall understanding of the environmental consequences of UV-oxidation of plastics remains incomplete (161).

Photo-oxidation, which can initiate formation and growth of cracks in plastics may also enhance biofilm formation through surface roughening. In turn, algal biofilms increase cracks, pores, surface areas, and further oxidise plastics and microplastics. These biofilm-initiated degradation mechanisms have synergistic interactions with other pollutants (42,162,163). For example, microplastics with biofilms adsorb or release pollutants (162), including antibiotics, with potential consequences for organisms.

6 Nano- and microplastics and human health

Humans are exposed to microplastics through ingestion, inhalation and skin contact. Exposure is primarily through ingestion of drinking water and food including crustaceans and other seafoods, sea salt, honey, beer, and other components of foods (164). The second route of exposure is through the inhalation of air and dust containing microplastics. Exposure of the skin is considered the least likely exposure route due to the protective barrier of the outermost layer (stratum corneum) of the skin. Studies have shown that microplastics smaller than 150 μ m can pass through the gastrointestinal epithelium in mammals (165), and thus the absorption of microplastics in humans is plausible. Smaller microplastics ($\leq 10~\mu$ m) appear to infiltrate tissues and pass through cellular membranes (165). Microplastics have been detected in human tissues collected in clinical settings, including placenta, lung, liver, colon, sputum, and bronchoalveolar lavage fluid. They have also been detected in blood, breast milk, saliva, urine, and faeces (including the first stool produced by a newborn) (165,166).

Concerns about the potential risk of microplastics and their leachates to human health have focused mainly on toxicity to the lungs, gastrointestinal tract, and liver; putative mechanisms include oxidative stress at the cellular level and inflammatory reactions at the tissue level (144,167). However, the majority of studies on the health impacts of plastics are limited by small sample sizes and may suffer from cross-contamination of samples during collection and processing. In addition, knowledge about the toxicity of microplastics under environmentally relevant conditions, with realistic exposure levels, is limited (144). Potential mechanisms of toxicity, and the role of microplastics as potential carriers of chemical contaminants and pathogens remain to be determined.

One potential leachate from degrading plastic is PFAS (Sect 5.1). While many studies have investigated potential health effects of PFAS exposure (168), there is ongoing research to clarify links with health outcomes. Human exposure to PFAS from plastics relative to other sources has not been fully quantified but is likely to be small.

The ecological, social and economic impacts of macro, micro- and nanoplastic pollution are inequitably experienced, often primarily affecting communities that are marginalised and vulnerable (169). Inequitable impacts of plastic pollution are apparent at all stages of the plastic life cycle as follows (170):

- Higher abundance of plastic litter due to poor waste management practices threatens the health of economically disadvantaged communities and damages their natural environments;
- Harm to people and ecosystems located near plastic production facilities from contamination of air, water and soil by plastic borne chemicals and microplastics;
- Inequities arising from the availability of higher grades of plastic resins and relatively more effective waste management practices in wealthier countries;
- Communities living near waste dumps that carry plastic trash and/or waterways polluted with floating plastic debris are especially vulnerable to negative health effects. Waste-pickers, in some countries overwhelmingly women of childbearing age, are especially subjected to potential risks of toxicity during pregnancy. Exposure of plastics to UV radiation in these locations further raises risks of exposure of the community to nano- and microplastics and leachates.

7 Knowledge gaps

Major questions remain concerning the fate and longevity of plastic waste in the environment, and the potential harmful effects of these plastics and their chemical additives on humans and other organisms. Further knowledge is needed on the risks to health and the environment from plastic pollution, and how such risk is impacted by the combined effects of UV radiation and climate change. Despite this knowledge gap, the precautionary principle in environmental science supports preventive action, even where all effects have not been fully quantified.

Weathering experiments in the laboratory have helped to identify the mechanism and rate of breakdown of plastics into micro- and nanoplastics (Sect. 3.1 and 3.4). However, there are still substantial knowledge gaps concerning the spectral sensitivity of UV photo-oxidation and the likelihood of complete plastic mineralisation. Furthermore, oxidation and degradation rates have not been quantified in the natural environment (e.g., in ocean, lakes, soils, and the atmosphere) where mechanical forces (e.g., wave action, wind), biofouling and breakdown by microorganisms modify the effects of solar UV radiation and rates of fragmentation. Thus, the overall fate, and longevity of environmental plastics remain largely unknown. Furthermore, substantial uncertainties persist concerning the quantitative contributions of mechanical fragmentation and biologically mediated fragmentation of plastics relative to that facilitated by photodegradation. Until the various factors that lead to the degradation of plastics are better understood, it is not possible to determine to what degree changes in solar UV radiation, which have been projected to be < 10% over the 21st century (Sect. 2), in tandem with climate change, will affect the fragmentation of plastic debris. This is a major knowledge gap that needs to be addressed before the effect of the Montreal Protocol and potential future amendments on the fate of plastics can be more robustly assessed.

8 Towards a more sustainable future

The Montreal Protocol has protected the biosphere from excessive UV-B radiation that would have made the planet inhospitable to many lifeforms. Relentless monitoring and the phase-out of 99% of ozone-depleting substances in most countries, has supported the effort of humankind to preserve the planet for generations to come, evidenced by indications of the recovery of the stratospheric ozone layer.

Stratospheric ozone depletion is considered a challenge that has been brought under control (171). Climate change and growing pollution, on the other hand, remain critical issues threatening the viability of our planet, exemplified in this assessment by plastic waste in the environment and the role of UV radiation and climate change in its breakdown.

By regulating the production and consumption of ozone-depleting substances the Montreal Protocol has reduced significant detrimental effects of UV radiation on many materials, including plastics. Weathering of materials is, however, a result of combined effects of all weathering agents, including temperature, precipitation, pollutants, freeze-thaw cycles, mechanical stresses, in addition to solar UV radiation. Climate change is raising the global average temperature to which outdoor materials are exposed, and extreme weather events are becoming more frequent, negatively impacting durability of these materials. This highlights the need for innovative new technologies and materials to successfully adapt to climate change. For plastics this would include developing durable materials with a lifetime tailored to their application. Moreover, as climate change is changing the behaviour of people, novel smart materials with high UV protection, UV detection, and/or thermochromic capacity are required to meet the demands of consumers.

Plastics have been intentionally designed for in-use functional performance, but rarely has endof-life fate of these materials been a dominant consideration in their design. There is a wide variety of grades of plastic resins, additives, and manufacturing that affect performance, weathering, and the lifetime of these materials and their impacts on the environment. Plastic debris persists after its intended life in the air, soil, water, and in living organisms, and there is a need to design novel plastics or plastic alternatives, where weathering and lifetime match the functional life of products, and which can be broken down into harmless substances, thus reducing accumulation of plastic debris in the environment. The design of plastics with tuneable durability can be customised for determining the end-of-life of the product, reducing both microplastic formation and post-use plastic accumulation (172). For example, PVC, the third most produced plastic, requires long durability when used in construction where it needs to last decades, while in some single-use medical materials a short in-use design life is adequate. Additionally, plastics can be designed for ease of recyclability (chemical, biological, mechanical), depending on their in-use needs, for instance, by designing products that use only a single plastic component. The concept of biodegradable plastics (biological recycling) involves developing plastics that are subject to complete mineralisation to CO₂, either in nature or in a commercial facility, within a certain timeframe. This timeframe is dependent on many environmental factors including temperature, UV radiation, and microbe types and needs to include effects of the changing environment. Therefore, many biodegradable plastics may not fully degrade in the environment and will instead end up as small plastics or microplastics for long periods of time (172). Evolving regulations should consider the desired function intended for the plastic materials as well as end-of-life management, including the recovery and processing in waste treatment systems.

Use of biobased, green, eco-friendly, sustainable materials is of growing interest to industry (173,174). Alternative, environmentally sustainable materials can replace plastics in various applications (e.g., transparent wood composite with thermal insulating capability and high UV-blocking properties to replace plastics or glass in energy-efficient buildings and photovoltaic devices (175,176)). Similarly, novel biodegradable composites based on cellulose and lignin can replace some of the conventional polymer-based products (e.g., tree-sapling shelters) to reduce their contribution to plastic pollution (177,178). Such development of eco-friendly alternatives for plastic materials intended for outdoor use is being recognised as a viable strategy in pursuing a sustainable future.

Stabilising additives affording UV-protection for use in coatings and fabrics (179,180) can also be made of bio-based materials e.g. lignin (181), chitosan (182,183), plant extracts (182,184), and low-carbon production processes (185,186). Similarly, more sustainable dyes and processes are being developed. For instance, a green tea product was used to dye wool fabrics through laccase-assisted polymerisation (187), while sodium lignosulfonate, an industrial bio-waste, was also successfully used as a dye and UV-protective finish of nylon fabric (188).

Finally, some progress has been made in the development of alternatives to phthalates (a class of chemicals that make plastics more durable) (174) and polybrominated fire retardants (189) used in relatively high-weight fractions in plastics. Overall, to mitigate future risks, every effort should be made to limit the release of hazardous additives from materials degrading with solar UV radiation.

This assessment has detailed some of the complex consequences of the photo-oxidation and weathering of a wide range of traditional plastics, resulting not only in a shortening of the useful lifespan of materials, but also in the release of micro- and nanoparticles, as well as hazardous leachates. Thus, it is essential that the entire cradle-to-grave life cycle of new additives and materials is subject to critical analysis to avoid potential environmental impacts.

9 Conclusions

There is a rapidly increasing awareness of the threat associated with the ubiquitous presence of plastic debris, as well as micro-, and nanoplastic particles in the environment, although the environmental and health effects of plastic pollutants are yet to be fully understood. The precautionary principle encourages preventive action even in the absence of extensive technical data, as expressed in the aim of the UNEP Intergovernmental Negotiating Committee, which aims to develop a comprehensive, legally binding international agreement to end plastic pollution.

This current assessment update has emphasised the importance of UV radiation in plastic degradation through photo-oxidation, and the acceleration of fragmentation into smaller fragments, including micro- and nanoplastics. Overall, UV radiation has negative effects on the fate of plastics; 1) by shortening the lifetime of plastic products and 2) by enhancing the degradation of plastic debris into micro- and nanoplastics. Projected decreases in UV-B radiation as a result of the Montreal Protocol are likely to extend the functional-life of plastic products but also decrease the UV-initiated degradation of plastics and therefore the formation of micro- and nanoparticles. Conversely, plastic debris is likely to have become more resistant to degradation in the environment. As part of a move towards a healthy sustainable planet, UV radiation and climate-mediated impacts on durability, weathering and fragmentation of plastics are key considerations in the design of new, innovative plastics to replace those

currently in use. Weathering and lifetime of these novel plastics, or plastic alternatives, will need to match the functional life of materials, while debris will need to be broken down into harmless substances, thus reducing accumulation of plastic in the environment.

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Supplementary Information for Section 2 of

Microplastics in the Environment in the Context of UV radiation, Climate Change and the Montreal Protocol

G. H. Bernhard¹, A. F. Bais², P. J. Aucamp³, I. Petropavlovskikh^{4,5}, S. A. Robinson⁶, and G. Chiodo⁷

This supplement provides more detailed information on Sect. 2 ("Factors affecting UV radiation throughout the 21st century") of the main text.

Since the publication of the last comprehensive assessment (*Bernhard et al.*, 2023) of the Environmental Effects Assessment Panel (EEAP) of the Montreal Protocol under the United Nations Environment Programme (UNEP), several studies have confirmed known or identified additional mechanisms that may affect stratospheric ozone and other factors controlling UV radiation throughout the 21st century. In the following, we assess these processes and their potential impact on UV radiation close to the Earth's surface. Changes in UV radiation caused by these mechanisms will to some degree also affect the degradation of plastics in terrestrial and aquatic environments and in the atmosphere.

SI 1. Dependence of UV radiation on stratospheric ozone recovery and increasing greenhouse gas concentrations

Recovery of stratospheric ozone throughout the 21st century depends greatly on future changes of atmospheric greenhouse gas (GHG) concentrations. This dependency results mainly from the fact that increases in GHGs, such as carbon dioxide, cool the upper stratosphere. This cooling reduces the rates of gas-phase chemical reactions that destroy ozone, and as a result, ozone concentrations increase. The evolution of annual-mean total column ozone¹ (TCO) for different latitude bands has been simulated with chemistry-climate models for the period 1950–2100 (*Keeble et al.*, 2021). These calculations were performed in the framework of the Coupled

¹Biospherical Instruments Inc., San Diego, California, USA.

²Laboratory of Atmospheric Physics, Department of Physics, Aristotle University, Thessaloniki, Greece.

³Ptersa Environmental Consultants, Pretoria, South Africa.

⁴Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Colorado, USA.

⁵ NOAA Global Monitoring Laboratory, Boulder, Colorado, USA.

⁶Securing Antarctica's Environmental Future & School of Earth, Atmospheric and Life Sciences, University of Wollongong, Wollongong, Australia.

⁷Institute for Atmospheric and Climate Science, ETH Zürich, Switzerland.

^{*}Corresponding author: G.H. Bernhard, Biospherical Instruments, Inc., California, USA E-mail: bernhard@biospherical.com

¹ Total column ozone or TCO is the amount of ozone in a vertical column extending from the Earth's surface to the top of the atmosphere. TCO is reported in Dobson Units (DU).

Model Intercomparison Project Phase 6 (CMIP6), which considered trajectories of future GHG emissions scenarios specified by "Shared Socio-economic Pathways" (SSP²) (*Meinshausen et al.*, 2020). Table 1 summarises projected changes in TCO between 2020 and 2100 for the latitude bands of 30°–60° S (southern mid-latitudes), 15° S–15° N (tropics), and 30°–60° N (northern mid-latitudes) extracted from Figure 7 by *Keeble et al.* (2021). Changes in TCO at mid-latitudes are generally positive. The largest increases in TCO in this latitudinal range are observed for scenarios with the greatest increase in GHGs (SSP3-7.0 and SSP5-8.5). Conversely, in scenarios with small increases in GHGs (SSP1-1.9 and SSP1-2.6), projected changes in TCO are small. Changes in the tropics are negative for most scenarios and remain small (i.e., <3%). The decrease in TCO in the tropics results from the expected acceleration of the Brewer–Dobson circulation, which strengthens the redistribution of ozone from the tropics to higher latitudes, leading to a decrease in lower stratospheric ozone. These projected changes in TCO agree largely with similar calculations with the Earth system model SOCOLv4 (*Karagodin-Doyennel et al.*, 2023).

Table 1. Projected percentage change in total column ozone (TCO) and the UV Index between 2020 and 2100 for different shared socio-economic pathway (SSP) scenarios and latitude bands. Changes in the UV Index were estimated from changes in TCO by applying a RAF of 1.2.

	Projected change between 2020 and 2100 [%]					
	Total column ozone			UV Index		
SSP scenario	30° N – 60° N	15° S – 15° N	30° S – 60° S	30° N – 60° N	15° S – 15° N	30° S – 60° S
SSP1-1.9	-2	-2	4	2	2	-4
SSP1-2.6	0	-2	4	0	2	-4
SSP4-3.4	2	-1	7	-3	1	-8
SSP2-4.5	4	-3	6	-5	4	- 7
SSP4-6.0	4	-1	7	-5	1	-9
SSP3-7.0	10	2	12	-12	-2	-14
SSP5-8.5	10	-3	12	-12	4	-14

Under the simplified assumption that the effects on UV radiation from clouds and aerosols remain constant throughout the 21st century, changes in UV radiation can be estimated from changes in TCO using Radiation Amplification Factors (RAF) (*McKenzie et al.*, 2022, *Micheletti et al.*, 2003). For erythemal ("sunburning") irradiance and high-Sun conditions, the RAF is about 1.2, meaning that a 1% reduction in ozone increases the erythemal irradiance by about 1.2%. Erythemal irradiance is typically quantified with the UV Index³, abbreviated UVI (*CIE*, 1998). Projected changes in the UVI throughout the 21st century can therefore be readily estimated from changes in TCO by setting RAF=1.2. The resulting changes in UVI are also shown in Table 1. Of note, thus-derived changes in the UVI in response to changes in TCO for the SSP4-6.0 scenario agree to within ±1% with the earlier projection by *Lamy et al.* (2019)

² Shared socio-economic pathway (SSP) scenarios describe a range of plausible trends in the evolution of society over the 21st century and were adopted by the Intergovernmental Panel on Climate Change (IPCC) for its Sixth Assessment Report. The pathways are used for climate modelling and research, as different socio-economic developments and political environments will lead to different GHG emissions and concentrations. They describe five climate futures (SSP1–SSP5) that are combined with assumed amounts of greenhouse gases that are emitted in years to come. The CMIP6 simulations are based on seven SSPs (SSP1-1.9, SSP1-2.6, SSP2-4.5, SSP3-7.0, SSP4-3.4, SSP4-6.0, and SSP5-8.5), which are named after a possible range of radiative forcing values in the year 2100 relative to pre-industrial values (1.9, 2.6, 4.5, 7.0, 3.4, 6.0, and 8.5 W m⁻², respectively), and have some equivalence to the "Representative Concentration Pathways" or RCPs used in IPCC's Fifth Assessment Report.

 $^{^{3}}$ The UV Index is calculated by weighting solar UV spectra with the action spectrum of erythema (CIE, 1998) and multiplying the result with 40 m²/ W.

discussed in Section 2 of the main text. This projection was based on time-invariant aerosol amounts and the RCP 6.0 scenario, which is similar to SSP4-6.0. This confirms that estimates based on more recent work are consistent within reasonable limits with earlier projections.

SI 2. Unexpected release of ozone depleting substances

It has recently been reported that atmospheric abundances of several chlorofluorocarbons (CFCs), namely CFC-113a, CFC-114a, CFC-115, CFC-13 and CFC-112a, have increased from 2010 to 2020 (*Western et al.*, 2023). While these ozone depleting substances (ODSs) were phased out globally in 2010 under the Montreal Protocol and its Amendments, their production is still allowed as a feedstock to produce other chemicals, such as hydrofluorocarbons (HFCs). Inadvertent release during the production of HFCs is likely the main cause for the observed increases in atmospheric concentrations of these CFCs. However, the increase in their concentrations is still small in absolute terms (e.g., when compared to the current escape of CFC-11 from containment in refrigeration, air-conditioning equipment and insulating foams (*Salawitch*, 2023)). The anticipated impact of these emissions on stratospheric ozone recovery is therefore minor. However, continuing emissions of the five CFCs mentioned above may negate some of the benefits gained under the Montreal Protocol if they continue to rise, which would also affect future UV radiation levels.

SI 3. Very short-lived substances and nitrous oxide

Very short-lived substances (VSLS) are ozone-depleting halogen-containing chemicals with a lifetime of less than six months. They are not regulated by the Montreal Protocol because they are mostly produced by natural processes, such as emissions from macroalgae (seaweed) and phytoplankton. However, some VSLS are of industrial origin and their atmospheric concentrations are increasing (Bridgeman et al., 2000, Hossaini et al., 2019). Furthermore, anthropogenic emissions of pollutants such as nitrogen oxides and volatile organic compounds have indirectly amplified the release of VSLS from natural sources (Saiz-Lopez et al., 2023). There is therefore concern that these emissions are a potential (but uncertain) threat to the recovery of the ozone layer (Bednarz et al., 2023). The relative role of these components will become more important over time as the concentrations of other regulated ODSs decline. The recent increase of VSLS could also explain about one quarter of the observed decrease of ozone concentrations in the tropical lower stratosphere (pressure layer of 30–100 hPa) (Son, 2023, Villamayor et al., 2023). The remaining decrease of ozone amounts in this region can be attributed to "tropical upwelling", which describes the transport of ozone-poor air from the troposphere into the stratosphere (Ball et al., 2020, Butchart, 2014). With continuing global warming from increasing GHG concentrations, this upwelling would become stronger (Garcia and Randel, 2008) and would further decrease ozone concentrations in the tropical lower stratosphere (Chipperfield et al., 2018). Recent model simulations by Villamayor et al. (2023) suggest that this GHG-driven ozone decline could be reduced by up to 25% by the end of the 21st century if anthropogenic VSLS emissions were to be controlled. However, resulting changes in UV radiation are expected to be smaller than 0.5% and thus negligible. On the other hand, since observed recovery rates of stratospheric ozone are also very small, small impacts from VSLSs could be large enough to nullify total ozone trends (Bednarz et al., 2023). In addition, leakage of some chloromethanes, which are VSLSs resulting from industrial production, can delay ozone recovery (Li et al., 2023). Lastly, industrial and agricultural emissions of nitrous oxide (N₂O), which is a potent greenhouse gas with a high ozone-depletion

potential, have increased since 2010 (*Davidson and Winiwarter*, 2023). Continued emissions of N₂O could also have an effect on atmospheric ozone and UV radiation, but this has not been quantified yet.

SI 4. Effect of climate change

Climate change resulting from increasing concentration of GHGs does not affect UV radiation only via changes in TCO but also via many other processes, including changes in cloud cover, aerosols, atmospheric circulation, and surface reflectance (or reflectivity). For example, a recent study based on the RCP 6.0 scenario (*Eleftheratos et al.*, 2022) provided evidence that cloud cover within the latitude band of 50° S–50° N will decrease between 2050 and 2100, resulting in increases in UV-B radiation by about 4%. This increase would add to the expected increase in UV radiation for the tropics discussed in Section SI 1.

Climate change will also lead to changes in atmospheric circulation patterns with effects on UV radiation at the Earth's surface. For example, high emissions of GHGs as modelled based on the SSP5-8.5 scenario will lead to a poleward shift of the belt of tropospheric westerly winds (sometimes referred to as the "westerly jet") in the Southern Hemisphere (*Bracegirdle et al.*, 2020, *Goyal et al.*, 2021). This shift in circulation will likely lead to increasing temperatures, cloud cover, and precipitation outside the summer season at southern latitudes south of 30° and in particular over Antarctica and the Southern Ocean. Increasing cloudiness would reduce UV radiation levels; however, a quantitative estimate is not available.

SI 5. Effects of aerosols on UV radiation

Economic growth in East Asia and India has caused large regional increases in pollution and concomitant increases in aerosol emissions over the last 30 years (Cherian and Quaas, 2020, Shaddick et al., 2020). In heavily industrialised regions (e.g., Eastern and South-East Asia), aerosols have reduced UV radiation close to the surface by more than 25% between 1960 and 2015 (Bais et al., 2015). As the result of new regulations (Tong et al., 2020), expected reductions in air pollutants in these regions will likely reduce aerosols over time and will gradually return UV radiation to more natural levels prevailing in unpolluted areas. For example, the Clean Air Act of the United States had a large impact on air pollution in North America (Ross et al., 2012), which had peaked in the middle of the 20th century (Bauer et al., 2020, Finney, 2017), but has greatly improved over the last ~50 years. While similar improvements in air quality are also expected for regions that are currently the most polluted (e.g., Central and Southern Asia, parts of the Middle East, and Sub-Saharan Africa), future trajectories of aerosols and other air pollutants are highly uncertain because attempts to improve air quality often compete with economic interests, population pressure, and other factors (*Riahi* et al., 2017). Outputs of chemistry-climate models for northern mid-latitude (30–60° N) sites, assuming the RCP 6.0 scenario (Lamy et al., 2019), projected large (-77%) decreases in the aerosol optical depth in this latitude belt, which would increase the UVI by about 6% between 2015 and 2090. These changes are of similar magnitude to those caused by changes in stratospheric ozone (Section SI 1). However, zonal mean changes in UVI are not representative for most regions and merely provide a qualitative estimate of changes in UV radiation. If all pollution sources in regions that are most polluted today were to disappear (for example, by eliminating fossil fuel consumption and transitioning to solar and wind power), increases in the UVI by more than 50% could occur in these regions over the course of the 21st century (Bais et al., 2015, Ipiña et al., 2021), thus returning the UVI to more natural levels.

Microplastics are also a part of the atmospheric aerosol burden and may affect climate and the transfer of radiation through the atmosphere. For example, they can act as cloud condensation nuclei as they undergo ageing (*Aeschlimann et al.*, 2022). However, given their low abundances, microplastics are currently not expected to have significant direct or indirect effects on UV radiation in the atmosphere (Section 4.1 of the main text).

SI 6. Effect of wildfires on stratospheric ozone and UV radiation

As a consequence of climate change, wildfires have become more frequent and more extreme. In addition to direct destruction of ecosystems and immediate harm to humans and other biota, wildfires are important sources of pollutants, including aerosols, which may be detrimental to human health and can also destroy stratospheric ozone as discussed below.

Smoke from wildfires can reduce the UVI at the Earth's surface by more than three orders of magnitude in extreme cases (Figure SI 1). However, it is difficult to extrapolate these observations in time and space. Furthermore, black carbon from wildfires that is deposited on snow lowers the albedo of snow, which leads to earlier snow melt. In turn, earlier melt may expose vegetation to UV radiation at times when snow would typically still cover the ground.

Superheated air from large wildfires can produce large-scale pyrocumulonimbus clouds, which can inject smoke and tropospheric air into the lower stratosphere (Allen et al., 2020, Hirsch and Koren, 2021, Kablick III et al., 2020, Khaykin et al., 2020, Ohneiser et al., 2020, Ohneiser et al., 2022). One recent example is the well-documented intrusion of smoke into the stratosphere from the Australian "Black Summer" wildfires of 2019/2020. Ozone-poor tropospheric air in the rising plume reduced TCO by up to 100 Dobson Units (DU) locally (Kablick III et al., 2020, Khaykin et al., 2020, Salawitch and McBride, 2022, Schwartz et al., 2020). Other observations following the Black Summer fires showed a substantial reduction in the abundance of ozone in the lower stratosphere between 30° S and 60° S, which peaked during May to August 2020 and was 6 to 7 DU below the average ozone column of 2012–2019 (Rieger et al., 2021). A different study showed that TCO over much of Southern Hemisphere midlatitudes during July to November 2020 was ~8 to 15 DU lower than normal (Solomon et al., 2022, Solomon et al., 2023). These studies suggests that the observed depletion of ozone is mostly caused by heterogeneous chemistry on aerosol particles from the wildfires. Considering that the average TCO at southern mid-latitudes is about 300 DU, a decrease by 6 to 15 DU corresponds to a relative decrease of about 2 to 5%. In turn, this decrease in TCO would lead to an increase in the UVI by about the same percentage. Most ozone loss occurred in latitudinal bands with large human populations and more terrestrial biota than at the poles. Since the Black Summer wildfires occurred during summer when the UVI was high, even a small relative decrease in TCO is concerning.

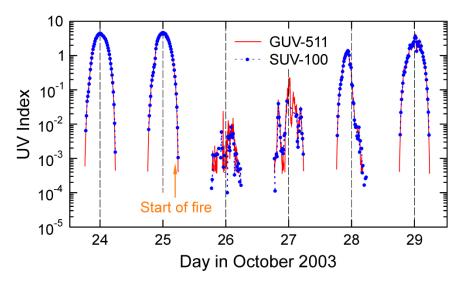


Figure SI 1. Example of the effect of wildfires on the UV Index. The figure shows measurements of the UV Index at San Diego, California (32° N), between 24 and 30 October 2003. In the afternoon of 25 October, the Cedar Fire (*Johnson*, 2004) started and became the most devastating wildfire in the history of San Diego county to date. More than 1,100 km² of land burned and about 2,800 buildings were destroyed.⁴ At noon on 25 October, before the start of the fire, the UV Index was 4.5. On the following day, which was also free of clouds, the UV Index did not exceed 0.024 and the maximum UV Index within ±30 minutes of local solar noon was only 0.004 (representing a reduction by more than three orders of magnitude compared to the previous day). Measurements were performed with a SUV-100 spectroradiometer (blue symbols) and a GUV-511 multi-filter instrument (red line) of the former National Science Foundation's UV monitoring network (*Booth et al.*, 1994). Measurements of the SUV-100 and GUV-511 radiometer were executed every 15 minutes and every 1 minute, respectively, when the Sun was above the horizon. The noise level of the SUV-100 corresponds to a UV Index of about 2×10^{-4} . Vertical dashed lines show local solar noon on the days indicated. The figure illustrates the effect of aerosols for one particular large fire but cannot be used to estimate the effect of fires on UV radiation in general.

Wildfires and volcanoes (Section SI 7) have also contributed to extensive and long-lasting Antarctic ozone depletion during the last three years (2020–2022) (*Damany-Pearce et al.*, 2022, *Solomon et al.*, 2023, *Yook et al.*, 2022). Ozone depletion in these years extended into late November and December when the solar elevation was high and exposure to UV radiation was more pronounced, thus likely exposing Antarctic marine and terrestrial biota to unusually high levels of UV radiation (*Bernhard et al.*, 2023). This period also corresponds with the timing of melt of snow and sea ice in spring (*Robinson*, 2023), which would otherwise offer protection to underlying organisms. This exposure was likely compounded by the dramatic reductions in Antarctic sea ice in recent years (*Fretwell et al.*, 2023, *Purich and Doddridge*, 2023).

SI 7. Volcanic eruptions

Volcanic eruptions can deposit large amounts of sulphur dioxide (SO₂), water vapour, and halogen-containing substances into the stratosphere, which can lead to ozone depletion for several years after the eruption. The classic example of the modern times is the eruption of Mt.

⁴ See:

Pinatubo in 1991, which decreased TCO by 6-8% in the tropics within one month of the eruption (*Kilian et al.*, 2020) and by about 3% globally (*WMO*, 2022).

On 15 January 2022, the sub-marine volcano of Hunga Tonga–Hunga Ha'apai (HT-HH) — located at 20.5° S in the South Pacific, about 700 km southeast of Fiji and 800 km southwest of American Samoa — erupted. It is the largest volcanic eruption in the 21st century to date. The height of the volcanic plume exceeded 50 km in altitude (Millán et al., 2022, Nedoluha et al., 2023) and extended into the mesosphere. The eruption led to a 5-fold increase of the stratospheric aerosol load (*Khavkin et al.*, 2022) and injected the largest amount of water vapour into the stratosphere of any eruption observed during the satellite era. The mass of water vapour injected into the stratosphere was estimated at 146 ± 5 Tg or $\sim 10\%$ of the stratospheric burden (Millán et al., 2022) and may take several years to dissipate. The added water vapour led to strong stratospheric cooling, which in turn may have induced changes in the large-scale circulation (Santee et al., 2023). Despite this large disturbance, observations of various atmospheric constituents by the Microwave Limb Sounder (MLS) on NASA's Aura satellite indicated only moderate enhancements in reactive chlorine throughout the southern middle and low-latitude stratosphere. As a result, Santee et al. (2023) concluded that the HT-HH eruption did not cause appreciable chemical ozone loss in the lower stratosphere of the Southern Hemisphere's mid-latitude in 2022. On the other hand, Wilmouth et al. (2023) found, also based on MLS data, that anomalies in lower stratospheric ozone resulting from the HT-HH eruption include widespread ozone reductions at Southern Hemisphere mid-latitudes and ozone increases in the tropics. Peak anomalies in monthly means averaged over 15° latitude bands were approximately -7% and +5%, respectively. As of this writing (November 2023), the science is not yet settled. In particular, chemical effects of the HT-HH eruption on stratospheric ozone and concomitant changes in UV radiation at the Earth's surface are still not completely understood.

As of May 2023, the strong positive stratospheric aerosol anomaly from HT-HH had already substantially abated. However, measurements of aerosol extinction provided by the Stratospheric Aerosol and Gas Experiment (SAGE III) on board the International Space Station suggest that stratospheric aerosol loading will not return to pre-eruption levels before 2024 (*Duchamp et al.*, 2023). Furthermore, stratospheric water vapour abundances remain historically high, with the extreme enhancement likely to endure for several more years (*Khaykin et al.*, 2022, *Millán et al.*, 2022). The HT-HH water vapour plume was effectively excluded from the 2022 Antarctic polar vortex and thus had little impact on that year's ozone hole; similarly, it did not reach northern high latitudes in time to influence Arctic ozone loss in the boreal spring 2023 (*Manney et al.*, 2023).

The sustained HT-HH water vapour enhancement, which led to strong stratospheric cooling that in turn induced changes in atmospheric circulation (*Santee et al.*, 2023), may have contributed to the relatively large size of the Antarctic ozone hole in the austral spring of 2023. As reported by NASA⁵ and the European Space Agency⁶, the ozone hole reached a size of 26 million km² on 21 September 2023. It was the 12th largest ozone hole on this day since 1979. During the last week in September 2023, the size of the ozone hole decreased conspicuously, likely due to dynamical effects (e.g., atmospheric waves originating in the troposphere that propagated into the stratosphere), and on 8 October 2023, the ozone hole's area, the minimum TCO within this area, and the minimum stratospheric temperature at latitudes south of 50° were close to their average values of the period 1979–2022. As of this writing (November 2023) these data are still preliminary and have not been fully verified. It is expected that water vapour from the HT-HH eruption will also lead to some ozone loss over the Arctic in the winter/spring

⁵ https://earthobservatory.nasa.gov/images/152023/modest-ozone-hole-in-2023

⁶ https://www.esa.int/Applications/Observing_the_Earth/Copernicus/Sentinel-5P/Ozone hole goes large again

season of 2023/2024. But since the effect will likely be small, it will be difficult to disentangle chemical ozone loss from ozone loss resulting from dynamical effects, such as the transport of ozone to lower latitudes.

It is currently unlikely that effects from the HT-HH eruption will lead to notable change in UV radiation at middle and low latitudes or significantly affect long-term trends in UV radiation. However, future volcanic eruptions that would emit larger quantities of halogen-containing gases (summarised by *Bernhard et al.* (2023)) than those released by the HT-HH eruption could lead to much greater effects on stratospheric ozone and UV radiation.

SI 8. Supersonic aircraft

The Scientific Assessment Panel's (SAP) latest report (WMO, 2022) assessed the effect of a hypothetical fleet of 500 or 1,000 commercial supersonic aircraft flying at cruise altitudes between 13 and 23 km in the lower stratosphere. Depending on scenario and flight altitudes, emissions of water vapour and nitrogen oxides from such a fleet could reduce TCO by up to 25 DU at high northern latitudes. Reductions in TCO at mid and low latitudes of the Northern Hemisphere would be considerably smaller, and the Southern Hemisphere would be less affected because most flights take place in the Northern Hemisphere. While no study has quantified the effect of a future fleet of supersonic aircraft on UV radiation, the estimated decrease in TCO suggests that erythemal UV irradiance could increase by several percent at mid-latitudes of the Northern Hemisphere.

SI 9. Solar radiation management

The effects of solar radiation management (a type of geoengineering) facilitated through stratospheric aerosol injections (SAI) is currently being extensively studied. Impacts on the atmosphere, including the ozone layer, have been discussed in the latest assessments by the SAP (Chapter 6 of *WMO*, 2022), the IPCC (e.g., Chapter 4 of *IPCC*, 2021), and the last two EEAP assessments (*Bais et al.*, 2019, *Bernhard et al.*, 2023). However, the effects of SAI on solar radiation in the UV and visible ranges have not been systematically explored, with few exceptions (*Madronich et al.*, 2018). Under present-day abundances of ODSs in the atmosphere, we expect that SAI would deplete polar ozone by up to 30 DU in Antarctica and by up to 18 DU in the Arctic (*Weisenstein et al.*, 2022), which would increase UV exposure at the surface. Conversely, under the very low ODS abundances reached by the end of the 21st century, models predict that TCO at mid-latitudes would increase by up to 40 DU (*Tilmes et al.*, 2022), which would decrease erythemal UV radiation at the surface by about 10–15%. However, the uncertainty of these predictions is large and a more systematic quantification on the effects on UV exposure is still missing.

SI 10. Nuclear war

A recent study used a state-of-the-art climate model with interactive chemistry to calculate the effects on TCO and UV radiation resulting from a regional or global nuclear war (*Bardeen et al.*, 2021). As summarised by *Bernhard et al.* (2023), a global-scale nuclear war would cause a 15 year-long reduction in the TCO with a peak loss of 75% globally and 65% in the tropics. Initially, soot would shield the surface from UV-B radiation, but eventually the UVI would become extreme: greater than 35 in the tropics for 4 years, and greater than 45 during the summer in the southern polar regions for 3 years. For a regional nuclear war, global TCO could be reduced by 25% with recovery taking 12 years.

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