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## Environmental contamination and climate change in Antarctic ecosystems: an updated overview

Roberto Bargagli  and Emilia Rota \*

Abiotic and biotic components of Antarctic ecosystems are valuable archives of past and current trends in global processes and play an important role in assessing emissions and long-range transport of persistent contaminants. After the ban on the production and use of alkyl-lead fuel additives, lead concentrations in Antarctic environmental matrices (snow, ice, sediments and biota) have decreased, just as the hole in the Antarctic stratospheric ozone layer is slowly shrinking following the ban on ozone-depleting gases. With the entry into force of the Stockholm Convention, the occurrence of persistent organic pollutants (POPs) in the Antarctic ecosystems could also decrease. However, the increasing anthropogenic sources of POPs in the Southern Hemisphere and the remobilization of those previously deposited in Antarctic ice could counteract the possible decreasing trend. Legacy pollutant concentrations in Antarctica are among the lowest reported in the global environment, with an exception of the bioaccumulation in various marine organisms of mercury (Hg) and cadmium (Cd) naturally occurring in Southern Ocean waters, or that of POPs in some long-lived seabirds with particular migration routes and life histories. However, despite the protection guidelines, long-range transport processes and especially the increase in human activities in Antarctica are sources of many persistent contaminants not yet subject to regulatory criteria and often lacking standardized sampling and analytical procedures. Chronic exposure to anthropogenic contaminants (legacy and of emerging interest) and pathogenic microorganisms near coastal scientific stations could cause synergistic or additive effects on marine biota. Most Antarctic marine organisms are endemic, with unique ecophysiological adaptations, and are also exposed to climate-related stressors. Warming and acidification of Southern Ocean waters along with increased melting of ice will likely affect the transport, pathways and environmental fate of persistent contaminants and could interfere with the metabolic processes of Antarctic organisms involved in the uptake and detoxification of environmental contaminants. Therefore, to implement environmental protection protocols around the coastal stations, the Council of Managers of National Antarctic Programs should evaluate the possible cumulative impact on biotic communities in the context of changing climatic and environmental conditions.

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### Environmental significance

Reports of new persistent synthetic chemicals, not yet subject to regulatory criteria, and plastic debris reaching Antarctica *via* long-range transport are continuously increasing. Scientific, tourism and fishing activities in Antarctica are also on the rise, inevitably contributing to localized environmental contamination and the introduction of alien species. The acidification of Southern Ocean waters and other climate-related stressors such as changes in sea ice cover and ocean freshening by glacial meltwater could reduce the resilience of Antarctic ecosystems, increasing the risk of biological effects of contaminants, especially in areas affected by human activities. This review discusses such possible cumulative impact. The most critical conditions and vulnerable species are also highlighted to guide future research and to implement protocols for human activity management and environmental monitoring particularly around science stations.

### Introduction

Pesticides and other synthetic organic compounds, neither produced nor applied in Antarctica, have been detected in Antarctic animal tissue since the 1960s.<sup>1,2</sup> In 1974, Molina and

Rowland<sup>3</sup> suggested that chlorofluoromethanes, used primarily in the Northern Hemisphere as refrigerants and aerosol propellants, could promote the destruction of stratospheric ozone through reactions catalyzed by chlorine atoms. Ten years later, Farman *et al.*<sup>4</sup> discovered a marked decrease in stratospheric ozone concentrations during the austral spring over Halley station (75°36'45"S 26°11'52"W) and showed that this "ozone hole" had started forming several years earlier. These

University of Siena, Department of Physics, Earth and Environmental Sciences, Via P. A. Mattioli, 4, IT-53100 Siena, Italy. E-mail: rota@unisi.it



discoveries increased global concern about the possible effects of UV-B and UV-C radiation and formed the basis for the implementation of the Montreal Protocol, one of the most successful environmental policies of the twentieth century.<sup>5</sup> Above all, it has emerged that, despite their remoteness and geographical isolation (increased by currents flowing clockwise around the continent, which is also surrounded by a cyclonic vortex of cold air), Antarctica and the Southern Ocean are linked to global environmental processes. However, although the Antarctic Treaty's Protocol on Environmental Protection (ATPEP; signed in Madrid in 1991 and entered into force in 1998) designated the region south of latitude 60°S as a "nature reserve, devoted to peace and science", it has no purview over global issues. Therefore, the growing global population, the continuing exploitation of natural resources, generation of wastes and release of environmental contaminants, including persistent organic pollutants (POPs), pose increasing threats to the mostly undisturbed nature of the Antarctic environment.<sup>6–10</sup> Despite some international agreements, such as the Minamata Convention to reduce the global Hg pollution and the Stockholm Convention to ban the production and use of some POPs, these compounds can persist in the environment for decades and, through repeated cycles of volatilization and condensation,<sup>11</sup> will continue to move along gradients in air temperature until they reach their final sinks in the polar regions. Climate change may also promote the remobilization and bioavailability of POPs previously deposited in Antarctica, through melting ice

and thawing of permafrost soils.<sup>10,12</sup> Global chemical production continues to grow, along with concerns for the ever-increasing number of reports on the occurrence of many new persistent synthetic chemicals, not yet subjected to regulatory criteria (contaminants of emerging interest, CEI), and plastic debris in the Antarctic environment (*e.g.*, ref. 13–18) (Fig. 1).

South of 60°S, all human activities are regulated by ATPEP. However, the increase in scientific, tourism and fishing activities in Antarctica<sup>19</sup> inevitably contributes to the introduction of alien species and localized environmental contamination through combustion of fuels, accidental oil spills, wastewater and waste production (*e.g.*, 20,21). Until the 1990s, at several Antarctic stations, wastes were simply disposed of in landfills, burned in the open air or dumped into the sea. Therefore, although limited in space, the impact of past human activities in some coastal areas has influenced the diversity of biotic communities and the functioning of ecosystems.<sup>8,21,22</sup> National organizations operating in Antarctica are mandated by ATPEP to prevent and monitor the impact of ongoing activities. However, many scientific stations and vessels lack wastewater treatment facilities. Where such facilities are present, the harsh Antarctic conditions often cause operational problems and malfunctions.<sup>23</sup> Several Antarctic coastal ecosystems are affected by pathogenic microorganisms and contaminants, such as metals, hydrocarbons, detergents, flame retardants, personal care products, pharmaceuticals and microplastics. An improvement in environmental monitoring and control

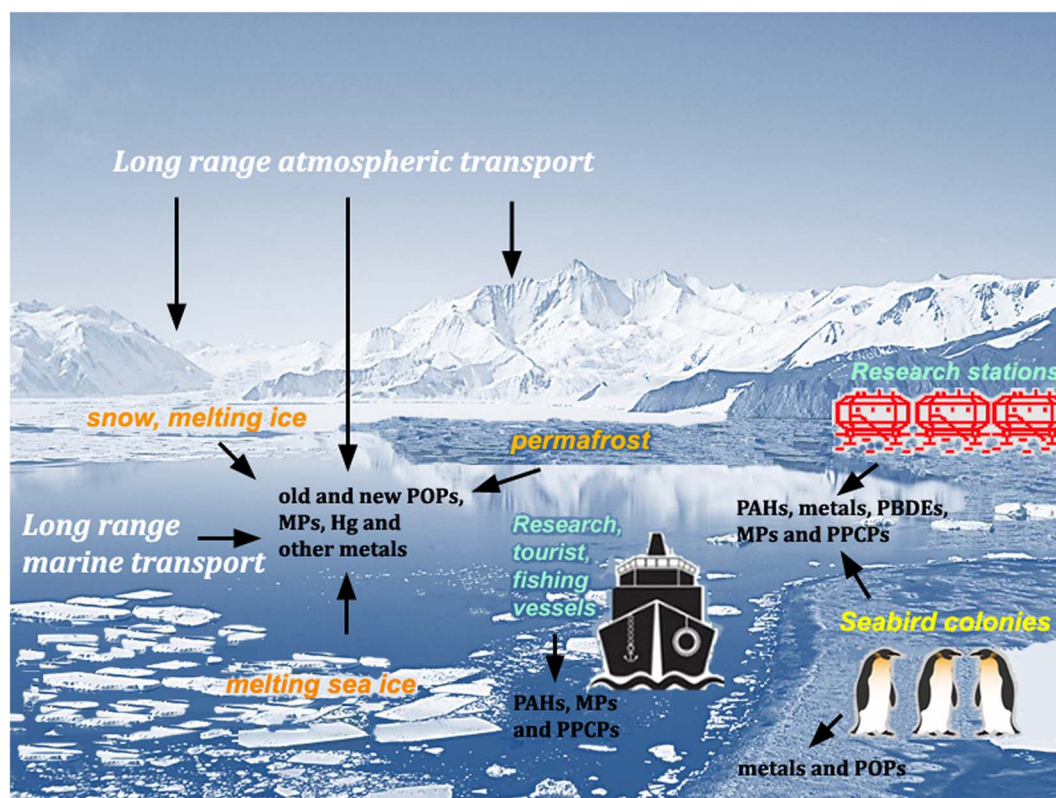


Fig. 1 Main sources of persistent contaminants in Antarctic ecosystems. POPs, persistent organic pollutants; MPs, microplastics; PAHs, polycyclic aromatic hydrocarbons; PBDEs, polybrominated diphenyl ethers; PPCPs, pharmaceuticals and personal care products.



protocols around scientific stations is therefore urgently needed (e.g., ref. 14, 15, 24 and 25).

In sharp contrast to the very poor terrestrial biotic communities of the Antarctic cold desert, coastal marine ecosystems host dense and diverse populations of benthic organisms. Through long evolutionary processes in isolation, they have acquired unique ecophysiological adaptations. By storing lipids as an energy source, they are prone to the accumulation of lipophilic and potentially toxic compounds such as POPs.<sup>26–29</sup> The involvement of benthic invertebrate communities in the transfer of energy and persistent pollutants to omnivorous fish and their predators lengthens the Antarctic food chain, thereby increasing the biomagnification of POPs and monomethyl mercury (MeHg)<sup>28,30,31</sup> and Cd bioaccumulation.<sup>32–35</sup> Thus, in some seabirds such as the south polar skua (*Stercorarius mac-cormicki*), concentrations of pollutants can reach levels close to those causing adverse health effects.<sup>36</sup> Furthermore, the Southern Ocean is among the seas most vulnerable to increasing CO<sub>2</sub> concentrations and water acidification.<sup>37</sup> Marine organisms may also experience additional global warming stresses, such as changes in sea-ice cover and the freshening of seawater due to melting glaciers. Therefore, climate-related stressors could reduce the resilience of Antarctic organisms and ecosystems, increasing the risk of possible biological effects of anthropogenic contaminants, especially in coastal areas affected by human activities. With these topics in mind, after 15 (ref. 6) and 23 years<sup>38,39</sup> from previous reviews, this review will update the knowledge on the occurrence of legacy and new anthropogenic contaminants in Antarctic ecosystems, and discuss the scientific evidence of their possible cumulative impact in the context of climate and environmental changes. Our aim is to summarize the most recent scientific acquisitions on the deposition of contaminants not in the Antarctic Plateau, nor throughout the continent, but above all in the ecosystems of the ice-free coastal areas and in the marine areas located near Antarctic stations, more impacted by scientific, logistical and tourism activities. The ecosystems of the Antarctic Peninsula and the surrounding archipelagos are the most exposed to such impacts. In the text, we refer to the “Scotia Arc” to indicate the island arc system (54.5 to 62°S, 65 to 25°W) located north of the Antarctic Peninsula and including, among others, South Georgia, the South Sandwich, South Orkney and South Shetland islands.

The most critical conditions and vulnerable species will also be highlighted to guide future research, and to implement protocols for the management of human activities and environmental monitoring around the scientific stations.

### Trace metals

Wet and dry atmospheric deposition contribute to the biogeochemical cycle of major and trace elements in Antarctic terrestrial ecosystems. The snow elemental composition shows that these elements originate mainly from local rock and soil dust, sea-salt spray, active volcanoes such as Mount Erebus or Deception Island, and natural or anthropogenic sources in South America, South Africa and Australia.<sup>40–43</sup> As a rule, past and ongoing

human activities in Antarctica are associated with highly localized depositions of metals, such as lead (Pb), copper (Cu), arsenic (As), nickel (Ni) and zinc (Zn) around scientific stations (e.g., ref. 44). The temporal distribution of Pb concentrations in Antarctic snow is paradigmatic of the long-range atmospheric transport and deposition of metals from anthropogenic sources in the Southern Hemisphere. The increase in Pb concentrations began at the beginning of the 20th century with mining and smelting activities, and especially with the global use of gasolines with alkyl-Pb additives. Values peaked in the 1970s and declined in the 1990s, following the use of ethanol fuel blended with gasoline in Brazil and unleaded gasoline in Australia and other countries.<sup>45</sup> In Antarctic snow samples collected in 2017, mean concentrations of Pb (4.4 pg L<sup>-1</sup>) were about half those recorded in 1970–1980 (9.0 pg L<sup>-1</sup>), and the contribution of metals from remote and local anthropogenic sources is probably currently lower than that from natural sources.<sup>46</sup>

Most Antarctic scientific stations are located in coastal ice-free areas, and historical and/or ongoing human activities have resulted in localized environmental contamination by metals<sup>21,34,47–49</sup> (Table 1). Despite the low soil formation rate, terrestrial ecosystems in the vicinity of stations can harbor lichens, mosses, arthropods, nematodes, rotifers, tardigrades and very diverse communities of microorganisms.<sup>6</sup> Moreover, coastal ice-free areas are essential breeding grounds for seabirds and seals. Penguins form large colonies, and transfer significant amounts of nutrients, heavy metals and POPs from the marine environment to terrestrial ecosystems through their excrements.<sup>50–52</sup> For example, according to Chu *et al.*,<sup>53</sup> the impact of metals from penguin guano on Ardley Island may exceed that of human activities near scientific stations. Through satellite digitization of visible disturbances around active and abandoned infrastructures, Brooks *et al.*<sup>54</sup> estimated that more than 5000 km<sup>2</sup> of Antarctic ice-free areas have been affected by human activities.

Several species of lichens and mosses have a wide geographic distribution in Antarctic ice-free areas and large-scale surveys, or those performed around scientific stations, demonstrate their reliability as biomonitors of atmospheric deposition of metals and other persistent contaminants (e.g., ref. 30 and 58–61). As shown in Table 2, baseline concentrations of metals in widespread Antarctic cryptogam species are in the same range as those measured in other lichen and moss species collected in reference areas of the Southern and Northern Hemispheres, prepared and analyzed with the same procedures.

Unlike other metals emitted from natural and anthropogenic sources, which are associated with atmospheric aerosol, mercury (Hg) is mainly present in the atmosphere as gaseous Hg<sup>0</sup>, with a lifetime of about one year.<sup>66</sup> Once deposited in terrestrial and aquatic ecosystems, inorganic Hg can be transformed by microorganisms into MeHg, a potent neurotoxin with a remarkably long biological half-life (some months instead of a few days or weeks for inorganic Hg). Thus, through a process of biomagnification, MeHg accumulates in primary producers and its concentrations increase in the muscle and other tissues of organisms along the food webs, reaching peak



**Table 1** Metal concentrations ( $\mu\text{g g}^{-1}$  dry wt; mean  $\pm$  SD) in Antarctic surface soils sampled in control areas and near active or abandoned infrastructures. NA, not analyzed

| Locations                                 | Cd              | Cu            | Hg              | Ni           | Pb            | Zn            | References |
|---|-----------------|---------------|-----------------|--------------|---------------|---------------|------------|
| <b>Victoria Land</b>                      |                 |               |                 |              |               |               |            |
| (Volcanic)                                | 0.13 $\pm$ 0.05 | 21 $\pm$ 8    | 0.04 $\pm$ 0.02 | 12 $\pm$ 9   | 8.8 $\pm$ 3.5 | 12 $\pm$ 9    | 38         |
| (Granitic)                                | 0.22 $\pm$ 0.08 | 16 $\pm$ 9    | 0.05 $\pm$ 0.03 | 10 $\pm$ 6   | 11 $\pm$ 6    | 10 $\pm$ 6    |            |
| <b>Larsemann Hills</b>                    | 0.04 $\pm$ 0.08 | 17 $\pm$ 15   | 0.03 $\pm$ 0.08 | 14 $\pm$ 6   | 1.6 $\pm$ 1.1 | 32 $\pm$ 19   | 55         |
| <b>Fildes Peninsula</b>                   |                 |               |                 |              |               |               |            |
| Manned stations                           | 0.17 $\pm$ 0.08 | 122 $\pm$ 32  | 0.02 $\pm$ 0.01 | 14 $\pm$ 5   | 16 $\pm$ 13   | 59 $\pm$ 9    | 56         |
| Baseline values                           | 0.09            | 89            | 0.01            | 10           | 5.4           | 51            |            |
| <b>Marambio Station</b>                   |                 |               |                 |              |               |               |            |
| Control sites                             | <0.8            | 15 $\pm$ 7    | NA              | 12 $\pm$ 4   | 44 $\pm$ 54   | 97 $\pm$ 103  | 47         |
|   | <0.8            | 8.2 $\pm$ 3.0 | NA              | 11 $\pm$ 8   | 10 $\pm$ 0.1  | 41 $\pm$ 8    |            |
| <b>O'Higgins Base</b> (near penguin col.) | 4.3 $\pm$ 1.5   | 422 $\pm$ 151 | NA              | 28 $\pm$ 10  | 28 $\pm$ 87   | 485 $\pm$ 182 | 57         |
| <b>Robert Island</b>                      |                 |               |                 |              |               |               |            |
| (Refuge)                                  | <0.2            | 107 $\pm$ 1   | NA              | 38 $\pm$ 0.5 | 102 $\pm$ 2   | 148 $\pm$ 5   | 48         |
| Control soil                              | <0.2            | 48 $\pm$ 0.4  | NA              | 40 $\pm$ 0.5 | 7.3 $\pm$ 0.5 | 44 $\pm$ 0.2  |            |

concentrations in long-lived species at higher trophic levels. Aquatic food webs are much more complex and longer than those of terrestrial ecosystems, and seabirds and marine mammals accumulate much more MeHg than their terrestrial counterparts. Although there appears to be no greater bioavailability of MeHg in the Southern Ocean than in other seas, its concentrations in seabirds such as the long-lived wandering albatross, *Diomedea exulans*, are probably among the highest ever reported for marine vertebrates (e.g., ref. 67 and 68). Analysis of contemporary and historical albatross feather specimens shows only a slight increase in Hg concentrations,<sup>69,70</sup> suggesting that metal accumulation is primarily a natural process due to species-specific life histories, metabolic

pathways, and the unique trophic web of the Southern Ocean. The wandering albatross feeds atop trophic webs and also frequents temperate waters (probably with higher MeHg bioavailability). Furthermore, molting and egg laying are important mechanisms for Hg excretion in seabirds. *D. exulans* replaces feathers over a period of years rather than annually, and has a low reproductive rate (one egg every two years). Seabirds and mammals can demethylate MeHg in the liver and accumulate selenium, an antagonist to Hg toxicity.<sup>71</sup> Hence, they are probably adapted to metabolize and tolerate MeHg intake without deleterious biological effects.<sup>6,72</sup>

Although there are very few local sources of Hg in Antarctica, a biomonitoring survey performed in the summers 1989/90 and

**Table 2** Metal concentrations ( $\mu\text{g g}^{-1}$  dry wt; mean  $\pm$  SD) in macrolichen (L) and moss (M) species from East Antarctica and other relatively uncontaminated areas in the Southern and Northern Hemispheres. NA, not analyzed

| Locations/species                | Cd              | Cu            | Hg              | Ni              | Pb              | Zn          | References |
|----------------------------------|-----------------|---------------|-----------------|-----------------|-----------------|-------------|------------|
| <b>Victoria Land</b>             |                 |               |                 |                 |                 |             |            |
| L <i>Umbilicaria decussata</i>   | 0.20 $\pm$ 0.10 | 4.8 $\pm$ 2.6 | 0.39 $\pm$ 0.27 | NA              | 0.50 $\pm$ 0.33 | 19 $\pm$ 4  | 39         |
| M <i>Bryum pseudotriquetrum</i>  | 0.21 $\pm$ 0.12 | 9.9 $\pm$ 3.3 | 0.14 $\pm$ 0.06 | 4.4 $\pm$ 2.1   | 2.2 $\pm$ 1.2   | 63 $\pm$ 20 |            |
| <b>Chilean Patagonia</b>         |                 |               |                 |                 |                 |             |            |
| L <i>Nephroma antarcticum</i>    | 0.15 $\pm$ 0.08 | 5.6 $\pm$ 1   | 0.07 $\pm$ 0.02 | 3.3 $\pm$ 1.9   | 0.74 $\pm$ 0.38 | 40 $\pm$ 13 | 62         |
| L <i>Usnea</i> sp.               | 0.08 $\pm$ 0.03 | 1.5 $\pm$ 0.3 | 0.14 $\pm$ 0.04 | 0.86 $\pm$ 0.36 | 0.49 $\pm$ 0.29 | 27 $\pm$ 9  |            |
| <b>Italian Alps/Apennines</b>    |                 |               |                 |                 |                 |             |            |
| L <i>Pseudevernia furfuracea</i> | 0.18 $\pm$ 0.09 | 5.4 $\pm$ 2.1 | 0.20 $\pm$ 0.06 | 1.7 $\pm$ 0.9   | 4.5 $\pm$ 2.9   | 41 $\pm$ 17 | 63         |
| <b>North-Eastern Italy</b>       |                 |               |                 |                 |                 |             |            |
| L <i>Pseudevernia furfuracea</i> | 0.21 $\pm$ 0.03 | 6.0 $\pm$ 0.5 | 0.17 $\pm$ 0.02 | 2.9 $\pm$ 1.7   | 5.4 $\pm$ 0.9   | 53 $\pm$ 5  | 64         |
| M <i>Hypnum cupressiforme</i>    | 0.23 $\pm$ 0.02 | 5.7 $\pm$ 0.3 | 0.13 $\pm$ 0.01 | 2.7 $\pm$ 1.2   | 3.4 $\pm$ 0.9   | 41 $\pm$ 11 |            |
| <b>Tuscany (Italy)</b>           |                 |               |                 |                 |                 |             |            |
| L <i>Flavoparmelia caperata</i>  | 0.26 $\pm$ 0.11 | 5.8 $\pm$ 1.3 | 0.17 $\pm$ 0.08 | 2.7 $\pm$ 1.9   | 3.9 $\pm$ 2.5   | 35 $\pm$ 7  | 65         |
| M <i>Hypnum cupressiforme</i>    | 0.19 $\pm$ 0.06 | 6.1 $\pm$ 1.6 | 0.12 $\pm$ 0.04 | 4.8 $\pm$ 3.1   | 2.7 $\pm$ 1.7   | 26 $\pm$ 9  |            |



1990/91 with the lichen *Umbilicaria decussata* across Victoria Land showed total concentrations of the metal in samples from ice-free areas in the Nansen Ice Sheet to be in the same range or higher than those measured in lichens of the same genus from contaminated sites in Europe.<sup>58</sup> In the Nansen Ice Sheet, there were no human, volcanic, or geothermal activities, and mean atmospheric Hg<sup>0</sup> in the Southern Hemisphere is lower than in the Northern Hemisphere. Therefore, there was no satisfactory explanation for the unexpected and localized Hg bioaccumulation. In the following years, it was demonstrated that in the coastal Arctic ecosystems facing ice-free marine areas in winter, the spring sunrise promotes photochemical reactions with the activation of bromine compounds which oxidize atmospheric Hg<sup>0</sup>, causing its deposition (so-called “Hg depletion events”;<sup>73</sup>). In winter, the sea in front of the Nansen Ice Sheet is free of ice. This is due to the recurring formation of the Terra Nova Bay coastal polynya. In spring, the depletion of Hg determines its accumulation in mosses, lichens, soils, lacustrine sediments and algal mats.<sup>74</sup> Interestingly, a recent survey of surface soils collected in Antarctic ice-free areas near scientific stations, penguin rookeries, coastal polynyas, and in control ice-free areas shows that Hg accumulation in soils is mainly dependent on their organic carbon content. In all the samples with an accentuated metal deposition, the value of the ratio [Hg ng g<sup>-1</sup>]/[OC%] is usually >11.<sup>75</sup>

Emissions of Hg<sup>0</sup> are increasing in some Southern Hemisphere countries<sup>76</sup> and global warming will likely reduce the sea-ice cover in some Antarctic coastal areas; thus, concern is

growing about Antarctica's potential role as the ultimate sink of Hg. Furthermore, studies on the metal cycling between air and snow in the Antarctic Plateau<sup>77,78</sup> and the Hg accumulation pattern in cryptogams collected along the Reeves Glacier<sup>79</sup> indicate that coastal ecosystems also receive Hg<sup>0</sup> via katabatic winds (*i.e.*, the cold and dense air masses sliding down-slope from the Antarctic Plateau towards the sea).

Since the earliest investigations on the elemental composition of marine organisms in the Southern Ocean, it was unexpectedly found that they can accumulate much higher Cd concentrations than those of related species from seas more impacted by anthropogenic activities.<sup>32,80,81</sup> In the highly productive waters of the Southern Ocean, the low input of trace elements such as Zn from the icy continent can limit the development of phytoplankton. Therefore, Cd is actively taken up by diatoms as a substitute for Zn to synthesize carbonic anhydrase (a metalloenzyme that supplies carbon for photosynthesis) (*e.g.*, ref. 82). From primary producers, the metal is transferred to consumers and accumulates in their kidneys and liver (or in the digestive gland of invertebrates). In general, the Cd concentrations in these organs do not increase with age and, depending on diet, may be higher in juveniles than in adults of the same species. Like Hg bioaccumulation, Cd bioaccumulation appears to be a natural process. During their evolution in the Southern Ocean, Antarctic marine organisms likely acquired metabolic pathways to regulate and tolerate Cd accumulation.<sup>7</sup>

**Table 3** Metal concentrations ( $\mu\text{g g}^{-1}$  dry wt; mean  $\pm$  SD) in feathers of penguins from different Antarctic areas. NA, not analyzed

| Locations/species                            | Cd              | Cu           | Hg              | Ni              | Pb              | Zn           | References |
|--|-----------------|--------------|-----------------|-----------------|-----------------|--------------|------------|
| <b>King George Island</b>                    |                 |              |                 |                 |                 |              |            |
| <i>Pygoscelis antarcticus</i>                | 0.21 $\pm$ 0.14 | 26 $\pm$ 5   | NA              | 0.28 $\pm$ 0.15 | NA              | 89 $\pm$ 20  | 86         |
| <i>Pygoscelis adeliae</i>                    | 0.14 $\pm$ 0.06 | 17 $\pm$ 2   | NA              | 0.24 $\pm$ 0.08 | NA              | 71 $\pm$ 11  |            |
| <i>Pygoscelis papua</i>                      | 0.14 $\pm$ 0.07 | 18 $\pm$ 6   | NA              | 0.27 $\pm$ 0.12 | NA              | 80 $\pm$ 28  |            |
| <i>P. papua</i> (chicks)                     | 0.06 $\pm$ 0.07 | 7 $\pm$ 2    | NA              | 0.01 $\pm$ 0.01 | 0.87 $\pm$ 0.86 | 81 $\pm$ 11  | 83         |
| <i>P. adeliae</i> (chicks)                   | 0.13 $\pm$ 0.08 | 13 $\pm$ 8   | NA              | 0.05 $\pm$ 0.03 | 0.24 $\pm$ 0.83 | 61 $\pm$ 20  |            |
| <b>Livingston Island</b>                     |                 |              |                 |                 |                 |              |            |
| <i>P. antarcticus</i>                        | 0.14 $\pm$ 0.11 | 29 $\pm$ 6   | NA              | 0.16 $\pm$ 0.07 | NA              | 117 $\pm$ 32 | 86         |
| <i>P. papua</i>                              | 0.14 $\pm$ 0.07 | 18 $\pm$ 2   | NA              | 0.20 $\pm$ 0.05 | NA              | 103 $\pm$ 11 |            |
| <i>P. antarcticus</i>                        | NA              | NA           | 0.67 $\pm$ 0.46 | NA              | NA              | NA           | 35         |
| <i>P. papua</i>                              | NA              | NA           | 0.22 $\pm$ 0.09 | NA              | NA              | NA           |            |
| <b>South Georgia</b>                         |                 |              |                 |                 |                 |              |            |
| <i>P. papua</i>                              | NA              | NA           | 0.85 $\pm$ 0.88 | NA              | NA              | NA           | 84         |
| <b>Antarctic Peninsula</b>                   |                 |              |                 |                 |                 |              |            |
| <i>P. antarcticus</i>                        | NA              | NA           | 0.62 $\pm$ 0.30 | NA              | NA              | NA           | 57         |
| <i>P. adeliae</i>                            | NA              | NA           | 0.35 $\pm$ 0.09 | NA              | NA              | NA           |            |
| <i>P. papua</i>                              | NA              | NA           | 0.31 $\pm$ 0.10 | NA              | NA              | NA           |            |
| Neko Harbor ( <i>P. papua</i> )              | 0.05 $\pm$ 0.07 | 14 $\pm$ 2   | NA              | 1.6 $\pm$ 1.6   | 0.06 $\pm$ 0.06 | 37 $\pm$ 6   |            |
| Doumer Island ( <i>P. papua</i> )            | 0.09 $\pm$ 0.07 | 15 $\pm$ 4   | NA              | 1.0 $\pm$ 1.2   | 0.10 $\pm$ 0.17 | 33 $\pm$ 4   |            |
| Stranger Point ( <i>P. papua</i> )           | 0.14 $\pm$ 0.09 | 20 $\pm$ 2   | NA              | 3.8 $\pm$ 2.4   | 0.60 $\pm$ 0.34 | 64 $\pm$ 11  |            |
| O'Higgins Base ( <i>P. papua</i> )           | 0.21 $\pm$ 0.28 | 21 $\pm$ 4   | NA              | 5.9 $\pm$ 8.2   | 0.63 $\pm$ 0.27 | 64 $\pm$ 11  |            |
| <b>East Antarctica</b>                       |                 |              |                 |                 |                 |              |            |
| Cape Bird ( <i>P. adeliae</i> )              | 0.11 $\pm$ 0.01 | 19 $\pm$ 0.3 | 0.59 $\pm$ 0.02 | NA              | 0.09 $\pm$ 0.02 | 75 $\pm$ 1   | 85         |
| Cape Crozier ( <i>Aptenodytes forsteri</i> ) | 0.04 $\pm$ 0.02 | 14 $\pm$ 1   | 1.35 $\pm$ 0.06 | NA              | 0.05 $\pm$ 0.06 | 68 $\pm$ 3   |            |



Like mosses and lichens, penguins have a circumpolar distribution. Due to their longevity (about 20 years) and tendency to return to their annual breeding sites, they are valuable bioindicators of temporal changes in the bioavailability of contaminants in the different foraging areas.<sup>83–85</sup> Comparison of the mean metal concentrations in penguin feathers from different Antarctic regions (Table 3) mainly shows higher bioavailability of Pb for colonies living in the Antarctic Peninsula and the Scotia Arc archipelagos, and higher bioaccumulation of Hg in feathers of emperor penguin from the Ross Sea. However, the latter penguin feeds at higher trophic levels than the other species and feather samples were collected in an area that may be affected by Hg emissions from the Mount Erebus volcano.<sup>85</sup> When comparing the elemental composition of penguin feathers, it should be noted that even for samples collected in the same breeding areas, the results are influenced not only by interspecies differences (*e.g.*, foraging habits, diet, migrations, molting pattern and detoxification mechanisms), but also by sex and stage of maturity.<sup>86</sup> Furthermore, Sun *et al.*<sup>87</sup> showed that feather sampling is itself a critical step since samples taken from different parts of the penguin body contained different concentrations of metals. By applying a standardized sampling protocol, they found higher As concentrations in the feathers of the Adélie penguin (range: from 0.62 to 2.95  $\mu\text{g g}^{-1}$  dry wt) than in those of seabirds from other seas (max 0.07  $\mu\text{g g}^{-1}$  dry wt), and higher concentrations of Cd, Cu, Hg, Ni, and Zn in samples from the Ross Sea than in those from the Antarctic Peninsula.

### Legacy and new persistent organic pollutants

The first synthetic pesticide (dichloro-diphenyl-trichloroethane, DDT) was produced in the 1940s. Due to its effectiveness in combating insect vectors of human diseases, it was later also extensively used against species harmful to crops and livestock production. In 1962, with the book “Silent Spring”, Rachel Carson<sup>88</sup> warned against the biological effects of pesticides. A few years later, Sladen *et al.*<sup>1</sup> found DDT in Antarctic penguins and seals. The discovery raised the question of how chemicals never used in Antarctica were able to reach

such a remote region. As later confirmed by Wania and Mackay,<sup>11</sup> since the first reports on the occurrence of pesticides in Antarctica, it was hypothesized that semi-volatile organic compounds could enter the atmosphere in warmer regions, and be transported by air masses towards the poles to then condense and settle. Shortly thereafter, other organochlorine pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and other POPs, mostly produced and used in the Northern Hemisphere, were detected in the Antarctic environment (*e.g.*, ref. 2 and 89–94).

Historically, the most frequent causes of environmental contamination in Antarctica have been oil spills during vehicle/aircraft refueling and spills caused by shipwrecks, collisions or accidents when transporting bunker fuel. Indeed, high concentrations of polycyclic aromatic hydrocarbons (PAHs) have been detected near some scientific stations.<sup>95–97</sup> At Arthur Harbor, the sinking of the Argentine supply ship *Bahia Paraiso* on 28 January 1989 released approximately 600 m<sup>3</sup> of diesel fuel. Because it was the middle to end of the seabird breeding season, thousands of seabirds were affected and some hundreds died.<sup>98</sup> Small amounts of oil on penguin plumage can cause waterlogging, reduced buoyancy and reduced thermal insulation. Furthermore, PAHs ingestion can cause histopathological changes in the liver, kidney and intestine, impaired osmoregulation and reduced fertility.<sup>28,99,100</sup>

In Antarctic terrestrial ecosystems, contamination by aliphatic and aromatic compounds reduces soil microbial diversity and promotes the development of hydrocarbon-degrading bacteria.<sup>101</sup> However, due to the extreme climatic and environmental conditions, the biodegradation of hydrocarbons proceeds very slowly. In marine sediments, a field experiment was performed that aimed at investigating the biological effects of various hydrocarbon products on the benthic macrofauna. The study showed that diesel fuel had the greatest initial impact, especially on annelids. However, after 5 years, the communities treated with diesel fuel seemed to recover faster than those treated with lubricating oils.<sup>29</sup>

Being largely due to local anthropogenic activities, rather than long-range atmospheric transport or local natural sources,

**Table 4** Concentrations of  $\Sigma$ PAHs (mean  $\pm$  SD or range, ng g<sup>-1</sup> dry wt) in Antarctic marine sediments and soils differently affected by anthropogenic activities

| Locations                            | Matrix                           | <i>n</i> of PAH species | $\Sigma$ PAHs       | References |
|--------------------------------------|----------------------------------|-------------------------|---------------------|------------|
| McMurdo Station (outfall)            | Coastal sediments                | 16                      | 779 $\pm$ 590       | 102        |
| Winter Quarter Bay                   |                                  |                         | 1095 $\pm$ 1082     |            |
| Cape Hermitage (control)             |                                  |                         | 36 $\pm$ 37         |            |
| Turtle Rock (control)                | Sediments (up to >1000 m depths) | 15                      | 5.7 $\pm$ 3.6       | 103        |
| Prydz Bay                            |                                  |                         | 18 $\pm$ 6 (13–31)  |            |
| Anvers Is., Palmer Station (outfall) | Sediments (18–24 m depth)        | 16                      | 32–302              | 104        |
| Reference area                       | Surface sediment (20–30 m)       | 21                      | 6–30                | 105        |
| Potter Cove, Carlini Station         |                                  |                         | 18–146              |            |
| South Fildes Pen. (some stations)    |                                  |                         | 19–143              |            |
| Reference areas                      | Coastal sediments                | 16                      | 4.6–16.6            | 106        |
| King George Island, Arctowski St.    |                                  |                         | 56–445              |            |
| King George Island                   |                                  |                         | 1.8–32.9            |            |
| Fildes Peninsula                     |                                  |                         | 61 (mean 2013–2019) |            |



contamination by PAHs in Antarctic marine sediments and soils is significantly higher near scientific stations than in reference areas (Table 4).

Bioaccumulation of PAHs has been reported in many species of marine organisms from contaminated coastal sites, but concentrations do not appear to increase along food webs.<sup>109</sup> Palmer *et al.*,<sup>102,104</sup> for example, measured higher levels in benthic invertebrate species, such as the soft coral *Alcyonium antarcticum* or the limpet *Nacella concinna*, than in their predators.

Other POPs listed under the Stockholm Convention, such as organochlorine pesticides, PCBs and PBDEs, have been reported in the Antarctic environment. Analyzing air and snow samples from the western Antarctic Peninsula, Khairy *et al.*<sup>110</sup> found the highest concentrations of these compounds in snow (suggesting the melting of ice and snow as a possible secondary source), while the vapor phases of hexachlorobenzene (HCB), PCBs, heptachlor and PBDEs prevailed in air. It is also probable that these latter compounds had originated from local sources. Although ATPEP bans the import and release of POPs in Antarctica, organohalogen compounds have been used as flame retardants in a range of household items, plastics, electronics, and materials used in the construction and/or renovation of scientific stations. Bengtson Nash *et al.*<sup>111</sup> found atmospheric PBDEs contamination around two stations. During the building of the Troll Station, they showed a marked increase in the concentrations of their penta-formulation congeners. As early as 2008, Hale *et al.*<sup>112</sup> had detected PBDEs in the indoor dust and sewage sludge of McMurdo Station and Scott Base. Their concentrations in sediments, fish and invertebrates from McMurdo Sound were in the same range as those measured in samples from urbanized North American areas. By analyzing legacy POPs in key species of the Ross Sea food web, such as *Euphausia superba* and *Pleuragramma antarctica* and their predators, Corsolini *et al.*<sup>113</sup> found the highest concentrations of PBDEs in Adélie penguins and skuas nesting near a long-term field camp. Markham *et al.*<sup>114</sup> detected PBDEs in all samples of phytoplankton, krill, fish and fur seal milk collected over a 14 year period. Moreover, between 2000 and 2014, the values increased in samples of fur seal milk, phytoplankton and zooplankton.

Most POPs reach Antarctica and the Southern Ocean through long-range transport processes, and Antarctic organisms are deemed to be reliable biomonitors of global POP emissions. As a rule, the concentrations of these contaminants in their tissues are lower than in related species from lower latitudes, and are usually much lower than those that would cause adverse health effects.<sup>115</sup> However, upon returning to Antarctica, opportunistic predators/scavengers (such as the south polar skua that migrate to the more polluted Northern Hemisphere during the austral winter) contribute to the contamination of terrestrial environments through their guano, abandoned eggs, and dead individuals.<sup>116</sup>

Following the entry into force of global conventions such as the Long-range Transboundary Air Pollution<sup>117</sup> and the Stockholm Convention,<sup>118</sup> legacy POPs have gradually been banned worldwide. However, there are few long-term surveys on POPs

concentrations in the Antarctic environment. Furthermore, the assessment of bioaccumulation temporal trends in the different study areas is made difficult by latitudinal variations in climatic and environmental conditions, and by differences in feeding and migratory behavior of organisms. Corsolini,<sup>119</sup> for example, highlighted the different temporal trends in PCB accumulation in a variety of marine species from West and East Antarctica. van den Brink *et al.*<sup>120</sup> found decreasing trends in PCBs, HCB and dieldrin levels in Adélie penguins, southern fulmars and pelagic fish from 1993–1994 to 2003–2004, even though their concentrations were steady or increasing in benthic organisms; thus, they questioned whether the POPs contamination in Antarctica is actually declining. Isla *et al.*<sup>121</sup> detected cytotoxic activity in extracts of marine sediments collected along thousands of kilometers of the Antarctic continental shelf and up to 1200 m depth. However, some more recent works would seem to indicate a decreasing trend of long-range transport and bioavailability of POPs in the Antarctic environment. Hao *et al.*<sup>122</sup> monitored the atmospheric concentrations of POPs in the Fildes Peninsula (King George Island) from 2010 to 2018. With the exception of HCB, they found low and declining levels of PCBs, HCHs, DDTs, and endosulfans. Summarizing the literature data on POP concentrations in penguin fat and eggs from 1964 to 2011, Ellis *et al.*<sup>123</sup> showed a decrease in the concentrations of DDTs, HCB and HCHs (hexachlorocyclohexane). In embryos from failed eggs of Wilson's storm-petrel collected on King George Island from 1998 to 2003 and 2014 to 2016, Kuepper *et al.*<sup>124</sup> found that concentrations of legacy pollutants were higher in 1998, 2001 and 2003, than in 2014–2016. A decrease in the bioaccumulation of HCB, HCHs, PCDDs (polychlorinated dibenzodioxins) and PCDF (polychlorinated dibenzofurans) was also reported by Cincinelli *et al.*<sup>31</sup> in the Antarctic fish *Trematomus bernacchii* over a 30 year period (early 1980s to 2010).

Among the new POPs listed in the Stockholm Convention are a few poly- and perfluoroalkyl substances (PFAS): perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorohexane sulfonate (PFHxS) and related compounds. Some of these proteinophilic compounds have been detected in Antarctic snow and waters,<sup>125,126</sup> seabirds and marine mammals.<sup>127,128</sup> In general, PFAS concentrations in Antarctica are lower than those reported for the Arctic or other remote regions. To assess possible trophic transfer along food webs, Gao *et al.*<sup>129</sup> analyzed sediments, algae, molluscs, fish, petrel and penguin feathers from King George and Ardley Islands. They found a unique PFAS profile that suggests long-range transport as the prevailing source. Furthermore, perfluorobutyric acid (PFBA) was predominant in all Antarctic organisms. No biomagnification was detected for the short-chain PFAS, such as C4–C7 perfluorocarboxylic (PFCA) and perfluorobutanesulfonic acids (PFBS), but trophic magnification factors of 2.09 and 2.92 were calculated for C-8 PFHxS and PFOS, respectively.

### Pharmaceuticals and personal care products

In Antarctica, there are more than 80 summer and year-round research stations, most of which are located in ice-free coastal



areas and discharge wastewater into the marine environment. Several stations do not have wastewater treatment plants, and where they are installed, the wastewater treatment plants often experience operational problems mainly due to the extreme climatic and environmental conditions and the great variability in station attendance.<sup>23</sup> Therefore, scientific and logistics personnel together with tourists are sources of alien microorganisms and many synthetic chemicals: pharmaceuticals and personal care products (PPCPs), micro- and nanoplastics. Also, due to the dry atmosphere and high levels of UV-B radiation, people operating in Antarctica make heavy use of sunscreens and moisturizers, and there is widespread consumption of personal hygiene products in order to prevent the spread of diseases. While many of these chemicals are not yet subject to regulatory criteria, they are increasingly being recognized as ubiquitous contaminants. Many PPCPs released into the environment usually undergo photochemical and biological degradation.<sup>130</sup> However, in Antarctic coastal ecosystems, their persistence is increased by seasonal formation of sea-ice, polar night and reduced metabolic rate of microorganisms in the cold waters of the Southern Ocean.

In the blubber of Antarctic fur seals collected in January–February 2004 on Livingston Island (Antarctic Peninsula), Schiavone *et al.*<sup>131</sup> found polycyclic musks in addition to pesticides, PCBs, PBDEs and polychlorinated naphthalenes (PCNs). These synthetic fragrances are used extensively in skin cream, soaps, detergents and deodorants, and can have anti-estrogenic effects. A few years ago, these compounds were also detected in East Antarctica in coastal waters collected near the Italian Station “Mario Zucchelli”.<sup>132</sup> In the same region, near McMurdo and Scott Base stations, Emnet *et al.*<sup>133</sup> found several personal care products and steroid hormones in samples of seawater, sea-ice and marine organisms. PPCP concentrations in seawater and sea-ice were in similar ranges, and many compounds were detected up to 25 km away from wastewater discharges.

The north of the Antarctic Peninsula is the Antarctic region most affected by research, tourism and fishing activities, and the human influence is also emphasized by the presence of a number of PPCPs. González-Alonso *et al.*<sup>134</sup> analyzed 25 selected pharmaceuticals and 21 recreational (licit or illicit) drugs in water samples from streams, ponds, glacier drains, and a wastewater discharge near Marambio Station. The highest concentrations were found in wastewaters, and analgesic and anti-inflammatory residues (acetaminophen, diclofenac and ibuprofen) were the most abundant pharmaceuticals, while caffeine and ephedrine were the most widespread recreational drugs. In water samples from Seymour/Marambio Island, King George Island and Deception Island, Olalla *et al.*<sup>15</sup> analyzed 54 substances belonging to drugs/medicines of abuse, endocrine disruptors, pyrethroids, perfluorinated compounds and sunscreens. By calculating the ratio of measured environmental concentrations of PPCPs to their predicted no-effect concentration, they found higher environmental risks for residues of acetaminophen, diclofenac, ibuprofen, the antibiotic clarithromycin, nonylphenol diethoxylate and long-chain PFASs. In untreated wastewater from Arctowski Station (Admiralty Bay, King George Island), among more than 170 substances

analyzed, Szopińska *et al.*<sup>18</sup> identified 34 PPCPs and other emerging contaminants. The highest environmental risk was calculated for residues of ketoconazole (azole antifungal), diclofenac, ibuprofen and caffeine. In wastewater and sea water, they also detected antibiotic and sulphonamide resistance genes. By analyzing a sample of phytoplankton from Port Foster Bay (Deception Island) by high-resolution Fourier-transform ion cyclotron-resonance mass spectrometry (FT-ICR-MS), Duarte *et al.*<sup>24</sup> found residues of 5 personal care products and 40 pharmaceuticals, including anticonvulsants, antihypertensives and beta-blockers, antibiotics, analgesics and anti-inflammatories.

Numerous multi-antibiotic resistant bacterial strains have been found in Antarctic ecosystems (*e.g.*, ref. 135). Antibiotic resistance genes can emerge naturally in microorganisms, especially in the extreme conditions of the Antarctic environment where bacteria can compete for nutrients.<sup>136</sup> However, Jara *et al.*<sup>137</sup> analyzed the antibiotic-resistance patterns and antibiotic-resistance genes in strains of bacteria from freshwater samples collected in human-affected and control areas in the Fildes Peninsula. They found that isolates from the impacted sites had a greater richness and diversity of antibiotic-resistance genes, and were resistant to synthetic and semi-synthetic drugs, while those from relatively undisturbed sites were highly susceptible to antibiotics. Therefore, there is growing concern about the impact of wastewater from scientific stations, which can modify the native resistome of microbial communities, and can also introduce antibiotic resistance gene carriers such as transposons, integrons and conjugative plasmids into the environment.<sup>18</sup>

### Microplastics

Plastic debris has become one of the most common and persistent synthetic wastes in the global environment. Microplastics (MPs, size 1–5000  $\mu\text{m}$ ), produced deliberately or by the fragmentation of larger debris, are among the most enduring evidence of past and recent human activities even in Antarctica.<sup>17</sup> In regions with the strongest human footprint, such as the Northern Antarctic Peninsula and the Scotia Arc, entanglement of seals in plastic waste or plastic ingestion by seabirds have been reported for forty years.<sup>138,139</sup> However, only in recent years, after the environmental impact of MPs had assumed global significance, have numerous investigations been conducted on the presence of MPs in the Antarctic environment. Most of the studies focused on coastal marine ecosystems with higher human pressure, and only plastic fragments  $>300 \mu\text{m}$  were often considered. Thus, the distribution pattern of MPs in the Southern Ocean, their background concentrations and potential impact on pelagic communities are currently unknown. Furthermore, it is very difficult to compare the available data and evaluate their reliability because of the differences in sampling and analytical methods among the different studies, and the lack of standardized protocols for assessing the contamination of samples in the field and in the laboratory. Further difficulties in assessing the potential impact of MPs arise from the spatio-temporal variations of the Southern Ocean



environmental characteristics, such as seasonal changes in sea-ice cover and exposure to UV-radiation. Depending on the polymer composition, these factors can contribute to the fragmentation and degradation of plastic wastes and influence their environmental fate.

Antarctic marine organisms include many endemic species with unique ecophysiological adaptations to the Southern Ocean. Without better knowledge of the spread of the tiniest plastic particles (nanoplastics, size < 1  $\mu\text{m}$ ) that are potentially more dangerous, it seems impossible to tell what impact these organisms will suffer. Although the Southern Ocean also probably receives plastic particles from lower latitudes through long-range marine and atmospheric transport,<sup>140</sup> their concentrations in open ocean waters appear to be very low. By sampling floating MPs (>100  $\mu\text{m}$ ) in subsurface waters from the Arctic to the Scotia Sea, Pakhomova *et al.*<sup>141</sup> found significantly lower concentrations in the Southern Hemisphere than in the Northern. In surface and subsurface waters of the Weddell Sea gyre, Leistenschneider *et al.*<sup>142</sup> measured MP concentrations of  $0.01 \pm 0.01 \text{ m}^{-3}$  and  $0.04 \pm 0.1 \text{ m}^{-3}$ , respectively. In addition, they found that about half of the particles sampled (>300  $\mu\text{m}$ ) originated from paints of the research vessel. In a circum-Antarctic survey, Kuklinski *et al.*<sup>143</sup> collected fibers that appeared to be plastic, but analysis *via* Fourier-transform infrared (FT-IR) spectroscopy showed that they were composed of silica (*i.e.*, likely of biogenic origin). By contrast, several surveys have reported relatively high concentrations of

MPs in seawaters, sediments and organisms in coastal ecosystems of the northern Antarctic Peninsula, South Georgia Island, and the Ross Sea, especially those directly affected by wastewater from scientific stations and/or rather intensive tourism and fishing activities (*e.g.*, ref. 16, 144 and 145). In general, fibers from washing clothes are among the most common MPs. In some coastal waters and sediments, their concentrations are in the same range as those reported in coastal environments outside Antarctica.

The Ross Sea is one of the largest marine protected areas in the world. Near the Italian scientific station “Mario Zucchelli”, synthetic fibers have been found in zoobenthic species<sup>146</sup> and in the fish *Trematomus bernacchii*.<sup>147</sup> Other scientific stations along the Ross Sea coasts such as McMurdo and Scott Base have been in operation for several decades. Zhang *et al.*<sup>148</sup> found more MPs in fish from the Ross Sea than in those from the nearby Amundsen Sea, where there are no scientific stations. The presence of MPs has also been reported in penguin scats, particularly in samples collected in the Antarctic Peninsula and the Scotia Sea.<sup>149–151</sup> Although these studies seem to suggest trophic transfer and possible biomagnification of MPs along food webs, Sfriso *et al.*<sup>146</sup> found 3–5 times higher concentrations in filter-feeder bivalves and benthic grazers than in omnivorous or predatory species of Antarctic invertebrates. Furthermore, Leistenschneider *et al.*<sup>152</sup> found that none of the 85 particles ingested by chicks of the emperor penguin (*Aptenodytes forsteri*, the only penguin species breeding around Antarctica during the

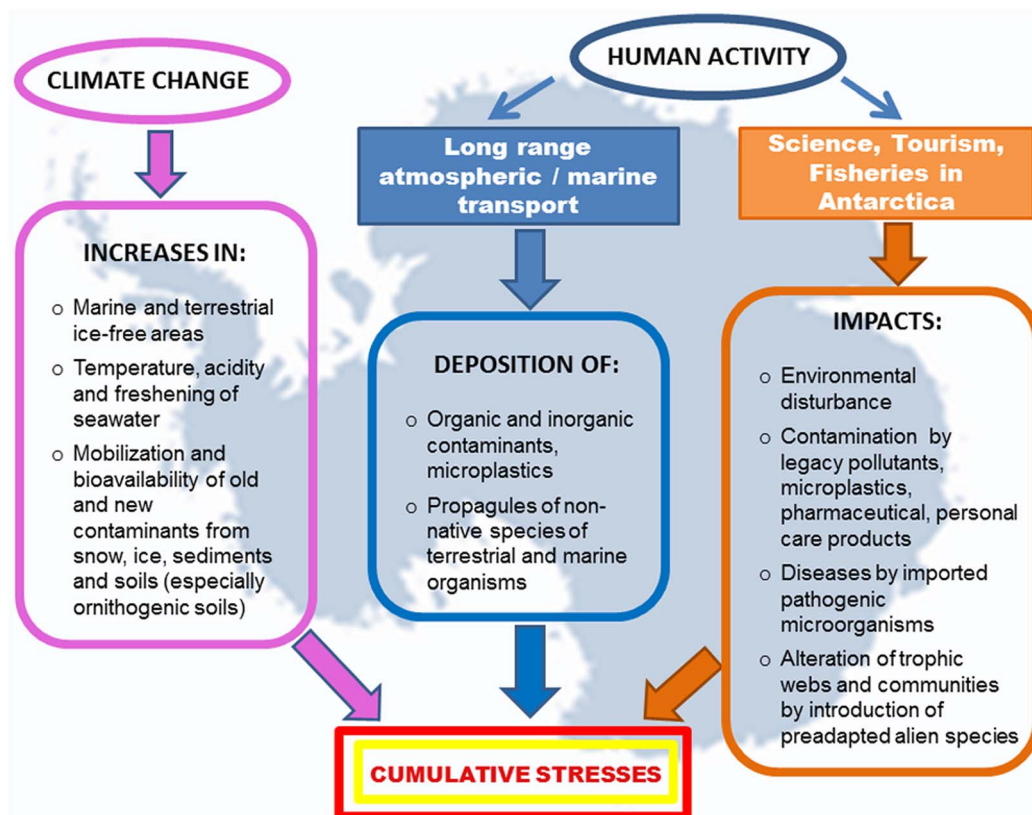


Fig. 2 Simultaneous and cumulative impacts of climate changes and human activities on Antarctic organisms and ecosystems.



austral winter) collected in Queen Maud Land were MPs, and the synthetic fibers found were due to contamination during the analysis and processing of the samples. Also, Garcia-Garin *et al.*<sup>153</sup> found that the fibers and fragments found in scats of male Antarctic fur seals (*Arctocephalus gazella*) collected at Deception Island (a hotspot of tourism and scientific activities in Antarctica) were silicate minerals and chitin fibers, and not MPs. Recently, the absence of MP particles (>80  $\mu\text{m}$ ) has also been reported in the stomachs of 10 ringed seals from the western Canadian Arctic.<sup>154</sup>

### Possible cumulative impacts of climate changes and environmental contaminants

With the exception of some local impacts in the vicinity of the scientific stations, marine and terrestrial ecosystems in continental Antarctica are scarcely affected by anthropogenic contaminants or by macroscopic climatic and environmental changes so far. By contrast, in the Antarctic Peninsula and the islands of the Scotia Arc, the larger and growing scientific, tourist and fishing activities constitute important local sources of metals, PAHs, PBDE, PCBs and PCPPs.<sup>155</sup> Rapid warming has led to the thinning and disintegration of ice shelves, the retreat and melting of ice sheets and the thawing of permafrost soils. The expansion of ice-free areas, together with the increase in liquid water availability, has promoted soil-formation processes and changes in terrestrial biotic communities.<sup>156</sup> Marine ecosystems harbour many endemic species, which through long evolutionary processes in isolation, have adapted to the cold waters of the Southern Ocean ( $-1.8$  °C). Compared to related species in other seas, these organisms tolerate much smaller temperature increases, which could impair their metabolism and ability to detoxify and eliminate environmental contaminants.

The role of climate change in shaping the responses of Antarctic marine organisms to environmental pollutants has recently been highlighted in coastal benthic communities at McMurdo Station.<sup>94,157</sup> Until the mid-1980s, the waste produced at the station was disposed of in snow pits, by open incineration or dumped directly into sea. In 1988, the US National Science Foundation initiated a dumpsite cleanup and long-term environmental monitoring.<sup>49</sup> Although the concentrations of most pollutants in sediments and marine organisms have progressively decreased to values typical of nearly pristine environments, Palmer *et al.*<sup>102,157</sup> found no signs of recovery in macrobenthic communities. Moreover, they found that temporal changes in species composition correlated with the Interdecadal Pacific Oscillation climatic index, and were also influenced by the Antarctic Oscillation climatic index and maximum sea-ice extent rather than by decreases in environmental pollution.

About 15 million  $\text{km}^2$  of sea-ice grows around Antarctica each year, and its summer melt promotes blooms of sympagic and pelagic communities at the ice edges. Sea ice intercepts and accumulates persistent contaminants from atmospheric deposition and seawater, and likely contributes to their uptake by sea-ice algae and other organisms in cryopelagic communities.

These communities play a crucial role in Southern Ocean productivity, and ice-algae are critical for the wintering of juvenile Antarctic krill (*Euphausia superba*, age class 0), the keystone species of Antarctic food webs.<sup>158</sup> However, after a few years of record highs, the sea-ice cover of the Southern Ocean has begun to exhibit a rapid decline since 2016 (the most pronounced since the beginning of 40 years of satellite observations;<sup>159</sup>). This decrease is likely due to progressive ocean warming and southward advection of atmospheric heat that adversely affects ocean productivity, and may also contribute to the transport of POPs and MPs from lower latitudes to the Antarctic environment.

Seawater acidification could be another climate-related stressor affecting the resilience of Antarctic marine organisms and increasing their sensitivity to anthropogenic contaminants.<sup>37</sup> In seawater, aragonite saturation is essential for calcifying organisms. Negrete-García *et al.*<sup>160</sup> estimated that the Southern Ocean could experience aragonite undersaturation by 2050. Preliminary laboratory experiments by Ericson *et al.*<sup>161</sup> indicate that adult *E. superba* specimens are resilient to one-year exposure to near-future levels of ocean acidification (1000–2000  $\mu\text{atm}$   $\rho\text{CO}_2$ ). However, other experiments showed inhibition of embryonic development of this key species at simulated concentrations of 2000  $\mu\text{atm}$   $\rho\text{CO}_2$ .<sup>162</sup> Furthermore, Morley *et al.*<sup>163</sup> have emphasized the sensitivity of *E. superba* to increasing water temperatures and sea-ice loss.

Any climatic and environmental stress can affect the biological thresholds of organisms for other stressors, such as environmental contaminants. Although no field data from Antarctic coastal ecosystems exist yet, some ecotoxicological experiments show impaired larval development or survival of Antarctic marine species exposed to the combined effects of water acidification and nanoplastics.<sup>164,165</sup> Additional cumulative stresses and threats to Antarctic organisms may arise from alien species and pathogenic microorganisms accidentally introduced by the growing number of scientists and tourists. Shimada *et al.*<sup>166</sup> found strains of *Legionella* spp., *Pseudomonas* spp., and *Mycobacterium* spp. in water facilities of the Syowa station and in waters collected in the surrounding glacial lakes. Again, climate change could play an important role in enabling the colonization and spread of pre-adapted and invasive alien species.

A wide range of microorganisms, microalgae and some invertebrate species have been found on the surface of plastic debris collected in the Antarctic Peninsula, and strains of bacteria with multiple antibiotic resistance have been isolated from a polystyrene fragment beached on King George Island.<sup>167</sup> Wastewater from scientific and tourist stations and vessels are also sources of PPCPs. Furthermore, the laundering of technical clothing releases plastic fibers, water repellents and flame-retardant chemicals. In the marine environment, plastic debris can adsorb and accumulate metals and hydrophobic organic contaminants in much higher concentrations than in the surrounding seawater.<sup>168</sup> Lu *et al.*<sup>169</sup> found that MPs affect the bioaccumulation and chronic toxicity of Cd in zebrafish. Since Antarctic marine organisms are already exposed to a naturally high bioaccumulation of Cd and Hg, ingestion of



MPs could contribute to their exceeding the tolerance thresholds for these metals (Fig. 2).

## Conclusions

Most of continental Antarctica and the Southern Ocean are minimally affected by local human activities, and receive persistent contaminants primarily through long-range transport processes. Therefore, levels of contamination in snow, water, soil, and sediment are among the lowest reported in the global environment. Several species of Antarctic lichens, mosses, seabirds and marine organisms with a circumpolar distribution are reliable biomonitors of global emissions of metals and POPs, and usually accumulate these contaminants to levels below or in the same range as those measured in related species from other remote regions. The main exception appears to be the “natural” accumulation of Cd and Hg, which is likely due to the unique features of the Southern Ocean environment and its food webs. The species-specific ecophysiological characteristics, migration routes and life histories of some long-lived seabirds (such as the south polar skua) may also contribute to significant bioaccumulation of some organic contaminants. However, as some recent surveys have suggested, after the declining Pb contamination, the POPs concentrations in Antarctic organisms are likely to be declining with the entry into force of global conventions banning POPs. Nonetheless, climate change can (directly or indirectly) affect the transport, pathways and environmental fate of persistent contaminants released in the Southern Hemisphere, and can also remobilize and make bioavailable those deposited in the past. Therefore, continental-scale monitoring with standardized procedures is needed to evaluate the long-term distribution pattern of legacy contaminants and their possible biological effects.

ATPEP bans the import and release of POPs in Antarctica, and provides stringent guidelines for the protection of its near-pristine environment and its value for studying global processes. However, the research results summarized in this review show that the global chemical production and the growing number of visitors and activities undertaken in certain Antarctic regions are sources of numerous (and quite overlooked) persistent contaminants. Several scientific and tourism stations and vessels lack wastewater treatment facilities, resulting in the release of metals, hydrocarbons, detergents, flame retardants, personal care products, pharmaceuticals, MPs and pathogenic microorganisms into marine ecosystems. Many of the chemicals are not yet subject to regulatory criteria. For some of them, there is also a lack of standardized methodologies for sampling and analytical determinations. Efforts directed at a reliable assessment of their occurrence and distribution appear to be particularly urgent in the marine ecosystems of the Antarctic Peninsula and the islands of Scotia Arc, where most human activities are concentrated. Moreover, these regions are more exposed to the transport of contaminants from South America, and have experienced conspicuous temperature increases in the recent past. In coastal marine ecosystems near scientific stations, chronic co-exposure to some contaminants of emerging interest and to pathogenic

microorganisms can give rise to synergistic or additive biological effects. Most Antarctic marine organisms are endemic species with unique ecophysiological adaptations to living in seawater with near freezing temperatures and tolerate only minimal variations. Small increases in water temperature can affect the properties of cell membranes and the metabolic processes involved in the absorption and detoxification of environmental contaminants. Thus, when evaluating biological responses to simultaneous exposure to metals, POPs, PCPPs, MPs, and pathogenic organisms, it is necessary to consider possible exacerbations due the concomitant impact of climate-related stressors and other anthropogenic disturbances.

The Southern Ocean is very sensitive to water acidification, and has shown a marked decrease in sea-ice formation in recent years. These processes can modify the biogeochemical cycling of nutrients, the productivity of marine ecosystems, and the composition of biotic communities. Warming and changes in sea-ice cover, along with rising Hg emissions in the Southern Hemisphere, could also enhance Antarctica's role as a metal “cold trap” through increased inputs of reactive halogens into the continental atmosphere and increased Hg depletion events.

## Conflicts of interest

There are no conflicts to declare.

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