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REVIEW

Air-Snow Interactions and Atmospheric Chemistry

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The presence of snow greatly perturbs the composition of near-surface polar air, and the higher concentrations of hydroxyl radicals (OH) observed result in a greater oxidative capacity of the lower atmosphere. Emissions of nitrogen oxides, nitrous acid, light aldehydes, acetone, and molecular halogens have also been detected. Photolysis of nitrate ions contained in the snow appears to play an important role in creating these perturbations. OH formed in the snowpack can oxidize organic matter and halide ions in the snow, producing carbonyl compounds and halogens that are released to the atmosphere or incorporated into snow crystals. These reactions modify the composition of the snow, of the interstitial air, and of the overlying atmosphere. Reconstructing the composition of past atmospheres from ice-core analyses may therefore require complex corrections and modeling for reactive species.

Snow can cover up to 50% of landmasses in the Northern Hemisphere (1). It forms a porous medium that remains permeable to gases over depths of several meters (2). The snow-

pack—the annually accumulated snow at high latitudes or altitudes—therefore offers a large internal surface for interactions with atmospheric gases.

Evidence for such interactions, and their impact on atmospheric chemistry, was found in the mid-1980s, when it was shown that at high latitudes, ozone could be destroyed completely at altitudes up to 1 km over large areas (3). Reactions of halogen species in the snowpack and on aerosol surfaces had to be invoked to explain this observation, which could not be understood on the basis of gas-

phase chemistry alone (4–8). Similarly, the rapid oxidation of lower atmospheric gas-phase elemental mercury (Hg) to reactive gas-phase and particulate-phase Hg (9–10) could only be explained once snowpack and/or sea-ice processes were invoked.

A detailed understanding of snow-atmosphere interactions is necessary for understanding current atmospheric processes, as well as for investigating those of the past using ice cores. In the past few years, extensive measurement campaigns in 2000 in Greenland (at Summit, 73°N) and the Canadian high Arctic (at Alert, 82°N) (Fig. 1) and in Antarctica (at South Pole in 1998–1999, and on the Antarctic coast at Neumayer, 70°S, in 1999) have provided evidence for the impact of the snowpack on many trace atmospheric species. As a result, some insights into the underlying mechanisms are emerging, although the overall picture is still not well understood.

Snowpack Chemistry

Because they control the oxidative capacity of the atmosphere through ozone production (11), nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$)

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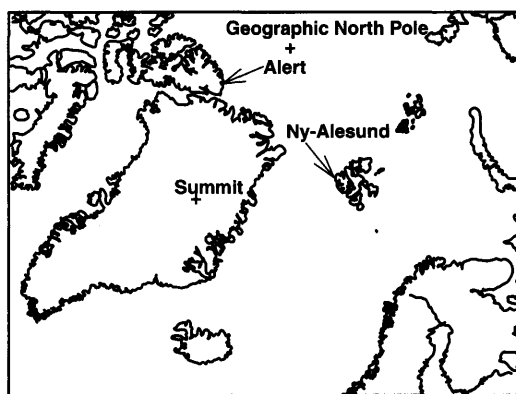
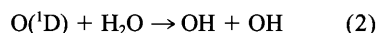
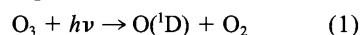


Fig. 1. Map of Greenland and of surrounding areas, showing the coastal location of Alert and the ice-cap location of Summit, where recent observation campaigns were conducted.

have received considerable attention. Daily cycles in NO_x concentrations have been observed during the polar spring and summer in the Arctic and Antarctic, with daytime maxima and night time (that is, when the Sun is very low on the horizon) minima (12–16). Gradient (Fig. 2) and flux measurements have shown that sunlit snowpacks emit NO_x , explaining a large part of the observed variations. HONO emissions from sunlit snowpacks have also been observed at Alert (17) and Summit (15). These emissions, followed by HONO photolysis that produces gas-phase OH, have a large impact on atmospheric boundary-layer OH and NO_x .

OH and HO_2 radical concentrations have been measured recently at South Pole (18). Atmospheric OH is normally produced by the reaction sequence shown below.



In polar regions, the rate of OH production from O_3 photolysis is reduced because of the high solar zenith angle and low water partial pressures, and one would therefore expect OH production to be low. Yet the concentrations measured at South Pole (18) or calculated for Arctic sites from steady-state calculations or models (19, 20) were as high as those found at lower latitudes and about 10 times higher than predicted by gas-phase chemistry models (19–21), pointing to a substantial influence of the snowpack. Increased OH concentrations decrease the lifetimes of many compounds including some pollutants, reduce their concentration near the surface, and provide a potentially important sink for longer lived species.

Concentrations of light aldehydes and acetone were also higher than expected over snowpacks. These compounds are intermediates in the oxidation of organic compounds and are an important source of HO_x ($\text{OH} + \text{HO}_2$) radicals, which largely determine the lifetime of trace gases in the atmosphere. At

Alert and Summit, elevated formaldehyde (HCHO) concentrations were found in snowpack interstitial air (22, 23), in amounts that increased as the solar elevation angle increased through the sunrise season. A snowpack photochemical production mechanism was proposed for the coastal site, whereas physical exchanges were suggested for the ice-cap sites. Daily cycles have been observed for HCHO , acetaldehyde (CH_3CHO), and acetone [$\text{CH}_3\text{C}(\text{O})\text{CH}_3$] (19, 24, 25) above the snow and in snowpack air at both coastal and ice-cap sites. Measured air-snow gradients imply fluxes of these species to the atmosphere during sunlit periods. Snowpack production of alkenes and alkyl halides was also observed, and a photochemical mechanism was postulated (26).

Molecular halogens such as Br_2 and BrCl are emitted by the snowpack both during the polar night and during sunlit periods (27). Halogens are involved in the large-scale ozone-destruction episodes mentioned above. They photolyze to produce reactive Cl or Br atoms, which destroy ozone in a chain reaction (5). Recent measurements have shown that the snowpack can also consume ozone directly (28, 29), independent of large-scale destruction episodes. Another important atmospheric oxidant, H_2O_2 , was observed to be taken up by the snowpack during the night and emitted during the day, resulting in a net uptake by snow (25).

These snow-air exchanges, and others not yet discovered, result in an atmospheric composition over snowpacks that differs substantially from that predicted by gas-phase chemistry models (Table 1). Snow-atmosphere interactions thus challenge our ability to understand and model atmospheric chemistry over a large fraction of Earth's surface. Moreover, polar snow can form glacial ice from which ice cores are extracted and analyzed (30). Processes taking place in surface snow affect the composition of the glacial ice, making it more difficult to decipher ice cores and reconstruct past climates and biogeochemical cycles. A detailed understanding of the processes involved in

air-snow interactions is therefore necessary for the development of reliable models of present and past atmospheric chemistry.

Physical and Chemical Interactions

Snow forms either by water vapor deposition or by the freezing of supercooled droplets. During formation and precipitation, it incorporates various gaseous and particulate contaminants (31). After deposition, atmospheric temperature changes and radiative heating and cooling of the snowpack result in temperature gradients and water-vapor fluxes that change with depth (Fig. 3). These fluxes determine snow metamorphism—the changes in crystal shapes and snow surface area and density caused by the transfer of water molecules between snow grains (32, 33).

The density of surface snow ranges from $\sim 0.01 \text{ g cm}^{-3}$ for fresh snow to 0.5 for wind-packed snow (34). Thus, much of the snowpack volume consists of air that can be readily exchanged with the atmosphere, and this is facilitated by “wind pumping” and the presence of irregularities on the snowpack surface (35). Numerous physical and chemical processes can affect trace gases in the snowpack (Fig. 3). These include purely physical processes such as adsorption (36), solid state diffusion (37) and cocondensation (38), and chemical reactions catalyzed by ice surfaces that can be initiated by light (22, 26) or by temperature [“dark” reactions, such as those that lead to the production of halogens (27)]. Some of these dark reactions are puzzling and seem to take place over long time scales, as indicated by the analysis of methyl bromide (CH_3Br) in Arctic firn air (39) down to a depth of 100 m (40). The rapid concentration increase of CH_3Br with depth observed is unexpected in air that is hundreds of

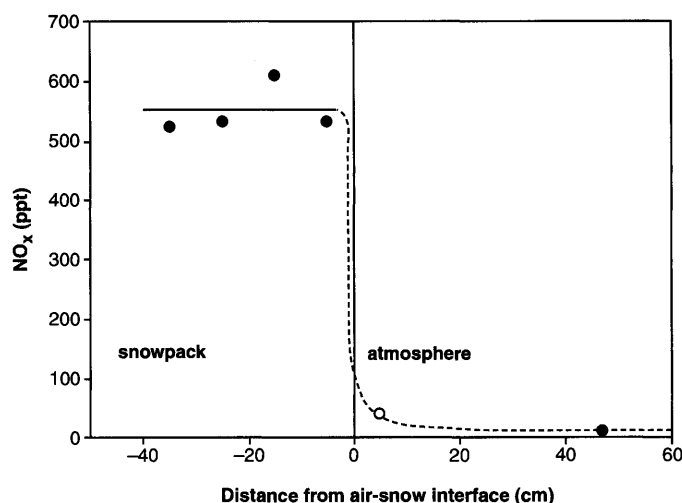


Fig. 2. Vertical profile of NO_x measured at Summit on 23 June 2000, showing that concentrations are much larger in the sunlit snowpack interstitial air than in the overlying atmosphere. The observed gradients result in fluxes of NO_x from the snow to the atmosphere. [Data from R. Honrath et al., Michigan Tech Univ.]

years old, and must involve biologically mediated processes and/or thermal condensed-phase chemistry.

Difficulties in understanding and characterizing these reactions are enhanced by a lack of knowledge of the physical and chemical nature of natural ice surfaces. A disordered layer, often called the quasi-liquid layer, exists on ice surfaces (41–43). Its thickness increases with temperature and ionic solute concentration, and its properties are intermediate between those of bulk ice and liquid water, complicating efforts to elucidate the reaction kinetics in this medium. Laboratory experiments that exposed ice surfaces to NaCl or sea salt have shown the formation of a surface liquid layer with high ionic concentrations (44). Such a medium can accelerate chemistry and photochemistry (45).

Interpretation of Observational Data

A mechanistic interpretation of observational data for snowpack emissions is difficult, but a tentative model (Fig. 4) can be derived from the existing observational data. Field studies in the Arctic and Antarctic indicate that snowpack chemistry can be driven by the photolysis of nitrate ions (NO_3^-) (46), which results in the release of NO_x (Fig. 2) and HONO to the snowpack air. This conclusion is supported by laboratory experiments on irradiated nitrate-doped ice (47). NO_3^- photochemistry leads to the formation of condensed-phase OH, and subsequently gas-phase OH, through the photolysis of HONO, also produced by NO_3^- photolysis (17) (Fig. 4).

OH formed in the snowpack can react with organic precursors to produce HCHO, acetaldehyde, and acetone (19, 48). These precursors could be humic material present as dissolved organic material or as particles in the snowpack. Support for the photochemical production of carbonyl compounds comes from observations and experiments at Alert involving the ultraviolet irradiation of natural snow (48).

These studies showed a good correlation between irradiation and HCHO production. Snowpack photochemical processes involving condensed-phase organic material may also produce alkenes and alkyl halides, as suggested from observations at Summit (26).

However, given the diverse and complex processes involved in exchanges between the snowpack and the atmosphere, the mechanism for production of a given

species probably depends on physical and chemical conditions and could vary from one site to another, as illustrated by the case of HCHO. Photochemical production was not considered necessary to explain HCHO emissions observed at Summit (23, 25) and various Antarctic sites (24, 49). Instead, physically driven exchanges were invoked as an explanation. The reason for the difference between sites may be that at

Alert, where some soil surfaces remain exposed all year long, the snow contains high concentrations of organic matter from a variety of biota (soil dust, seasonal plants, small mammals, ice algae). In Greenland and Antarctica, there are no major local sources of organic matter. Snowpack photochemical production may thus be an important input for atmospheric HCHO at Alert, whereas physical exchanges would be more important at other sites. Physical exchanges would still take place at Alert, and HCHO emission simply upon heating snow was observed (48). Photochemical production may also contribute to HCHO production at places such as Summit, as suggested by shading experiments (50).

The physical mechanisms responsible for air-snow exchanges of trace gases are not clearly identified. Adsorption/desorption (23, 49) and cocondensation/sublimation (24) have been proposed in the case of HCHO. Perrier *et al.* (51) concluded that HCHO was not located on the snow crystal surfaces and proposed that exchanges by solid-state diffusion were involved. Measurements of the adsorption isotherms of HCHO on ice, and of its diffusion coefficient and solubility in ice, are necessary for a convincing interpretation.

Global Impacts

Snowpack photochemistry can clearly have a marked impact on the composition of surface snow (and that of ice that forms glaciers and ice caps). The global impact of this chemistry may be substantial. Knowing the fraction of Earth's surface that is snow covered and assuming that on average, the top 10 cm of snow

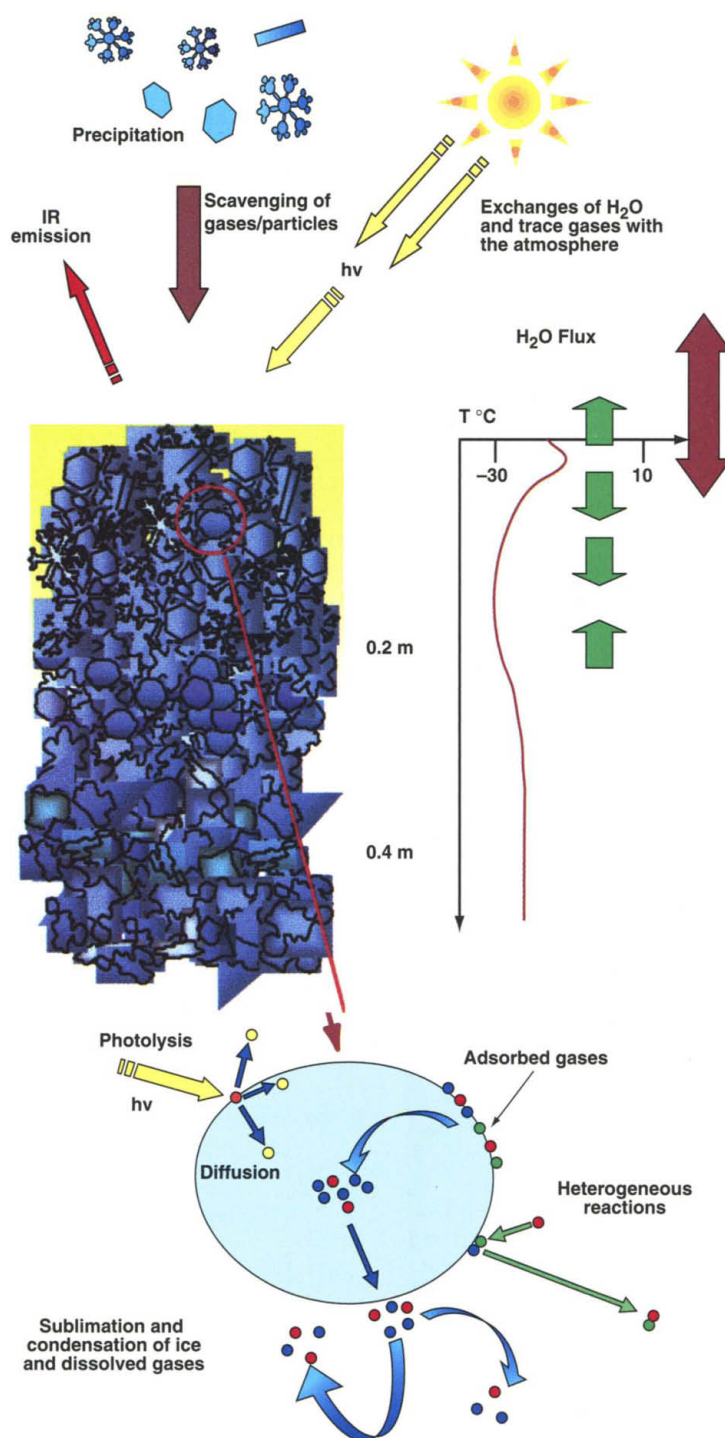


Fig. 3. Physical and chemical processes involved in air-snow interactions at the snowpack scale, and at the snow-crystal scale.

Table 1. Measured (or calculated) concentrations of gaseous species at Alert at the end of April 2000, compared with values predicted by models that include gas-phase chemistry only.

Species	Value measured over snow	Prediction by gas-phase chemistry (19)
HCHO	200 pptv	70 pptv
CH ₃ CHO	80 pptv	40 pptv
NO _x	25 pptv	1 pptv
HONO	20 pptv	1 pptv
OH	0.03 pptv*	0.003 pptv
HO ₂	3.7 ppt*	0.9 ppt
O ₃	As low as 0.07 ppb	30–34 ppbv
Hg ⁰	0.02 pptv	0.17 pptv

*Calculated in (19, 20).

are subject to wind pumping, and given an effective flow rate through that snow of $0.5 \text{ cm}^3 \text{ s}^{-1}$, we estimate that an air volume equivalent to the volume of the whole atmosphere passes through snowpack on a time scale of ~ 3 months. Obviously, this will directly affect the lower atmosphere, but there is clearly a large potential for removing particles and water-soluble gases from the atmosphere and emitting snowpack reaction products back into the atmosphere. For example, this process manifests itself in the partitioning of persistent organic pollutants toward the colder poles (52), as well as the complete removal of lower atmospheric ozone at sunrise over the Arctic Ocean (5).

Snowpack perturbations of atmospheric chemistry will depend on meteorological factors, particularly on the rate at which snowpack emissions are mixed vertically by turbulence in the lower troposphere (the boundary layer). Owing to strong radiative cooling and low absorption of solar radiation by the surface, the boundary layer is often very stable in polar regions, and this is particularly true at South Pole (14). As a result of this poor vertical mixing in the polar lower atmosphere, snowpack emissions of photolabile substances such as HONO and HCHO remain confined to a thin layer near the surface, where they can have pronounced effects. For example, a median NO_x concentration of 225 parts per trillion by volume (pptv) at the sunlit South Pole has been observed; gas-phase chemistry would predict only a few pptv (14). At Alert or Summit, where boundary-layer mixing can be more effective than at South Pole, the NO_x concentration is rarely above ~ 20 to 30 pptv (15, 16).

Atmospheric stability also leads to high HO_x levels, which maintain the halogen chemical cycle, producing high BrO concentrations in polar marine environments (53). It has been hypothesized (9, 10) that these high BrO concentrations result in the rapid depletion of otherwise long-lived elemental Hg from the boundary layer. Thus, even though this chemistry is confined to the boundary layer, it could have a large impact on the

global cycle of mercury (10), and perhaps other toxic pollutants. It is noteworthy that this chemistry results in the conversion of atmospheric gas-phase elemental mercury to more bioavailable forms that are transferred to the snow-covered environment and subsequently enter the hydrological cycle upon snowmelt. However, recent evidence for additional reductive processing in the snowpack after deposition complicates the analysis (54). Ozone is also relatively long-lived but is rapidly removed in the boundary layer of the Arctic and of the coastal regions of Antarctica (55).

Implications for Ice-Core Interpretation

Analyses of buried snow and of interstitial air are used to reconstruct past trends in atmospheric composition. Snowpack processes that affect the composition of both media must be taken into account in their interpretation. From snowpack actinic flux data at Alert (56), the photolytic lifetime of NO₃[−] in snow in summer is calculated to be about 40 days. Radiation is considerably attenuated at depths of a few centimeters (56), but most deposited nitrogen could still be photochemically processed in areas with low rates of snow accumulation, such as Antarctica, from where many ice cores originate. This factor complicates the interpretation of nitrate ice-core data, and of other species affected by snowpack processes. For example, the relatively high radical (e.g., HO₂) concentrations in firm air could also severely complicate the interpretation of ice-core H₂O₂, because this species can be produced in the firm air through the HO₂

self-reaction. These problems are not necessarily intractable, however, and elaborate models can usefully reproduce observed air-snow relationships for some species, including H₂O₂ (57).

Photochemical processing by reaction with OH in the boundary layer will also be important for species that do not interact with snow, and that can be used in past climate studies, such as nonmethane hydrocarbons. The OH-lifetime of propane at -15°C is 5 days, sufficiently short for its boundary-layer concentration to be reduced relative to its concentration in the free troposphere. Thus, the ice-core record for species that react rapidly with OH will be influenced by the trend in NO₃[−] deposition to the snowpack, which affects gas-phase OH concentrations. The difference in concentrations of these species between the boundary layer and the free troposphere must be studied to assist in converting ice-core values of short-lived species into values that have appropriate global relevance.

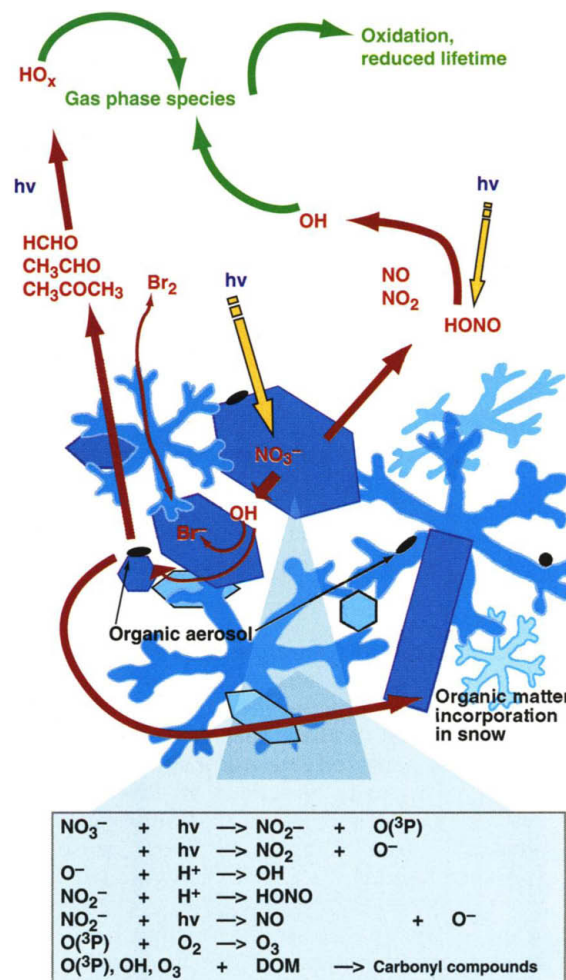


Fig. 4. Some of the effects of the photolysis of the nitrate ion NO₃[−], contained in snow, on the chemistry of snowpack interstitial air and of atmospheric air. Products of nitrate photolysis, which include OH, can oxidize both inorganic and organic compounds contained in the snowpack. Reaction products modify snow and atmospheric compositions.

Concluding Remarks

It is increasingly recognized that the snowpack is a multiphase reactor in which physical exchange processes, heterogeneous reactions, and photochemical reactions take place. Quantitative understanding is, however, lacking, hampering efforts to simulate snowpack processes. A major problem is that the physical and chemical nature of the surface of snow and ice is not well understood. In particular, it is not clear what effect ionic species contained in snow have on ice surface structure, composition, and chemistry. The composition of most of the snowpack organic carbon has not been determined, and even the inorganic chemistry involving halogen oxidation is ill-defined. The microphysical location of reactive species (particle phase, dissolved in ice, or adsorbed on ice) must also be known if quantitative understanding is to be achieved. Laboratory experiments can help to quantify elementary physical and chemical processes, while model studies can be implemented to assess their global- and regional-scale impacts.

Air-snow interactions may affect the chemical composition of the global atmosphere. The rapid decrease in the global extent of snow cover (58) highlights the need to improve our understanding of this intriguing and highly interdisciplinary area of physical science.

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REVIEW

Environmental Change and Antarctic Seabird Populations

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Recent changes in Antarctic seabird populations may reflect direct and indirect responses to regional climate change. The best long-term data for high-latitude Antarctic seabirds (Adélie and Emperor penguins and snow petrels) indicate that winter sea-ice has a profound influence. However, some effects are inconsistent between species and areas, some in opposite directions at different stages of breeding and life cycles, and others remain paradoxical. The combination of recent harvest driven changes and those caused by global warming may produce rapid shifts rather than gradual changes.

The broad scientific consensus is that the warming of Earth's climate since the 1970s has been at a rate greater than at any time in the last thousand years (1). This has generated concern about the consequential biological and ecological changes, affecting the range and distribution of species; their phenology

and physiology; the cycles, composition, and interactions of communities; and the structure and dynamics of ecosystems (2).

There is a widespread belief that Antarctic ecosystems represent more pristine environments than elsewhere on our planet and that the current phase of climate change poses a

new challenge to the survival of Antarctic wildlife.

Some of the strongest signals of global climate warming have come from polar regions, especially the Antarctic, where large increases in air temperature and extensive melting of ice shelves have been observed (3–5). It might be supposed, therefore, that concurrent changes in biological responses should be evident, particularly in species at higher levels in food chains, which might integrate and/or amplify effects. However,

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