Ice sheets and nitrogen

Eric W. Wolff

British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK

Snow and ice play their most important role in the nitrogen cycle as a barrier to land–atmosphere and ocean–atmosphere exchanges that would otherwise occur. The inventory of nitrogen compounds in the polar ice sheets is approximately 260 Tg N, dominated by nitrate in the much larger Antarctic ice sheet. Ice cores help to inform us about the natural variability of the nitrogen cycle at global and regional scale, and about the extent of disturbance in recent decades. Nitrous oxide concentrations have risen about 20 per cent in the last 200 years and are now almost certainly higher than at any time in the last 800 000 years. Nitrate concentrations recorded in Greenland ice rose by a factor of 2–3, particularly between the 1950s and 1980s, reflecting a major change in NO\textsubscript{x} emissions reaching the background atmosphere. Increases in ice cores drilled at lower latitudes can be used to validate or constrain regional emission inventories. Background ammonium concentrations in Greenland ice show no significant recent trend, although the record is very noisy, being dominated by spikes of input from biomass burning events. Neither nitrate nor ammonium shows significant recent trends in Antarctica, although their natural variations are of biogeochemical and atmospheric chemical interest. Finally, it has been found that photolysis of nitrate in the snowpack leads to significant re-emissions of NO\textsubscript{x} that can strongly impact the regional atmosphere in snow-covered areas.

1. Introduction

In comparison with biologically active terrestrial and ocean surfaces, ice is not a very dynamic source or sink of nitrogen compounds. However, it nonetheless plays an important role as a significant part of Earth’s surface, and as an archive of changes in atmospheric composition. In addition, there is some interesting chemistry associated with N compounds in ice. In this paper, all these aspects of nitrogen and ice will be addressed. Although the major focus will be on ice sheets because of their large area, other icecaps and glaciers are also discussed, in so much as they can provide localized archives of past deposition of N compounds.

The first role of ice and snow in the N cycle is as a barrier between the underlying land or ocean surface and the atmosphere. Permanent ice sheets (mainly Antarctica and Greenland) cover over 10 per cent of the land surface, whereas seasonal snow (mainly in the northern hemisphere) covers a maximum of about a further 30 per cent [1]. At its maximum in spring, Arctic sea ice covers approximately 5 per cent of the ocean’s surface, whereas Antarctic sea ice covers around 6 per cent of the world’s oceans in austral spring. There is some limited microbial activity near the surface, especially in warmer, wetter, snow and ice. However, the most obvious implication is that the biological N exchanges that would normally occur must be scaled back to account for the land and ocean areas that are covered in snow and ice.

However, the ice sheets and glaciers do of course receive an input of N compounds from the atmosphere through wet and dry deposition, and in the next section I carry out an annual budget, and an inventory, of N compounds in permanent ice sheets. Seasonal snow cover acts only as a delay for material to reach the underlying surface when the snow melts. Changes with time of the deposition of N compounds to the ice sheets (as determined from ice cores) can (with care) be used to understand the changing regional atmospheric burden of N compounds and to test estimates of emission changes. In a further section such changes, both in the recent past and the more distant past, are considered, studying both anthropogenic and natural changes. Finally, the

Cite this article: Wolff EW. 2013 Ice sheets and nitrogen. Phil Trans R Soc B 368: 20130127.

http://dx.doi.org/10.1098/rstb.2013.0127

One contribution of 15 to a Discussion Meeting Issue ‘The global nitrogen cycle in the twenty-first century’.

Subject Areas:
environmental science

Keywords:
- ice
- nitrate
- ammonium
- nitrous oxide
- trends
- ice cores

Author for correspondence:
Eric W. Wolff

e-mail: ewwo@bas.ac.uk

© 2013 The Author(s) Published by the Royal Society. All rights reserved.
Table 1. Estimate of total inventory of N compounds in the Greenland and Antarctic ice sheets. See text for further details of the calculations. The uncertainty for nitrate and ammonium is large, mainly because of the difficulty of estimating a depth and spatially-averaged concentration from relatively sparse measurements.

<table>
<thead>
<tr>
<th></th>
<th>mean concentration</th>
<th>inventory (with large ±)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Greenland</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2O</td>
<td>260 ppbv</td>
<td>0.1 Tg N</td>
</tr>
<tr>
<td>NO3</td>
<td>60 µg kg⁻¹</td>
<td>30 Tg N</td>
</tr>
<tr>
<td>NH4⁺</td>
<td>7 µg kg⁻¹</td>
<td>10 Tg N</td>
</tr>
<tr>
<td><strong>Antarctica</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2O</td>
<td>260 ppbv</td>
<td>0.7 Tg N</td>
</tr>
<tr>
<td>NO3</td>
<td>40 µg kg⁻¹</td>
<td>200 Tg N</td>
</tr>
<tr>
<td>NH4⁺</td>
<td>1 µg kg⁻¹</td>
<td>220 Tg N</td>
</tr>
</tbody>
</table>

chemistry of N compounds within snow, firn and ice is assessed, considering especially processes by which they may be re-released to the atmosphere.

2. Nitrogen compounds in snow and ice

Cold, polar ice sheets, in which there is little or no melting, contain chemicals (including nitrogen compounds) in two separate phases [2]. First, material deposited as aerosol and directly from the gas phase onto the snow surface is contained within the snow phase. Second, polar ice contains air bubbles, which are enclosed as the ice is compressed with depth. These bubbles contain a sample of all the stable gases in the atmosphere. The main N compound contained in the air bubbles is N2O, whose changing concentration, because of its role as a greenhouse gas, is of interest.

The inorganic N compounds found in the snow phase are nitrate and ammonium. Nitrate (NO3⁻) is present in polar ice at concentrations typically between 10 and 1000 µg kg⁻¹ (0.2–15 µM), and ammonium (NH4⁺) at typically 0.5–300 µg kg⁻¹ (0.03–20 µM). The lower concentrations within this range for both compounds are typically seen in central Antarctica, and the causes of the wide range of concentrations will be considered later. It is likely that some dissolved organic nitrogen compounds are present in polar ice, but there are no quantitative data in the literature [3].

Estimates of the total inventory of N2O, NO3⁻ and NH4⁺, and of the annual budget of the two snow-phase chemicals, in the Greenland and Antarctic ice sheets are shown in tables 1 and 2. In order to make these approximate estimates, the total volume and annual snow accumulation rate (in ice equivalent) are used. It is assumed that the air bubbles occupy 10 per cent (at ambient pressure, roughly estimated from the accumulation-weighted mean altitude of each ice sheet) of the ice volume. This is followed by an approximate estimate of the concentration in recent snow in each of Greenland and Antarctica, and of the average concentration in the ice sheet (taking account that the ice sheets each contain a mixture of interglacial and glacial ice). For this exercise, no attempt to make a formal areal weighting (for which there anyway may be insufficient data) has been made: for that reason, the budget and inventory estimates should be considered accurate only to within about 30 per cent.

Because of its much greater volume, Antarctica contains the larger mass of N compounds in its inventory. Nitrate is the dominant compound in each case. The total inventory in the ice sheets (of around 260 Tg N) is of course very small compared with the inventories in soils and oceans, and is of the same order of magnitude as the annual turnover of N between the atmosphere and land or the atmosphere and ocean [4]. Similarly, the annual budget of N compounds deposited onto the ice sheets (table 2) is very small, of order 0.1 per cent of the total global deposition of nitrate and ammonium from the atmosphere.

Table 2. Estimate of annual budget of N compounds from the atmosphere to the Greenland and Antarctic ice sheets. See text for further details. The uncertainties are rather large, mainly because of the difficulty of making a precipitation-weighted spatial average from sparse data.

<table>
<thead>
<tr>
<th></th>
<th>mean concentration</th>
<th>deposition (with large ±)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Greenland</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3⁻</td>
<td>0.015 Tg N a⁻¹</td>
<td></td>
</tr>
<tr>
<td>NH4⁺</td>
<td>0.003 Tg N a⁻¹</td>
<td>0.02 Tg N a⁻¹</td>
</tr>
<tr>
<td><strong>Antarctica</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3⁻</td>
<td>0.02 Tg N a⁻¹</td>
<td></td>
</tr>
<tr>
<td>NH4⁺</td>
<td>0.002 Tg N a⁻¹</td>
<td>0.02 Tg N a⁻¹</td>
</tr>
</tbody>
</table>

3. Natural sources and sinks of N compounds found in ice sheets

N2O is a well-mixed trace gas in the atmosphere, with a lifetime of about 120 years. As discussed in earlier papers [5], pre-industrial sources are mainly biological, resulting from nitrification and denitrification in soils and the ocean. Additional anthropogenic sources are discussed in the next
section. N$_2$O is removed mainly by chemistry occurring in the stratosphere.

Nitrate is a member of the oxidized nitrogen family of chemical species (often written as NO$_y$). It can be present in the gas phase as HNO$_3$ and in aerosol as HNO$_3$ or as nitrate salts. It is formed by oxidation of NO$_2$ either directly or via N$_2$O$_5$ or the NO$_3$ radical, and is lost mainly by photolysis, by reaction with OH and by deposition. However, because there are many interconversions between NO$_y$ species, whereas nitrate is the member of NO$_y$ that can be archived in ice, it is perhaps more useful to think about the sources of NO$_y$. The natural sources of NO$_y$ are terrestrial (including ammonia oxidation, biomass burning and soil exhalation), plus lightning production of NO and production in the stratosphere [6,7]; however, there is no clear understanding of the extent to which each of these sources has contributed to the input of nitrate to each polar ice sheet.

Ammonium salts archived in polar ice sheets from pre-industrial times derived from emissions of ammonia from both terrestrial and marine sources [6,8], largely of biological origin. Ammonia is easily entrained into aerosol and re-deposited. It is, therefore, generally assumed that the most important emission source for Greenland snow is the terrestrial systems of North America, whereas sources for Antarctica are generally assumed to be in the surrounding Southern Ocean.

4. Ice-core records: anthropogenic change in N$_2$O

Because of its long atmospheric lifetime (approx. 120 years), changes in N$_2$O measured in Greenland or Antarctic ice cores can be considered to represent changes in emissions (or sinks) at global scale. Nitrate and ammonium, with much shorter lifetimes against deposition, must be considered of regional interest, with each ice core representing changes in particular source areas.

After carbon dioxide (CO$_2$) and methane (CH$_4$), nitrous oxide (N$_2$O) is the next most important long-lived anthropogenic greenhouse gas. It also acts as an ozone-depleting substance in the stratosphere [9], and is currently the most important one. Routine atmospheric measurements were started only in recent decades, so our knowledge of the increase of N$_2$O in the atmosphere comes mainly from polar ice cores. They show that N$_2$O was relatively steady at 260–270 ppbv for the last two millennia until about 1850. Since 1850 there has been an increase to about 320 ppbv, with a steeper rate of rise since 1950 (figure 1). The increase is consistent with enhanced emissions from fertilized agricultural lands. A recent isotopic study, using Antarctic firn air samples along with archived air samples from Cape Grim in Tasmania, also confirms this assessment [12]. The isotopic measurements are consistent with the suggestion that the mechanism of enhanced N$_2$O emissions from soil, resulting from fertilizer use, is through activation of nitrification processes.

5. Ice-core chemical records

Ammonium is mainly deposited as aerosol, while nitrate can be deposited as aerosol and as nitric acid adsorbed directly from the gas phase onto ice surfaces. Concentrations can depend on emissions, but also on transport strength and pathways, strength of deposition en route and on the efficiency of deposition at the ice-core site. The use of concentration profiles from ice with time as indicators of changing emissions implicitly assumes that all other factors, while undoubtedly showing significant variability, have not exhibited a trend. This is probably a reasonable assumption in the relatively stable climate conditions of the last century, but is unlikely to be true when comparing over much longer timescales, such as between glacial and interglacial conditions [13]. In addition, while tracers such as ammonium are irreversibly deposited to the snow surface, nitrate can be re-emitted from the snow either by re-evaporation of nitric acid or through photolysis. This really affects mainly sites in central Antarctica with very low snow accumulation, and will be discussed later, but for now, it prohibits us from assessing trends in emissions using data from strongly affected sites.

6. Ice-core records: anthropogenic change in nitrate

First, considering nitrate and starting with Arctic records, several records covering the last century have been published.
more closely related to regional emissions of NO$_x$ from the Siberian Arctic. Taken together all these records indicate that the Arctic atmosphere is strongly affected by anthropogenic NO$_x$ emissions originating further south, in line with understanding gained from studies of Arctic Haze [26].

In contrast to Greenland, data from Antarctica, although showing considerable year-to-year noise, show no significant trend over the twentieth century ([20,21]; figure 2). Antarctica is very distant from major industrial or urbanized areas, and this result suggests that nitrate over the Southern Ocean and Antarctica is still largely of natural origin.

Nitrate trends have been measured at high-altitude glaciers and icecaps in mid-latitudes, representing more regional sources (see table 3 for a summary of the main sites outside Greenland and Antarctica that are discussed in this paper). For such ice-cores sites, very high altitude is a prerequisite in order to avoid significant melting. For the European Alps, a number of studies have derived nitrate records covering the last century [27,28]. A comprehensive and more recent study was carried out at Col du Dôme, at 4250 metres above sea level (m.a.s.l.) in the French Alps [18] (figure 2). The very high snow accumulation rate (approx. 3 m water equivalent per year) meant that it was possible to consider summer and winter snow layers separately. The authors concluded that the summer input is influenced mainly by emissions from within 1000 km of the site, while the winter input comes from a wider area comparable with the size of Europe. They found that there had been an approximately fivefold increase in summer nitrate concentration over the last century, with the strongest rate of increase between 1960 and 1980, in agreement with at least one estimate [29] of emissions from France, Italy, Switzerland and Spain (WE4 nations). For winter, although concentrations are lower, the increase over the century is still a factor 4 between 1950 and 1990, levelling off in the last decade of the twentieth century. This seemed to be consistent with inventory estimates of emissions changes from all of Europe [30]. The summer values imply, in contrast to some emissions inventories, that NO$_x$ emissions from the WE4 nations had not stabilized after 1990. Using the anthropogenic emissions inventories and the background pre-industrial concentration of nitrate, it was possible to estimate the natural emissions from both the WE4 countries and Europe as a whole.

At the northwestern end of the Tibetan Plateau, a core has been collected at 7010 m.a.s.l. at Mount Muztagata [19] (figure 2). NO$_x$ concentrations increased by a factor of approximately 2, mainly between about 1980 and 2000. The atmospheric flow suggests that the main sources to this site are from the west, and the increase appears consistent with the inventory trends in regional emissions from central and southwest Asia (semicircle of countries from Pakistan to Kazakhstan). At the eastern end of the Himalayas, the situation is less clear: nitrate concentrations have increased significantly over recent decades compared with their 1000-year background at Dasuopu (7000 m.a.s.l.) [31], but the data resolution is insufficient to give a clear timing or magnitude of any increase. At the nearby East Rongbuk Glacier, the increase is less clear [32]. New records extending into the twenty-first century, after the strongest period of industrialization in the surrounding nations (India, China), are certainly required. Finally in Asia, an ice core further north, at Belukha in the Siberian Altai (4062 m.a.s.l.) shows a convincing increase (factor close to 2) between 1950 and 1980 [33],

![Figure 2. Nitrate in recent decades at various sites. From the top: Greenland sites B16 (dashed red, 73.94° N, 37.63° W) and B21 (solid blue, 80.00° N, 41.14° W) [15]; Col du Dôme (summer values, 5 year running mean) in the French Alps [18]; Mount Muztagata, central Asia (5 year running mean) [19]; Law Dome (red dashed, 66.78° S, 112.82° E) [20] and Siple Dôme (blue solid, 81.65° S, 148.81° W) [21], Antarctica (both 5 year running means).](http://rstb.royalsocietypublishing.org)
although this sits on a very noisy background. For this core, as for some of the other non-polar ice cores where the combination of latitude and altitude is not sufficient to ensure cold summers, care must be taken in interpreting trends because the high percentage of melt layers in the core indicates that some percolation of water (and hence ionic load) could have occurred.

7. Ice-core records: anthropogenic change in ammonium

For ammonium, there is no clear recent trend in Greenland [34], although this would have to be discerned from a noisy background, that is largely owing to the dominance of biomass burning spikes in the record [35]. By splitting the annual snowfall into approximately monthly slices, it appears as if an upward trend since 1950 can be observed in the winter/spring concentrations [34], when Greenland sees a greater proportion of airmasses from Eurasia [36], but not in the summer, when airmasses are most frequently from North America. The lack of an increase has to be treated a little cautiously, not only because of the noisy signal, but also because the conversion of ammonia to aerosol, and therefore its deposition efficiency, both en route and in Greenland, will have altered as sulfate and nitrate have increased. Nonetheless, at face value, this suggests that Greenland in summer (which dominates the annual budget) is still seeing ammonium from undisturbed (northern) North American ecosystems [34] or from marine sources. Unsurprisingly, ammonium concentrations in Antarctic snow show no anthropogenic trend.

In the European Alps, three different records show an upward trend in ammonium concentration, mainly between about 1950 and 1980 [27,37]. As with the nitrate signal, the record from Col du Dôme has been split into seasons, and the main increase (factor 3) is in summer, when the concentrations are also highest. Encouragingly, concentrations estimated from combining emissions estimates with a multi-layer atmospheric dispersion model were consistent with atmospheric concentrations estimated by inverting the ice-core values [37]: this gives some confidence to uncertain emissions estimates.

In Asia, large increasing trends in ammonium concentrations are observed at Mount Muztagata (approx. factor 3 increase, 1960–1990) [19], East Rongbuk Glacier (~factor 2, 1950–1980) [38] and Belukha (factor 1.6, 1950–1980, followed by plateau) [33]. Modelling work is needed to separate out the influence of higher emissions from that of increased concentrations of sulfate and nitrate that may neutralize gaseous NH₃, leading to greater NH₄⁺ deposition. It is also suggested that a part of the increase may arise from the strengthening of natural ammonia emissions from plants and soils owing to increasing temperature [38]. Still, it seems likely that a large part of each increase is related to increased agricultural emissions, and that these ice-core trends can be used to constrain poorly known emission estimates for the regions influencing these core sites.

An unusual trend has been observed in ammonium concentrations in an ice core from the Bolivian Alps (Illimani). The year-to-year variations [39] have been calibrated against temperature anomalies in the Amazon Basin (most airmasses at Illimani track back over the Amazon): a remarkably good correlation was found. This was used to propose that ammonium in this ice core could be used as a proxy for temperature across the Amazon Basin further back in time. Ammonium increased by about a factor 3 from 1700 to 2000 (figure 3), which was then interpreted as an Amazon Basin increase of about 0.6°C over this period. Kellerhals et al. [39] suggest that the mechanism for the observed relationship is that higher temperatures lead to greater emissions of NH₃ from soils, and from vegetation through
changes in the temperature-dependent canopy compensation point. This is intriguing but surprising, as the calibration requires that a 1°C increase in temperature leads to a factor of 3 increase in ammonia emissions. Further work is clearly needed, as this is an important result that challenges current understanding, and yet offers the potential for a rather precise temperature proxy.

8. The long perspective: N₂O

The Antarctic ice-core record extends back 800,000 years (800 ka). N₂O has been measured on several long cores; there can be artefact issues [40], in which a very high scatter is observed at some depths. This is believed to be owing to either chemical or biological [41] production in the ice. Although the exact cause has not yet been proven, it is possible to filter out the scattered data by excluding measurements from ice with a high dust concentration (it is expected that higher levels of both chemical and biological material are present in such ice), and to confirm that the filter works by comparing different ice cores [5]. Because of this need to exclude some parts of the core, the record is not yet complete throughout the last 800 ka, but the general relationship between climate and N₂O concentration is now clear (figure 5). N₂O tends to be high during warmer periods: typically 200 ppbv during colder times and 280 ppbv during warmer periods (figure 4) [5]. It is important to note that, until the twentieth century, the concentration had never risen above 300 ppbv; it is now above 320 ppbv.

During cold glacial periods, climate is dominated by a millennial scale dynamic, with Greenland showing very rapid jumps in temperature (Dansgaard–Oeschger (D–O) events) that are accompanied by sharp jumps in CH₄ concentration. Antarctica shows subdued out-of-phase climate changes that are paralleled by slow CO₂ changes. N₂O [42] also changes on millennial scales, but with a dynamic different to either CH₄ or CO₂: N₂O does increase across most D–O events, but its increase is typically smoother, and begins during the D–O cold phase, when CH₄ is still low. Natural sources of N₂O are nitrification and denitrification, with an estimated ratio of about 2 : 1 for soils and oceanic emissions [44]. The changes in N₂O on glacial and millennial scales are, therefore, believed to arise from marine and/or low-latitude terrestrial changes. Isotopic data [45] suggest that the ratio of marine to terrestrial production has not changed much in the last 33 ka, which includes the last glacial termination. This implies that both sources increased in strength by approximately 40 per cent across the termination.

9. The long perspective: nitrate

Over the last 800 ka, nitrate in central Antarctic ice varies very strongly (factor 5 higher in last glacial maximum (LGM), 21 ka ago, compared with present). However, it shows a very strong correlation with the concentration of calcium [13] (figure 5). In central Antarctica, nitrate is very readily lost from the ice (see later section), and it appears that high dust (represented by calcium) concentrations help to stabilize it. Thus, the glacial–interglacial changes do not, unfortunately, hold any information about sources of nitrate, but rather indicate the role of dust in stabilizing the deposited
nitrates. Even where dust concentrations are low, the residual variability at sites in central Antarctica seems to be controlled by the snow accumulation rate, with greater preservation when the accumulation rate is a little higher. This offers the possibility to use nitrate as an aid to estimating past snowfall rates [46]. One should expect to be able to use nitrate concentrations in coastal regions of Antarctica (where snow accumulation is higher), under climate conditions close to those of today (i.e. the Holocene period, last 11 ka) to understand changes in the past sources of nitrate to Antarctica. One hope has been that we might learn about past input of nitrate from the stratosphere [47]. However, the discovery (using measurements of isotopes of O and N in nitrate) that much of the nitrate deposited in coastal Antarctica may be recycled after emission from snow in central Antarctica [48] suggests that even this will be challenging. Although nitrate is routinely measured in Antarctic ice cores, its interpretation in terms of sources remains speculative and challenging.

Interpretation is also difficult in Greenland: the glacial atmosphere there was also subject to hugely increased concentrations of dust, which are likely to have radically altered the deposition processes for nitrate. Having said that, nitrate is rare in having very similar average concentrations in the LGM and the Holocene; changes can be seen [49] at the glacial termination, but they are tiny compared with the vast factorial changes in all other chemical content. Nitrate does show clear annual cycles that are used as a component of the layer-counted dating of Greenland ice cores. There has been a widespread paradigm in the solar–terrestrial physics community that large spikes of nitrate concentration in ice cores could be used to define the statistics of occurrence of solar energetic particle events [50]. However, it has now been clearly shown that this is not the case [51]: most of the spikes are due to the passage of biomass burning plumes (discussed under ammonium).

In summary, nitrate is routinely measured in ice cores. The difficulties in interpreting its concentrations have been recognized for a long time, but the study of processes over the last two decades has mainly raised additional questions. As a result, there is still limited understanding of the natural sources of nitrate to the ice sheets, or of their change over time. Improved modelling of all the confounding factors is urgently required to improve this situation, as there is undoubtedly important information about natural NO$_x$ tied up in the data.

11. Snow as a source of NO$_x$ to the atmosphere

It has been shown that snowpacks are a strong source of NO$_x$ to the atmosphere [56–58]. The mechanism has been shown to be photolysis of nitrate in the snow. The strength of the source is perhaps not surprising because it can be shown that the inventory per unit area of nitrate in the top few centimetres (photic zone) of snowpacks is much higher than the inventory per unit area for the lowest kilometres of the troposphere. However, for NO$_x$ to be released, it must be available at the surface of snow crystals, not trapped within them; this is evidently the case.

The photochemistry of snow (of which nitrate photolysis is only one example) has been reviewed thoroughly, and I will not repeat that material here [58]. However, the effects of nitrate photolysis have been observed particularly strongly at South Pole, where the very shallow boundary layer leads to concentrations of NO as high as 500 pptv [59], and to a highly oxidizing environment, with high OH, and ozone production. Even the more modest concentrations of NO$_x$ seen at coastal Antarctic stations seem to be dominated by snowpack emissions during at least the summer months [60]. Nitrate photolysis should be a significant source of NO$_x$ emissions at any snow-covered site (including snow on sea ice and seasonal snow at mid-latitudes). It is unlikely to be a significant source at global scale [58] but could be a major influence on boundary layer chemistry at remote regions where NO$_x$ would otherwise be at low concentration.

12. Conclusions

This review has shown that snow can be a significant local source of NO$_x$ affecting atmospheric chemistry in a shallow
but important skin above the surface. However, the most important role of snow and ice must remain its influence as a cap on exchanges that would otherwise occur, and this should be remembered when modelling such exchanges.

The other major role of ice is that it provides, through ice-core records, archives of past change in deposition of the two main compounds nitrate and ammonium, and of the long-lived greenhouse gas N₂O. The rise of N₂O in the last two centuries is clearly seen, while the rise in nitrate at various sites around the globe (but not yet Antarctica) should allow some validation of otherwise poorly known emission inventories. An increase in ammonium is not yet as clearly imprinted at high latitudes. Care must be taken in interpreting trends, where transport and chemical form may also have altered with time. There may be good scope for work of this sort at further sites to delineate more regional emissions, but modelling is most likely required to interpret the findings fully and correctly.

Finally, over long time periods, the change in N₂O (low in cold periods) gives clues about large-scale changes in terrestrial and marine emissions. Nitrate is very hard to interpret over long time periods, but ammonium may provide a helpful constraint on the timing of increased terrestrial influence from North America coming out of the last glacial period, and on the (apparently small) change in marine emissions of ammonium in the relevant part of the Southern Ocean over glacial cycles.

I thank the many colleagues in the ice-core community that have made data available for a synthesis such as this one. This work is part of the British Antarctic Survey Polar Science for Planet Earth Programme, and was financially supported by the Natural Environment Research Council.

References


