



A reassessment of Antarctic plateau reactive nitrogen based on ANTCI 2003 airborne and ground based measurements

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Abstract

The first airborne measurements of nitric oxide (NO) on the Antarctic plateau have demonstrated that the previously reported elevated levels of this species extend well beyond the immediate vicinity of South Pole. Although the current database is still relatively weak and critical laboratory experiments are still needed, the findings here suggest that the chemical uniqueness of the plateau may be substantially greater than first reported. For example, South Pole ground-based findings have provided new evidence showing that the dominant process driving the release of nitrogen from the snowpack during the spring/summer season (post-depositional loss) is photochemical in nature with evaporative processes playing a lesser role. There is also new evidence suggesting that nitrogen, in the form of nitrate, may undergo multiple recycling within a given photochemical season. Speculation here is that this may be a unique property of the plateau and much related to its having persistent cold temperatures even during summer. These conditions promote the efficient adsorption of molecules like HNO₃ (and very likely HO₂NO₂) onto snow-pack surface ice where we have hypothesized enhanced photochemical processing can occur, leading to the efficient release of NO_x to the atmosphere. In addition, to these process-oriented tentative conclusions, the findings from the airborne studies, in conjunction with modeling exercises suggest a new paradigm for the plateau atmosphere. The near-surface atmosphere over this massive region can be viewed as serving as much more than a temporary reservoir or holding tank for imported chemical species. It defines an immense atmospheric chemical reactor which is capable of modifying the chemical characteristics of select atmospheric constituents. This reactor has most likely been in place over geological time, and may have led to the chemical modulation of some trace

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species now found in ice cores. Reactive nitrogen has played a critical role in both establishing and in maintaining this reactor.

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1. Introduction

During the last decade there has been a growing interest in the atmospheric chemistry of polar regions (Domine' and Shepson, 2002 and references therein). Among the reasons for this increased interest is the relevance of this chemistry to the interpretation of chemical signatures in polar ice cores. The latter can provide insights about major geophysical events in the earth's past history as well as point to changes that have occurred in the planet's climate (Legrand and Delmas, 1987; Legrand and Feniet-Saigne, 1991). An understanding of atmospheric chemistry is relevant because it provides one of the critical inputs for evaluating the air-to-snow "transfer function" for a chemical proxy species. An evaluation of this transfer function requires that all of the processes that modulate the concentration of a chemical species be known from its point of origin to the point of deposition. As applied to the generic species "reactive nitrogen," earlier efforts to interpret ice cores have resulted in minimal success (Legrand and Kirchner, 1990; Legrand and Mayewski, 1997; Wolff, 1995). Having the ability to interpret the levels of nitrogen in ice cores potentially could provide important insights about the planet's past atmospheric chemical fluctuations, particularly as related to its oxidizing capacity. The significance of "reactive nitrogen" lies in the fact that in the chemical form of NO it has a major impact on the levels of both OH and O₃, the two most important oxidizing agents in the earth's atmosphere (Finlayson-Pitts and Pitts, 2000 and references therein).

Reflecting the uncertainties that still exist in interpreting ice-core nitrate levels are several recent studies showing that polar snow fields can release significant emissions of NO_x (Honrath et al., 1999, 2000; Jones et al., 2000; Ridley et al., 2000; Davis et al., 2001; Beine et al., 2002a, b). One of the major mechanisms identified as being responsible for these emissions is the UV photolysis of nitrate ions in firn (Honrath et al., 1999, 2000). Possibly even more

complex processes may generate still other nitrogen species such as HONO (Zhou et al., 2001; Beine et al., 2002a, b). Collectively, these field observations have led to a flurry of laboratory studies designed to better understand the detailed photochemical and physical processes operating within polar firn (Dubowski et al., 2001, 2002; Boxe et al., 2003; Cotter et al., 2003).

Nowhere has this newly identified polar-atmospheric source of NO_x resulted in larger perturbations to the background levels of this species than observed at South Pole (SP), Antarctica (Davis et al., 2001, 2004a, b). In two of the earliest field studies carried out in 1998 and 2000 (e.g., Investigation of Sulfur Chemistry in Antarctica (ISCAT), observed NO levels were found to range from a low of 10 pptv to a high of ~600 pptv, with median levels estimated at 223 and 86 pptv, respectively. As previously found in the Arctic (Honrath et al., 1999, 2000), shading experiments at SP, along with measurements of snow surface nitrate levels (Dibb et al., 2004), have all pointed to the importance of nitrate photolysis as the dominant source of NO. Reflecting these enhancements in NO, 24h averaged atmospheric hydroxyl radical (OH) concentrations have been measured at 2×10^6 molecules cm⁻³, rivaling in magnitude time averaged values found in the tropical marine boundary layer (Mauldin et al., 2001, 2004). Not surprisingly, the near surface atmosphere at SP has also been found to be a net-photochemical source of ozone (Crawford et al., 2001; Chen et al., 2004; Helmig et al., 2007a).

Davis et al., in their 2004 paper, undertook a detailed examination of the possible causes for the highly elevated levels of NO at SP. Specifically, they explored the possible reasons why the SP environment might support higher NO levels than observed at other polar sites (e.g., Summit, Alert, Neumayer, and Halley Bay) where median values are typically an order of magnitude lower. Using data from the 1998 and 2000 ISCAT studies, Davis et al. (2004a) concluded that among the important factors favoring SP were: (1) 24 h of continuous sunlight during summer; (2) a strong tendency for shallow planetary

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