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Investigating the sensitivity of surface-level nitrate seasonality in Antarctica to primary sources using a global model

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HIGHLIGHTS

- Model simulations are used to assess sources of TNIT ($HNO_3 + NO_3^-$) in Antarctica.
- Adjoint analysis is used to evaluate impacts of surface versus stratospheric sources.
- TNIT in May–July is attributed to HNO_3 from NO_x emissions as far north as 25°S.
- In other seasons, TNIT is transported in the form of PAN.
- PSC sedimentation may contribute to observed peaks in concentrations in August.

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ABSTRACT

Determining the sources of total nitrate (TNIT $\equiv NO_3^- + HNO_3$) reaching Antarctica is a long-standing challenge. Here we analyze the monthly sensitivity of surface-level TNIT in Antarctica to primary sources using a global 3-D chemical transport model, GEOS-Chem, and its adjoint. Modeled seasonal variation of TNIT concentrations shows good agreement with several measurement studies, given that the lack of post-depositional processing in the model leads to an expected underestimate of maximum values in November through January. Remote NO_x sources have the greatest impact May–July, during when the model background concentrations are sensitive to NO_x emissions from fossil fuel combustion, soil, and lightning originating from 25°S to 65°S. In this season, NO_x is transported to Antarctica as TNIT, which is formed above continental source regions at an altitude of 5–11 km. In other seasons, more NO_x is transported as a reservoir species (e.g., peroxyacetyl nitrate, PAN) through the free troposphere, transforming into TNIT within a cone of influence that extends to 35°S and above 4 km altitude. Photolysis of PAN over Antarctica is the main driver of modeled NO_x seasonality. Stratospheric production and loss of tracers are relatively unimportant in monthly sensitivities in GEOS-Chem, driving only a few percent of surface level variability of TNIT. A small peak concentration in August is captured by the model, although some measured values in August fall outside the range of simulated concentrations. Modifications to the model to represent sedimentation of polar stratospheric clouds (PSCs) lead to increased surface level August TNIT concentrations. However, this simple representation does not explicitly account for PSC particle deposition or disappearance of the tropopause in the middle of winter, and thus the influence of stratospheric nitrate sources estimated in this study is likely a lower bound.

1. Introduction

TNIT ($\equiv NO_3^- + HNO_3$) is an oxidation product of nitrogen oxides ($NO_x \equiv NO + NO_2$) in the atmosphere associated with important environmental issues such as aerosol concentrations and the oxidative capacity of the atmosphere. A significant fraction of NO_x is sequestered as TNIT and then removed from the atmosphere by wet

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and dry deposition, providing nitrogen to the surface where it serves as a key ecosystem nutrient. Given its environmental importance, there are interests in understanding past variability of atmospheric NO_x. Numerous studies have reported seasonal and historical variations in TNIT concentrations in Antarctica, yet the mechanisms and sources driving these variations are still not well quantified.

As a proxy for historical variability of atmospheric NO_x, ice cores from polar regions provide chronologically preserved records of TNIT (Wilson and House, 1965; Legrand et al., 1988; Mayewski and Legrand, 1990; Legrand and Kirchner, 1990; Jacobi et al., 2000; Jones et al., 2011; Wolff et al., 2012). Greenland ice core NO_3^- records show that the Northern Hemispheric NO_3^- burden has doubled since the mid twentieth century due to anthropogenic emissions (Mayewski et al., 1986). In contrast, impacts of human activity on NO_3^- are not as prominent in Antarctic ice cores (Mayewski and Legrand, 1990). Aerosol measurements at the surface are also used to constrain recent trends and seasonal variability of nitrate (Savoie et al., 1993; Wagenbach et al., 1998; Weller et al., 2002; Savarino et al., 2007; Jones et al., 2008). Antarctic measurements consistently show minimum levels of TNIT in April–June, a small peak in August, and a steady increase afterward until maximum levels are reached in November–January (Savoie et al., 1993; Savarino et al., 2007; Jones et al., 2011; Weller et al., 2011).

To interpret the significance of Antarctic ice-core and aerosol measurements, three important types of processes that influence Antarctic surface-level TNIT must be considered. First, variations in TNIT burden are impacted by long-range tropospheric transport of species emitted outside Antarctica. Emissions of NO_x include surface sources (fossil fuel, biofuel, soil exhalation, biomass burning), lightning, and aircraft emissions. TNIT may be transported directly, as NO_x or aerosol nitrate, or as reservoir species such as peroxyacetyl nitrate (PAN). PAN is produced by chemical reactions between hydrocarbons and NO_x and has a highly temperature dependent lifetime (1 h at 298 K, 5 months at 250 K). Once it ascends to the free troposphere, it can be transported to the polar regions and then decomposed upon descent into NO_x by thermal decomposition or photolysis (Mills et al., 2007; Jacobi et al., 2000; Jones et al., 2011).

Second, stratospheric influences in Antarctic TNIT include sedimentation of polar stratospheric clouds (PSCs) and HNO_3-rich airmass mixing across the tropopause. One of the major components of PSCs is HNO_3 (Carslaw et al., 1995; Pitts et al., 2007). The polar vortex provides a favorable environment for PSCs to form and grow; subsequent sedimentation of PSCs is responsible for removal of gas-phase HNO_3 in winter from the Antarctic stratosphere, i.e., denitrification (Fahey et al., 1990; Carslaw et al., 1994). Also, an enhanced polar vortex can result in disappearance of the tropopause above Antarctica (Rubin, 1953) leading to more active airmass mixing between the stratosphere and troposphere (Savoie et al., 1993; Wagenbach et al., 1998; Weller et al., 2002).

Lastly, TNIT deposited on snow can recycle several times by reemission to the atmosphere by HNO_3 evaporation or photochemical reduction into NO_x (Weller et al., 2004; Savarino et al., 2007; Jones et al., 2008). This process, so called post-depositional processing, has been suggested to cause observed TNIT maximum concentrations in late spring and early summer (Savarino et al., 2007; Jones et al., 2008; Weller et al., 2011).

The variety and complexity of these sources and mechanisms make it challenging to relate observed Antarctic TNIT to atmospheric NO_x (Zeller and Parker, 1981; Röthlisberger et al., 2000; Savarino et al., 2007; Wolff et al., 2008). While local meteorology and post-depositional processing influence the high TNIT concentrations in summer by active photochemistry within Antarctica, the original source of TNIT for this recycling remains to be quantified (Wolff et al., 2008). Specifically, it is of interest to determine the contribution of continental emissions versus stratospheric input, the role of different types of natural versus anthropogenic emissions, and the chemical mechanisms by which TNIT is processed and transported to Antarctica in the troposphere.

Atmospheric chemical transport models provide a means of investigating the importance of possible sources of Antarctic TNIT. Although there have been modeling studies investigating atmospheric transport towards Antarctica (Krinner and Genthon, 2003; Stohl and Sodemann, 2010), most have been limited to nonreactive tracers (e.g., black carbon, radon) and thus focused on transport of airmass and decay of tracers. A more comprehensive modeling study, considering critical processes for reactive tracers such as chemical reactions, emissions, and dry deposition, has been conducted for Antarctic CO (van der Werf et al., 2013). However, due to the complicated characteristics of NO_x chemistry and transport, there has not to our knowledge been a comprehensive modeling attempt at analyzing sources of Antarctic TNIT until now.

In this study, we use the global 3-D chemical transport model GEOS-Chem and its adjoint to quantify sensitivities of surface level Antarctic TNIT to its precursor processes. These include emissions, and production and loss of tracers resulting from tropospheric and stratospheric chemistry. In doing so, we evaluate the model by comparing the modeled seasonality with measurements from previous studies, although we expect the model to underestimate austral summer observations due to a lack of post-depositional processing in the model.

2. Model description

We use GEOS-Chem (Bey et al., 2001) version 8-02-04 with updates described below to estimate the TNIT concentrations over Antarctica. GEOS-Chem is a global 3-D atmospheric chemical transport model driven by meteorological input from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (www.geos-chem.org). The version of the model employed in this study uses GEOS-5 meteorological fields at 2° latitude $\times$ 2.5° longitude horizontal resolution, with 47 vertical layers up to 0.01 hPa. The model's tropospheric chemical mechanism consists of more than 290 reactions and 90 gas and aerosol species. Aerosols are assumed to be externally mixed. $SO_4^{2-}-NO_3^{-}-NH_4^{+}$ thermodynamic equilibrium is calculated using RPMARES (Park et al., 2004), which is based on the MARS-A routine of Binkowski and Roselle (2003). More comprehensive aerosol treatment including sea-salt (Na^+ and Cl^-) and crustal ions (K^+, Ca^{2+}, and Mg^{2+}) is available using another thermodynamic scheme in the model, i.e., ISORROPIA, however, we use RPMARES due to the lack of an adjoint of ISORROPIA until very recently (Capps et al., 2012). Carbonaceous and size-resolved dust aerosols are based on Chin et al. (2002), Park et al. (2003), and Fairlie et al. (2007). Wet deposition includes sub-grid scavenging in convective updrafts, large scale in-cloud rainout and below-cloud washout (Liu et al., 2001). Dry deposition is calculated using a resistance-in-series model (Wesely, 1989; Wang et al., 1998).

A new stratospheric chemistry scheme is implemented for this study. The standard version 8-02-04 of GEOS-Chem applies zonal mean production and loss rates to 23 gaseous species, as archived from earlier 2-D models (Bey et al., 2001). The new linearized stratospheric chemistry (Murray et al., 2012), updated in the adjoint model as well for this study, uses monthly climatological 3-D production and loss rates from the GMI (Global Modeling Initiative) Combo model (http://gmi.gsfc.nasa.gov) for 24 gaseous tracers above the tropopause, including CO, O_3, NO_x, and HNO_3. These production and loss rates only reflect gas-phase chemistry.