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Investigating the Atmospheric Production of Perchlorate: Inference from Polar Ice Cores

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INVESTIGATING THE ATMOSPHERIC PRODUCTION OF PERCHLORATE:

INFERENCE FROM POLAR ICE CORES

BY

THOMAS S. COX

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INVESTIGATING THE ATMOSPHERIC PRODUCTION OF PERCHLORATE: INFERENCE FROM POLAR ICE CORES

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy in Chemistry degree and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ABBREVIATIONS

%CV – Coefficient of Variation

2D-IC – Two-Dimensional Ion Chromatography

ALC – Annual Layer Counting

CFA – Continuous Flow Analysis

CFC – Chlorofluorocarbon

DU – Dobson Unit

EESC – Equivalent Effective Stratospheric Chlorine

ESI – Electrospray Ionization

ESI-MS/MS – Tandem Mass Spectrometry with Electrospray Ionization

EPA - Environmental Protection Agency

HCFC – Hydrochlorofluorocarbon

HPLC-ESI-MS/MS – High Performance Liquid Chromatography-Tandem Mass Spectrometry with Electrospray Ionization

IC – Ion Chromatography

IC-ESI-MS/MS – Ion Chromatography-Tandem Mass Spectrometry with Electrospray Ionization

LLOQ – Lower Limit of Quantification

LOD – Limit of Detection

MDF – Mass Dependent Fractionation

MIF – Mass Independent Fractionation

MRM – Multiple Reaction Monitoring

NIS – Sodium/Iodide Symporter

NMD – Nonmass Dependent

NOAA – National Oceanic and Atmospheric Administration

NSS – Non-Sea Salt

PRIC – Polar Research Institute of China

PSC – Polar Stratospheric Cloud

S/N – Signal-to-Noise

SDSU – South Dakota State University

SP04C1 – 2004 South Pole Core 1

SPC14 – 2014 South Pole Shallow Core

SWE – Snow Water Equivalent

TTU – Texas Tech University

WAIS – West Antarctic Ice Sheet

WDC05B – 2005 WAIS Divide Core B

WDC13 – 2013 WAIS Divide Shallow Core

WEA – Water Equivalent per Year

WMO – World Meteorological Organization

WOUDC – World Ozone and Ultraviolet Radiation Data Centre

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ABSTRACT

INVESTIGATING THE ATMOSPHERIC PRODUCTION OF PERCHLORATE: INFERENCE FROM POLAR ICE CORES

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2017

Perchlorate (ClO_4^-) in the environment is of concern, because of potential health risks to humans, among other reasons. Evidence suggests that the majority of environmental perchlorate is formed in the atmosphere (likely in the stratosphere), in chemical processes involving ozone and stratospheric chlorine. A lack of knowledge in regards to the processes has resulted in a limited understanding of the environmental conditions and variables that influence perchlorate production and consequently perchlorate prevalence and variability in the environment. In this study, perchlorate was measured, using an established ion chromatography-electrospray ionization-tandem mass spectrometry (IC-ESI-MS/MS) technique, in over 1,600 snowpit and ice core samples collected at several Antarctic locations. Several ice core records were developed covering the 20th century; however, interpretation of the records is complicated by depositional and post-depositional processes that affect perchlorate concentrations in snow. It appears that wet deposition is significant at sites where accumulation is high and dry deposition is significant where accumulation is low; additionally, perchlorate concentration in snow may undergo significant changes (~50% decrease) at low accumulation sites. Yet, the records suggest that perchlorate is produced from activated chlorine species (chlorine free radicals) in the stratosphere and that increases in stratospheric chlorine - due to anthropogenic emissions of chlorine compounds (CFCs) - are likely driving the increasing trend of perchlorate production. Furthermore, perchlorate variability appears to also be indirectly influenced by stratospheric temperature and stratospheric sulfate aerosols.

1. Introduction

1.1 Perchlorate in the environment

Perchlorate (ClO_4^-) contains one chlorine atom bound to four oxygen atoms in a tetrahedral geometry, in which chlorine is in the most oxidized form. Perchlorate is nonvolatile, highly stable, unreactive and persistent in nature [*Brown and Gu*, 2006]. It is also highly soluble and capable of mobilizing in aquatic environments [*Parker*, 2009]. In aqueous environments perchlorate anion demonstrates rather nonreactive and stable behavior [*Gu and Coates*, 2006; *Parker*, 2009]. This nonreactive behavior of perchlorate can be explained by the difficulty of the reduction of the molecule in nature; common abiotic processes do not reduce perchlorate in the environment because of a high kinetic barrier [*Srinivasan and Viraraghavan*, 2009; *Ye et al.*, 2012]. As a result, perchlorate may persist for many years under typical surface water and groundwater conditions [*Sturchio et al.*, 2014]. Due to the stable and unreactive behavior of perchlorate, many studies have focused on determining the fate of perchlorate in the environment and its mitigation [*Brown and Gu*, 2006; *Motzer*, 2001; *Trumpolt et al.*, 2005; *Urbansky*, 2002].

1.1.1 Health concerns

Perchlorate is a contaminant of concern because it constitutes a significant health risk to humans. The human Na/I symporter (NIS) has a 30-fold higher affinity for perchlorate than for iodide [*Sijimol et al.*, 2015], and as a result, perchlorate will competitively inhibit the uptake of iodide through the NIS to the thyroid gland [*Leung et al.*, 2010; *Tran et al.*, 2008]. This will adversely affect the production of thyroid hormones, and a deficiency of thyroid hormones has severe health effects especially for fetuses, infants, and young children. Because the thyroid hormones are crucial for neurodevelopment in the early stages of life, their deficiency can cause irreversible impairment in the nervous system, particularly in the brain [*Sijimol et al.*, 2015]. Exposure to perchlorate comes from perchlorate in the environment, likely via the consumption of perchlorate-contaminated food and water [*Kumarathilaka et al.*, 2016; *Sijimol et al.*, 2015; *Steinmaus*, 2016].

1.2 Sources of environmental perchlorate

1.2.1 Anthropogenic perchlorate

Environmental perchlorate has been associated with human activities. Perchlorate salts are produced by electrolysis of NaCl brines [*Schumacher*, 1960] in quantities on the order of 10^7 kg year^{-1} [*Dasgupta et al.*, 2006]. Perchlorate is a strong oxidizing agent and has been used in a variety of industrial and consumer products including missile fuel, fireworks, and vehicle airbags. Perchlorate usage appears to be widespread across the United States [*Motzer*, 2001; *Steinmaus*, 2016]. Approximately 90 percent of industrial perchlorate production is dedicated to making ammonium perchlorate for solid propellant in rockets and missiles [*Dasgupta et al.*, 2006; *Motzer*, 2001; *Trumpolt et al.*, 2005].

1.2.2 Natural perchlorate

Chilean nitrate fertilizers have been confirmed as containing perchlorate-bearing minerals [*Hunter*, 2001; *Susarla et al.*, 1999; *Urbansky et al.*, 2001]. Significant amounts of perchlorate salts occur in the nitrate deposits of Atacama Desert in Chile, providing the first indication that perchlorate has a natural source [*Calderon et al.*, 2014; *Ericksen*, 1981]. The natural occurrence of perchlorate was thought to be confined to the nitrate deposits in the Atacama Desert, Chile [*Jackson et al.*, 2006], and that perchlorate in the general environment derived exclusively from anthropogenic sources. However, the measurement of perchlorate in pre-anthropogenic groundwater in the southwest U.S. [*Plummer et al.*, 2006; *Rao et al.*, 2007] has shown that natural sources exist outside the Atacama Desert. Perchlorate has been found in precipitation (generally < 0.1 µg L^{-1}) [*Rajagopalan et al.*, 2009], in soil (generally < 10 mg kg^{-1}) [*Winkler et al.*, 2004], and in groundwater at concentrations ranging from levels of about 0.01 to > 100 µg L^{-1} [*Parker*, 2009; *Winkler et al.*, 2004], in arid regions where perchlorate has been concentrated by evaporation. Additionally, perchlorate has been detected in the soils of the Dry Valleys, Antarctica [*Jackson et al.*, 2016; *Kounaves et al.*, 2010], an area that is unlikely to be directly impacted by human activities. Since perchlorate has been found to be widespread in the environment with trace amounts present on all continents, it is likely that perchlorate is produced naturally.

1.3 Isotopic composition of perchlorate

Stable oxygen and chlorine isotopic ratios of perchlorate can be used in combination with the radioactive isotope ^{36}Cl for discriminating between natural and synthetic perchlorate [*Böhlke et al.*, 2005; *Jackson et al.*, 2010; *Sturchio et al.*, 2006] as well as gaining insight into how natural perchlorate is produced [*Bao and Gu*, 2004; *Sturchio et al.*, 2009]. By assessing triple-oxygen isotope ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$), *Bao and Gu* [2004] demonstrated that perchlorate from Atacama Desert soil is distinctly different from the synthetically produced samples. A study by *Böhlke et al.* [2005] successfully utilized stable isotope analysis ($^{37}Cl/^{35}Cl$ and

$^{18}O/^{17}O/^{16}O$) to differentiate the natural and synthetic sources of perchlorate. Based on similar approaches, non-anthropogenic perchlorate occurrences have been identified in many places throughout the world [*Jackson et al.*, 2006; *Parker et al.*, 2008; *Plummer et al.*, 2006; *Rajagopalan et al.*, 2006; *Rao et al.*, 2007]. Although isotopic investigations were originally applied to perchlorate contamination to distinguish sources, research regarding the isotopic composition of non-anthropogenic perchlorate has led to improved understanding of its origin and the key reactants involved in its formation [*Bao and Gu*, 2004; *Jackson et al.*, 2010; *Sturchio et al.*, 2009].

1.3.1 Oxygen isotopes

There is specific evidence that significant nonmass-dependent (NMD) fractionation occurs in the oxygen isotopes of ClO_4^-. In most processes, isotopes undergo mass-dependent fractionation (MDF) in proportion to the difference in mass between the isotopes. In the case of oxygen isotopes measured with respect to ^{16}O, the amount of ^{17}O atoms relative to ^{16}O atoms is half that of ^{18}O relative to ^{16}O, thus usual isotopic fractionation gives a straight-line relationship defined by $\delta^{17}O$ is approximately 0.5 x $\delta^{18}O$. (A more precise determination of the mass-dependent line is $\delta^{17}O = 0.52 \times \delta^{18}O$.) Deviations from this straight-line relationship are termed NMD or mass-independent fractionation (MIF). MIF is measured as the deviation off the straight line, which is represented by the notation $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ [*Farquhar and Johnston*, 2008; *Thiemens*, 2006].

Research has shown that ozone production leads to mass-independent fractionation of oxygen isotopes[*Thiemens and Heidenreich*, 1983], whereby ozone is isotopically enriched with a $\Delta^{17}O$ range from 25 to 40 ‰ [*Johnston and Thiemens*, 1997; *Krankowsky et al.*, 1995]. The $\Delta^{17}O$ of natural perchlorate from the Atacama varies from +4.2 ‰ to +12.8 ‰ with an average of +8.7 ‰ [*Böhlke et al.*, 2005; *Jackson et al.*, 2010; *Sturchio et al.*, 2006]. Large positive $\Delta^{17}O$ values in natural perchlorate samples (Figure 1) indicate that natural perchlorate was formed by oxidation of chlorine species via reactions with ozone in the atmosphere. A factor of four difference between the $\Delta^{17}O$ of perchlorate (4.2–12.8 ‰) and O_3 (30–40 ‰) suggests that O_3 (or ozone-derived oxidants) contributes one oxygen atom in four to natural perchlorate [*Bao and Gu*, 2004]. Synthetic perchlorate samples have $\Delta^{17}O$ values of 0.0 ± 0.1‰ indicating that mass-independent isotopic fractionation is insignificant during perchlorate production processes [*Bao and Gu*, 2004; *Sturchio et al.*, 2006].

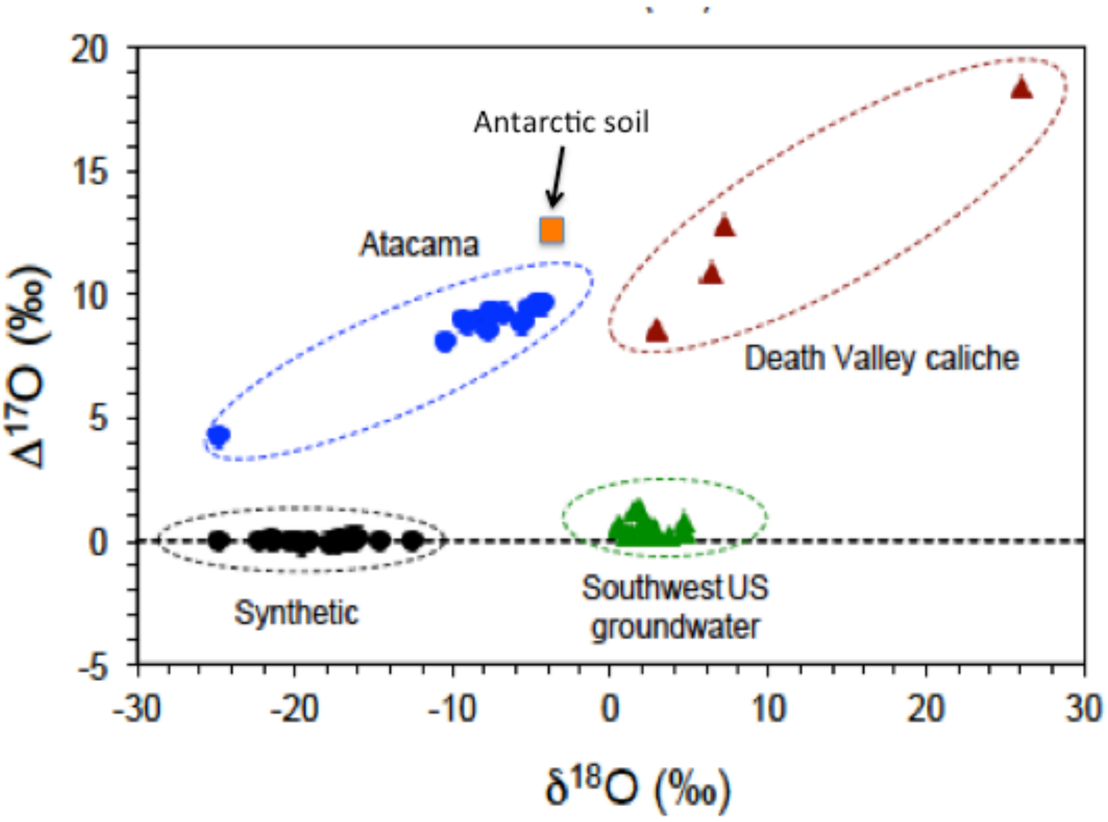

Figure 1. $\Delta^{17}O$ (per mil) versus $\delta^{18}O$ (per mil) values for samples of synthetic ClO_4^-, Atacama ClO_4^-, and Southwest U.S. ClO_4^-. Southwest ClO_4^- is subdivided into Southern High Plains and Death Valley. Figure adapted from *Sturchio et al.* [2012] and data is from *Böhlke et al.* [2005]; *Jackson et al.* [2016]; *Kounaves et al.* [2010]; *Sturchio et al.* [2006]**.**

1.3.3 Chlorine isotopes

^{36}Cl, a cosmogenic radionuclide with a half-life of 301,000 years, is produced in the atmosphere by cosmic-ray spallation of ^{40}Ar [*Lal and Peters*, 1967; *Lehmann et al.*, 1993]. Chlorine isotope ratios of perchlorate are unusual. Natural perchlorate displays $^{36}Cl/Cl$ ratios that are distinct from synthetic perchlorate (Figure 2). Natural perchlorate from the western U.S. and Antarctica has $^{36}Cl/Cl$ atom ratios that are orders of magnitude higher than those of synthetic perchlorate. High ^{36}Cl abundances are found in the stratosphere [*Lal and Peters*, 1967], indicating stratospheric chlorine is involved in perchlorate production. It has been suggested that a tropospheric formation pathway exists [*Dasgupta et al.*, 2005; *Furdui and Tomassini*, 2010]; however, high ^{36}Cl/Cl ratios indicate that some natural perchlorate is formed in the stratosphere [*Sturchio et al.*, 2009].

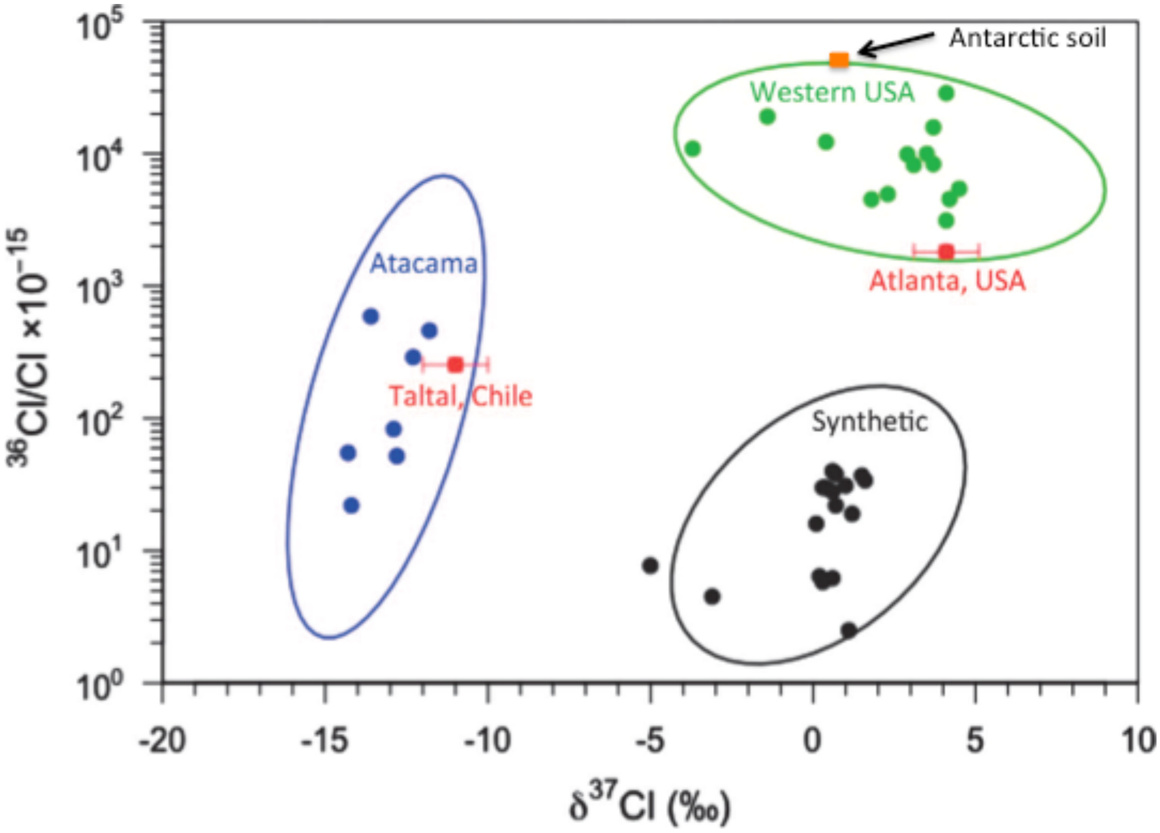

Figure 2. ^{36}Cl/Cl (atom ratio) versus δ^{37}Cl (‰) in representative samples of synthetic ClO_4^-, Atacama ClO_4^- and Southwest US ClO_4^-. Chlorine isotope ratios of perchlorate extracted from pooled human urine samples are indicated in red. Figure adapted from *Sturchio et al.* [2009] and data is from *Böhlke et al.* [2005]; *Kounaves et al.* [2010]; *Poghosyan et al.* [2016]; *Sturchio et al.* [2006].

Furthermore, chlorine isotope ratios of perchlorate extracted from pooled human urine samples from two geographically distinct sample populations (Atlanta, USA and Taltal, Chile) (Figure 2) strongly indicate that natural perchlorate is the dominant source of perchlorate exposure [*Poghosyan et al.*, 2016]. It had been previously assumed that perchlorate contamination is a localized problem, mostly affecting regions near military-related facilities or other locations of major anthropogenic releases [*ITRC (Interstate Technology & Regulatory Council)*, 2007; *Richardson*, 2003] and that human exposure to perchlorate was generally isolated to these contaminated regions. It is apparent that as perchlorate is ubiquitous in the environment, human exposure to perchlorate is also widespread.

1.4 Records of environmental perchlorate

Knowledge of the magnitude of natural (likely atmospheric) perchlorate source and its contribution, relative to that from current and past human activities, to the current environmental perchlorate budget is critical to evaluating the impact of proposed regulation and remediation of perchlorate and therefore crucial to decision-making processes. Preliminary analysis by *Dasgupta et al.* [2006] estimated the strength of the atmospheric perchlorate source, based on measured perchlorate concentrations in rainfall and precipitation rates, to be 0.1-0.6 Gg (10^9 g) per year for the United States. In a more recent study, *Rajagopalan et al.* [2009] estimated the total annual perchlorate flux across the conterminous United States to be 0.05 Gg, roughly half or less of the earlier estimate. These values illustrate the large uncertainty in estimating the strength of the natural source.

It is highly likely that records of environmental perchlorate will allow for the assessment of the magnitude and strength of the natural source. The first step has been taken in the preliminary estimates of the magnitude of the natural source in the U.S. [*Dasgupta et al.*, 2006; *Rajagopalan et al.*, 2009]. However, the data used in these analyses are limited to regional measurements and do not allow an estimate of decadal or longer-scale variability of the natural source. Therefore, an alternative assessment is needed to determine the magnitude and variability of perchlorate in the current and past environment. An important goal of environmental perchlorate research ought to be an accurate understanding and description of the natural production of perchlorate, including the influence of important environmental variables. In addition to being an alternative method to evaluate source strengths and variations, well-dated perchlorate records will also likely contain clues to the atmospheric chemical processes, i.e., oxidation chemistry.

Currently, few records of perchlorate in the environment exist and there is a limited understanding of the processes that contribute to perchlorate occurrence in the environment. *Kounaves et al.* [2010] and *Andraski et al.* [2014] have suggested that the production and deposition of natural perchlorate is likely to account for a significant fraction of the total perchlorate in the environment. And yet, research on atmospheric perchlorate production and deposition has been relatively scarce. Isotopic data indicate ozone and stratospheric chlorine are involved in perchlorate formation, strongly suggesting that perchlorate is produced in the atmosphere. The magnitude and variability of environmental perchlorate is thus linked to atmospheric (likely stratospheric) chemistry and the atmospheric environment in general. Proxy records on historic ClO_4^- depositional rates can be obtained in subsoil and groundwater samples [*Plummer et al.*, 2006; *Rajagopalan et al.*, 2009; *Rao et al.*, 2007] but provide limited information on what factors influence perchlorate production in the atmosphere. It is likely that perchlorate records will contain clues to various atmospheric chemical processes (i.e., oxidation chemistry), and close examination of the perchlorate deposition patterns over time may reveal the impact of environmental variables such as climate conditions and the atmospheric oxidative capacity.

1.5 Ice core records of perchlorate

Many chemical species in the atmosphere deposit with snow and are preserved in polar ice sheets. Ice cores (ice cylinders typically ~ 10 cm in diameter) can be recovered by drilling into the ice sheets hundreds or even thousands of meters thick [*EPICA members*, 2004]. Ice cores are useful tools for uncovering environmental changes by providing chronological records of chemical and climate variations. Insights into the paleo-environmental information contained in polar ice sheets can be obtained by extracting species of interest from ice cores. Ice cores extracted from the Antarctic and Greenland ice sheets [*North GRIP community members*, 2004; *Petit et al.*, 1999] have the potential to provide very detailed information on past atmospheric characteristics, from sub-annual to orbital time scales (10^5 years). Ice core studies also offer the considerable advantage that multiple physical, chemical and biological records are obtained from the same ice matrix and thus can be compared on exactly the same time scale. This reduces the dating uncertainty and allows the examination of synchronous interactions between climate, ecosystems and, more recently, human societies.

Measurement of perchlorate in polar snow and ice can yield both short and long records of perchlorate in the environment. For example, in recently published work [*Furdui and Tomassini*, 2010; *Peterson et al.*, 2015b; *Rao et al.*, 2012], perchlorate was found in Arctic snow and ice core samples at extremely low concentrations detectable with highly sensitive techniques [*Jiang et al.*, 2013; *Peterson et al.*, 2015a]. The investigations on perchlorate in Arctic snow suggest that perchlorate concentrations appear to be higher in recent snow (post-1980) than in older snow with the increase possibly attributable to anthropogenic influence [*Peterson et al.*, 2015b]. In addition, *Furdui and Tomassini* [2010] found that recent environmental perchlorate trends may be related to ozone variation. However, these findings are preliminary and key factors affecting perchlorate variability have yet to be investigated. In addition, it is not known if the perchlorate trends found in the Arctic also exist in Antarctica, as few measurements have been made for perchlorate in Antarctic snow [*Jackson et al.*, 2016; *Jiang et al.*, 2013]. Preliminary data from the Antarctic [*Jackson et al.*, 2016; *Jiang et al.*, 2013] also suggest that perchlorate levels are several orders of magnitude higher than the North American and Arctic levels. The reason behind this large difference is unclear.

1.6 Objectives

The overall goal is to develop ice core records of perchlorate. These records can be used not only to determine past exposure, but also to study atmospheric chemistry and to assess variations in atmospheric chemistry and potentially in climate. Proper interpretation of perchlorate records will require adequate working knowledge of the atmospheric chemical processes and climatic conditions that influence perchlorate production. This work seeks to improve our knowledge of perchlorate production in the atmosphere and of how environmental and climatic variables influence perchlorate production. Furthermore, as perchlorate in polar ice sheets originates in the atmosphere, improved understanding about the air-to-snow transfer of perchlorate is also necessary to properly interpret data from polar snow and ice. It is also not known if perchlorate is irreversibly deposited and preserved within the snowpack. Whereas many chemical impurities are irreversibly deposited and preserved in polar snow and ice, some species are not-well preserved and undergo post-depositional processes that alter their concentration, and consequently, alter the records of these species in ice cores. As such, in order to properly interpret perchlorate profiles from ice cores, it is also necessary to determine the quality of preservation of perchlorate in polar snow and ice. In this work, perchlorate was measured in snowpit and ice core samples collected at several Antarctic locations to achieve the following objectives:

(1) detect any trends in Antarctic perchlorate over the 20th century and compare to the increasing trend in the Arctic
(2) determine the key drivers of natural perchlorate production
(3) explore depositional characteristics of perchlorate at various ice core sites as well as investigate the stability of perchlorate in the polar snowpack

These objectives will be accomplished through the development of several high resolution and well-dated ice core records of perchlorate from Antarctica. The high temporal resolution of the records will allow for the assessment of sub-annual variations in perchlorate concentrations in relation to changes in the environment.

Such information can give insight into how environmental/atmospheric conditions influence perchlorate production; it is possible that perchlorate may be used in future long-term (millennial-scale) ice core records as a proxy to assess past variations in atmospheric chemistry and climate.

2. Ice cores and chemical measurement

Snowpit and ice core samples were collected at several Antarctic locations covering West Antarctica, the South Pole, and East Antarctica to investigate the possible spatial distribution of perchlorate deposition. Additionally, several ice cores were collected from similar locations - but 10 years apart in time – to explore the preservation of perchlorate within the snowpack. Two ice cores were collected from the South Pole, one in 2004 and the other in 2014, whose records overlap in time. Two ice cores were also collected from a site in West Antarctica, one in 2005 and one in 2013, whose records overlap in time. Overlapping ice cores were collected at two locations (South Pole and West Antarctica) to study the preservation of perchlorate at a low accumulation location (South Pole) as well as a moderately high accumulation location (West Antarctica).

2.1 Ice Core collection

The West Antarctic Ice Sheet (WAIS) Divide ice core site (79°28' S, 112°05' W, elevation 1766 m) (Figure 3) has an average snow accumulation rate of 20 cm water equivalent per year (w.e.a^{-1}) [*Banta et al.*, 2008]. Five ice cores were drilled at the WAIS Divide site during the 2004-2005 austral field season and the top 30 m of one core (WDC05B) was used for this study. Due to the fragile nature of the surface snow and the likelihood that the upper meters would be destroyed during drilling, the top 1.4 m of snow were not collected and the WDC05B core begins at 1.4 m from the surface. The core was cut with a band saw into samples of approximately 4 cm in depth interval, producing 780 samples for all 30 m.

A 10 m deep hand augur firn core was drilled within the vicinity (within ~20 km) of the WAIS Divide site in January 2013. In this work, this core will be referred to as the WDC13 core. This core was melted and sampled at the Dartmouth College ice-core chemistry laboratory, using a continuous melter system with fraction collection. The melter system collected samples continuously with a sampling interval of approximately 5 cm, producing 201 samples for all 10 m. Samples were bottled and shipped to the ice core chemistry laboratory at South Dakota State University (SDSU).

In January 2013, a set of snow samples were collected at 3 cm intervals from a 2.8 m snowpit near the WAIS Divide ice core site. The snow samples were placed in pre-cleaned containers and kept frozen during transport and storage.

South Pole (elevation 2850 m) (Figure 3) has a moderate snow accumulation rate of 8.4 cm w.e.a^{-1} [*Ferris et al.*, 2011]. During the 2004-2005 austral summer, several ice cores were drilled at a site 4.7 km from the Amundsen-Scott South Pole Station [*Ferris et al.*, 2011]. The top 15 m of one core (SP04C1) was used for this study. The core was cut with a band saw into samples of about 4 cm in depth interval, producing 470 samples for all 15 m.

A 10 m deep hand augur firn core was drilled at the South Pole in December 2014. In this work, this core will be referred to as the SPC14 core. This core was also melted and sampled using the Dartmouth melter system with a sampling interval of 10-15 cm, producing 86 samples for all 10 m. Samples were bottled and shipped to the ice core chemistry laboratory at SDSU.

Dome A (80°22′ S, 77°22′ E, elevation 4093 m) is located on the East Antarctica Plateau (Figure 3). Previous investigation has shown that Dome A has an average snow accumulation rate of 2.3 cm w.e.a^{-1} [*Jiang et al.*, 2012]. During the 2009-2010 austral summer, a 3 m snowpit was excavated at Dome A and samples were collected by pushing pre-cleaned vials horizontally into one wall in 5 cm intervals. All samples were kept frozen in the vials during transport and storage at Polar Research Institute of China (PRIC).

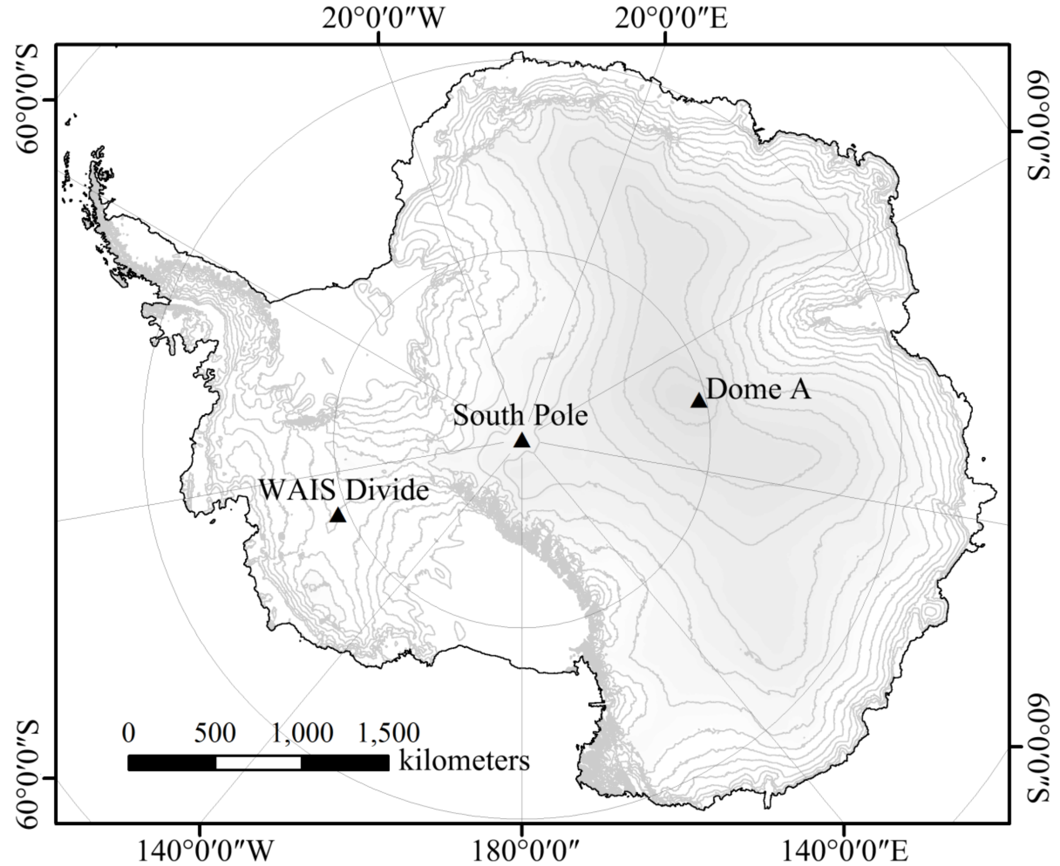

Figure 3. A map of Antarctica showing the location of the South Pole, WAIS Divide, and Dome A ice core and snowpit sites.

2.2 Major ion analysis

Each ice core sample was analyzed for its soluble major-ion content (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) using a ThermoFisher (formerly Dionex) DX600 ion chromatography (IC) system with conductivity detection. A Dionex AS11 (2×250 mm) column, an ASRS300 (2 mm) suppressor and NaOH eluent was used to separate major anions and a Dionex CS12 (2×250 mm) column, a CSRS300 (2 mm) suppressor and H_2SO_4 eluent was used to separate major cations. The uncertainty of ion concentrations measured with this method, as described in previous work [*Cole-Dai et al.*, 1997b], is less than 10% relative standard deviation (RSD) of the measured concentrations. Concentrations for major ions are reported in $\mu g\ L^{-1}$ (parts-per-billion). Cation concentrations were not measured for the samples corresponding to 1.4 – 4 m depth of the WDC05B core due to a malfunction with the IC system. The malfunction was corrected and cation data were collected for the remainder of the core.

2.3 Analytical techniques for measuring perchlorate

Perchlorate is likely to occur in environmental waters at extremely low levels (low parts per billion to parts per trillion). Due to the lack of sensitivity among analytical instrumentation and techniques that were available until the mid-1990s, the detection of perchlorate in nature was impractical [*Motzer*, 2001]. However, in 1997, the California Department of Health Services developed and introduced what became U.S. EPA Method 314.0 with a detection limit of 4 $\mu g\ L^{-1}$ [*Helperin et al.*, 2001]. Following the establishment of the EPA method, perchlorate began to be detected in water sources not previously suspected of being contaminated [*Brown and Gu*, 2006; *Trumpolt et al.*, 2005]. Subsequent new developments in analytical techniques [*El Aribi et al.*, 2006; *Koester et al.*, 2000; *Winkler et al.*, 2004] resulted in worldwide perchlorate detection [*Jackson et al.*, 2015]. With new advances in analytical instruments and techniques, perchlorate has been found to be ubiquitous in the environment with trace concentrations found on every continent [*Jackson et al.*, 2015].

As the preliminary work by *Jiang et al.* [2013] suggests, perchlorate concentrations in snow and ice from the Antarctic are in the low ng L^{-1} to well over several hundred ng L^{-1}. As such, the measurement of perchlorate in snow and ice samples requires an ultra-sensitive analytical technique. Ion chromatography (IC) with conductivity detection has demonstrated a detection limit of 0.5 μg L^{-1} [*Liu and Mou*, 2003]. Two-dimensional ion chromatography (2D-IC) with conductivity detection has been shown to achieve a much lower limit of detection (LOD) at 55 ng L^{-1} [*Wagner et al.*, 2007]. However, as perchlorate levels in Antarctic ice are expected to be in the low ng L^{-1} range, more sensitive methods are required.

The application of mass spectrometry with electrospray ionization (ESI) to perchlorate measurement has been able to achieve even lower LODs than conventional chromatography techniques [*EPA*, 2005; *Magnuson et al.*, 2000]. The pairing of liquid chromatography with tandem mass spectrometry (HPLC-ESI-MS/MS) resulted in a much lower LOD of 9-50 ng L^{-1} [*Backus et al.*, 2005; *Noot et al.*, 2012; *Winkler et al.*, 2004]. Finally, the use of ion chromatography-tandem mass spectrometry with electrospray ionization (IC-ESI-MS/MS) demonstrated the most success in the measurement of low levels of perchlorate in aqueous samples with detection limits near or slightly below 1 ng L^{-1} [*El Aribi et al.*, 2006; *Furdui and*

Tomassini, 2010; *Rao et al.*, 2012]. An IC-ESI-MS/MS method utilizing 10-fold online pre-concentration for the determination of perchlorate in Antarctic snow developed by *Jiang et al.* [2013] was able to achieve an even lower limit of detection of 0.2 ng L^{-1}. However, the method developed by *Jiang et al.* [2013] was not verified for precision at the low ng L^{-1} level, as the perchlorate concentrations in the Antarctic snow samples analyzed in that study ranged from 10 to 300 ng L^{-1}. The method used in this study was an IC-ESI-MS/MS method developed for the quantification of perchlorate at the sub-ng L^{-1} levels without pre-concentration [*Peterson et al.*, 2015a]. There is typically a large number of samples in ice core studies. Thus sample throughput is important. As such, rapid determination (i.e., without pre-concentration and approximately 15 minute run time) of extremely low perchlorate concentrations in snow and ice samples is desirable.

2.3.1 Perchlorate analysis by IC-ESI-MS/MS

Perchlorate was separated from the sample matrix and other matrix species using a ThermoFisher (formerly Dionex, Sunnyvale, CA) DX500 ion chromatography system consisting of an IP25 isocratic pump and a CD25 conductivity detector. Samples were loaded into the system from 5 mL vials using a Dionex AS40 autosampler. The samples were injected onto a Dionex IonPac AS16 (2 x 250 mm) analytical column with a 600 μL injection loop and perchlorate was eluted from the column with 60 mM sodium hydroxide (NaOH) at a rate of 0.3 mL min^{-1}. The effluent was suppressed using an AERS-500 (2 mm) suppressor. The post-column additional mixing of 90% (v/v) acetonitrile: 10% water solution with the effluent at

0.3 mL min^{-1} was necessary to decrease the surface tension and aid in the nebulization of the sample.

Ultrapure deionized water (18 MΩ) was used throughout the sample preparation procedures for cleaning glassware and other containers and for solution preparation. All chemicals used for eluent preparation are reagent grade. The acetonitrile in the 90% acetonitrile-deionized water mixture is HPLC grade. Analytical grade potassium perchlorate ($KClO_4$) from Acros Organics (Geel, Belgium) was used to prepare a 1000 mg L^{-1} (ClO_4^-) stock standard in deionized water. A 1.00 μg L^{-1} intermediate perchlorate solution was prepared from the 1000 mg L^{-1} stock. Perchlorate calibration standards (1.00, 2.50, 5.00, 10.00, 20.00, 50.00 ng L^{-1}) in deionized water were prepared daily by dilution from the intermediate standard solution.

2.3.2 Optimized mass spectrometer parameters

The optimized ion source and the high-purity nitrogen collision gas parameters, as well as the compound specific parameters are shown in Table 1. Similar methods utilizing AB SCIEX API 3200 mass spectrometers [*Furdui and Tomassini*, 2010; *Jiang et al.*, 2013] obtained similar - albeit slightly higher - detection limits of 0.2 ng L^{-1} and 0.3 ng L^{-1}. Although the API 3200 is very similar to the QTRAP 5500, the latter includes a linear ion trap in Q3, which increases extraction efficiency and thus sensitivity.

Table 1. Ion source and high purity nitrogen gas parameters for the AB SCIEX QTRAP 5500 triple quadrupole mass spectrometer optimized for low perchlorate detection limit

Parameter	Optimized Condition
Source temperature	600.0 °C
Ion spray voltage	-3,000.0 V
Curtain gas	20 psi
Ion source gas 1	40 psi
Ion source gas 2	15 psi
Collision gas	Medium

The mass chromatogram of a 0.10 ng L^{-1} perchlorate solution is shown in Figure 4. The perchlorate peak at 10.2 min is seen at both mass-to-charge 99 ($^{35}ClO_4^-$) and 101 ($^{37}ClO_4^-$). The 99/101 peak area ratio of 3:1 verifies that the detected species is perchlorate.

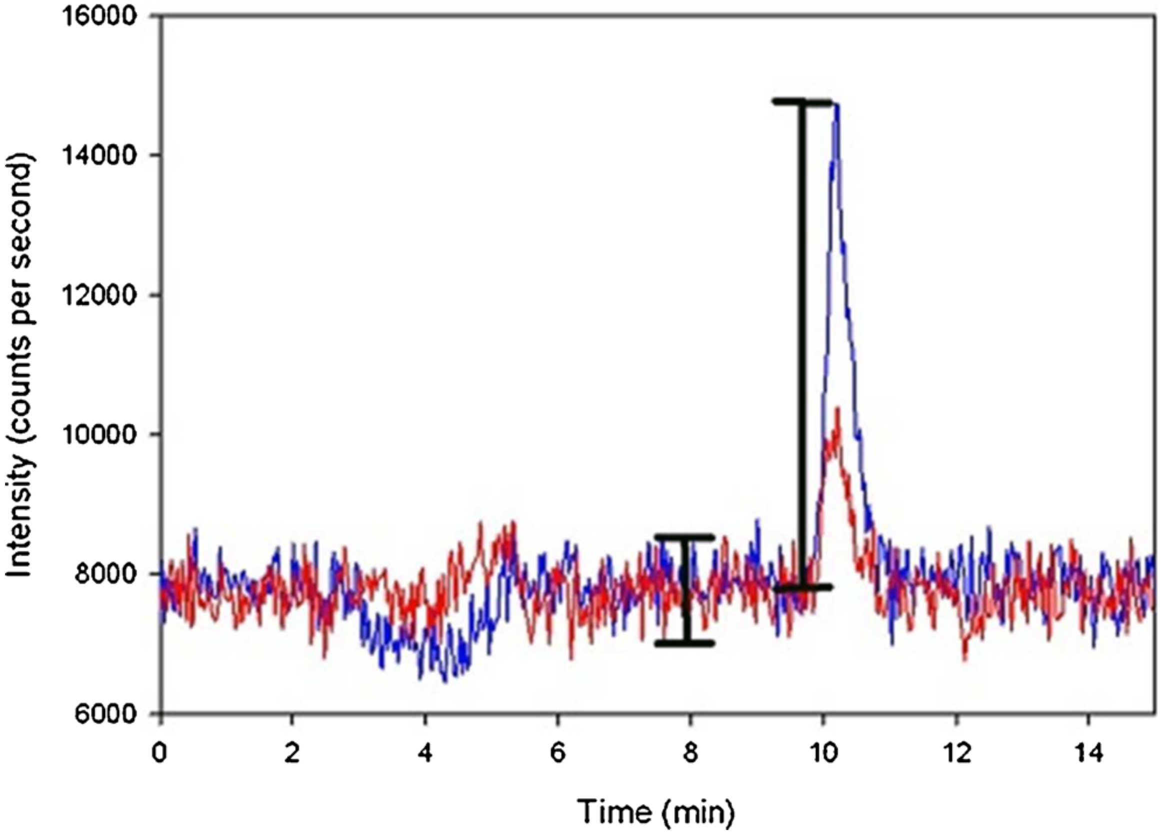

Figure 4. Mass chromatogram for a 0.10 ng L^{-1} standard used to determine the LOD (S/N>3). The blue signal represents $^{35}ClO_4^-$. The red signal represents $^{37}ClO_4^-$.

A set of five perchlorate standards were used for calibration. The calibration curve was constructed by plotting the $^{35}ClO_4^-$ peak area against concentration, and the data were fitted using least squares linear regression. The criteria [*EPA*, 2012] used to establish the dynamic range were a relative standard deviation of less than 20% (Table 2). A dynamic range of 1–50.0 ng L^{-1} was used in this study.

Table 2. Quality control data for the analysis of perchlorate by IC-ESI-MS/MS.

Nominal Concentration (ng/L)	Intraassay recovery (%)[a]	Interassay recovery (%)[b]	Intraassay precision (%CV)[a]	Interassay precision (%CV)[b]
1.00	97.38	98.46	7.80	12.76
9.00	97.25	98.27	3.76	6.73

[a]Mean for 1 day of validation (n = 3)
[b]Mean for 3 days of validation (n = 9)

To determine the limit of detection, the peak-to-valley baseline noise of the mass chromatogram was estimated. A concentration of 0.1 ng L^{-1} (n=6) yielded a signal three times the baseline noise (Figure 4) and was estimated to be the LOD.

2.3.3 Selectivity

The main chemical impurities in polar snow are inorganic acids and salts [*Legrand and Mayewski*, 1997]. Meltwater samples of Antarctic snow and ice contain the following main ionic species at the micrograms per liter level or below: Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. With chromatographic and mass spectrometric separation, no interferences from the matrix species are expected. This is illustrated with the chromatogram (Figure 5) of a typical snow sample. The perchlorate peak elutes at approximately 10.2 min (Figure 5), in samples with a variety of ionic species, indicating that perchlorate is separated from the other ionic species and no other species co-elutes with perchlorate.

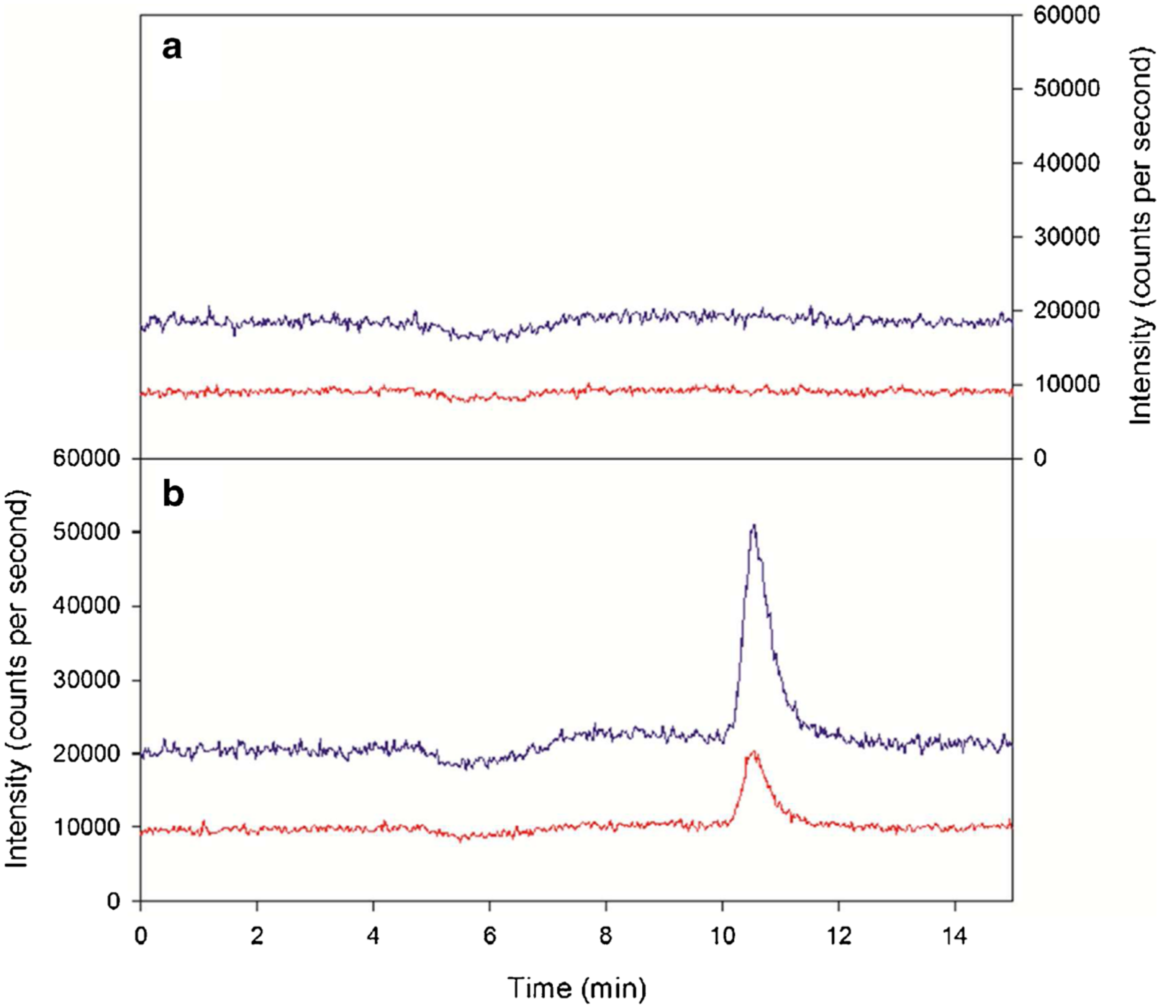

Figure 5. A mass chromatogram of a sample with no perchlorate (a) and a mass chromatogram of a sample containing perchlorate (b). There are no peaks co-eluting with perchlorate (10.2 min). The blue signal is $^{35}ClO_4^-$ and the red signal is $^{37}ClO_4^-$.

2.3.4 Interlaboratory comparison

An interlaboratory comparison was performed to validate the IC-ESI-MS/MS method for perchlorate analysis. Perchlorate standards and meteorite samples prepared and analyzed at Texas Tech University (TTU), Lubbock, Texas, USA, were measured independently using the method developed in our laboratory. The results of this study are presented in Table 3. The percent deviation between the measured concentration by the TTU laboratory and those measured in our laboratory is less than 10% for those standards that fall within our dynamic range (i.e., 1-50 ng L^{-1}). The slightly higher deviations for the meteorite sample concentrations are likely the result of the concentrations outside the typical dynamic range established for the ice core samples. No dilution of the samples to within the dynamic range was performed due to limited sample volume. The comparison with the analytical data from another established laboratory contributes to the validation of the new method.

An interlaboratory compatibility test of the IC-ESI-MS/MS method at SDSU and the method used by *Jiang et al.* [2013] for application to Antarctic snow samples was performed. The comparison was performed to confirm the agreement of the two methods. This was accomplished when a set of Dome A snow samples and perchlorate standards with concentrations ranging from 10 to 500 ng L^{-1} prepared at the Polar Research Institute of China laboratory was analyzed at the SDSU laboratory; the concentrations obtained by the SDSU laboratory were within ±5% of the nominal concentrations prepared and measured at PRIC using the method established by *Jiang et al.* [2013].

Table 3. Results of an interlaboratory comparison study in which samples and standards prepared at Texas Tech University (TTU) were analyzed using the IC-ESI-MS/MS method at South Dakota State University (SDSU)

Sample	TTU Concentration (ng L^{-1})	SDSU Concentration (ng L^{-1})	Percent deviation
Purified water	<1	<LLOQ	N/A
1 ng L^{-1}	1.18	1.3	9.2
5 ng L^{-1}	5.78	6.0	3.7
10 ng L^{-1}	11.3	12.1	6.6
Fayetteville 10	52	64.2	19.0
Fayetteville 10 fusion layer	140	157.3	11.0

2.4 Sample preparation

All ice core samples that were processed at SDSU (WDC05B and SP04C1 cores) were cut from each respective core in a –20 °C freezer using a bandsaw as described in *Peterson et al.* [2015a]. The band saw blade was cleaned first with ethyl alcohol and then with deionized water, and then cleaned by cutting frozen ultrapure deionized water samples repeatedly. As with all analysis of ice cores for chemical impurities, the exterior of ice cores is presumed to become contaminated during ice core drilling and transport; the ice cores, therefore, must be decontaminated in sample preparation. Prior to melting and analysis, samples were decontaminated with the removal of all previously exposed surfaces. Because of the porous nature of the firn, exposed surfaces must be removed by mechanical means. In this case, during cutting, the operator wore pre-cleaned vinyl gloves to maneuver the ice, and freshly cut, clean surfaces of the ice were kept from coming into contact with the saw bench surface. After all previously exposed surfaces had been removed, the sample (approximately 3.5 x 3.5 x 4.0 cm) was allowed to melt in a capped clean sample container (plastic specimen cup) at room temperature followed by analysis with IC-ESI-MS/MS for perchlorate as well as IC for major ions. Prior to ice core samples being placed in sample containers (plastic specimen cups) for analysis, the cups were washed thoroughly and repeatedly with deionized water and allowed to dry at room temperature on a clean air bench.

The Dome A snowpit samples were melted at room temperature and analyzed with a ThermoFisher ICS3000 IC system for concentrations of major ions . Perchlorate measurement was performed on an ICS2000 IC system coupled to an AB SCIEX API 3200 ESI-MS/MS in the State Key Laboratory of Environmental Chemistry and Ecotoxicology, Chinese Academy of Sciences. Detailed procedures for IC-ESI-MS/MS analysis for the Dome A snowpit samples have been described previously[*Jiang et al.*, 2013].

2.5 Operational blanks

In order to assess the degree of contamination introduced during the preparation of ice core samples and the efficacy of decontamination, deionized water was frozen in a clean container and was used to create operational blanks. An operational blank was prepared in the same way as the ice core samples, where the outside surfaces were removed using the band saw. An uncleaned blank was prepared without removing the outside surfaces to represent the contamination that would be introduced when no precautions to remove contamination were implemented.

Cleaned and uncleaned blanks were prepared on three separate occasions. Each blank was analyzed in triplicate for a total of nine measurements for each type of operational blank. The results from this study are summarized in Table 4. The concentrations in the uncleaned blanks (2.7 ng L^{-1}) indicate that removal of exposed surfaces is necessary. The sources of contamination are likely unwashed vinyl gloves, which were used to handle the ice prior to cutting, and the saw bench. The level in the cut blanks was above the LOD, but below the LLOQ (Table 4). This level of contamination in the firn samples does not affect the interpretation of the perchlorate records sampled and melted at SDSU (SP04C1 and WDC05B).

Table 4. Results of analysis of operational blanks for contamination assessment

Sample type	Mean ClO_4^- concentration (ng L^{-1})	Concentration range (ng L^{-1})	Standard deviation (ng L^{-1})
Decontaminated	0.17	0.11-0.21	0.04
No decontamination	2.70	0.40-5.39	2.17

2.6 Dating Methods

The establishment of reliable chronologies for ice cores is critical in ice core studies. Depending on the required accuracy and the time period and the ice core location (high or low annual accumulation rate), various methods can be used to determine the ages of layers in an ice core. These methods include counting the annual layers (strata) of snow and ice, using computer models to estimate the age-depth relationship along an ice core when the annual layers are too thin to be counted, and “dating horizons” such as well-known volcanic eruptions.

2.6.1 Annual layer counting

Seasonal variations in isotopic composition and impurity content of the snowfall provide the basis for a distinct annual signal in the snowpack, which may be preserved in the ice. The ability of an ice core to provide (sub-)annual information depends on the accumulation rate [*Legrand and Mayewski*, 1997]. It typically ranges from a few centimeters of snow per year on the high plateau in East Antarctica to several meters at coastal sites of Greenland and on low latitude glaciers [*Legrand and Mayewski*, 1997]. In the upper part of an ice sheet, snow slowly compacts into incompressible ice. Due to the continuous accumulation of snow, older snow and ice become buried in the ice sheet over time.

The ratios of stable oxygen and hydrogen isotopes of H_2O molecules in glacier ice (expressed as $\delta^{18}O$ and δD values) reflect seasonal variations in local temperature at the time of precipitation [*Dansgaard*, 1964]. In ice cores from high accumulation sites, such as the DYE-3 core from southern Greenland, the seasonal variation of $\delta^{18}O$ and δD may be traced 8,000 years back in time [*Vinther et al.*, 2006]. However, at lower accumulation sites, mixing of sublimated water molecules during the transition from snow to ice reduces, or completely erases, the amplitude of the seasonal cycle [*Legrand and Mayewski*, 1997]. Moreover, ice flow-induced layer thinning combined with the diffusion of H_2O molecules within the firn ultimately obliterates the seasonal $\delta^{18}O$ and δD cycles even in high-accumulation areas [*Johnsen et al.*, 2000]. Therefore, in cores from moderate accumulation sites and in deeper parts of cores from high accumulation sites, other impurities that exhibit seasonality and are less prone to diffusion must be employed for annual layer detection.

An annual signal may be present in the impurity content of an ice core, as many impurities display a seasonal variation [*Legrand and Mayewski*, 1997]. In Greenland, for example, dust concentrations generally reach a maximum during spring, whereas the amount of sea-salt aerosols peaks during winter [*Rasmussen et al.*, 2006]. The annual dust cycle can sometimes be identified from the visible layering of an ice core [*Svensson et al.*, 2005], but most impurity records are obtained by measurements on melted samples, often using a melting device and a high-resolution continuous flow analysis (CFA) system [*Cole-Dai et al.*, 2006; *Röthlisberger et al.*, 2000a].

Impurity records contain non-annual signatures, e.g. input from volcanic eruptions, biomass burning, and other episodic sources [*Legrand and Mayewski*, 1997] that cause a seasonal or annual signal to become ambiguous for a period of several years. For this reason, the development of several impurity records of different origin from the same core is recommended when establishing a chronology [*Ferris et al.*, 2011; *Rasmussen et al.*, 2006; *WAIS Divide Project Members*, 2016]. High-resolution CFA datasets have allowed for multi-parameter layer identification in ice cores from both hemispheres [*Sigl et al.*, 2013]. Annual layers have been identified back to ~30,000 years before present in an ice core drilled on the West Antarctic Ice Sheet Divide [*WAIS Divide Project Members*, 2016]. These ice-core chronologies rely on identifying annual layers, which can be laborious and inherently subjective [*Steig*, 2008]. Yet, annual layer counting is also a very flexible approach that can accommodate changes in the expression of annual layers, data quality, and resolution.

2.6.2 Constant accumulation rate

Another technique to date an ice core is the use of snow accumulation rates. This technique involves using the average annual snow accumulation rate at a specific location to determine the age at a certain depth. Time stratigraphic horizons from known volcanic eruptions are one of the ways to determine mean annual accumulation rates. A mean accumulation rate can be calculated between two adjacent volcanic events and the accumulation rate is assumed constant to date the intervening snow layers [*Cole-Dai et al.*, 2000; *Igarashi et al.*, 2011]. The use of accumulation rates for dating is complicated by the compression of annual layers with increased depth. As a result, snow annual layer thickness decreases with increasing depth. Thus, the snow depths need to be converted into amount of snowfall in water equivalent, which is not dependent on the depth in the core. Rather than use the depth interval in snow, the average snow water equivalent (SWE) depth is used to date the ice core.

2.7 Dating the ice cores

2.7.1 South Pole snow

When compared to the appearance of annual summer depth hoar layers in South Pole snow, sodium and magnesium concentration cycles are unambiguously annual [*Cole-Dai and Mosley-Thompson*, 1999; *Legrand and Delmas*, 1984]. Sodium measurements in South Pole snow and ice show that sodium concentrations peak every year in austral winter from an influx of sea salt aerosols [*Wolff et al.*, 2003]. Sea salt aerosol is derived from small bubbles bursting over the open ocean. However, for Antarctica, sea ice surfaces rather than open water have been suggested as the dominant source of sea salt aerosol [*Huang and Jaeglé*, 2016; *Rankin et al.*, 2000; *Wolff et al.*, 2003]. Fresh sea ice is covered by saline brine and it has been shown that blowing snow and small ice crystals growing on these salty surfaces represent effective sources of sea salt aerosol in coastal and inland Antarctica [*Huang and Jaeglé*, 2016; *Rankin et al.*, 2000; *Yang et al.*, 2008]. More sea ice is formed during the winter months than the summer months, thus resulting in higher sea salt aerosol concentrations over the Antarctic ice sheet in winter compared to summer. This results in higher concentrations of sea salt aerosol species (Na^+, Mg^{2+}) in winter snow and lower concentrations in summer snow [*Cole-Dai and Mosley-Thompson*, 1999]. Annual cycles in Mg^{2+} and Na^+ concentrations were discernable throughout the SP04C1 core (Figure 6) and were used to date this core. In the counting procedure, the Na^+ cycles served as the primary annual layer indicator, and Mg^{2+} cycles were used as a complementary indicator, particularly when Na^+ cycles appeared ambiguous (Figure 6). Using this annual layer counting (ALC) technique, the core was determined to cover the period from 1920 to 2005. The appearance of volcanic sulfate from the Pinatubo eruption (1991) during 1993–1995 and the Agung eruption (1963) during 1964-1965 [*Cole-Dai and Mosley-Thompson*, 1999; *Ferris et al.*, 2011] displayed in Figure 7 supports the accuracy of the annual layer counting.

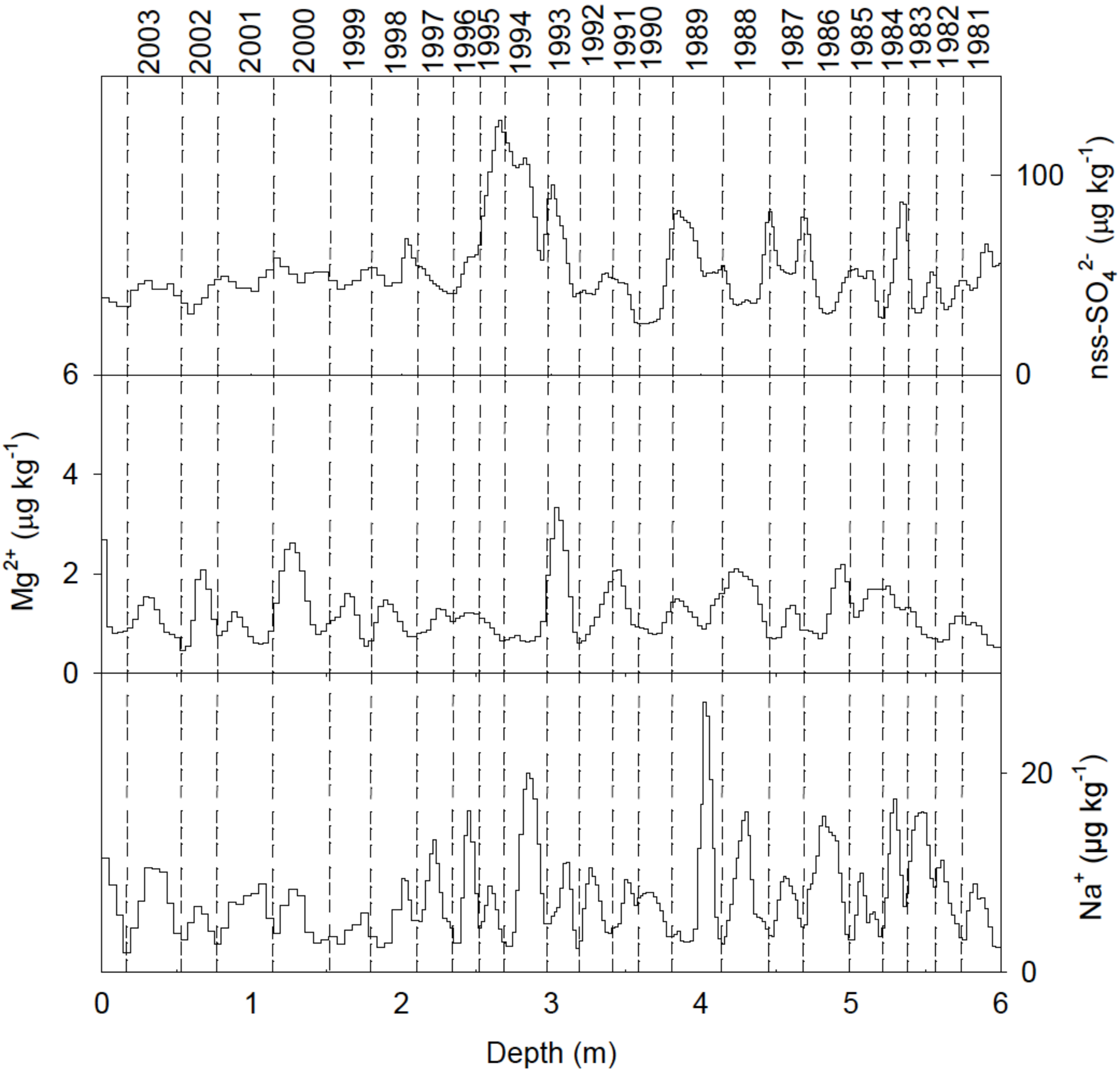

Figure 6. Concentrations of (a) SO_4^{2-} (b) Mg^{2+} (c) Na^+ from the 2004 South Pole firn core (SP04C1) in depth 0-6 m. All data has been smoothed using unweighted 3-sample running mean. Annual layers are counted (years denoted by dashed lines) using summer minima in Na^+ and Mg^{2+} concentrations, where Na^+ was used as the primary layer indicator and Mg^{2+} as the complimentary indicator.

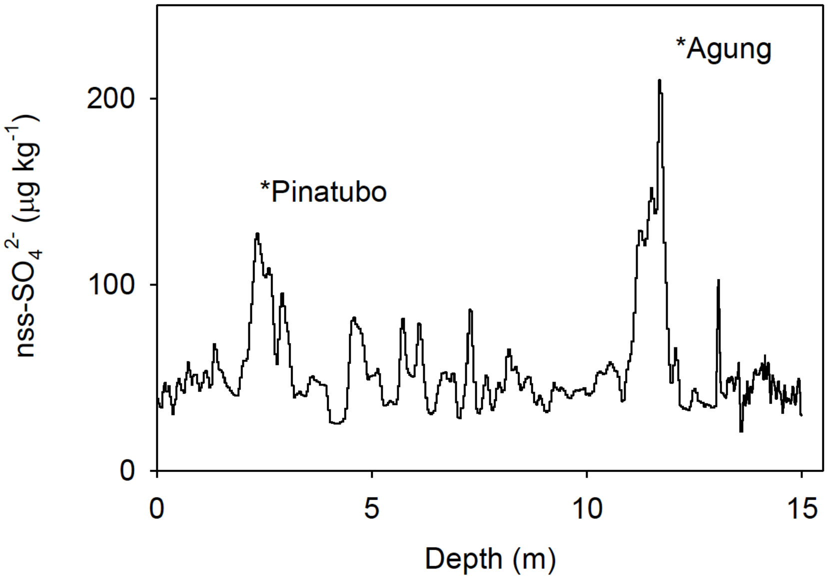

Figure 7. Concentrations of SO_4^{2-} throughout the 2004 South Pole firn core (SP04C1) clearly show the sulfate fallout from the Mt. Pinatubo (1991) and Mt. Agung (1963) volcanic eruptions between depths 2.6-3.0 m and 7.6-7.9 m, respectively. Data has been smoothed using unweighted 3-sample running mean.

The sampling resolution for the SPC14 core is not high enough to date the core by counting seasonal variations of the ions (e.g., Na^+). Therefore, the SPC14 core was dated using average accumulation rate determined from the 2014 snow surface and the volcanic sulfate deposition from the Pinatubo eruption in 1993-95 and the Agung eruption in 1964-65 (Figure 8).

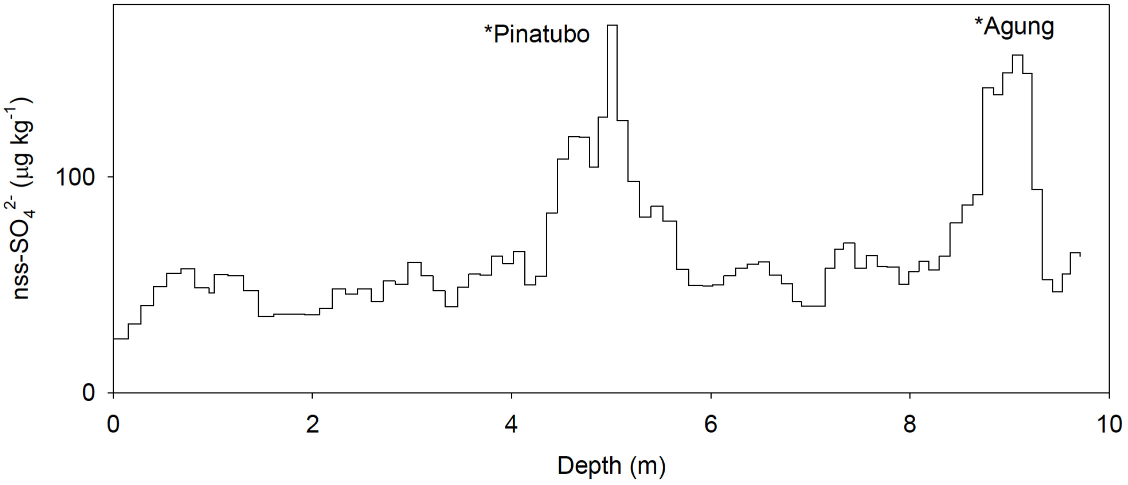

Figure 8. Depth profile of SO_4^{2-} concentrations in the 2014 South Pole (SPC14) 10 m firn core display the sulfate fallout from the Mt. Pinatubo (1991) and Mt. Agung (1963) volcanic eruptions between depths 4.6-5.0 m and 8.7-9.2 m, respectively.

The average accumulation rate can be determined by converting snow depth to water-equivalent depth. Snow depth can be converted to water-equivalent depth using the empirical relationship:

$$D_{w.e.} = \tfrac{1}{3} AZ^3 + \tfrac{1}{2} BZ^2 + CZ \qquad (1)$$

Where A is -4.8 (10^{-4}), B is 0.0196, C is 0.350, $D_{w.e.}$ is depth (m w.e.), and Z is depth in meters of firn at South Pole [*Mosley-Thompson et al.*, 1995; *Mosley-Thompson et al.*, 1999]. Based upon density measurements at South Pole, this relationship has been verified as a good estimate of water-equivalent to a snow-depth of 15 m [*Mosley-Thompson et al.*, 1995; *Mosley-Thompson et al.*, 1999].

The 2014 South Pole firn core was dated to cover the period 1962-2014 using average accumulation rate of 8.3 cm w.e.a^{-1} determined from the 2014 snow surface and the volcanic sulfate deposition from the Pinatubo eruption in 1993-95 and the Agung eruption in 1964-65 and an age-depth (w.e.) profile developed. This determined accumulation rate is similar to the previously determined average accumulation rate of 8.4 cm w.e.a^{-1} for the twentieth century at South Pole[*Mosley-Thompson et al.*, 1999].

2.7.2 WAIS Divide snow

The major source of non-sea-salt (nss) sulfate to West Antarctic ice sheet is biogenic sulfur that results from biological activity in the surrounding oceans during the Southern Hemisphere summer months [*Legrand and Mayewski*, 1997]. The nss-sulfate concentrations in μg kg^{-1} can be calculated by subtracting the concentration of sea-salt-derived sulfate from the total sulfate concentration, using Na$^+$ as a sea-salt reference species and the sulfate-to-sodium ratio in bulk sea water of 0.252 [*Dixon et al.*, 2005; *Holland*, 1984]:

$$(\text{nss-SO}_4^{2-}) = (\text{SO}_4^{2-}) - 0.252(\text{Na}^+) \quad (2)$$

The strong seasonality of biogenic sulfur released to the atmosphere results in well-defined annual oscillations of sulfate in WAIS Divide snow and ice cores [*Dixon et al.*, 2005]. Biogenic source sulfate reaches a peak during the austral summer months [*Minikin et al.*, 1998]. As such, nss-sulfate concentrations in snow peak from November to January and display a regular minima from May to August [*Dixon et al.*, 2005; *Minikin et al.*, 1998].

Annual cycles in nss-sulfate and Na$^+$ concentrations were discernable throughout the WDC05B core and were used to date this core. In the counting procedure, the nss-SO$_4^{2-}$ cycles served as the primary annual layer indicator, and

Na^+ cycles were used as a complementary indicator, particularly when nss-SO_4^{2-} cycles appeared ambiguous during large volcanic events. Using this annual layer counting technique, the WDC05B core was determined to cover the period from 1929 to 2002 (Figures 9 and 10). The appearance of volcanic sulfate from the Pinatubo eruption (1991) during 1993–1994 and the Agung eruption (1963) during 1964-1965 in West Antarctic snow [*Sigl et al.*, 2013] supports the accuracy of the annual layer counting (Figures 9 and 10). The analysis of the top 30 m of the WDC05B ice core yielded an annually resolved 73 year continuous chronology of snow chemical content.

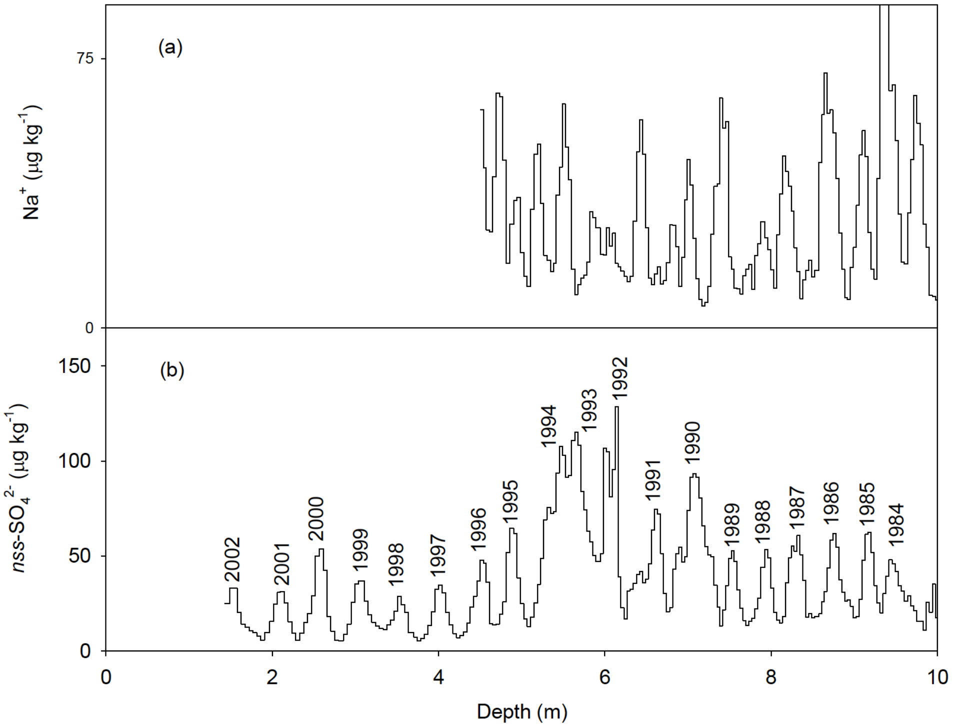

Figure 9. Concentrations of (a) Na^+ (b) nss-SO_4^{2-} from the 2005 WAIS Divide firn core (WDC05B) in depth 0-10 m. All data has been smoothed using unweighted 3-sample running mean. Annual layers are counted for austral summer peaks and winter minima in nss-SO_4^{2-} concentrations. Na^+ winter maxima are used as a complimentary indicator when nss-SO_4^{2-} peaks are ambiguous (i.e., depths 5.25-6 m). Note that the top 1.4 m of the core were not collected and thus not available. Sodium data were not developed for the top 4 m.

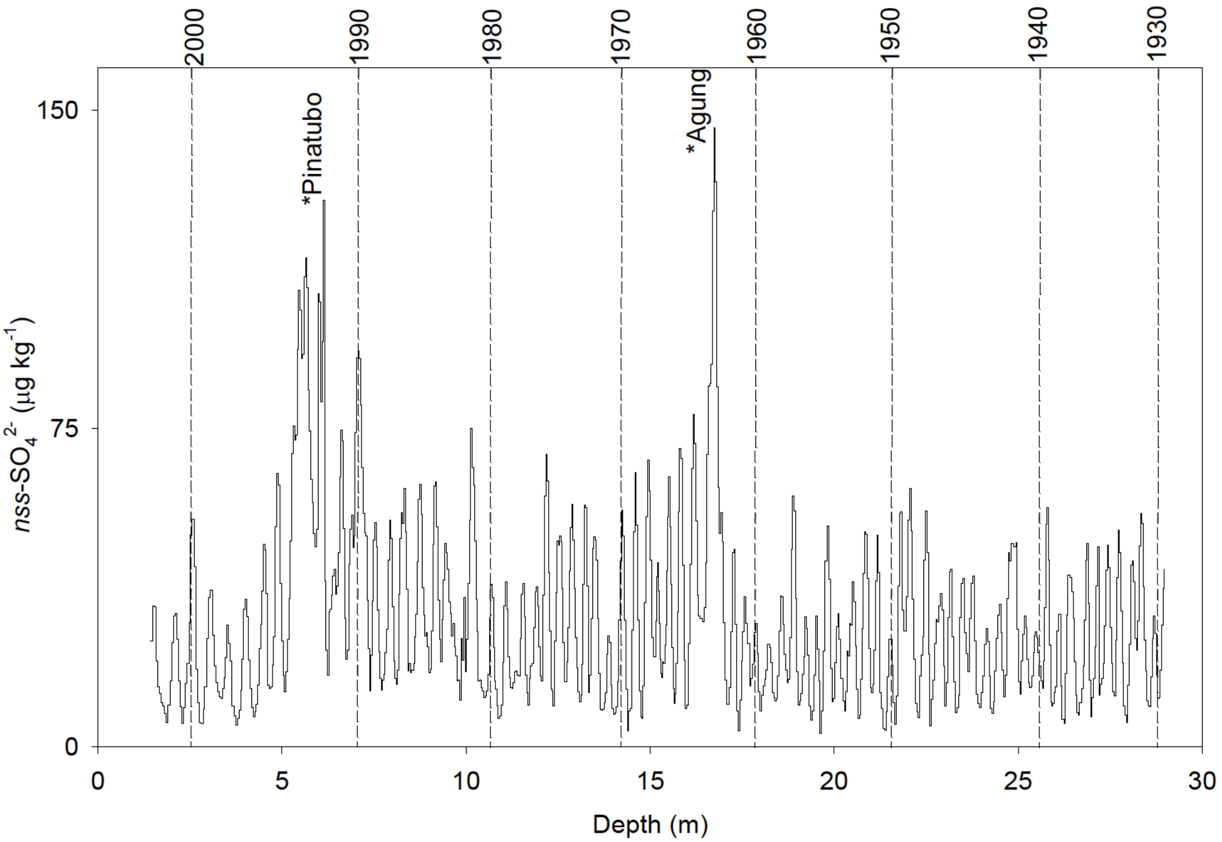

Figure 10. Depth profile of nss-sulfate concentrations in the 2005 WAIS Divide 30 m firn core (WDC05B) clearly show the sulfate fallout from the Mt. Pinatubo and Mt. Agung volcanic eruptions between depths 5.25-6 m and 16.5 -17 m, respectively. Data are smoothed with an unweighted three-sample running mean.

The 2013 WAIS Divide shallow snow core was dated using ALC of nss-sulfate (Figure 11) to cover the time period 1992-2013. The volcanic sulfate deposition from the eruption of Mt. Pinatubo in 1991 (the Pinatubo eruption deposition is seen in 1993-94 in Figure 11) supports the accuracy of the annual layer counting.

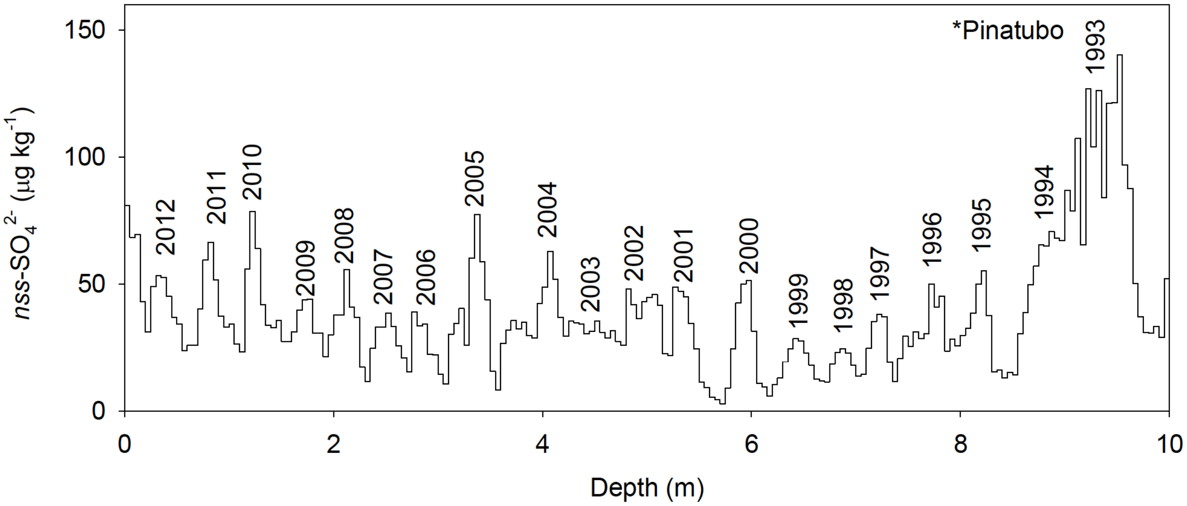

Figure 11. Concentrations of nss-SO$_4^{2-}$ from the 2013 WAIS Divide (WDC13) 10 m firn core. All data has been smoothed using unweighted 3-sample running mean. Annual layers are counted for austral summer peaks and winter minima in nss-SO$_4^{2-}$ concentrations.

The Dome A snowpit samples were dated using average annual snow accumulation rate of 2.36 cm w.e. calculated between the 2010 snow surface and the volcanic sulfate deposition from the eruption of Mt. Pinatubo in 1991 at the snow depth of 1.35 m (Figure 12) . The snowpit covers the time period from 1967 to 2010.

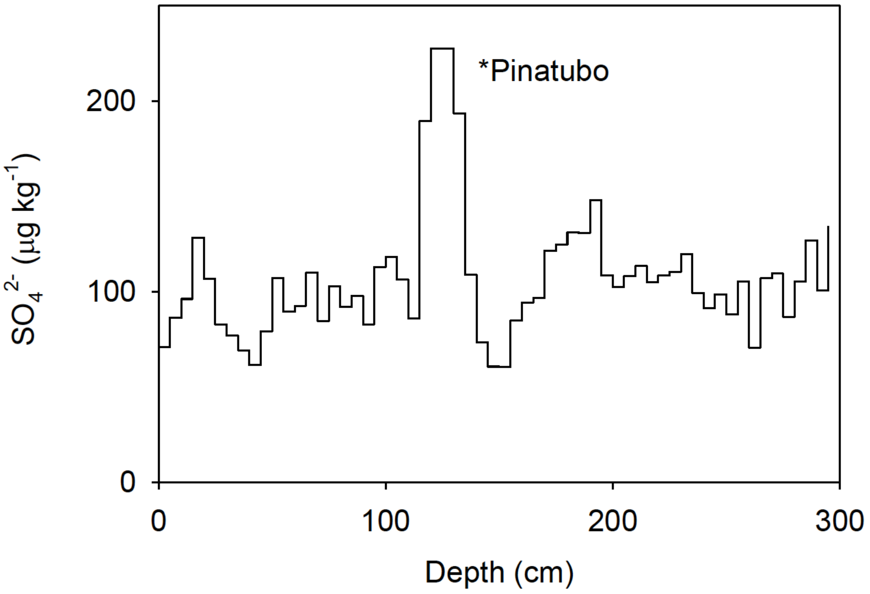

Figure 12. Depth profile of concentrations of sulfate in the Dome A snowpit displays the sulfate fallout from the Mt. Pinatubo (1991) volcanic eruption at 1.35 m snow depth.

2.7.3 Monthly dating

The temporal resolution of the discrete sampling and chemical analyses is high for all ice cores analyzed, with a range of 5 to 16 samples/measurements per year. The high-resolution analysis captures the annual peak-valley-peak variations in the concentration of nss-SO_4^{2-} in WAIS Divide snow [*Dixon et al.*, 2005] and of Na^+ in South Pole snow [*Cole-Dai et al.*, 1997a]. These cycles can be counted beginning at the top of a core to determine the depth-age relationship. Several of the cores (SP04C1, WDC05B, WDC13) used in this work are dated with this annual layer counting method resulting in high dating accuracy. To determine the months within an annual layer, the assumption is made that the snow accumulation rate during a year is constant. The annual layer thickness in water equivalent is subsequently divided into twelve equal parts representing the months. The measured concentrations of the chemical species in snow/ice samples within the year, weighted by the portions of the samples in a month, are attributed to the 12 month intervals. Because nss-SO_4^{2-} concentration peaks in mid-summer (December-January) in West Antarctica snow [*Dixon et al.*, 2005], the start of the annual layer in the WDC05B and WDC13 cores is assigned the month of January. The same approach is taken to convert the annual layer thickness into months in the SP04C1 core, where the annual layer marker is Na^+. Because Na^+ concentration reaches an annual minimum in mid-summer (December-January) in South Pole snow [*Cole-Dai and Mosley-Thompson*, 1999], the start of the annual layer in the SP04C1 core is assigned the month of January.

2.8 Data analyses

2.8.1 Dating smoothing

The continuous analysis of the SP04C1, WDC05B, and WDC13 ice cores yielded an average of 5-16 samples per year. Annual perchlorate concentration was determined by averaging the perchlorate concentrations of samples in the annual depth interval between two adjacent Na^+ (SP04C1) concentration minima or *nss*-SO_4^{2-} (WDC cores) concentration peaks. Where indicated, perchlorate concentrations were smoothed used the negative exponential smoothing function in a graphing software (SigmaPlot®, Systat Software Inc.), in which the data is weighted with a Gaussian weight function and fitted with a quadratic line.

2.8.2 Power spectral analysis

Any time series can be expressed as a combination of cosine (or sine) waves with differing periods and amplitudes (maximum/minimum value during the cycle). This fact can be utilized to examine the periodic (cyclical) behavior in a time series. In the area of time series called power spectral analysis, a time series can be viewed as a sum of cosine waves with varying amplitudes and frequencies. One goal of an analysis is to identify the important frequencies (or periods) in the observed series. A starting tool for doing this is the periodogram, which graphs a measure of the relative importance of possible frequency values that might explain the oscillation pattern of the observed data, and can be used to identify the dominant periods (or frequencies) of a time series.

A common example of utilizing a periodogram to identify any significant periods or regular oscillations that would otherwise be masked in the time series is the solar cycle. This can be done with Fast Fourier Transform and a publicly available dataset that lists the sunspot activity from the year 1750 until 1980 [*Minikin et al.*, 1998]. The series of data below (Figure 13) is semi-annual sunspot activity (smoothed number of sunspots) for 459 time periods. This is semi-annual data, so this is 459 divided by 2 is 229.5 years worth of data. The following time series plot shows ups and downs, but it is difficult to judge the span(s) of any regular periodicity.

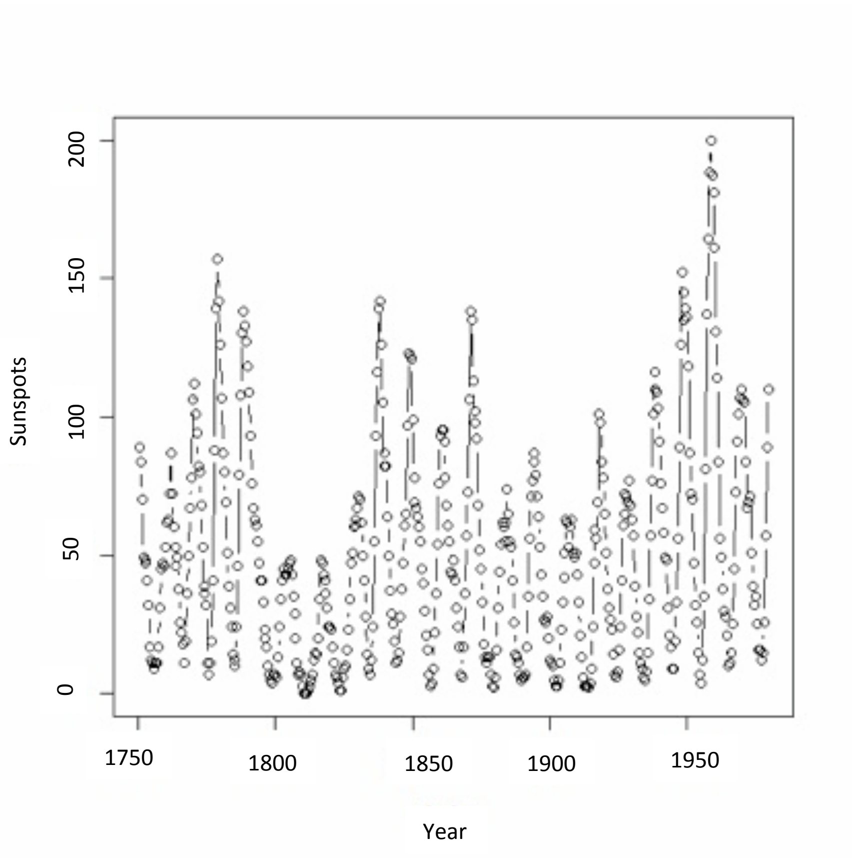

Figure 13. Semi-annual sunspot activity from the year 1750 until 1980. Figure from *Donahue and Baliunas* [1992].

To apply Fast Fourier Transform on this data, it needs to be detrended. This is done by calculating the difference in sunspots with the previous year. Once the dataset is detrended, the Fast Fourier Transform function is then applied to the Sunspots dataset [*Donahue and Baliunas*, 1992; *Toman*, 1966]. The result of this transform is the complex vector, Y. The periodogram for the sunspot activity shows the magnitude of Y squared, which is called the power, and a plot of power versus frequency (Figure 14). The periodicity can be determined by dividing 1/ frequency peak to determine the time period [*Donahue and Baliunas*, 1992]

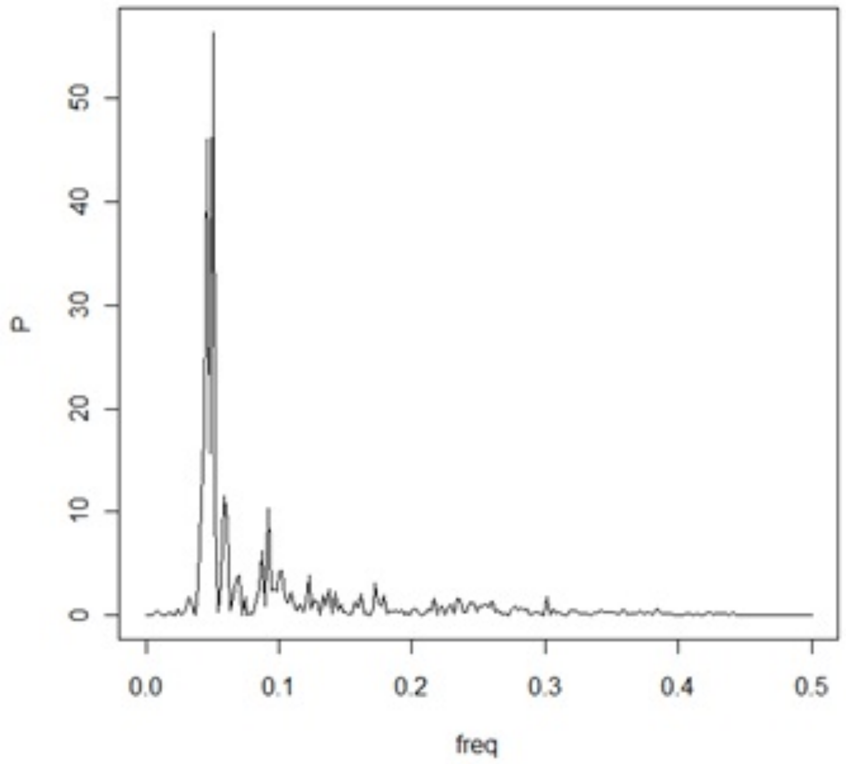

Figure 14. Example periodogram displaying power spectral analysis of sunspot activity (y-axis is Power and the x-axis is frequency) indicating a dominant peak occurs around a frequency of 0.05.

The dominant peak area occurs around a frequency of 0.05 (Figure 14). This corresponds to a period of about 1 divide by 0.05 is equivalent to 20 time periods. That is equivalent to 10 years since this is semi-annual data. Thus there appears to be a dominant periodicity of about 10-11 years in sunspot activity. This 10-11 year cyclical variation in sunspot counts, as discovered in 1843 by astronomer Samuel Heinrich Schwabe, is commonly known as the Sunspot Cycle [*Donahue and Baliunas*, 1992; *Toman*, 1966].

3. Depositional and post-depositional processes

Ice core records of perchlorate may provide insight into changes in source, what factors influence atmospheric perchlorate production, and how changes in the atmospheric concentration relate to changes in climate. Previous studies [*Furdui and Tomassini*, 2010; *Jackson et al.*, 2016; *Peterson et al.*, 2015a; *Peterson et al.*, 2015b; *Rao et al.*, 2012] have assumed that variations in perchlorate concentrations in snow are direct representation of variations in atmospheric concentrations of perchlorate. This assumption has been made in the past in regards to other ionic species in snow (i.e., nitrate, chloride, fluoride, etc.) [*Dominé et al.*, 1995; *Mayewski and Legrand*; *Neftel and Fuhrer*, 1993; *Staffelbach et al.*, 1991]. It was later determined that various depositional and post-depositional processes [*Curran et al.*, 2002; *Legrand et al.*, 1996; *Rothlisberger et al.*, 2002; *Santachiara et al.*, 2016; *Wagnon et al.*, 1999] can significantly affect the concentrations of these species in snow and complicate the interpretation of their records from ice cores. If it is assumed that perchlorate concentrations are stable in polar snow and are not significantly altered during or after deposition, this assumption should be verified. Without verification, interpretations of snow and ice core records of perchlorate could very well be incorrect and misleading. Thus, when past changes in atmospheric chemistry are to be derived from perchlorate records, the processes influencing the deposition and preservation of perchlorate ion in polar snow and ice should be examined. The deposition of perchlorate and the preservation of perchlorate concentration within the snowpack post deposition have not been previously explored. The perchlorate concentrations in snow and ice after extended periods of time depend not only on its atmospheric concentrations, but can also be influenced by the incorporation into to depositing snow and by possible alteration to the snow concentrations by physical and chemical processes inside the snowpack. Understanding of how these processes work to produce the amount of perchlorate observed in ice is needed if paleo-atmospheric concentration is to be inferred from ice core measurements.

3.1 Deposition

The chemical composition of polar snow depends on atmospheric components (gases and aerosols) and their deposition to the surface snow. Deposition of chemical species to the surface snow can be generalized into two categories: wet deposition and dry deposition. In polar regions, wet deposition occurs primarily by way of precipitation (snowfall). Aerosol are scavenged or removed from the atmosphere via nucleation scavenging – a process by which particles serve as cloud condensation nuclei [*Davidson et al.*, 1996]. In general, water vapor condenses on the condensation nuclei surface and continues to do so as a water droplet or snowflake is formed. In addition, some species may be incorporated, either by dissolution or adsorption, into droplets or snowflakes. As each snowflake grows from the initial condensation nuclei (aerosol or particle), the chemical composition in each snowflake is assumed to be the same at a given site and more accumulation (or less) will not change the concentration. However, the concentration in a flake may (actually likely to) be different between sites, even at sites with the same accumulation rate, because the concentration in flake is dependent on site-specific atmospheric conditions (scavenging efficiency). If the atmospheric conditions and scavenging efficiency are the same among various locations, then the concentrations of chemical species are likely to be similar across various locations despite differing accumulation rates [*Legrand and Delmas*, 1987; *Legrand and Mayewski*, 1997].

Dry deposition is simply the sedimentation (via gravity) of aerosol from the atmosphere directly onto the surface. It is likely that in most high-altitude polar regions that are characterized by very cold temperatures, dry air, and very low accumulation rate of snow, a large fraction of impurities undergo dry deposition [*Davidson et al.*, 1996; *Legrand and Delmas*, 1987; *Legrand and Mayewski*, 1997]. This distinction between depositional processes is important as snow concentrations at dry deposition sites can be influenced by accumulation rate: if the same amount of a chemical species dry deposits at a constant rate, increasing snow accumulation dilutes the concentration of the specie in snow. This dilution leads to variations in snow and ice core concentrations influenced by accumulation rate, even if atmospheric concentrations remain unchanged. Thus, an accurate interpretation of ice core data therefore requires knowledge of the deposition mechanism as well as the snow accumulation rate in the past in order to properly interpret ice core records from sites where dry deposition is significant.

3.1.1 Perchlorate deposition

Perchlorate concentrations within the snowpack are quite similar among various locations in Greenland, the Canadian Arctic, and North America despite dissimilar accumulation rates (Table 5). All of the Arctic locations where perchlorate level has been measured in snow experience moderate to high amounts of annual accumulation. The similarity in perchlorate concentration despite a wide range of accumulation rates suggests that perchlorate incorporation into surface snow in the Arctic is dominated by wet deposition.

Table 5. Surface snow (top 1 m) perchlorate levels and snow accumulation rates for various locations in the Antarctic, Arctic, and North America. Similarity among North American and Arctic levels despite varying accumulation rates suggest wet deposition is significant at high accumulation sites whereas the dissimilarity in the Antarctic levels suggests dry deposition is significant at low accumulations sites.

	Mean ClO_4^- Values (ng kg^{-1})		
Site	Surface snow	Accum. rate (cm w.e.a-1)	Ref.
Eclipse Ice Field, Canada	2.2 ± 2.0*	130	*Rao et al.* [2012]
Upper Fremont Glacier, USA	1.8 ± 0.7	76	*Rao et al.* [2012]
Devon Ice Cap, Canada	4.2 ± 2.5	24	*Furdui and Tomassini* [2010]
Summit, Greenland	1.7 ± 1.0	24	*Peterson* [2016]
Tunu, Greenland	6.0 ± 3.9	12.5	*Peterson* [2016]
Basin, Greenland	1.1 ± 0.5	41	*Peterson* [2016]
WAIS Divide	24 ± 16	20	This work
South Pole	70 ± 32	8.4	This work
Dome A	294 ± 67	2.3	This work

*Standard deviation (1σ)

In Antarctic surface snow, perchlorate levels are quite dissimilar and it appears surface concentrations are an order of magnitude greater at Dome A than at South Pole or WAIS Divide (Table 5). Two of the Antarctic locations (Dome A, South Pole) experience very low amounts of accumulation annually. It appears that perchlorate concentrations in surface snow are inversely proportional to the snow accumulation rate. The lower the snow accumulation, the higher the concentrations. This suggests that perchlorate probably undergoes significant dry deposition in Antarctica. It has been suggested [*Legrand and Mayewski*, 1997; *Legrand et al.*, 1999; *Legrand and Delmas*, 1984] that dry deposition is the dominant sink for atmospheric aerosols on the Antarctic plateau (i.e., South Pole, Dome A) and wet deposition predominates in the coastal and/or lower elevation areas of Antarctica (such as WAIS Divide). Dry deposition dominates the Antarctic plateau (South Pole and Dome A) because these sites experience very cold temperatures, dry air, and very low accumulation rates – meteorological and environmental conditions that promote dry deposition over wet deposition [*Gjessing*, 1984; *Santachiara et al.*, 2016; *Wolff et al.*, 1998].

The contributions from wet and dry deposition may be studied by analyzing the relationship between deposition flux and accumulation rate for a given site. Annual accumulation is calculated as the depth interval between two annual layer indicators (i.e., sulfate peaks at WAIS Divide, sodium minima at South Pole), whereas annual flux is the total mass deposited in a unit area during the year. Annual flux is calculated according to

$$Annual\ flux = \sum_{i=1}^{n} Sample\ (i)\ size\ \text{x}\ concentration(i). \qquad (3)$$

The annual perchlorate flux is compared with annual accumulation for a South Pole and WAIS Divide (Figure 15). There does not appear to be any correlation between the yearly precipitation and perchlorate flux at South Pole (Figure 15a; $R=0.05$, $n=14$, $p<0.05$); however, a positive correlation (Figure 15b; $R=0.90$, $n=14$, $p<0.001$) between annual accumulation and perchlorate flux at WAIS Divide suggests wet deposition - and not dry deposition – may be significant at WAIS Divide. Thus, it may be that wet deposition of perchlorate is significant at sites of high accumulation and dry deposition of perchlorate is significant at sites of low accumulation.

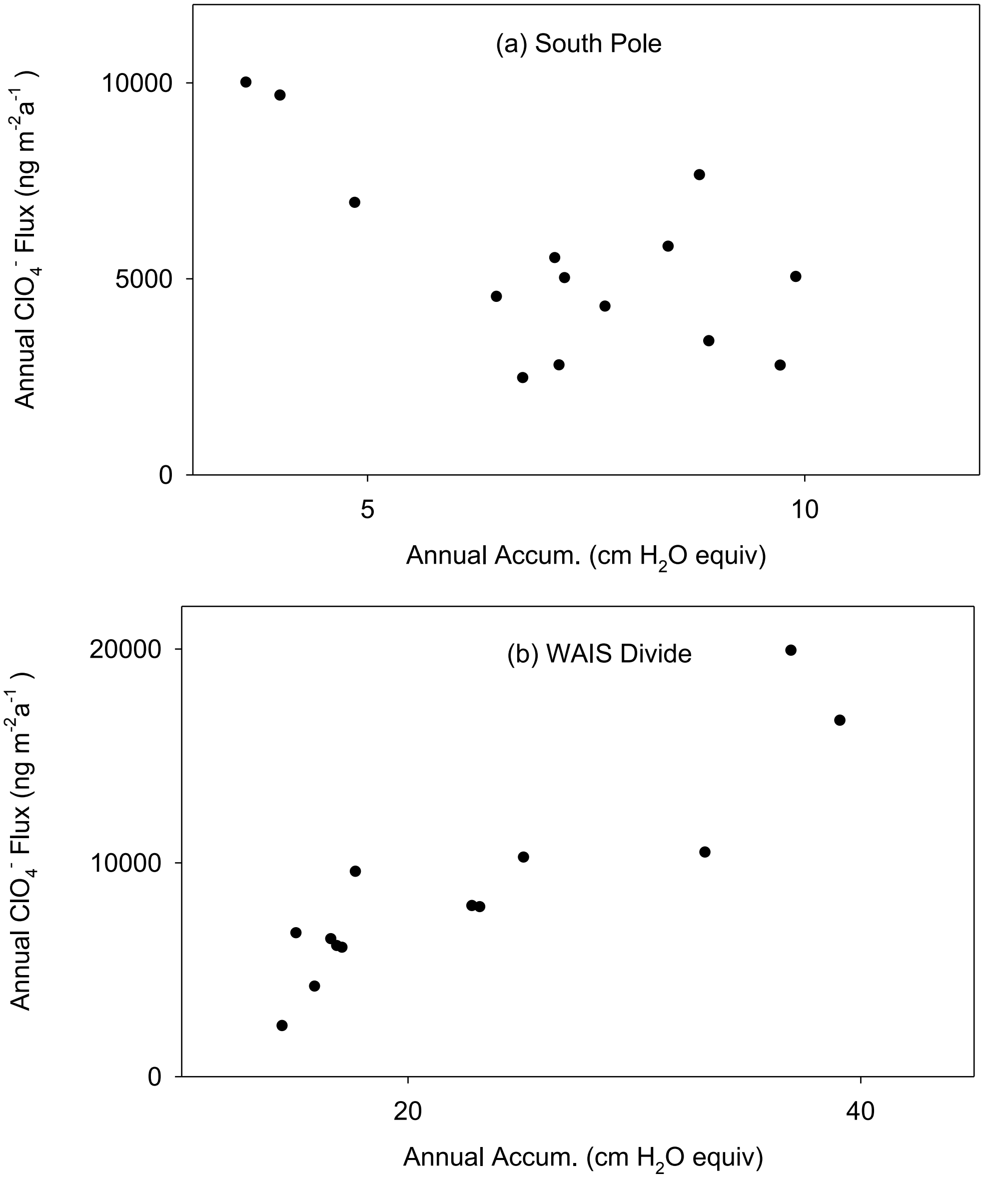

Figure 15. Annual accumulation versus annual perchlorate flux for (a) South Pole and (b) WAIS Divide. There does not appear to be any correlation between the annual amounts of precipitation and perchlorate flux at South Pole. However, a positive correlation between annual accumulation and perchlorate flux at WAIS Divide suggests wet deposition - and not dry deposition - is significant at WAIS Divide.

3.2 Post-depositional processes

Post-depositional processes affect the composition of polar snow and ice [*Curran et al.*, 2002; *Rothlisberger et al.*, 2002; *Santachiara et al.*, 2016]. The common processes that influence the composition of polar snow after deposition include sublimation of snow, volatilization of chemical species, and chemical and photochemical reactions in snow [*Santachiara et al.*, 2016]. These processes affect and alter the chemical composition of the snow surface, firn, and ice core, and therefore the actual air-to-snow transfer function.

It has been observed that at Antarctic locations of low snow accumulation, concentrations of certain chemical species in snow decrease with time or depth [*Röthlisberger et al.*, 2000b; *Wagnon et al.*, 1999; *Weller et al.*, 2004]. For example, at the South Pole, *Mayewski and Legrand* [1990] found that nitrate concentrations in near-surface snow are significantly higher than concentrations in deeper snow. They suggested that higher nitrate concentrations in snow fallen since the 1980s were due to increased fallout from stratospheric denitrification related to the development of the Antarctic ozone hole. However, subsequent studies [*Mulvaney et al.*, 1998; *Rothlisberger et al.*, 2002] found that the decreasing trend with depth observed at low-accumulation sites is the result of post-depositional loss of nitrate from the snowpack. The longer nitrate remains exposed to sunlight in near-surface snow, the greater the post-depositional loss and the lower the nitrate concentration becomes, consequently the decreasing concentration with depth (time). The emission of gaseous NO_x from the photolysis of nitrate in snow is recognized as the main mechanism for nitrate post-depositional loss [*Honrath et al.*, 2000;

Rothlisberger et al., 2002]. Similarly, post-depositional loss of chloride has been observed at low-accumulation locations; chloride loss is primarily due to release of volatile HCl from the snowpack [*Legrand et al.*, 1996; *Wagnon et al.*, 1999], rather than due to photochemical process.

At the time of this work, it was not known if perchlorate experiences significant changes in concentration post deposition within the polar snowpack. Thus, in order for proper interpretation of snow and ice core records of perchlorate, it is necessary to address the following questions: (1) is perchlorate removed or lost from the snowpack? (2) if perchlorate is lost from the snowpack, can this loss be quantified? (3) what, if any, site characteristics influence these post-depositional changes. As this is the first work to investigate post-depositional changes of perchlorate in polar snow, there is limited information and knowledge of perchlorate behavior in polar regions. However, there have been numerous studies surrounding post-depositional behavior of nitrate and chloride within the polar snow, and we can use these two species and their respective behaviors for comparison with perchlorate.

3.2.1 Perchlorate: a decreasing trend with depth

Perchlorate concentrations in the 2004 South Pole core (SP04C1) are highly variable. Relatively high concentrations (50– 150 ng kg^{-1}) in the top 3 meters of the core gradually decrease to values around 5 ng kg^{-1} over the deepest 5 meters of the core (Figure 16). This data are similar to the range and variability of perchlorate that *Jackson et al.* [2016] reported in surface snow in the McMurdo Dry Valleys, Antarctica.

The decrease in perchlorate concentration with depth at South Pole appears to be similar to the decreasing trends of nitrate and chloride and, therefore, suggests that the perchlorate trend could be the result of post-depositional loss.

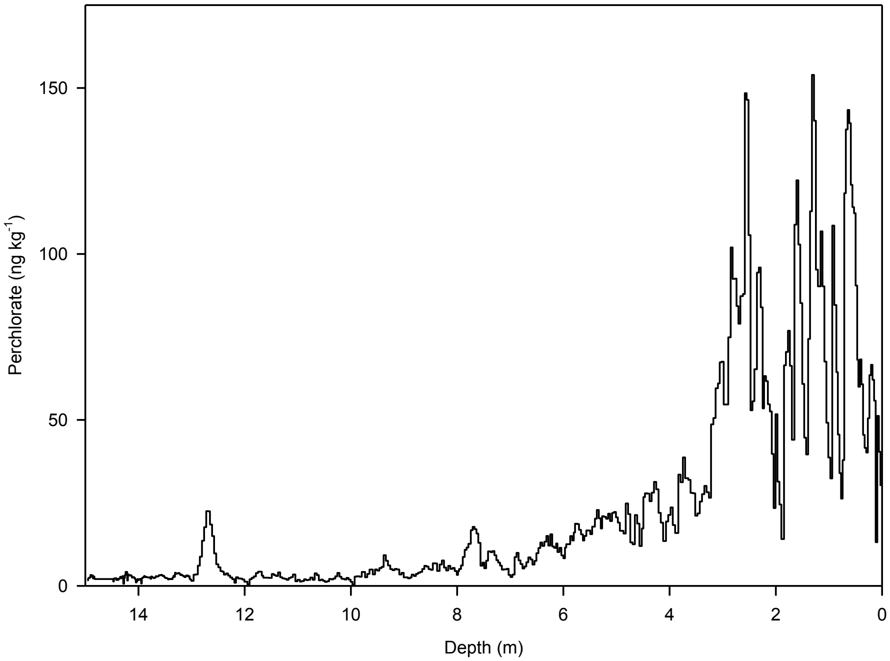

Figure 16. Depth profile of ClO_4^- concentrations in the South Pole 2004 (SP04C1)15 m firn core. Data are smoothed with an unweighted three-sample running mean.

3.2.2 Post-depositional loss of perchlorate in South Pole snow

A more recent record of perchlorate from the South Pole was developed via the analysis of the 2014 shallow core samples (SPC14). This profile (Figure 17), covering the time period 1962-2014, displays several years that overlap with the 2004 South Pole record. The SPC14 perchlorate profile also displays a decreasing trend with depth (Figure 17).

The question of whether perchlorate undergoes post-depositional changes within the snowpack can be addressed by comparing the more recent SPC14 record of perchlorate with the SP04C1 record. As these two ice cores were drilled at the same location, the environmental conditions influencing perchlorate concentration in snow are assumed to be the same in the two cores and time remains the only distinct factor influencing perchlorate concentrations between the two cores. If perchlorate concentrations are similar in each core during the overlapping years, then it is likely that perchlorate is preserved in South Pole snow and the interpretation of the record is less complex. If perchlorate concentrations are dissimilar in each core during the overlapping years, then it is likely that perchlorate is not preserved without change in South Pole snow and the interpretation of the record becomes quite complicated. The decrease in concentration in the SPC14 core appears to occur in the early 2000s, which is inconsistent with the timing of the decrease observed in the SP04C1 record (Figure 16), thus, reinforcing the hypothesis of a previous ice core and snow-pit study that the preservation of perchlorate in snow in questionable. Furthermore, perchlorate concentrations during the overlapping years of the SP04C1 and SPC14 records appear to be different, with the SPC14 concentrations significantly less than the SP04C1 concentrations (Figure 18). This suggests that post-depositional changes resulting in a net loss of perchlorate concentration are significant in the upper snow layers at South Pole, providing further support for post-depositional loss of perchlorate within the polar snowpack.

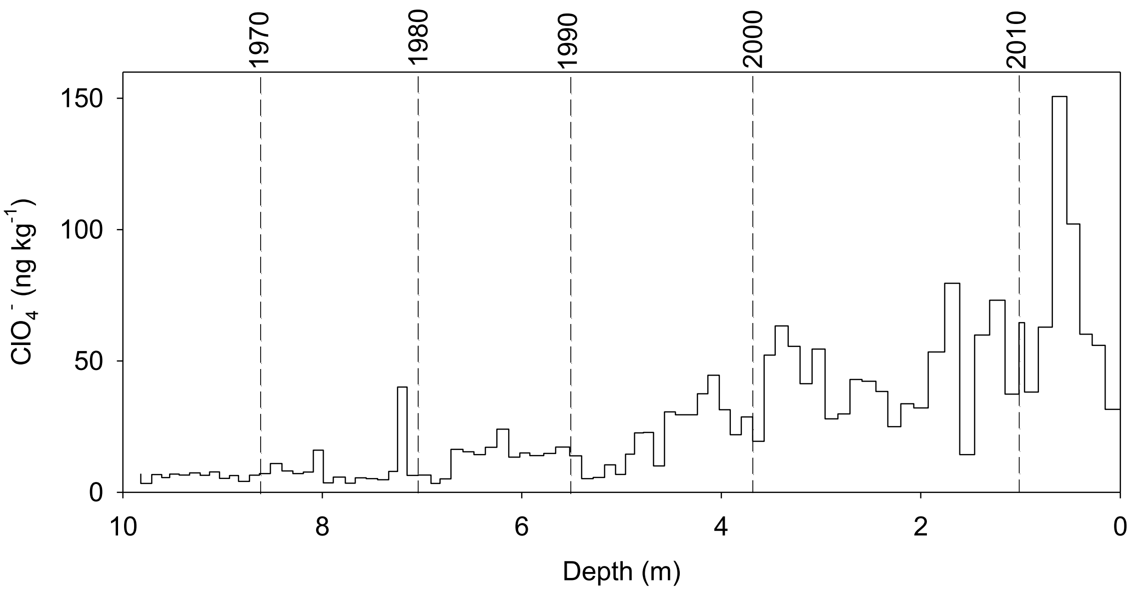

Figure 17. Profile for perchlorate from the 2014 South Pole shallow (SPC14) core.

It is likely that perchlorate undergoes significant changes in concentration post deposition within the polar snowpack. Thus, in order for proper interpretation of snow and ice core records of perchlorate, it is necessary to answer the following questions: (1) how is perchlorate removed or lost from the snowpack, (2) how much is lost from the snowpack, and (3) what, if any, site characteristics influence these post-depositional changes.

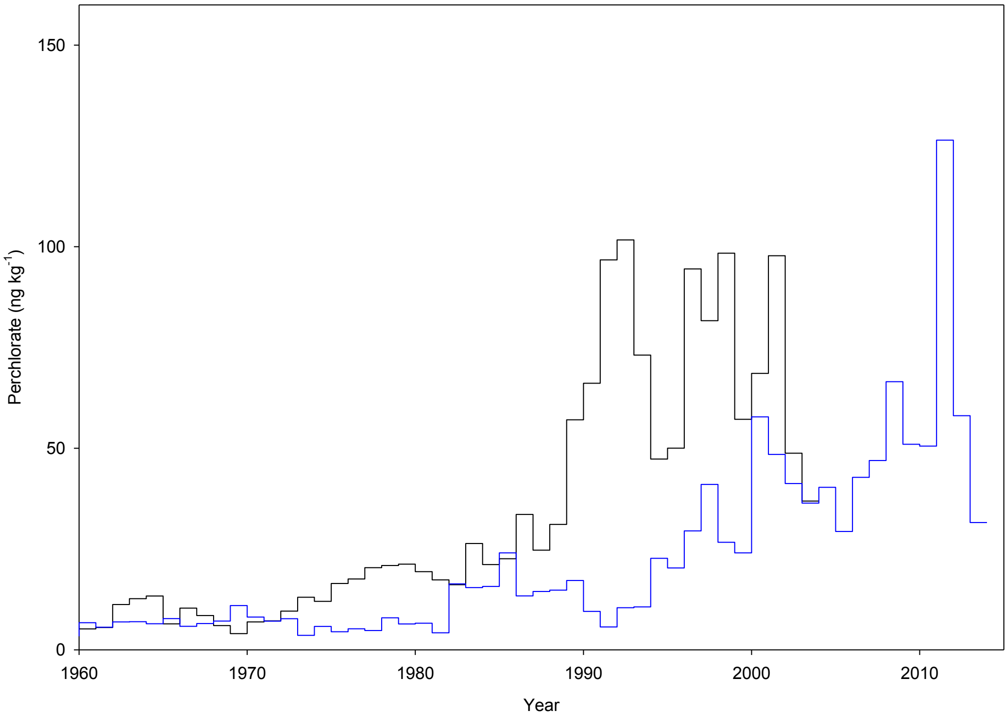

Figure 18. A comparison of the two overlapping perchlorate records from the South Pole: annual averages from the SP04 core (black) and the SPC14 core (blue).

3.2.3 Perchlorate loss mechanism

A similar decreasing perchlorate trend with depth is also evident in the Dome A samples (Figure 19). It has been observed [*De Angelis and Legrand*, 1995; *Diehl et al.*, 1995; *Dominé et al.*, 1995; *Legrand et al.*, 1996; *Wagnon et al.*, 1999; *Weller et al.*, 2004] at sites on the East Antarctic plateau that chloride concentration also display a decreasing trend with depth. Recall that chloride is a chemical species that undergoes post-depositional change, with chloride loss attributed primarily due to release of volatile HCl from the snowpack. This loss mechanism can be considered for perchlorate, yet loss of perchlorate as perchloric acid ($HClO_4$) is unlikely because perchloric acid is not considered a volatile compound [*Mendiratta* *et al.*, 2000] and has a low vapor pressure at room temperature [*Pearce and Nelson*, 1933; *Robinson and Baker*, 1946]. At the extremely cold temperatures in polar snow, perchloric acid would likely have an even lower vapor pressure. This suggests that, if perchlorate undergoes post-depositional loss in Antarctic snow, the process is likely not due to vaporization.

Recall that the photolysis of nitrate in snow is recognized as the main mechanism for nitrate post-depositional loss. This same mechanism can be considered for perchlorate. It has been previously assumed that photolytic loss of perchlorate is negligible [*Jaegle et al.*, 1996]. Furthermore, the rate of decreasing perchlorate with depth is much lower than that of nitrate at Dome A (Figure 19). Photolysis experiments of concentrated (6 M) aqueous $HClO_4$ resulted in production of ClO_2^- [*Huie and Peterson*, 1983]. Yet, an aqueous solution of 3 M $HClO_4$ was not observed to undergo any photolytic decomposition [*Huie and Peterson*, 1983]. As perchlorate concentrations in polar snow are not concentrated enough to undergo photochemical activity, it is highly unlikely that photolysis is responsible for the change in perchlorate concentration post deposition. As such, the process(es) causing the changes in perchlorate concentration in the polar snowpack remains undetermined and further research into the behavior of perchlorate is necessary.

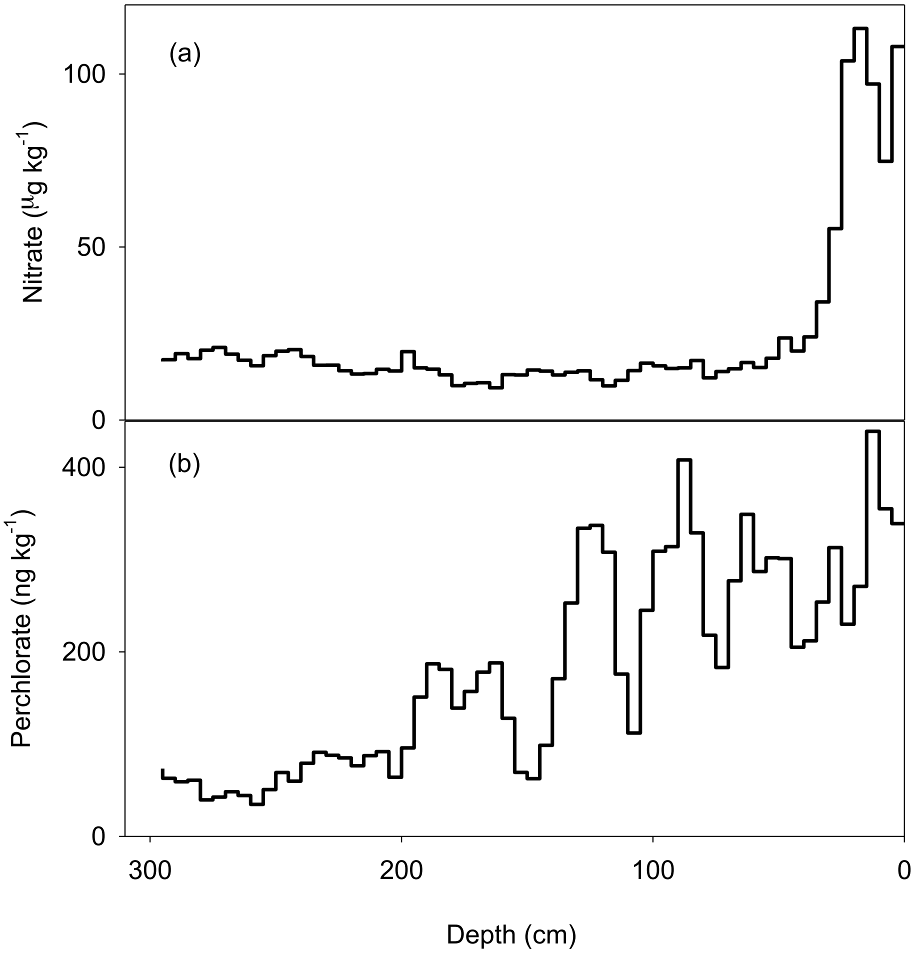

Figure 19. Depth profiles of (a) nitrate and (b) perchlorate from the Dome A snowpit. The decrease of nitrate due (due to post-depositional loss) is more rapid than that of perchlorate.

3.2.4 Quantifying post-depositional loss

By comparing the respective concentrations from the 2004 and 2014 South Pole records during the overlapping years, the post-depositional loss of perchlorate may be quantified. The annual mean perchlorate levels for both records during the overlapping years are listed in Table 6.

Table 6. A comparison of the annual mean concentrations from the South Pole perchlorate records (SP04 and SPC14). Percent loss is determined by the following equation: $\% \boldsymbol{Loss} = \frac{(C_{SP04} - C_{SPC14})}{C_{SP04}} * \mathbf{100}\%$ where C_{SP04} and C_{SPC14} are the respective mean concentrations from that record for a given year.

Annual Mean ClO_4^- (ng kg^{-1})			
Year	SP04C1	SPC14	% Loss
2004	36.9	36.4	1.4
2003	48.8	41.2	15.4
2002	97.8	48.5	50.4
2001	68.6	57.8	15.7
2000	57.2	24.0	58.0
1999	98.4	26.7	72.9
1998	81.6	41.0	49.8
1997	94.5	29.5	68.8
1996	50.0	20.3	59.4
1995	47.3	22.7	52.0
1994	73.1	10.7	85.4
1993	101.7	10.4	89.7
1992	96.7	5.7	94.1

AVG: 54 ± 28 %

In several of the more recent years, the difference between the two records is less than 20%. However, by the depths representing the year 2000, there is as a 50% difference between the two records (Table 6). There is an average annual loss of 50% of perchlorate between the years 1984-2004, suggesting that perchlorate undergoes significant post-depositional changes resulting in loss of concentration within the snowpack at South Pole. As the small difference (less than 20%) in relative concentration during the most overlapping recent years (2003-2004) indicates minimal loss, it is likely that post-depositional process(es) influencing perchlorate does not take place in the surface snow. It appears loss became significant by the year 2002; this year corresponds to approximately 3.8 m depth in the SPC14 core. A significant amount (95%) of light does not penetrate below the top 10-20 centimeters of the snowpack [*Beaglehole et al.*, 1998; *Perovich*; *Warren et al.*, 2006] and very little light is expected to penetrate to approximately 3.8 m snow depth, thus further supporting the inference that photolysis is not the process causing the loss of perchlorate. Although the significance of this depth (where the loss of perchlorate begins to occur) is not fully understood at this time, it may be useful in interpreting future ice core projects involving perchlorate.

3.3 Preservation of perchlorate in snow

As the loss mechanism or post-depositional process(es) influencing perchlorate concentration in polar snow remain uncertain, it is possible that perchlorate loss may also occur in WAIS Divide snow. Perchlorate concentrations in the 2005 WAIS Divide core (WDC05B) are variable with moderate concentrations on the range of 10 - 60 ng kg^{-1} in the top 3 m that gradually decrease to values around 5 ng kg^{-1} over the deepest 5 m of the core (Figure 20).

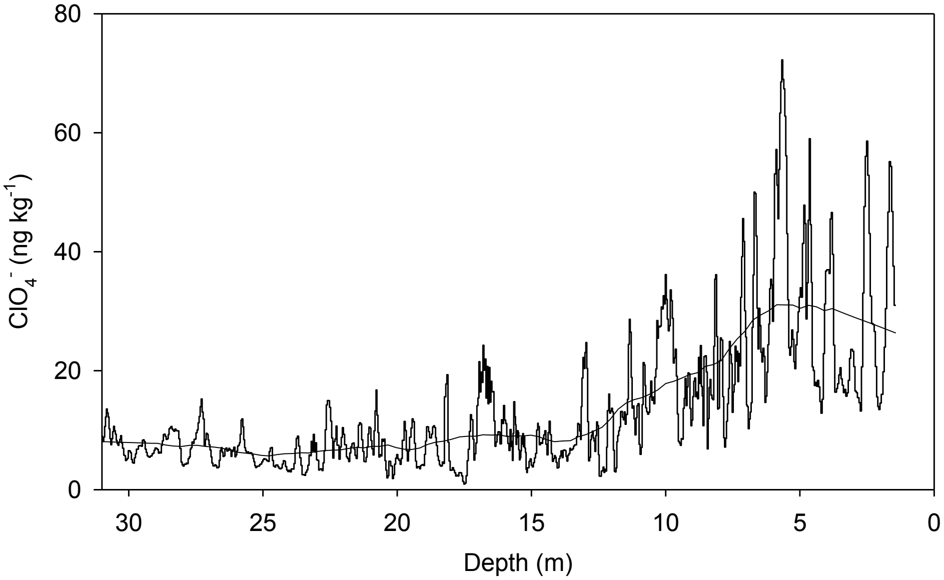

Figure 20. Depth profile of ClO_4^- concentrations in the top 30 m of the 2005 WAIS Divide (WDC05B) core. The smooth solid line represents perchlorate data smoothed by using a negative exponential smoothing function in SigmaPlot.

The decreasing trend in the WAIS Divide core is much more gradual than that of the South Pole or Dome A profiles. Additionally, a more recent perchlorate profile developed from a 2013 WAIS Divide shallow core (WDC13) does not display a decreasing trend (Figure 21). The WDC13 core was determined to cover the time period 1992-2013, with several years of data overlapping with the 2005 record.

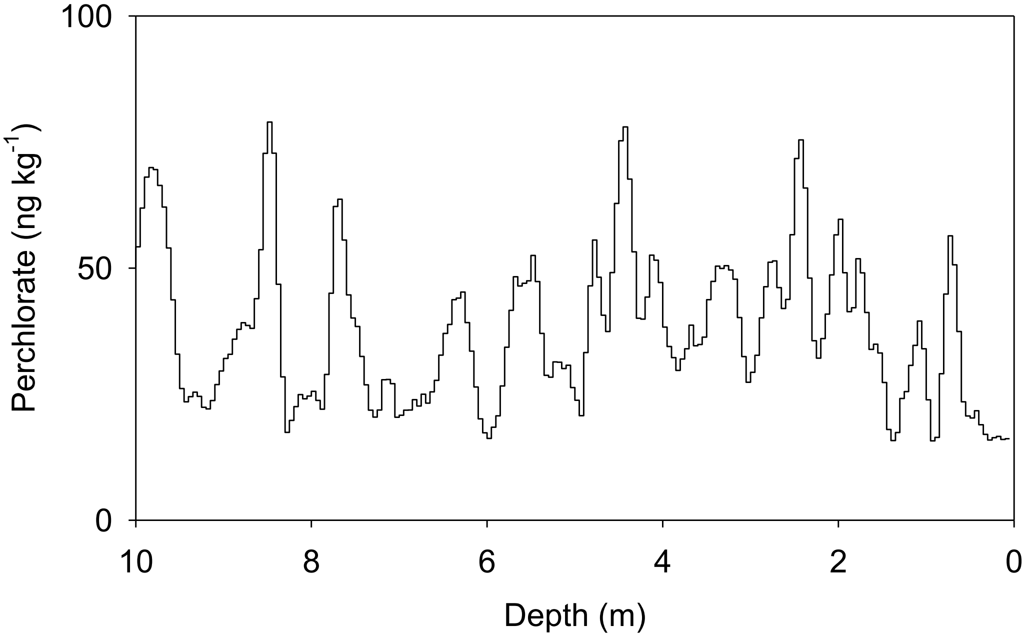

Figure 21. Depth profile of ClO_4^- concentrations in the 2013 WAIS Divide 10 m shallow core. Data are smoothed with an unweighted three-sample running mean.

A comparison of the two WAIS Divide perchlorate profiles indicates similar levels during the overlapping years (Figure 22). This suggests that perchlorate is irreversibly deposited and thus preserved without alteration within the snowpack at WAIS Divide. As such, it is likely that perchlorate is preserved and does not experience changes in concentration in the snow at WAIS Divide; whereas, perchlorate is not preserved well and does experience changes in concentration in South Pole or Dome A snow. This is similar to the preservation of nitrate, in that nitrate undergoes post-depositional changes in the snow on the Antarctic plateau (i.e., South Pole, Dome A) but not West Antarctica [*Rothlisberger et al.*, 2002].

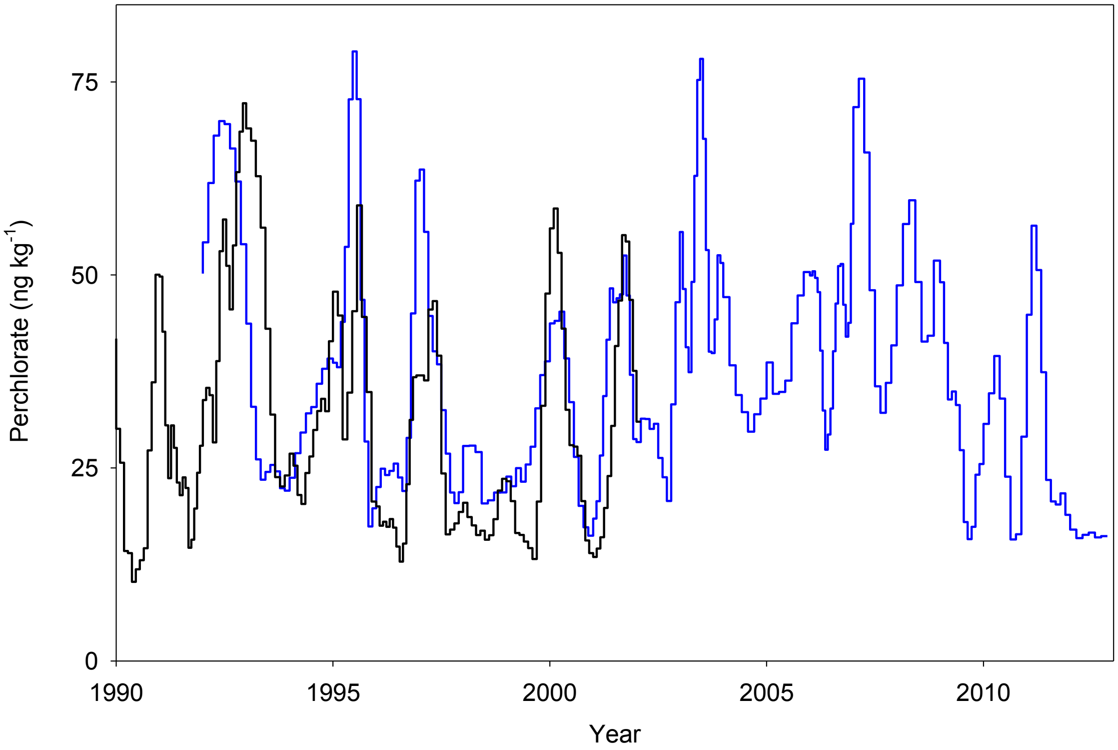

Figure 22. A comparison of the two overlapping perchlorate records from WAIS Divide: the 2005 record (WDC05B) in black and the 2013 (WDC13) record in blue.

3.4 Characteristics of sites with post-depositional changes

Many post-depositional processes affect the composition of glacial ice. These processes affect and continuously alter the chemical composition of the snow surface, firn, and ice core. Post-depositional losses are partly well documented and described, especially for low accumulation sites in Antarctica and central Greenland [*De Angelis and Legrand*, 1995; *Delmas et al.*, 2004; *Legrand et al.*, 1996; *Rothlisberger et al.*, 2002; *Röthlisberger et al.*, 2000b; *Wagnon et al.*, 1999]. The influence of accumulation rate and temperature on the chemical concentrations has also been described in several previous investigations [*Legrand et al.*, 1996; *Rothlisberger et al.*, 2002; *Wagnon et al.*, 1999].

3.4.1 Accumulation Rate and Temperature

As nitrate concentrations in polar snow are related to the accumulation rate [*Rothlisberger et al.*, 2002; *Röthlisberger et al.*, 2000b], a relationship may also exist between perchlorate concentrations and accumulation rate. At low-accumulation sites (<10 cm w.e.a^{-1}), the typical nitrate profile of the top meters shows a sharp decrease with depth and stable concentrations with little variation thereafter [*Mayewski and Legrand*, 1990; *Röthlisberger et al.*, 2000b]. The decrease in nitrate concentration in the upper snow layers is attributed to post-depositional concentration changes. At sites with higher accumulation rates such as WAIS Divide, the typical nitrate profile looks quite different; the surface concentrations are lower than in the low-accumulation sites, but they decay less, so that generally higher mean concentrations and annual fluctuations are seen below the surface [*Fischer et al.*, 1998; *Rothlisberger et al.*, 2002; *Röthlisberger et al.*, 2000b; *Wagenbach et al.*, 1998; *Wolff*, 1995]. The loss is due to the longer nitrate remains exposed to sunlight in near-surface snow, the greater the post-depositional loss and the lower the nitrate concentration becomes, consequently the decreasing concentration with depth (time). A similar relationship between perchlorate and accumulation rate may also exist. Table 7 shows that the surface concentrations of perchlorate are lower at a high accumulation site (WAIS Divide) than in the low-accumulation sites (South Pole, Dome A), but the degree of decrease is less, so that generally higher mean concentrations and annual fluctuations are seen below the surface. It may be that at sites with higher accumulation, perchlorate is buried at a sufficient rate so that it does not remain in surface snow for an extended period of time, thus limiting the effects of the post-depositional processes.

Table 7. Accumulation rate, mean annual surface temperature, and mean surface snow (top 1 m) perchlorate concentrations for South Pole, Dome A and WAIS Divide. Climatology data for South Pole, Dome A, and WAIS Divide obtained from *Lazzara et al.* [2012] *Hou et al.* [2007] and *Fegyveresi et al.* [2016] respectively.

Site	Mean Surface Snow ClO_4^- Values (ng kg^{-1})	Mean Temp. (C)	Accum. rate (cm w.e.a^{-1})
South Pole	70 ± 32*	-49	8.4
Dome A	294 ± 67	-59	2.3
WAIS Divide	24 ± 16	-31	20

*Standard deviation (1σ)

Another factor which may potentially influence perchlorate concentration in snow is temperature. As seen with nitrate, at colder temperatures the ice-air concentration ratio of HNO_3 is shifted toward higher snow concentrations at a given atmospheric concentration [*Abbatt*, 1997]. This is due to a tendency for a higher uptake of nitrate in the snowflake surface from the air at lower temperatures [*Rothlisberger et al.*, 2002]. A similar tendency may occur with perchlorate, as there are higher perchlorate concentrations in surface snow at sites with colder temperatures (Table 7). However, the relationship of perchlorate concentration and surface temperature is merely speculative and requires future work.

3.5 Conclusion

The surface snow perchlorate levels in the Arctic and North America are similar in concentration and range despite varying rates of accumulation. In the Antarctic, however, surface snow perchlorate levels appear to be inversely proportioned to the snow accumulation rate: the lower the snow accumulation, the higher the concentrations. This relationship between snow accumulation and concentration suggest that perchlorate undergo significant dry deposition at low accumulation sites, whereas the similar concentrations in the Arctic suggest wet deposition at high accumulation sites. It is likely that wet deposition of perchlorate is significant at sites of high accumulation and dry deposition is significant at sites where accumulation is low such as South Pole and Dome A. This is important as dry deposition can complicate ice core records of perchlorate in that changes in accumulation can dilute or enhance perchlorate concentrations even if atmospheric concentrations or the amount deposited remains unchanged. As such, an accurate interpretation of perchlorate data from low accumulation sites therefore requires knowledge of the mean snow accumulation rate over the past.

It is also likely that perchlorate is reversibly deposited in snow at low accumulation sites and undergoes significant post-depositional loss of approximately 50% of initial concentration. Other chemical species (i.e., nitrate, chloride) that undergo photochemical process or volatile acid gas formation result in decrease of concentration with depth (time) post deposition. These behaviors are considered for perchlorate loss. Perchloric acid is not known to be volatile and it is highly unlikely that perchloric acid volatilizes in the extremely cold temperatures in polar snow. It is also unlikely that the mechanism causing post-depositional loss of perchlorate is photolysis, as perchlorate has only been observed to undergo photolysis in aqueous solutions of concentrations greater than 3 M [*Huie and Peterson*, 1983]. As such, the mechanism causing the loss of perchlorate concentration in snow remains unclear and further research into the behavior of perchlorate within the polar snowpack is necessary.

It is likely that perchlorate undergoes dry deposition and post-depositional loss at low accumulation sites. There may be a relationship between dry deposition and post-depositional loss of perchlorate. Perchlorate aerosol that is dry deposited may be situated in the thin liquid-layer on the snowflake surface. It has been suggested [*Boxe and Saiz-Lopez*, 2009; *Marcotte et al.*, 2015; *Weller et al.*, 2004] that processes taking place in the superficial thin liquid-layer alter the concentrations of ionic impurities on the snowflake (and consequently the snowpack). Similar to other ionic species, the process causing the loss of perchlorate may also be related to dry deposition and the thin liquid-layer of snowflakes. However, this suggested relationship between dry deposition and post-depositional loss is purely speculative and also requires future work. Although, as perchlorate is preserved within the snow at WAIS Divide, it is likely that at sites with higher accumulation, perchlorate is buried at a sufficient rate so that it does not remain in surface snow for an extended period of time, thus limiting the effects of the post-depositional processes. This indicates that although perchlorate is not preserved in the snowpack at Dome A or South Pole, it is preserved well in WAIS Divide snow – thus allowing for a viable ice core record of perchlorate from the Antarctic that is uncomplicated by post-depositional loss that can be used to investigate the atmospheric production of perchlorate.

4. Long term perchlorate trend: implications for production

Time-series of the ionic composition in polar ice cores can provide detailed direct and proxy records of seasonal to millennial scale fluctuations in climate, atmospheric chemistry, and volcanic activity. One of the motivations of this work was to explore how atmospheric chemistry, climate, and volcanic activity influence perchlorate levels. Even though questions surrounding the source(s) and air-to-snow transfer of perchlorate have not all been entirely resolved, the notion remains that ice cores from polar ice sheets (Greenland and Antarctica) likely hold the best hope [*Peterson et al.*, 2015b; *Roberts*, 2009] of retrieving detailed paleoatmospheric records of perchlorate.

The physical and chemical environments of Greenland and Antarctica share some similarities but are also quite different. The Arctic and Antarctic have opposite land-sea arrangements: in the Arctic there is an ocean surrounded by continents, while the Antarctic is a continent surrounded by oceans. These differences in the arrangement of land and water contribute to differences in each polar region's climate, oceanic and atmospheric circulation patterns, and sea ice [*Legrand and Mayewski*]. Therefore ice core records of perchlorate from both Greenland and Antarctica are needed to investigate global changes in perchlorate levels. There are currently several ice core records of perchlorate from the Arctic [*Furdui and Tomassini*, 2010; *Peterson et al.*, 2015a; *Peterson et al.*, 2015b]; however, prior to this work, few data on perchlorate in the Antarctic exist [*Jiang et al.*, 2013].

4.1 Perchlorate trends in Arctic snow

Peterson [2016] recently compiled a 300-year perchlorate record from a Greenland ice core that reveals environmental perchlorate concentrations were remarkably stable between 1700 and 1980 (Figure 23). *Peterson* [2016] reported that average perchlorate concentration between 1700 and 1850 (1.0 ± 0.7 ng kg^{-1}) is the same as that between 1850 and 1980 (1.0 ± 0.9 ng kg^{-1}). This is strong evidence that the onset of the Industrial Revolution or the use of Chilean nitrate fertilizers since 1830 did not increase the level of perchlorate in Greenlandic snow. In contrast, the average perchlorate concentration between 1980 and 2007 (2.7 ± 2.1 ng kg^{-1}) is higher by almost a factor of 3 than the pre-Industrial Revolution concentrations [*Peterson*, 2016]. Table 8 shows that this large increase in environmental perchlorate since 1980 was also observed in ice core records from other Greenland locations [*Peterson*, 2016]. Ice core records from Wyoming, USA and Yukon, Canada [*Rao et al.*, 2012] also display similar amounts of increase in perchlorate since 1980 (Table 8).

The North American and Arctic perchlorate profiles were developed from locations that experience moderate to high amounts of annual accumulation, ranging from 12.5 to 130 cm. w.e.a^{-1} (Table 5). The overlapping perchlorate profiles from both South Pole and West Antarctica suggest that perchlorate undergoes post-depositional loss only at very low accumulation sites (less than 10 cm. w.e.a^{-1}). Thus, it is unlikely that the North American and Arctic perchlorate profiles are influenced by post-depositional loss.

The increasing trend in perchlorate levels since 1980 in both North American and Arctic snow indicates additional perchlorate likely entered the environment. Despite limited available data on industrial perchlorate production, analysis by *Dasgupta et al.* [2005] suggested that more perchlorate may have been released into the environment because the industrial production of perchlorate increased around 1980. The most likely human activities contributing to environmental perchlorate are perchlorate's use as an oxidizer in large scale activities [*Dasgupta et al.*, 2006]. The impact of perchlorate as an oxidizer in space shuttle launches could be detected in ice core records. This is because when perchlorate is used as an oxidizer in space shuttle launches, it is often released into the atmosphere where it can undergo more widespread distribution [*Lang et al.*, 2002].

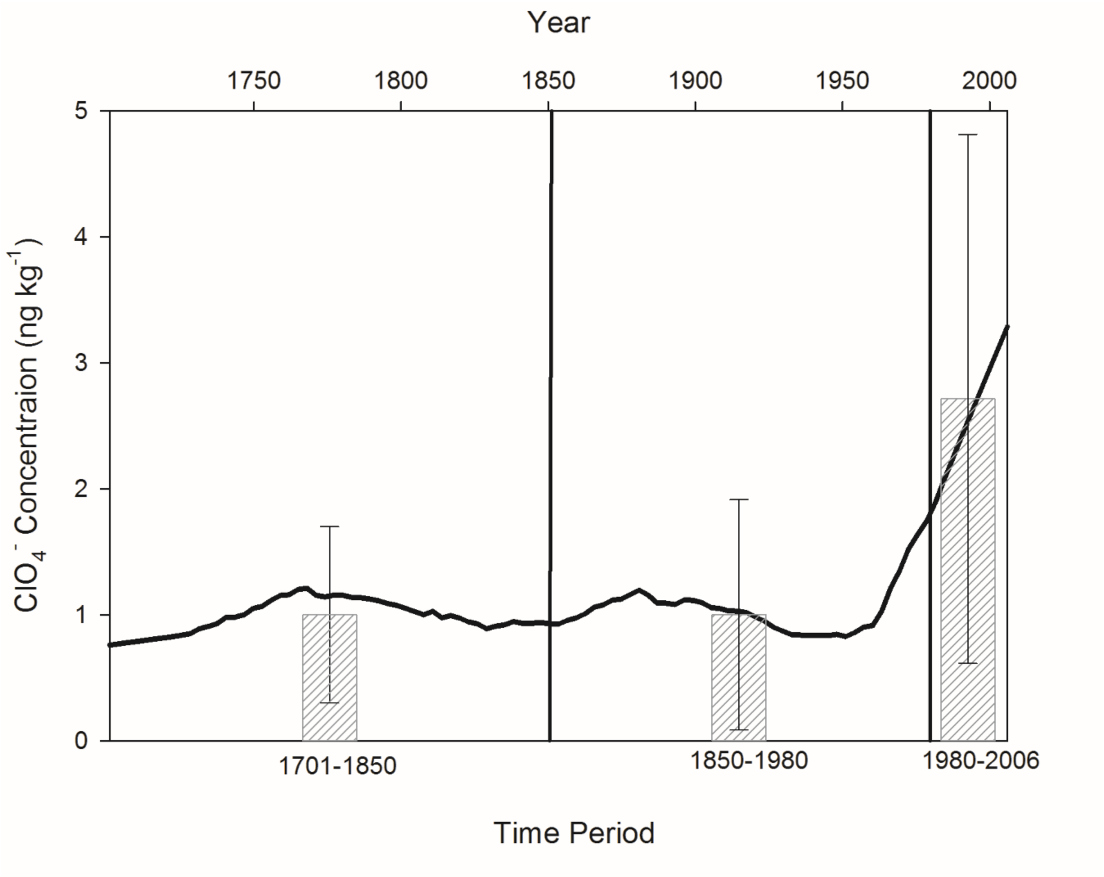

Figure 23. Perchlorate concentrations in Summit, Greenland snow (1700-2007). The bold black line is annual perchlorate concentrations that have been smoothed using a running average with a 0.1 sampling proportion. The vertical bars represent the average perchlorate concentration for each time period, with standard deviation as error bars. Figure adapted from *Peterson* [2016].

Due to its high solubility and the low volatility of perchlorate salts, perchlorate pollution from disposal is likely removed via precipitation and generally remains localized [*Dasgupta et al.*, 2006; *Rajagopalan et al.*, 2009]. Perchlorate in localized pollution may become airborne and is likely associated with dust [*Vella et al.*, 2015], which is generally not transported efficiently in the atmosphere [*Maher et al.*, 2010], and therefore, is unlikely to be recorded in polar snow. Because of the tendency of perchlorate pollution to remain localized to the source of the release [*Dasgupta et* *al.*, 2006; *Gu and Coates*, 2006], the disposal of perchlorate by manufacturing plants and perchlorate users unlikely explains the significant increase in perchlorate levels after 1980 in the Greenland ice core records. Thus, it is more likely the direct release of perchlorate from anthropogenic applications is not a significant cause of the increase since 1980. It seems likely that there is another source of perchlorate, or that atmospheric conditions changed in a way that promotes the atmospheric production of perchlorate and is contributing to the post-1980 increase that is observed throughout Greenland and in the Canadian Arctic.

Table 8. Comparison of mean perchlorate levels in snow and ice samples from various sites in the Northern Hemisphere: Greenland, northern Canada, and Wyoming, USA.

	Mean ClO_4^- Values (ng kg^{-1})		
Site	Post-1980	Pre-1980	Ref.
Eclipse Ice Field, Canada	2.2 ± 2.0*	0.6 ± 0.3	*Rao et al.* [2012]
Upper Fremont Glacier, USA	1.8 ± 0.7	N/A	*Rao et al.* [2012]
Summit, Greenland	2.7 ± 2.1	1.0 ± 0.8	*Peterson* [2016]
Tunu, Greenland	3.6 ± 3.5	1.0 ± 1.1	*Peterson* [2016]
Basin, Greenland	2.8 ± 3.1	0.9 ± 0.6	*Peterson* [2016]

*Standard deviation (1σ)

4.2 Perchlorate trends in Antarctic snow

Perchlorate records from Antarctic snow (South Pole, West Antarctica, Dome A) covering the 20th century allow for the comparison of perchlorate trends between the Arctic and the Antarctic. However, it is likely that the trends at South Pole and Dome A are significantly influenced by post-depositional loss processes**.** Significant post-depositional change in perchlorate concentration does not appear to occur in WAIS Divide snow; this is likely due to the much higher rate of accumulation at WAIS Divide than at South Pole and Dome A. The Arctic records of perchlorate are from sites that also have accumulation rates higher than those of South Pole and Dome A. Thus, it is unlikely that perchlorate undergoes significant post-depositional alteration at these sites.

Despite post-depositional alterations at South Pole and Dome A, at all three Antarctic sites, perchlorate concentrations are in general very low ng kg^{-1} prior to the 1970s, and begin to increase in the late-1970s and the increase accelerates starting in the mid-1980s (Figure 24). The timing of the increasing trend is consistent with perchlorate data from the Arctic, with higher levels in recent snow (post-1980) than in older snow [*Peterson et al.*, 2015b; *Peterson*, 2016; *Rao et al.*, 2012].

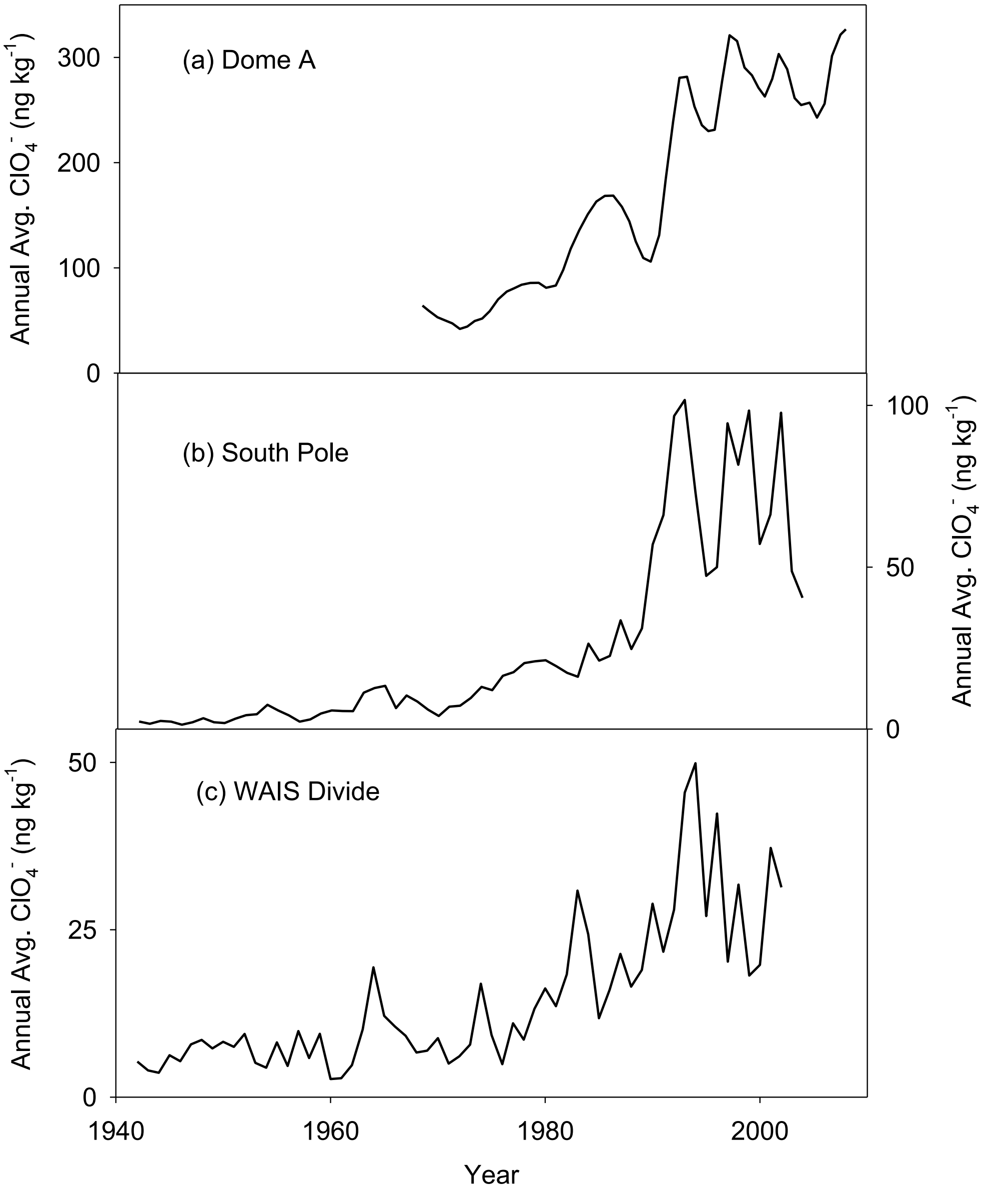

Figure 24. Mean annual perchlorate levels for three sites in Antarctica: (a) Dome A (b) South Pole (c) West Antarctica show perchlorate concentrations are in general low ng kg^{-1} prior to the 1970s, and begin to increase in the late-1970s with the increase accelerating in the mid-1980s.

4.3 Influence from the Antarctic ozone hole

The increase of perchlorate in Antarctic snow since the 1970s coincides with the appearance and growth of the Antarctic stratospheric ozone hole (significant loss of ozone during austral spring) over the Antarctic. Annual average perchlorate concentration and annual average total column ozone [*National Oceanic & Atmospheric Administration (NOAA)*, 2015] from the South Pole and WAIS Divide are plotted in Figure 25. Total column ozone over Antarctica began to decrease in the mid-1970s [*Farman et al.*, 1985]. Ozone loss became more drastic in the period between 1980 and the mid-1990s and has continued to the present day [*National Oceanic & Atmospheric Administration (NOAA)*, 2015; *WMO/GAW Ozone Monitoring Community*, 2015]. Correlational analysis shows that, before the initial appearance of the ozone hole around 1980, there is little or no correlation between total column ozone and South Pole annual average perchlorate ($R = -0.05$, $n=14$, $p>0.05$). A significant negative correlation is seen in post-1980 South Pole data ($R = -0.58$, $n=22$, $p<0.001$) and post-1980 WAIS Divide data ($R = -0.61$, $n=30$, $p<0.001$), which suggests that perchlorate production is affected by stratospheric ozone level. Isotopic evidence suggests the involvement of ozone in perchlorate formation (Sec 1.3) and previous works [*Bao and Gu*, 2004; *Dasgupta et al.*, 2005; *Rao et al.*, 2010] have suggested that high ozone concentrations enhance perchlorate production. Thus, it was expected that total column ozone and Antarctic perchlorate would be positively correlated. However, the negative correlation between perchlorate and ozone after the initial appearance of the Antarctic ozone hole indicates that perchlorate production is not enhanced by stratospheric ozone on a long-term (decadal) or interannual basis.

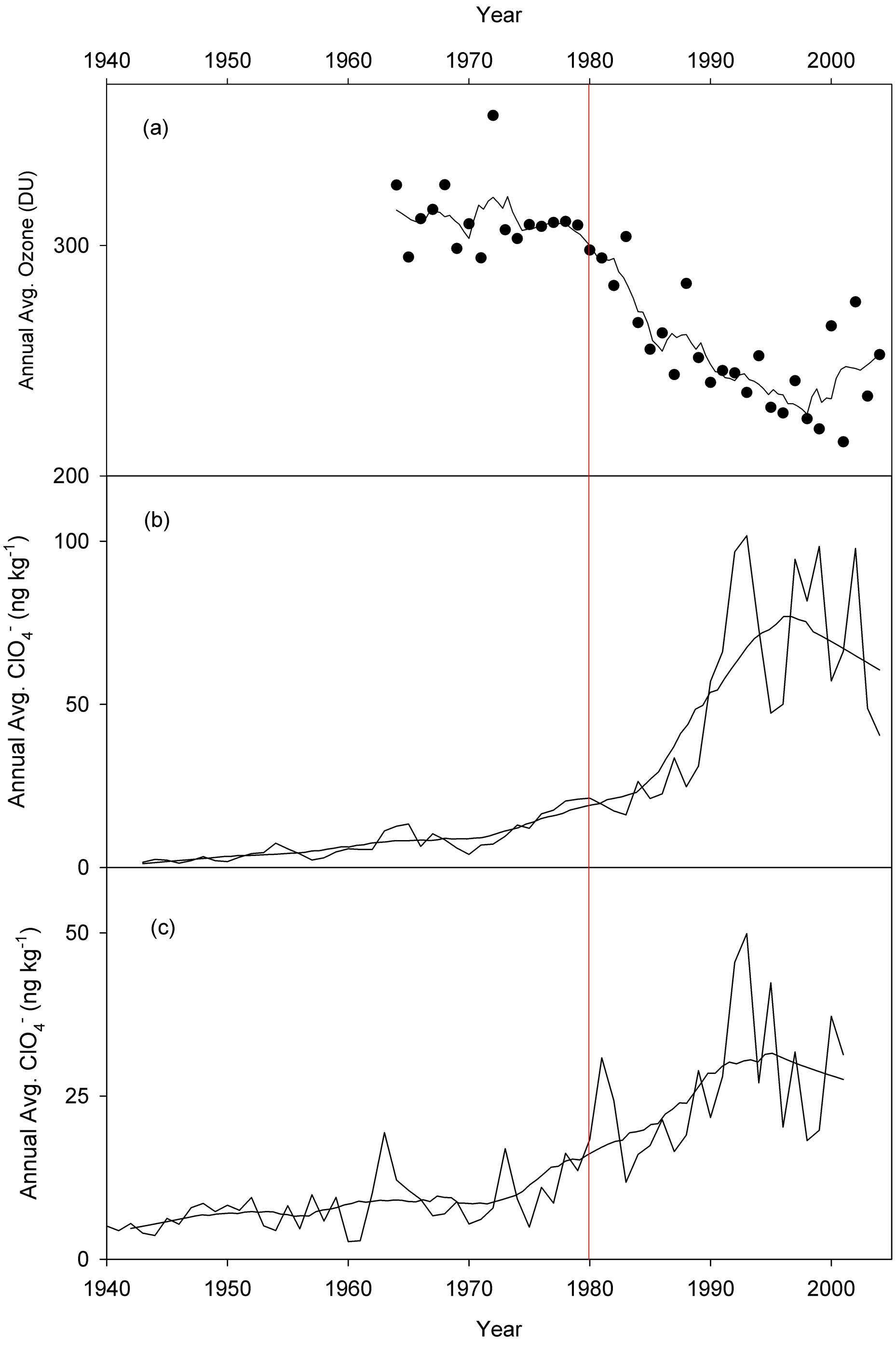

Figure 25. Profiles of (a) annual average ozone over South Pole (b) annual average perchlorate concentration at South Pole and (c) annual average perchlorate concentration at WAIS Divide for the years 1940 to 2005. Ozone data obtained from *National Oceanic & Atmospheric Administration (NOAA)* [2015]. The red line indicates the year 1980 when ozone layer drastically began to weaken. Solid black lines represent perchlorate data smoothed by using a negative exponential smoothing function in SigmaPlot.

4.4 Stratospheric chlorine and the global increasing trend in perchlorate

As discussed in section 1.3.3, chlorine isotopic data [*Jackson et al.*, 2016; *Sturchio et al.*, 2009] indicate that stratospheric chlorine is involved in perchlorate formation. There have been significant increases in stratospheric chlorine over the 20th century, particularly since the 1970s (Figure 26). The timing of the increasing trend in stratospheric chlorine is analogous with the timing of the recent increases in perchlorate in the Arctic, the Antarctic, and North American ice core records.

4.4.1 Sources of stratospheric chlorine

Methyl chloride is the largest natural source of stratospheric chlorine and is mainly derived from biogenic sources (fungi, salt marshes, algae), oceans, and soil [*Gribble*, 2003; *Yokouchi et al.*, 2000]. Prior to the twentieth century, methyl chloride was likely the only source of stratospheric chlorine [*von Clarmann*, 2013; *World Meteorological Organization*, 2014]. Firn air measurements from ice cores indicate that methyl chloride levels have only increased by 10% during the latter half of the twentieth century [*Aydin et al.*, 2004]. Anthropogenic sources of stratospheric chlorine include mainly emissions of chlorocarbons, chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFCs) [*World Meteorological Organization*, 2014]. Anthropogenic emissions of chlorine compounds have been identified as the key factor in increased levels of chlorine in the stratosphere [*Montzka et al.*, 1999; *Schauffler et al.*, 2003; *WMO and UNEP*, 2003] during the latter half of the 20th century (Figure 26).

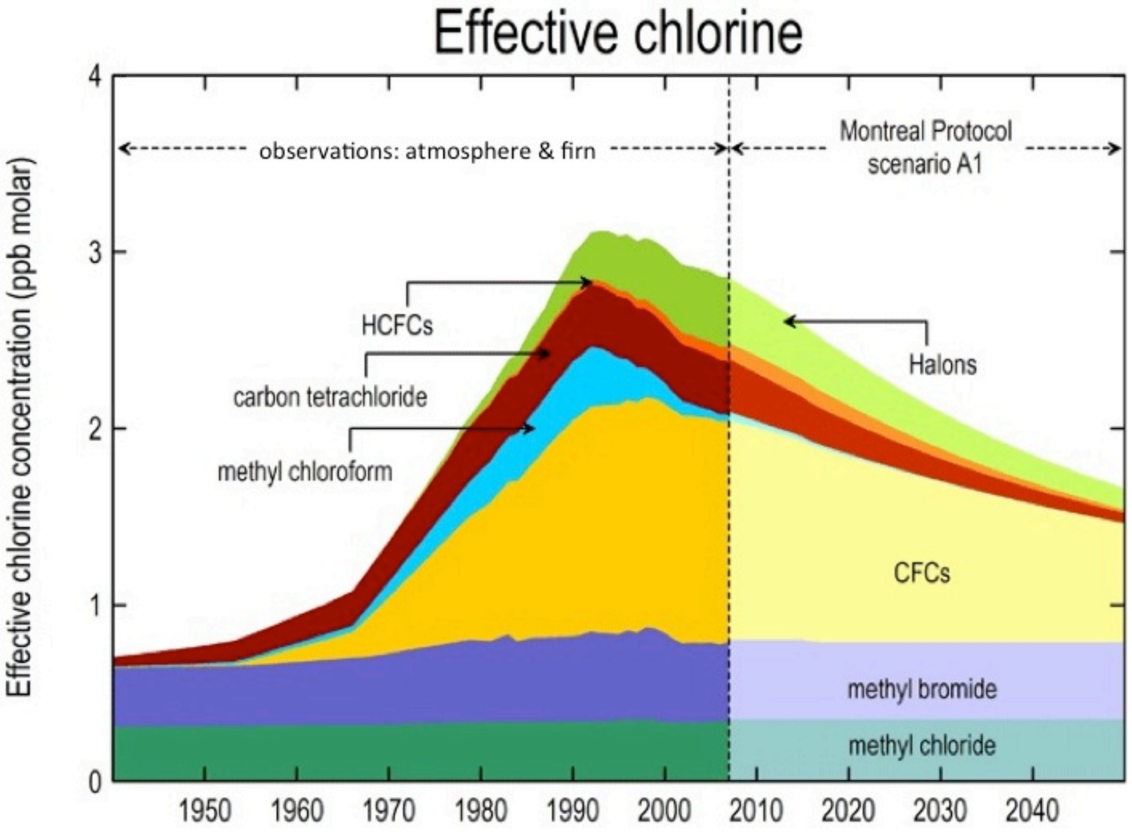

Figure 26. Effective chlorine levels in the Southern Hemisphere atmosphere from in situ measurements at Cape Grim, on the Cape Grim Air Archive and on Antarctic firn air. The future scenario is from *Schauffler et al.* [2003] in WMO Scientific Assessment of Ozone Depletion: 2010. Image from *Fraser et al.* [2013]

CFCs were invented in the 1930s, produced only anthropogenically and widely used as refrigerants and propellants [*Molina*, 1996] and are the main group of anthropogenic chlorine compounds [*Elkins et al.*, 1993; *WMO/GAW Ozone Monitoring Community*]. After the Montreal Protocol banned the production of CFCs, HCFCs production and use as a refrigerant increased [*Elkins et al.*, 1993]. The most abundant anthropogenic chlorine source gases are CF_2Cl_2 (CFC-12), CCl_3F (CFC-11), CHF_2Cl (HCFC-22), CH_3CCl_4 (methyl chloroform), and CCl_4 [*Montzka et al.*, 1996]. These gases are released into the environment and, being rather inert in the troposphere, are more likely than other common pollutants to enter the stratosphere [*Prinn et al.*, 1995; *von Clarmann*, 2013]. The transport of chlorine gases to the stratosphere, where they break down readily, is very slow [*Montzka et al.*, 1996]. Thus, the atmospheric residence times of these chlorine compounds range on the order of decades for some to over a century for others [*Rigby et al.*, 2013]. For example, CFC-11 and CFC-12 have lifetimes of 55 years and 140 years [*Elkins et al.*, 1993], respectively. These long residence times result in the accumulation of chlorine species in the atmosphere [*World Meteorological Organization*, 2014]. Using CFC-11 as an example, Figure 27 shows that anthropogenic chlorine compounds have accumulated throughout Earth's atmosphere. The use and emission of CFCs has led to a global increase of ~3 ppbv (approximately 400% increase) in the concentration of chlorine in the stratosphere in the latter half of the 20th century [*World Meteorological Organization*, 2014].

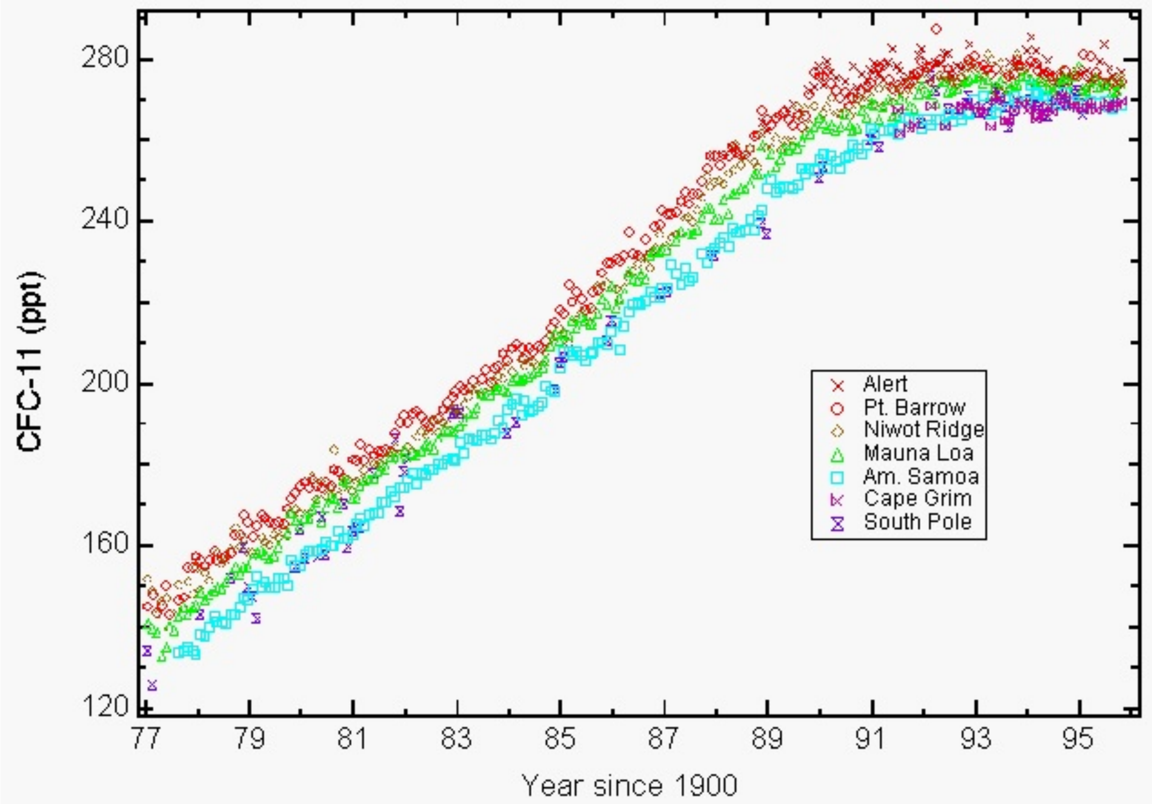

Figure 27. The accumulation of chlorofluorocarbon-11 (CFC-11) in the atmosphere at Hawaii, American Samoa, Alaska, Greenland, Australia, and South Pole. Image courtesy of *National Oceanic & Atmospheric Administration (NOAA)* [2015].

Volcanic eruptions can emit large quantities of chlorine into the atmosphere [*Varekamp et al.*, 1984] and it was previously suggested [*Mankin and Coffey*, 1984; *Pinto et al.*, 1989] that HCl emitted from volcanic eruptions contributed to the stratospheric chlorine budget. However, the majority of HCl emitted from volcanic eruptions is efficiently washed out via precipitation in the troposphere before it can enter the stratosphere [*Harris et al.*, 1992; *Tabazadeh and Turco*, 1993; *Vierkorn-Rudolph et al.*, 1984].

4.4.2 A proxy for stratospheric chlorine: EESC

The amount of chlorine in the stratosphere may be represented by equivalent effective stratospheric chlorine (EESC) – a parameter based on emission calculations and ozone depletion potentials [*Newman et al.*, 2007]. Figure 28 shows that global EESC levels began to increase sharply in the 1970s and peaked in 1996-97 [*World Meteorological Organization*, 2014]. The pattern of perchlorate increase in South Pole and WAIS Divide snow parallels the increasing trend of stratospheric chlorine (Figure 28). The strong positive correlation (R = 0.884, n = 61, p < 0.01; R = 0.828, n=71, p<0.005) between EESC and perchlorate at South Pole and WAIS Divide, respectively, suggests that the perchlorate increase in recent snow may be caused by the increase in stratospheric chlorine.

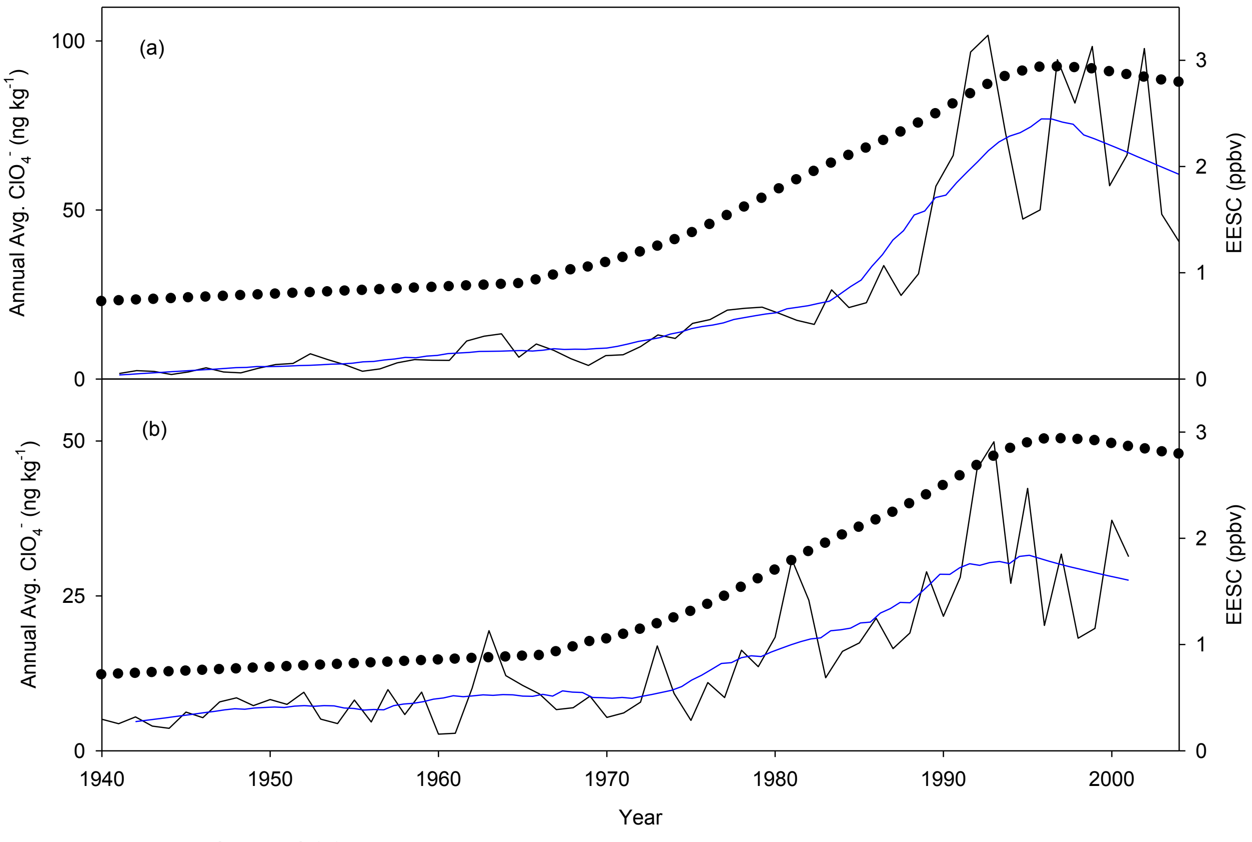

Figure 28. Profiles of (a) annual average perchlorate concentration at South Pole and (b) annual average perchlorate concentration at WAIS Divide and EESC data (dots) for the period of 1940 to 2005. EESC data obtained from *World Meteorological Organization* [2014]. Black lines represent annual averages and blue lines represent perchlorate data smoothed by using a negative exponential smoothing function in SigmaPlot.

Emissions of anthropogenic chlorine compounds such as CFCs have significantly increased over the latter half of the twentieth century (Figures 26 and 27), thus resulting in enhanced stratospheric chlorine levels in the Antarctic, the Arctic, as well as the mid-latitudes (Figure 27). Ice core records show that perchlorate levels also increased significantly during the same time period in North America and the Arctic [*Peterson*, 2016; *Rao et al.*, 2012]. Chlorine isotopic evidence [*Sturchio et al.*, 2009] supports the involvement of stratospheric chlorine in atmospheric perchlorate production. Furthermore, *Roberts* [2009] has suggested that perchlorate production is promoted by long-lived CFC and chlorocarbon compounds in the stratosphere. Thus, the perchlorate trend in polar snow supports the suggestion that stratospheric chlorine can impact perchlorate production and that recent increases in stratospheric chlorine (due to anthropogenic emissions) have caused stratospheric perchlorate production to increase significantly.

4.5 Stratospheric chlorine chemistry and perchlorate formation

Ice core records indicate perchlorate levels in the Arctic and Antarctic have increased significantly over the recent decades. Yet, mean perchlorate levels in the Antarctic are several orders of magnitude greater than the levels in the Arctic (Table 9). Although the amounts of stratospheric chlorine are similar in both the Arctic and Antarctic [*Clerbaux and Cunnold*, 2007], there are fundamental differences in what happens to stratospheric chlorine in the Antarctic than in the Arctic [*Solomon et al.*, 2014]. Due to colder temperatures in the stratosphere during the polar winter, more stratospheric chlorine becomes activated (as chlorine radicals) in the Antarctic than in the Arctic [*Solomon et al.*, 2014].

Table 9. Mean perchlorate levels in post-1980 snow are significantly higher in the Antarctic than in the Arctic (Greenland, northern Canada) and North America (Wyoming, USA).

	Mean ClO_4^- Values ($ng\ kg^{-1}$)	
Site	Post-1980 snow	Reference
Eclipse Ice Field, Canada	2.2 ± 2.0*	*Rao et al.* [2012]
Upper Fremont Glacier, USA	1.8 ± 0.7	*Rao et al.* [2012]
Summit, Greenland	2.7 ± 2.1	*Peterson* [2016]
Tunu, Greenland	3.6 ± 3.5	*Peterson* [2016]
Basin, Greenland	2.8 ± 3.1	*Peterson* [2016]
South Pole, Antarctica	74 ± 21	This work
Dome A, Antarctica	273 ± 80	This work
WAIS Divide, Antarctica	24 ± 16	This work

*Standard deviation (1σ)

The Arctic winter stratosphere is generally warmer than the Antarctic, and the Arctic also warms up earlier in the spring. These two factors taken together result in lower amounts of activated chlorine species in the Arctic than the Antarctic, and also explains why ozone depletion in the Arctic is generally much less than in the Antarctic [*Solomon et al.*, 2014]. Several works [*Dasgupta et al.*, 2005; *Kang et al.*, 2006; *Rao et al.*, 2010; *Roberts*, 2009] have proposed the involvement of chlorine radicals (activated chlorine) in perchlorate formation. As such, these distinct differences in chlorine activation may explain the large difference in perchlorate concentrations between the Arctic and Antarctic.

4.5.1 Stratospheric chlorine chemistry and ozone depletion

Due to their inertness, CFCs do not break down when released and can persist in the troposphere for more than 100 years. Over time, air currents carry them into the stratosphere. Antarctic ozone depletion is associated with enhanced stratospheric chlorine from CFCs and heterogeneous chemistry under cold conditions [*Solomon et al.*, 2014]. *Molina and Rowland* [1974] initially suggested that, when exposed to UV radiation in the stratosphere, CFCs would disassociate and form chlorine radicals. For instance, radiant energy of wavelength less than 215 nm will break the covalent bond between one of the chlorine atoms and the carbon atom in CF_2Cl_2 [*Clerbaux and Cunnold*, 2007; *von Clarmann*, 2013]:

$$CF_2Cl_2 + h\nu\ (<215\text{ nm}) \rightarrow CF_2Cl + Cl\bullet \qquad (1)$$

Molina and Rowland [1974] proposed that each chlorine radical would then destroy a molecule of ozone with the formation of a chlorine monoxide radical (ClO•) and a molecule of oxygen (Reaction 2). The chlorine monoxide radical would then in turn react with an oxygen atom to yield another molecule of oxygen and another chlorine radical (Reaction 3), which could then start the chain over again. The net result would be the destruction of a molecule of ozone.

$$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2 \qquad (2)$$

$$ClO\bullet + O \rightarrow Cl\bullet + O_2 \qquad (3)$$

This hypothesis was later revised [*von Clarmann*, 2013]: chlorine released from chlorine source species is not fully available as Cl or ClO, but forms chlorine reservoir species (HCl and $ClONO_2$) through Reactions 4 and 5 [*Lipson et al.*, 1999; *McElroy and Salawitch*, 1989; *Stolarski and Cicerone*, 1974; *von Clarmann*, 2013], where M is a third body molecule such as N_2 or O_2:

$$Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet \qquad (4)$$

$$ClO\bullet + NO_2 + M \rightarrow ClONO_2 + M \qquad (5)$$

HCl and $ClONO_2$ are much less reactive than chlorine radicals [*von Clarmann*, 2013], and their predominance leads to a reduced efficiency of the catalytic chlorine cycle (Reactions 2-3). Approximately 70% of stratospheric chlorine is present as HCl [*Michelsen et al.*, 1996; *Nassar et al.*, 2006] with another 15% of stratospheric chlorine as sequestered as $ClONO_2$ [*Douglass et al.*, 1995; *Michelsen et al.*, 1996; *von Clarmann*, 2013] and unavailable for ozone destruction reactions. However, reactive chlorine can be released from the reservoir species via Reaction 6 [*Abbatt and Molina*, 1992; *Douglass et al.*, 1995; *Molina et al.*, 1987] yielding Cl_2 that can easily generate radicals.

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \qquad (6)$$

A low efficiency of approximately 2×10^{-21} cm^3 $molecule^{-1}$ s^{-1} was predicted [*Atkinson et al.*, 1987; *Friedl et al.*, 1986] for this reaction in the gas phase. However, research [*Borrmann et al.*, 1997; *Burkholder et al.*, 1993; *Friedl et al.*, 1986; *McElroy and Salawitch*, 1989] has demonstrated the critical role of reactions taking place in stratospheric aerosols at low temperature. Temperatures in the wintertime Antarctic stratosphere are sufficiently cold to cause formation of persistent ice-like clouds called polar stratospheric clouds (PSCs) in the lower part of the stratosphere [*Peter*, 1997; *Solomon et al.*, 2014]. Reaction 6 can proceed efficiently at a rate constant of 1×10^{-19} cm^3 $molecule^{-1}$ s^{-1} [*Abbatt and Molina*, 1992; *Friedl et al.*, 1986; *Molina et al.*, 1985] – approximately two orders of magnitude faster - when they heterogeneously occur on the surface of ice crystals of PSCs than in the gas-phase (homogeneous reactions) [*Drdla et al.*, 1993; *Peter*, 1997; *Solomon et al.*, 1986].

Production of photochemically active diatomic chlorine from the reservoirs in the presence of PSCs results in Cl_2 accumulating in the polar winter [*Borrmann et al.*, 1997; *Solomon et al.*, 2014]. In the early spring, sunlight returns and causes Cl_2 to disassociate to form two chlorine radicals (Reaction 7) [*Solomon*, 1999; *Yudin et al.*, 1997]. These radicals start the catalytic chlorine cycle that depletes ozone until the radicals become sequestered as reservoir (inactive) chlorine species [*von Clarmann*, 2013]. Hence the large depletion of ozone with the appearance of sunlight every austral spring in the Antarctic.

$$Cl_2 + h\nu \rightarrow 2\ Cl\bullet \qquad (7)$$

It should be noted that the same basic chlorine activation mechanisms operate in both hemispheres [*Solomon et al.*, 2014]. The Antarctic winter stratosphere is generally colder than the Arctic, thus resulting in more PSCs in the Antarctic than in the Arctic. A greater abundance of PSCs results in more heterogeneous reactions and more chlorine activation over the southern pole than the northern pole [*Solomon et al.*, 2014]. This ultimately results in significant ozone depletion every spring in the Antarctic whereas in the Arctic, significant ozone depletion occurs less frequently and has only been observed during cold Arctic winters [*Solomon et al.*, 2014].

4.5.2 Atmospheric perchlorate formation

Despite the inference that natural perchlorate is formed atmospherically, the key reactions involved are presently unknown and the proposed formation pathway remains speculative [*Bao and Gu*, 2004; *Kang et al.*, 2008; *Roberts*, 2009]. Several studies [*Dasgupta et al.*, 2005; *Jackson et al.*, 2006; *Kang et al.*, 2006; *Rao et al.*, 2010] have proposed various pathways that are constrained by isotopic data, but little is known about the steps involved in the formation of atmospheric perchlorate.

A reaction scheme to form perchlorate was proposed in 1975 by *Simonaitis and Heicklen* [1975], who further suggested that perchlorate, which is not subject to photodecomposition and radical attack [*Schumacher*, 1960; *Simonaitis and Heicklen*, 1975], may be an important sink for stratospheric chlorine and suggested a formation scheme. *Dasgupta et al.* [2005] expanded on the initial scheme but suggested that chlorate radicals ($\bullet ClO_3$) may be formed as an intermediate via reaction 2a (Table 10) and may then be acted on by $\bullet OH$ to produce stable $HClO_4$. Table 10 (adapted from *Dasgupta et al.* [2005]) represents an expanded version of the Simonaitis-Heicklen view, and some of these reactions (reactions 1a, 2a, and 4a) are part of the well-known chlorine-ozone reaction chain [*von Clarmann*, 2013] while others (reaction 3a) are part of the chlorine monoxide dimer cycle [*von Clarmann*, 2013]. It may be that perchlorate is formed as a minor product of chlorine-ozone photochemical reactions [*Kang et al.*, 2006; *Kang et al.*, 2008; *Kim et al.*, 2013; *Rao et al.*, 2010].

Table 10. Known stratospheric chlorine-ozone reactions that may lead to perchlorate formation

reaction number	reactions
1a	$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
1b	$ClO\bullet + O_3 \rightarrow ClO_4^-$
2a	$Cl\bullet + O_3 + M \rightarrow ClO_3 + M$
2b	$ClO_3 + OH \rightarrow HClO_4$
3a	$ClO\bullet + ClO\bullet + M \rightarrow Cl_2O_2$
3b	$Cl_2O_2 + O_3 \rightarrow ClO_3 + ClO_2$
3c	$ClO_3 + OH \rightarrow HClO_4$
4a	$ClO\bullet + O_3 + M \rightarrow ClO_2 + M$
4b	$ClO_2 + O + M \rightarrow ClO_3 + M$
4c	$ClO_3 + OH \rightarrow HClO_4$

Recent laboratory studies [*Carrier and Kounaves*, 2014; *Carrier and Kounaves*, 2015; *Kang et al.*, 2006; *Kim et al.*, 2013; *Kopitzky et al.*, 2002; *Rao et al.*, 2010; *Wilson et al.*, 2016] have suggested that perchlorate can form from ClO_2 and ClO_3, and that the amount of perchlorate formed from ClO_2 is an order of magnitude higher than the amount of perchlorate formed from ClO_3 [*Carrier and Kounaves*, 2015; *Rao et al.*, 2010]. It may be that ClO_2 is a more likely intermediate for perchlorate formation than ClO_3, and that any reaction pathway involving the oxidation of ClO_2 to ClO_4 does not appear to take place through a ClO_3 intermediate as suggested by reactions 4a-4c. Another possible explanation is that the perchlorate forms through multiple pathways, and the formation pathway with ClO_2 as an intermediate is faster than the pathway with ClO_3 as an intermediate. However, this speculation requires future work in modeling and experimentation to determine the formation pathway(s) of perchlorate. Additionally, ClO_2 is regularly observed in the polar stratosphere [*Miller et al.*, 1999], with a greater abundance over Antarctica [*Miller et al.*, 1999; *Sanders et al.*, 1993] than over the Arctic [*Brandtjen et al.*, 1994; *Miller et al.*, 1999] whereas ClO_3 has not been observed in the stratosphere [*Santee et al.*, 2008].

There are observations of particle-bound perchlorate in the stratosphere [*Murphy and Thomson*, 2000]. The formation mechanism of perchlorate in the stratosphere is not known with certainty, but preliminary measurements show that ClO uptake on H_2SO_4 or ice-covered surfaces could be involved [*Martin et al.*, 1979b]. Preliminary work suggests some production of perchlorate from photochemical and ozone-initiated reactions of aqueous solutions of oxychlorine anions [*Kang et al.*, 2006; *Rao et al.*, 2010], especially from ClO_x species, but key intermediates and even the reaction order remain to be determined. It has been suggested that a tropospheric formation pathway for perchlorate exists [*Dasgupta et al.*, 2005; *Rao et al.*, 2012], with lightning involved in the formation of chlorine radicals. However, as lightning is infrequent in the Antarctic [*Mackay and Fraser-Smith*, 2011], stratospheric chlorine chemistry (likely involving ClO_x species) may be the sole natural source of atmospheric perchlorate [*Roberts*, 2009]. Stratospheric ClO_x chemistry is driven by long-lived chloro-, chlorofluoro- and bromocarbon compounds [*von Clarmann*, 2013]. There are higher UV radiation fluxes in the stratosphere than in the troposphere [*Madronich et al.*, 1995], which results in a higher amount of radical Cl species [*Solomon et al.*, 2014; *von Clarmann*, 2013]. For these reasons, there are higher abundances of ClO_x compounds in the polar stratospheric than troposphere [*von Clarmann*, 2013]. The higher abundances of ClO in the stratosphere make higher oxides of Cl such as OClO and possibly compounds such as Cl_2O_3 [*von Clarmann*, 2013]. Although ClO_x species such as OClO and Cl_2O_3 are not stable against photolysis [*Burkholder et al.*, 1993], a small fraction could react in the aerosol phase to form chlorate and perchlorate, through hydrolysis and disproportionation reactions [*Catling et al.*, 2010; *Kopitzky et al.*, 2002; *Prasad and Lee*, 1994]. Additional chemistry involving the nitrogen compounds such as $ClONO_2$, $ClNO_2$ and $BrONO_2$ could be important, as those are also relatively abundant in the stratosphere. Details of such a perchlorate formation mechanism are quite uncertain, but are crucial for understanding how perchlorate formation may impact the environment, how much is formed, and what other atmosphere species or processes it may depend on. As the key processes in perchlorate formation remain unknown, the suggestion that various ClO_x species may be key intermediates or involved remains speculative.

4.6 Conclusion

Antarctic perchlorate levels noticeably increase from the 1970s to the present day – similar to the increasing trend in Arctic perchlorate data. However, Antarctic perchlorate levels are several orders of magnitude higher than Arctic perchlorate levels. Ozone and stratospheric chlorine are implicated in perchlorate formation via isotopic data [*Jackson et al.*, 2010; *Sturchio et al.*, 2012], polar stratospheric chlorine chemistry and the Antarctic ozone hole are explored in relation to perchlorate production. Antarctic perchlorate levels are inversely correlated with ozone – suggesting perchlorate production is not enhanced by increases in stratospheric ozone on a long-term basis. Antarctic perchlorate levels are strongly correlated with stratospheric chlorine levels – suggesting that recent anthropogenic CFC emissions have driven perchlorate production to increase three-fold. Chlorine radicals have been proposed as intermediates in atmospheric perchlorate formation [*Dasgupta et al.*, 2005; *Kang et al.*, 2009; *Roberts*, 2009]. As chlorine radicals are more abundant in the Antarctic stratospheric than the Arctic stratosphere (due to colder temperatures in the Antarctic winter and more chlorine activation) [*Solomon et al.*, 2014], it may be that abundance of activated chlorine is the explanation for the difference in perchlorate between the Arctic and the Antarctic. As perchlorate formation from photochemical and ozone-initiated reactions of various oxychlorine anions has been demonstrated in the laboratory [*Carrier and Kounaves*, 2014; *Kang et al.*, 2006; *Rao et al.*, 2010], it could be that perchlorate is formed as a minor product of stratospheric chlorine-ozone photochemical reactions, but this suggestion is merely speculative. Furthermore, future work is necessary to understand the inverse relationship between total column ozone and Antarctic perchlorate levels.

5. Short-term perchlorate variations

Several chemical species in polar snow and ice core records display short-term (annual and sub-annual) variations that fluctuate on a seasonal cycle, often a result of variations in aerosol source strength and transport efficiency. Annual oscillations of certain chemical impurities and their use as time markers for annual layers to date ice cores have already been discussed (Sec. 2.6.1). Chemical species with established seasonal oscillations can also be useful in determining the seasonality of other species, such as perchlorate, which may provide information about their sources. Examining the short-term variations of perchlorate in polar snow may help to elucidate the details of its formation, production, and transport in the polar environment.

5.1 Short-term variations of perchlorate in the Arctic

Furdui and Tomassini [2010] noted a correlation between perchlorate concentrations at Devon Island, Canada and ozone concentrations measured at nearby Resolute Bay, Canada, and found that both reached maximum concentrations concurrently, suggesting that ozone plays a key role in the formation of perchlorate. Perchlorate concentrations in Greenland snow display a weak seasonal pattern: perchlorate levels appear to peak in late spring / early summer each year and show a slight correlation with total column ozone, suggesting that ozone is involved in the formation of perchlorate (Figure 29). Maximum ozone concentrations in the Arctic are generally reached in the late winter and early spring [*WMO/GAW Ozone Monitoring Community*, 2015], in which winter is defined as December-February and spring is defined as March-May (Figure 29). *Peterson* [2016] has suggested that the reason that the perchlorate peak concentrations occur slightly later than the annual maximum ozone concentrations could be due to a lack of activated chlorine (radical chlorine species) in the late winter-early spring. The production of perchlorate is likely also dependent on radical chlorine, and the lack of sunlight in the late winter and early spring does not allow for the generation of radical chlorine species.

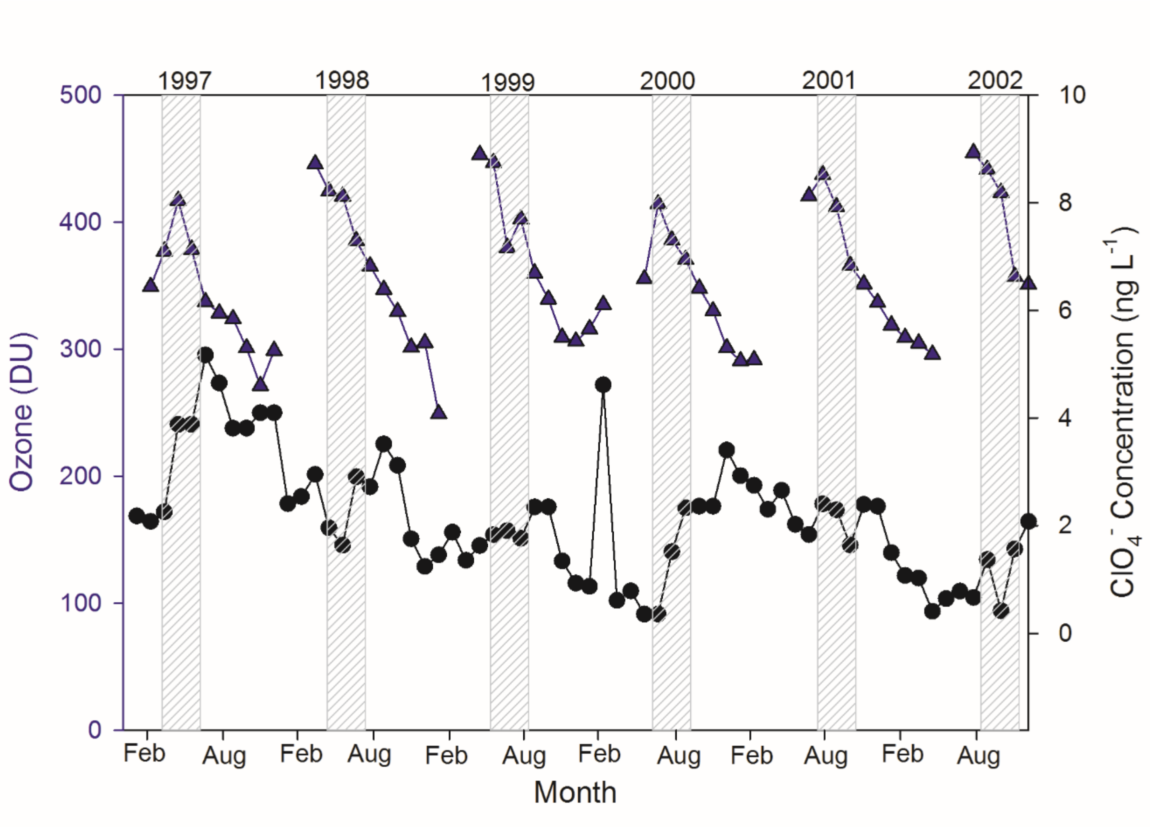

Figure 29. Monthly total ozone column concentrations (triangles) from Sondrestrom, Greenland [*WMO/GAW Ozone Monitoring Community*, 2015] and average monthly perchlorate concentrations (black circles) in SM07C2. The gray shaded bars (with years labeled on the top axis) indicate the boreal spring (March-May). Figure from *Peterson* [2016]

5.2 Short-term variations of perchlorate in the Antarctic

The South Pole perchlorate record suggests that the stratospheric ozone hole over Antarctica influences perchlorate production. As annual average total column ozone over the South Pole began to decrease due to the ozone hole, perchlorate levels began to increase (Figure 30), suggesting less ozone in the stratosphere results in a greater production of perchlorate. A proposed explanation is that the ozone hole in the stratosphere allows short wavelength (UV) solar radiation, which is normally filtered out by the ozone layer, to penetrate into the troposphere where it may enhance the production of oxidants such as the OH free radical and ozone [*Ehhalt et al.*, 1990; *Gligorovski et al.*, 2015]. Due to higher tropospheric oxidant levels, perchlorate production in the troposphere becomes enhanced - despite depletion of ozone in the stratosphere. Based on this scenario, perchlorate concentrations would increase during and/or surrounding the appearance of the annual stratospheric ozone hole [*Crawford et al.*, 2017] in the austral spring,. Increased perchlorate concentration during the months of the stratospheric ozone hole would support this hypothesis and may indicate that in the Antarctic, perchlorate forms primarily in the troposphere rather than the stratosphere.

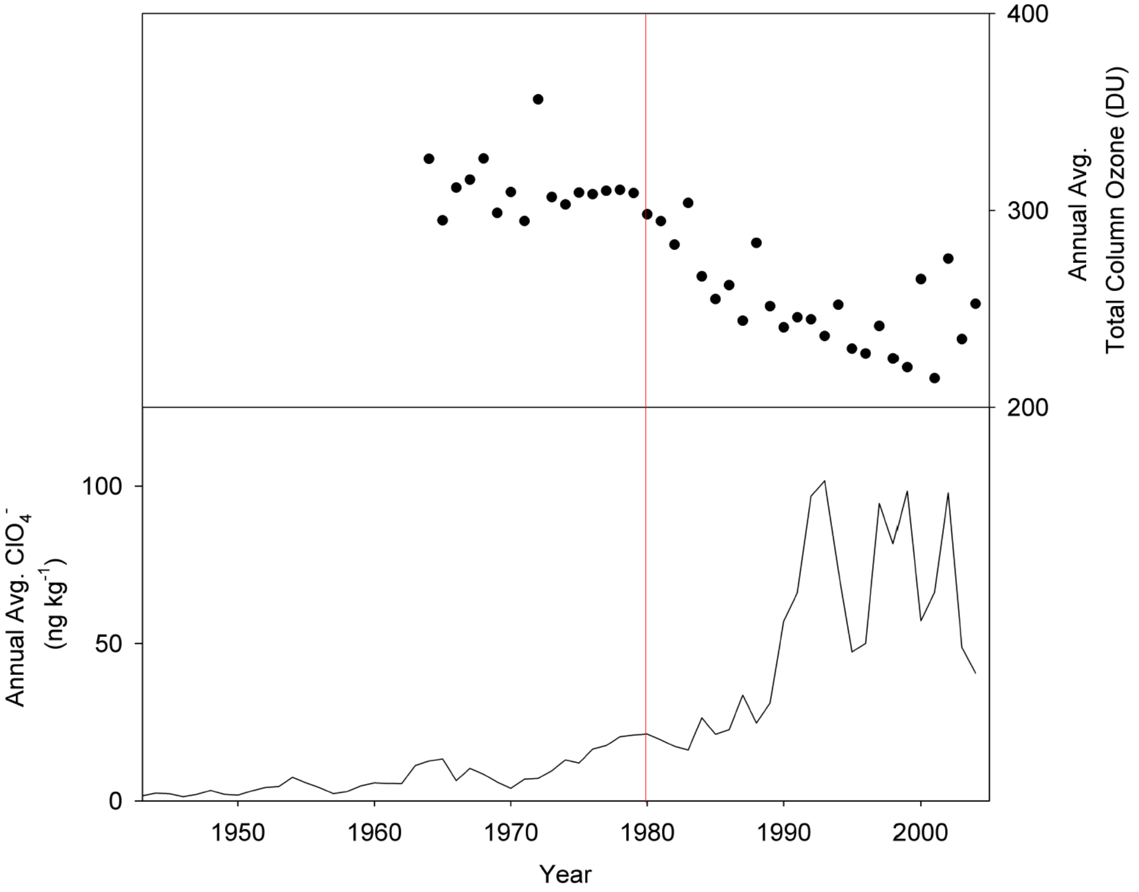

Figure 30. Profiles of (a) annual average total column ozone and (b) annual average perchlorate at the South Pole. The initial appearance of the ozone hole in 1980 is indicated by the solid red line.

The stratospheric ozone hole occurs in the austral springtime during the months of September – October. To determine the influence of the stratospheric ozone hole on perchlorate production and test the hypothesis that the penetration of ultra-violet radiation into the troposphere may result in an increase in tropospheric perchlorate production, the short-term variability of perchlorate at South Pole during the most recent years can be examined. It is assumed that during the most recent years (top 3 m depth) at South Pole and their respective variations are representative of the atmospheric production and are not strongly influenced by post-depositional process(es) at this age (depth). Perchlorate has strong oscillations (maxima and minima) during the most recent years at the South Pole (Figure 31); the oscillations appear to occur on a ~1.5 yr cycle between the years 1994 and 2004.

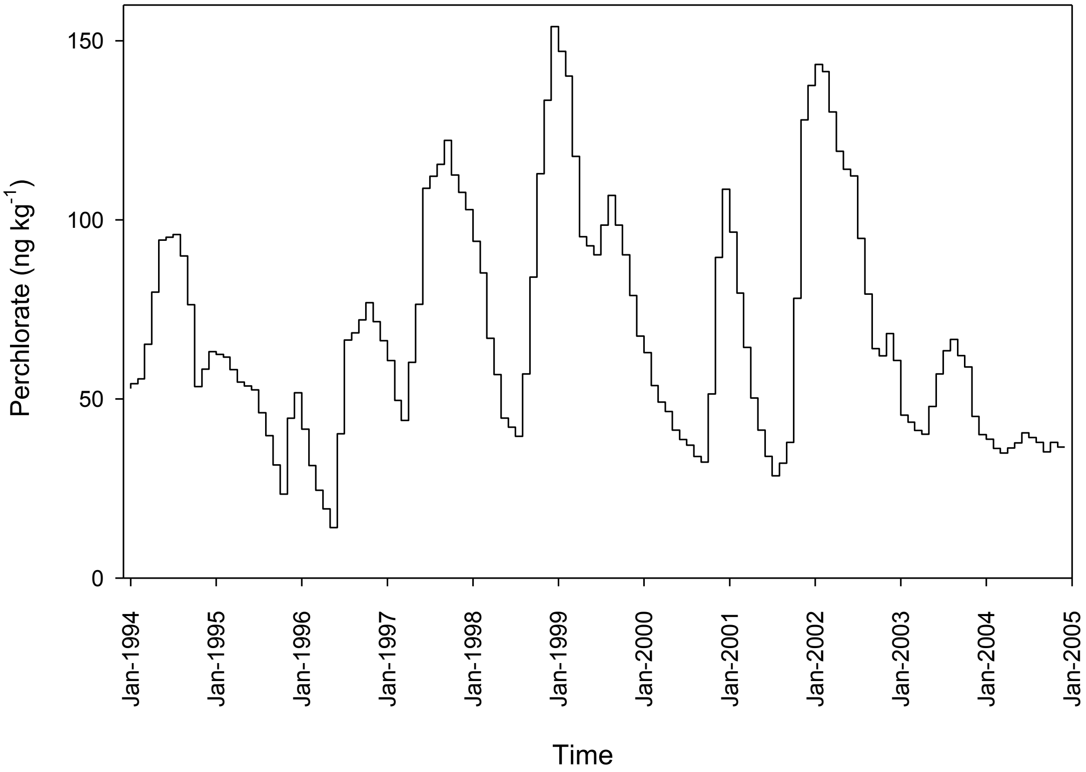

Figure 31. Mean monthly perchlorate concentrations in South Pole snow show that fluctuations in perchlorate at the South Pole are intra-annual but the maxima and minima do not appear to occur on a seasonal basis. The oscillations appear to occur on a ~1.5 yr cycle between the years 1994 and 2004.

There does not appear to be a seasonal pattern nor do the oscillations appear to occur on an annual cycle. As such, this data provide evidence against the tropospheric production hypothesis.

5.3 Sub-annual variations of perchlorate in West Antarctica snow

Perchlorate in the snow pit samples collected from WAIS Divide, Antarctica revealed that perchlorate concentrations in recent West Antarctic snow exhibit a different and much stronger seasonal signal than that at Greenland and South Pole. The average monthly perchlorate concentrations were determined using the monthly dating technique described in Sec. 2.7.3 and a monthly timescale developed. According to the monthly time scale, perchlorate maxima appear annually in the austral fall (March-April). The minima occur regularly in the spring (September-October), when column ozone reaches the lowest levels (Figure 32). The monthly average column ozone at South Pole is also plotted in Figure 32, which clearly shows the appearance of the stratospheric ozone hole in early austral spring (September and October) of each year. The low perchlorate concentrations during the austral spring, which occur annually during the years 2008-2012, do not support our hypothesis of enhanced tropospheric perchlorate production on the stratospheric ozone depletion.

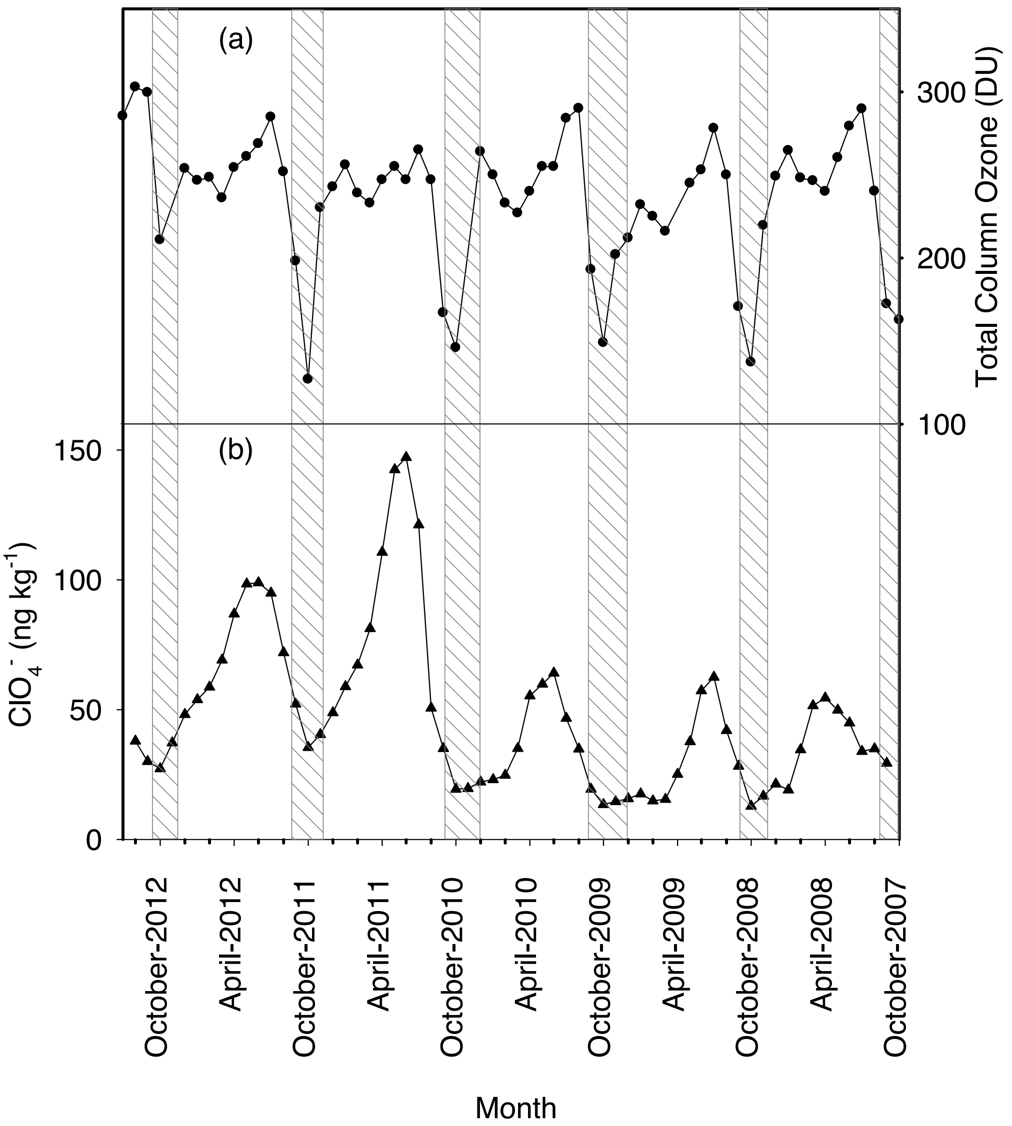

Figure 32. Profiles of (a) monthly total column ozone over South Pole and (b) monthly perchlorate concentrations in the WAIS Divide snowpit (2008-2012). The shaded periods (September-October) mark the coincident ozone and annual perchlorate minimum. South Pole ozone data are obtained from World Ozone and Ultraviolet Data Center (WOUDC)[*WMO/GAW Ozone Monitoring Community*, 2015].

On the contrary, the consistency of seasonal variation in perchlorate concentration and, in particular, the annual minimum during the austral spring, suggests a relationship between perchlorate levels and ozone concentration opposite of what was initially hypothesized. The data show that perchlorate production is reduced when stratospheric ozone concentrations are low. A moderate positive relationship exists between monthly average total ozone and monthly average perchlorate ($R=0.316$ $n=56$, $p<0.05$) . This relationship suggests that, during ozone depletion events, the perchlorate production rate is dependent on the amount of ozone in the stratosphere. Ozone concentrations can impact perchlorate production because ozone can be a key reactant in the perchlorate formation reactions [*Rao et al.*, 2010]. If the atmospheric production of perchlorate over Antarctica and, in general, in the polar regions occurs primarily in the stratosphere, rather than the troposphere [*Sturchio et al.*, 2009], the decrease in stratospheric ozone concentrations would result in reduced perchlorate concentration in spring snow.

Perchlorate concentrations reach annual minima in the spring and summer and maxima during the fall and winter in the WAIS Divide snowpit. *Peterson* [2016] has suggested that these regular oscillations are due to a fine balance of the key reactants – ozone and active chlorine. *Peterson* [2016] has proposed that although there is more activated chlorine available for perchlorate production in the spring, ozone concentrations are low during this time. In this proposed scenario, it is likely that ozone limits the rate of perchlorate production in the springtime. However, during the summer, ozone levels return to normal abundance but activated chlorine levels are low and become the limiting reactant. *Peterson* [2016] suggested that the austral autumn peak in perchlorate concentrations at WAIS Divide occurs when neither active chlorine nor ozone is at their lowest levels and both are readily available, and concluded that perchlorate production depends on a delicate balance between activated chlorine and ozone concentrations. This is due to the close relationship between activated chlorine and ozone. As activated chlorine in the stratosphere increases, ozone levels decrease.

However, observations of activated chlorine in the stratosphere over the Antarctic do not support this qualitative mechanism as proposed by *Peterson* [2016]. Approximately 90% of activated/ reactive chlorine in the stratosphere is as ClO during the winter months [*Santee et al.*, 2008; *Solomon et al.*, 2006; *von Clarmann*, 2013]. Figure 33 displays the time series of ClO measured in the stratosphere over the Southern and Northern Hemispheres. It is apparent that in the Southern Hemisphere, ClO becomes enhanced in the sunlit portions of the vortex by at least late May/early June every year [*Santee et al.*, 2008; *Solomon et al.*, 2006]. Then ClO levels are at maximum concentration in the austral winter (June-August) [*Santee et al.*, 2008; *Solomon et al.*, 2006] and then consistently remains enhanced in mid-September [*Santee et al.*, 2008], with a rapid decrease in concentration by October. Thus elevated levels of reactive chlorine persist for 4–5 months in the Southern Hemisphere.

Activated chlorine levels appear to be at a minimum during the austral autumn when perchlorate concentrations peak in the WAIS Divide snowpit (Figure 24). The seasonal oscillations of ClO do not display any increase or change in concentration above the background level during the months when perchlorate concentrations peak in West Antarctic snow (Figure 33) - which is in contrast to the suggestion by *Peterson* [2016] that there is sufficient chlorine activation in the austral autumn to reach maximum perchlorate production. Figure 33 shows that there is a minimal amount of activated chlorine in the Antarctic during the months when perchlorate peaks – indicating that ClO is not likely involved in perchlorate formation in the Antarctic. This does not, however, discount that other short-lived activated chlorine species (i.e., OClO, Cl_2O_2 etc.) could be involved in perchlorate formation and explain the seasonal oscillations of perchlorate in West Antarctic snow. The examination of the entire 82-year ice core record of perchlorate at WAIS Divide may provide more information.

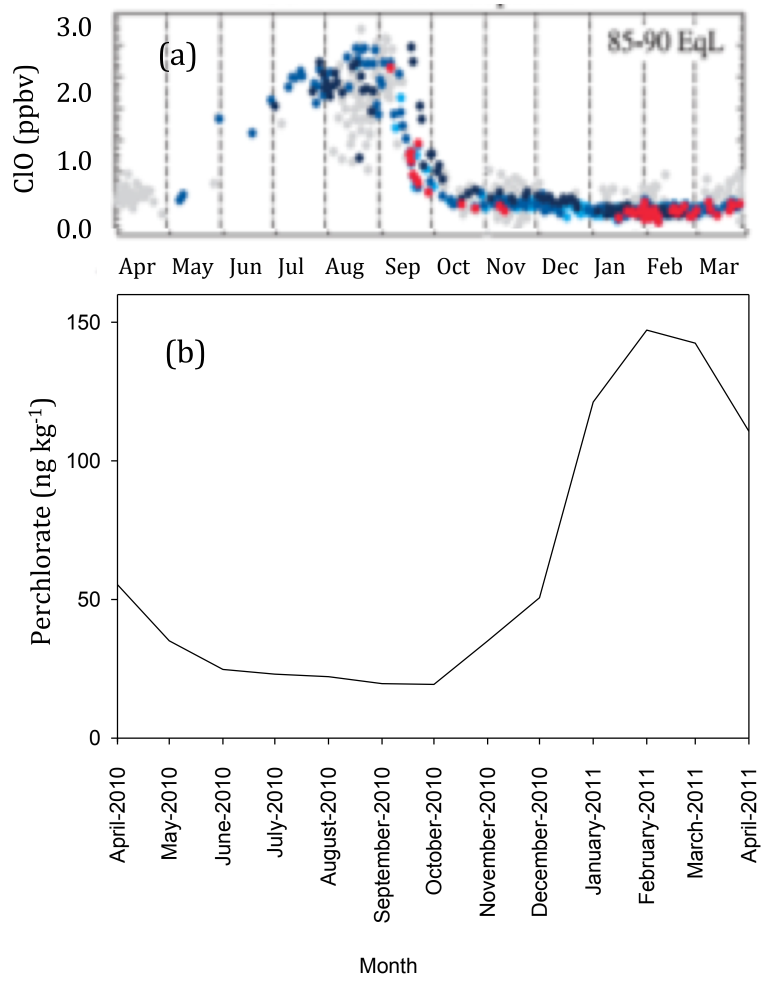

Figure 33. Time series of (a) ClO measurements at 50 hPa (19 km altitude) via satellite (MLS) for the (left) 85-90° S latitudinal bin over the southern pole. Grey dots represent data averaged over the period 1991-2000; blue dots represent different years between 2003-2006; red dots represent data from 2007. Dashed lines demark calendar month. Adapted From *Santee et al.* [2008]. Monthly average perchlorate concentrations (b) from the WAIS Divide snowpit for the time period April 2010-2011.

5.3.1 Inconsistent intra-annual variability in WAIS Divide ice core record

There are large fluctuations (maxima and minima) of perchlorate throughout the WAIS Divide ice core records (WDC05B and WDC13) (Figure 34); however, these oscillations are not as regular or as distinct as the oscillations observed in the

WAIS Divide snowpit. The perchlorate maxima and minima do not appear to occur with as consistent or regular timing in the WAIS Divide ice cores as in the WAIS Divide snowpit. Oscillations occur irregularly, with some peak-to-peak cycles occurring every ~1.5 years during the 1990s and 2000s while during the 1940s and early 1950s the cycles occur on an annual regularity – similar to the annual cycle of perchlorate in the snowpit data (Figure 34, left insert). Yet, the annual oscillations that are apparent in the snowpit data – maxima in autumn/winter, minima in summer – are apparent in approximately 15% (~12 years) of the entire 82-year perchlorate record at WAIS Divide. There are no consistent seasonal patterns or annual cycles in the time periods before or after the initial appearance of the ozone hole (pre- and post-1980). This lack of consistency does not provide support for the idea that the appearance of the stratospheric ozone hole has a significant influence on the seasonal production of perchlorate.

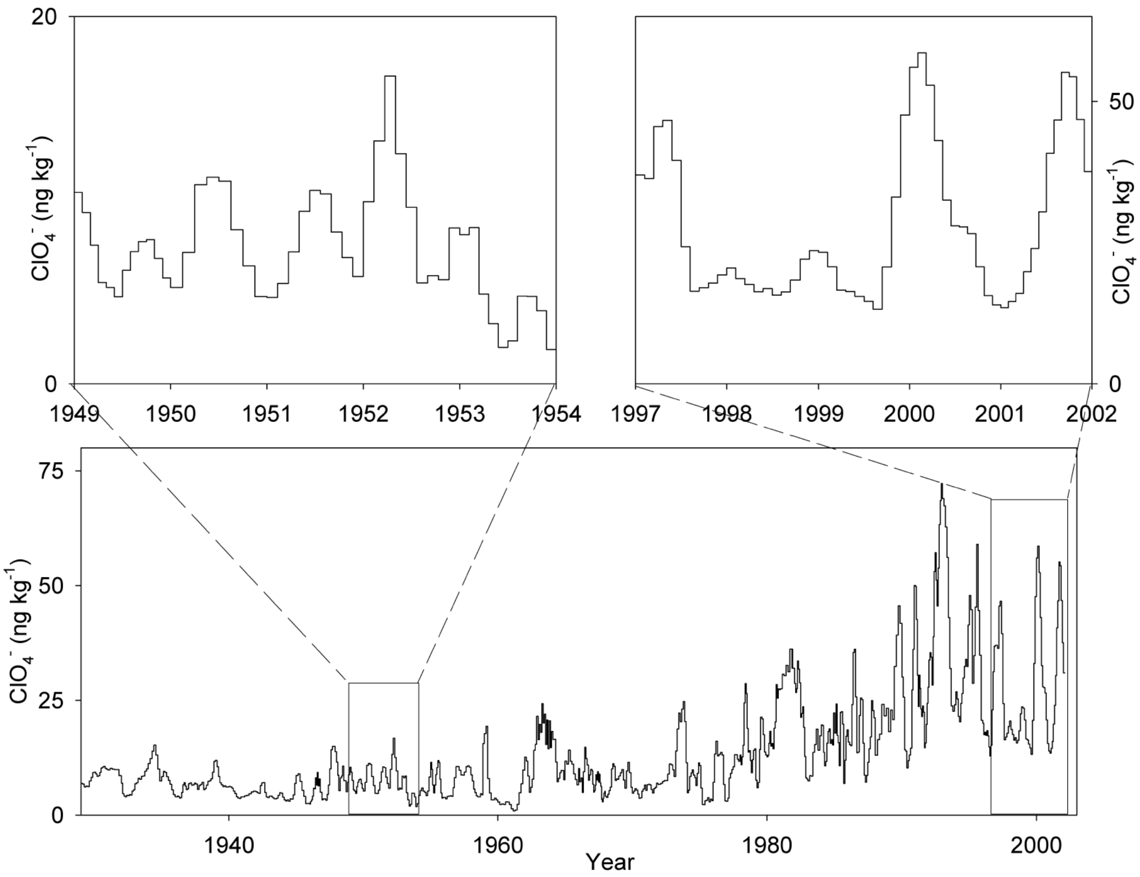

Figure 34. Temporal snapshots of WAIS Divide perchlorate at periods before and after the appearance of the Antarctic ozone hole (pre- and post-1980).

5.4 Potential factors influencing perchlorate variability

It is likely that Antarctic perchlorate is produced in the stratosphere, and as such, there is a range of factors that may influence the amount of perchlorate deposited to the snowpack. The variations of perchlorate in polar snow and ice may result not only from changes in production, but also from local and regional transport processes. In order to properly interpret short-term variations in ice core records of perchlorate, it is imperative to explore and eventually understand the impact of the factors and processes influencing short-term perchlorate production but also those influencing perchlorate transport from the stratosphere to the snowpack.

5.4.1 Influence of stratospheric temperature on perchlorate variability

Nedoluha et al. [2016] observed an anti-correlation between column activated chlorine and temperature over twenty years of activated chlorine measurements – colder temperatures in the stratosphere correlated with higher abundances of ClO. Total column activated chlorine was observed to be strongly anticorrelated with stratospheric temperature anomalies, both on a daily and on a year-to-year basis. This is physically reasonable since colder temperatures increase the availability of polar stratospheric clouds, and these clouds will in turn provide the surfaces for chlorine activation [*Molina et al.*, 1987; *Solomon*, 1999]. Making use of this anticorrelation, *Nedoluha et al.* [2016] calculated a linear dependence of the column ClO on temperature but noted that other dynamical effects might also influence ClO trends (e.g., changes in the Brewer–Dobson circulation).

Chlorine oxide species (such as ClO) may be a key factor in stratospheric perchlorate production. And as ClO (and likely ClO_x) abundance is very sensitive to interannual variations in temperature, it may be that perchlorate production is also sensitive to variations in stratospheric temperature. Figure 35 shows that annual average perchlorate from WAIS Divide and annual stratosphere temperature anomalies are anti-correlated (Spearman's correlation: $R=-0.58$, $n=47$, $p<0.001$) between the years 1979-2005, implying that colder stratospheric temperatures result in more perchlorate production. A similar, yet weaker, inverse relationship (Spearman's correlation: $R=-0.33$, $n=43$, $p<0.05$) was also observed (Figure 36) between stratospheric temperatures in the Northern Hemisphere and annual mean perchlorate levels from Summit, Greenland between the years 1979-2005. It may be that perchlorate production is also enhanced as a result of increased abundance of PSC and chlorine activation due to colder temperatures in the polar stratosphere.

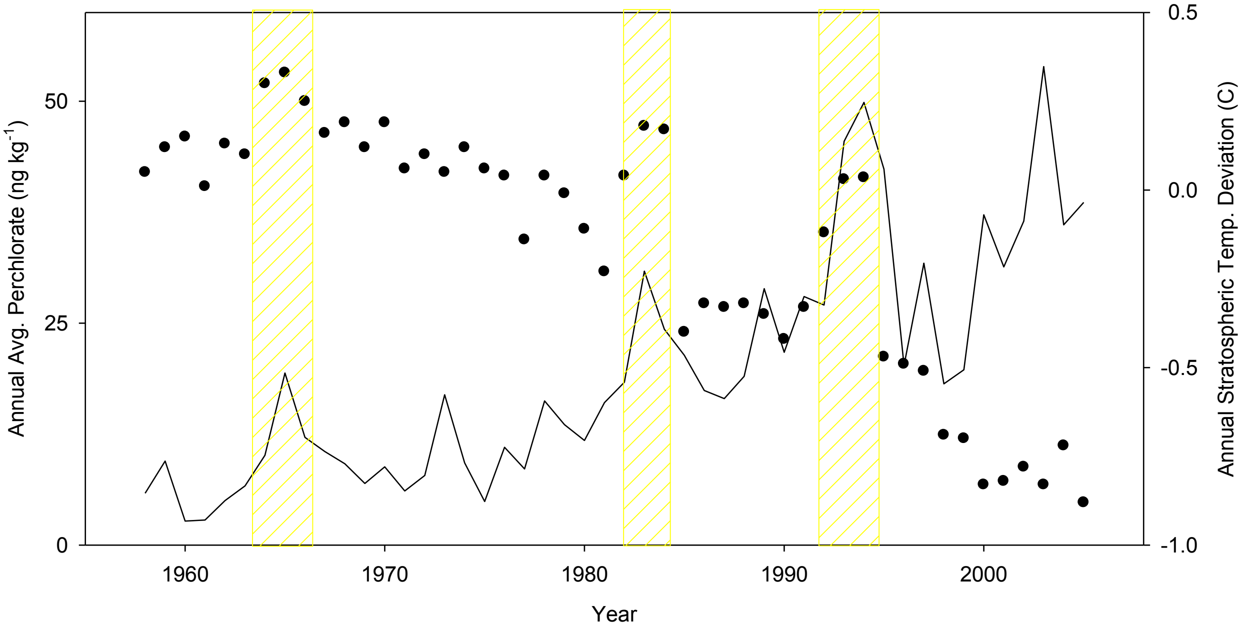

Figure 35. WAIS Divide annual average perchlorate concentrations (lines) and annual temperature deviations (dots) from the 15-year average of 1961-1975. There is a decreasing temperature trend that is coherent in timing with the increasing trend of perchlorate. Periods when increased levels of perchlorate correspond to distinct warming in the stratosphere are highlighted (1963-65, 1983-84, 1992-94). Temperature data from *Sterin* [2007].

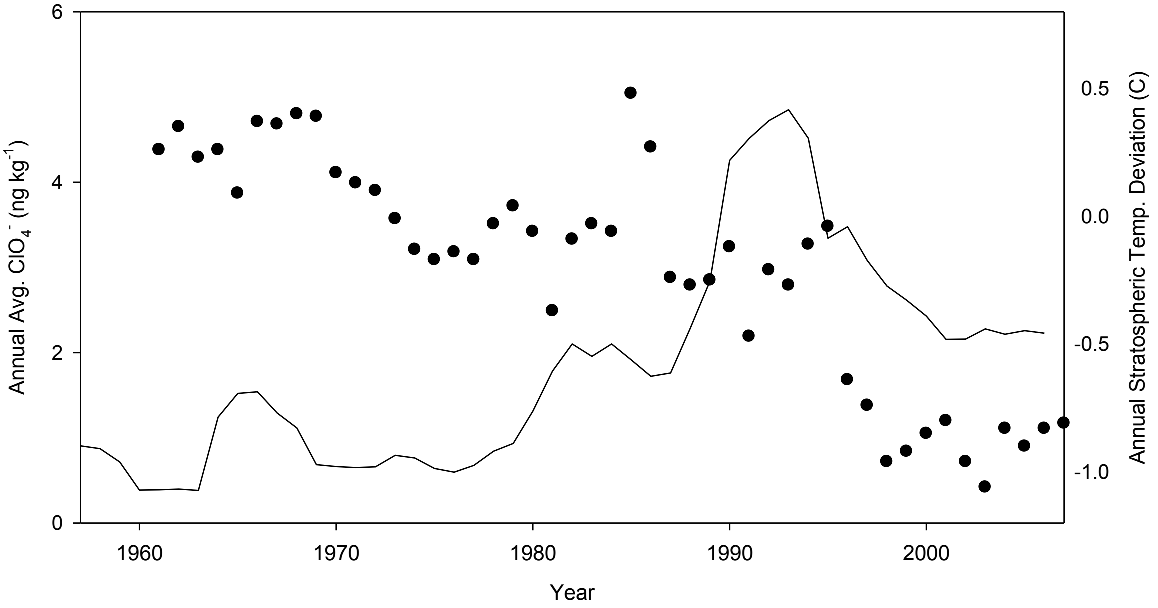

Figure 36. Annual average perchlorate concentrations (lines) from the Summit core and annual temperature deviations (dots) from the 15-year average of 1961-1975. There is an inverse relationship between stratospheric temperatures and annual average perchlorate concentrations in the Arctic. Perchlorate data from *Peterson* [2016] and temperature data from *Sterin* [2007].

There is however, a noticeable anomaly in the relationship between stratospheric temperature and Antarctic perchlorate levels during the years 1992-1994: there appears to be perchlorate increase associated with distinct warming in the stratosphere (Figure 35). The warming of the stratosphere during this time period has been largely attributed to the eruption of Mt. Pinatubo [*Labitzke and McCormick*, 1992; *McCormick et al.*, 1995; *Randel et al.*, 1995]: the second-largest volcanic eruption of the 20th century.

Several studies have suggested a potential link between sulfate from volcanic eruptions and elevated perchlorate concentrations [*Catling et al.*, 2010; *Gu and Coates*; *Jaegle et al.*, 1996; *Martin et al.*, 1979a], but due to limited data this link has remained speculative. In the 300-year perchlorate record from Greenland, *Peterson* [2016] noted substantially elevated perchlorate levels during brief periods. These peaks in perchlorate concentrations coincide in time (depth) with the appearance of volcanic sulfate peaks seen in ice core records. *Peterson* [2016] suggested that very large, explosive volcanic eruptions influence perchlorate production in the stratosphere – proposing that volcanic H_2SO_4 aerosols enhance chlorine activation and thus perchlorate production. Solomon et al.[*Solomon et al.*] suggested that volcanic H_2SO_4 aerosols in the stratosphere were likely responsible for the increased chlorine activation observed over Antarctica following the 1991 Pinatubo eruption. There also appear to be increased levels of perchlorate during distinct warming in the stratosphere during the years 1963-65 and 1983-84 (Figure 35). These two stratospheric warming events also correspond to very large volcanic eruptions: Mt. Agung in 1963 and El Chichon in 1982. A direct connection between an increase of stratospheric temperature and an increase in volcanic aerosols has been observed during the El Chichon eruption [*Labitzke et al.*, 1983]. Similar to PSCs, this suggests that volcanic aerosols provide surface area for heterogeneous chlorine activation, facilitate chlorine radical formation and, consequently, enhance perchlorate production despite stratospheric warming.

5.4.2 Transport of perchlorate from stratosphere to the snow surface

Properly interpreting perchlorate records from ice cores hinges on a thorough understanding of the physical processes that control the production, transport and deposition of perchlorate to the ice sheets. Assuming perchlorate undergoes similar processes and exhibits behavior as other specie transported from the stratosphere (i.e., ^{10}Be, volcanic sulfate) [*Cole-Dai et al.*, 1997a; *Heikkilä et al.*, 2013; *Jordan et al.*, 2003], it is likely that perchlorate attaches to ambient aerosol soon after its formation. The perchlorate-bearing aerosol is then transported downward through meteorological processes (stratosphere-troposphere air-mass exchange) and deposited on the snow surface, either by wet or dry deposition.

There are irregular year-to-year fluctuations throughout the 82-year record at WAIS Divide. As seen with other stratospheric aerosols, it may be that factors other than changes in production (i.e., atmospheric transport) influence the yearly amounts of perchlorate in ice cores.

Perchlorate may have a residence time similar to that of ^{10}Be – which is primarily produced in the stratosphere [*Nagai et al.*, 2000]. ^{10}Be has an average atmospheric residence time of months in the stratosphere and days to weeks in the troposphere [*Heikkilä et al.*, 2013; *Jordan et al.*, 2003; *Pedro et al.*, 2011b; *Raisbeck et al.*, 1981]. Deposition can occur by both wet (precipitation related) and dry (turbulent and gravitational) processes [*Davidson et al.*, 1996].

To better visualize the monthly distribution of perchlorate concentration in West Antarctic snow, a box and whisker plot is used, which is a way of displaying the distribution of data based on the following: minimum, lower (25%) quartile of the data, median, upper (75%) quartile of the data, and maximum. The average perchlorate concentrations for each month of the year were determined (Sec 2.7.3) for the more recent decades (1980-2013) from the WDC05B and WDC13 cores. In order to focus on the timing and structure of the seasonal variations of perchlorate rather than on absolute concentrations, each month of the seasonal variation is shown as an anomaly from the annual mean value of the perchlorate record. The box and whisker plot for mean monthly perchlorate at WAIS Divide (Figure 37) indicates that the median does not vary throughout the year. However, the quartiles, minima and maxima in the plot vary less in the austral winter months than in the spring and summer months. There are also fewer outliers during the winter months than the rest of the year, suggesting there is less variability during the winter than the summer or spring and is similar to the variability of ^{10}Be observed in an Antarctic snow pit [*Pedro et al.*, 2006]. A significant fraction of the variability of ^{10}Be in the snowpit was attributed to the vertical transport and stratosphere-to-troposphere exchange of air masses [*Pedro et al.*, 2006; *Pedro et al.*, 2011b]. It is not known if or how stratosphere-to-troposphere exchange influences or affects the concentrations of perchlorate observed in Antarctic snow. The possibility exists that some of perchlorate's variability may be due to transport of perchlorate from the stratosphere to the troposphere and deposition on the snowpack, and requires further work to better understand the vertical transport of perchlorate.

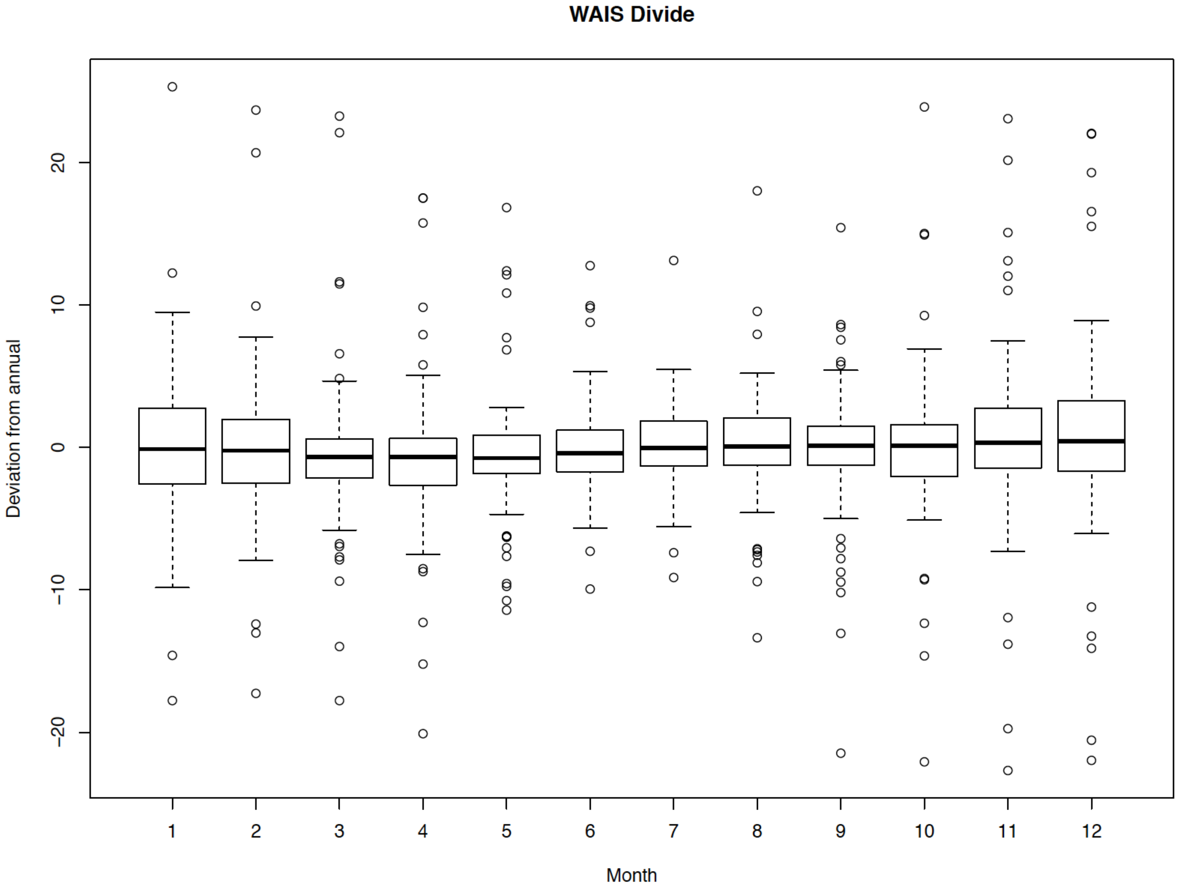

Figure 37. A box and whisker plot displays the median (bold line) of the monthly mean WAIS Divide perchlorate concentrations, the lower and upper quartiles (25% and 75% indicated by upper and low boxes) and the minimum and maximum values as well as outliers (circles). Each month of the seasonal variation is shown as an anomaly from the annual mean value of the perchlorate record. The median does not vary throughout the year, however, the quartiles, minima and maxima in the plot vary less in the austral winter months than in the spring and summer months, suggesting that there is less variability in perchlorate concentration during the winter than the summer or spring.

5.4.3 Fluctuations in stratosphere-to-troposphere exchange

The polar vortex is a large area of low pressure and cold air surrounding each of the Earth's poles. Cold air is contained within the polar vortex by the polar-front jet stream - an eastward-moving belt of strong stratospheric winds that separates warm tropical air in the midlatitudes from cold air in the polar regions

[*Waugh and Polvani*, 2010]. The mass of cold air descends adiabatically. The strength of the polar vortex varies with the season, but it is strongest during the winter season in each hemisphere, when the temperature contrast between the pole and the Equator is greatest [*Waugh and Polvani*, 2010]. It may weaken or disappear entirely during the warmer months of the year. The vertical transport of volcanic aerosols from the stratosphere to the troposphere is facilitated by the enhanced stratosphere-to-troposphere exchange associated with the polar vortex [*Cole-Dai et al.*, 1997a; *Jordan et al.*, 2003].

The interpretation of stratospheric aerosol (i.e., ^{10}Be, stratospheric sulfate) records from ice cores is complicated by the relatively long transport path from the origin of the aerosol in the atmosphere to the snowpack and the scavenging processes removing the aerosol from the atmosphere [*Gautier et al.*, 2016; *Pedro et al.*, 2011a; *Pedro et al.*, 2011b; *Toohey et al.*, 2013]. Elevated concentrations of stratospheric aerosol markers are reported to arrive to Antarctic stations in autumn and winter [*Raisbeck et al.*, 1981; *Sanak et al.*, 1985; *Toohey et al.*, 2013; *Wagenbach*, 1996]. Some of the perchlorate peaks in the WAIS Divide record coincide in time with the increased stratospheric subsidence that is expected to occur during winter [*König‐Langlo et al.*, 1998; *Pedro et al.*, 2011b], suggesting that some peaks in perchlorate concentration could be the result of enhanced stratosphere-to-troposphere exchange associated with the polar vortex and not from production. Pedro et al.[*Pedro et al.*, 2012] has suggested that a similar combination of meteorological and vertical transport processes is responsible for the transport of stratospheric particles (i.e., ^{10}Be) in the Arctic, and that direct descent of stratospheric aerosols from the polar stratosphere to the troposphere during the autumn-winter over both poles. As such, perchlorate levels in Arctic snow may also be influenced by enhanced stratospheric transport. In the Arctic, the seasonal maximum in stratospheric input is seen in the late winter to spring [*Heikkilä et al.*, 2013; *Toohey et al.*, 2013], which is consistent with the occasional maxima of perchlorate levels in Greenland snow. It has been estimated that approximately 30% of the variance in the ^{10}Be record in polar snow is due to changes in atmospheric transport [*Heikkilä et al.*, 2013; *Pedro et al.*, 2011a; *Pedro et al.*, 2011b], irrespective of changes in solar activity or production. It may be that changes in vertical transport may also have a significant influence on the variance in perchlorate ice core records. However, improvements in simulating perchlorate transport and deposition to the Arctic and the Antarctic as well as highly resolved perchlorate records from other Antarctic sites are suggested.

5.5 Determining cyclical nature in a time series using a periodogram

Any time series can be expressed as a combination of cosine (or sine) waves with differing periods and amplitudes (maximum/minimum value during the cycle). This fact can be utilized to examine the periodic (cyclical) behavior in a time series. Power spectral analysis, cosine waves with varying amplitudes and frequencies, are separated by frequency and identified. One goal of power spectral analysis is to identify the important frequencies (or periods) in the observed series. A graphic way to view this is the periodogram. The periodogram graphs a measure of the relative importance of possible frequency values that might explain the oscillation pattern of the observed data. This can be a helpful tool for identifying the dominant cyclical behavior in a series, particularly when the cycles are not related to the commonly encountered annual cycle.

5.5.1 Periodicity in the WAIS Divide perchlorate record?

Fast Fourier Transform is applied to the WAIS Divide perchlorate monthly time series (Figure 38). The x-axis is frequency, where 1/frequency is equal to number of months. There are peaks at approximately 0.035 and 0.05 (Figure 38), which would be equivalent to 28 months and 20 months, respectively. However, the scale of the y-axis indicates that the peaks in frequency do not appear different from the noise or background signal. There may be a periodicity of lower frequency (decadal or centennial) for perchlorate that is not apparent due to the relatively short length (time) of the 82-year record; for example, the sunspot cycle of 10-11 years may not be apparent in a 70-year record of sunspot activity.

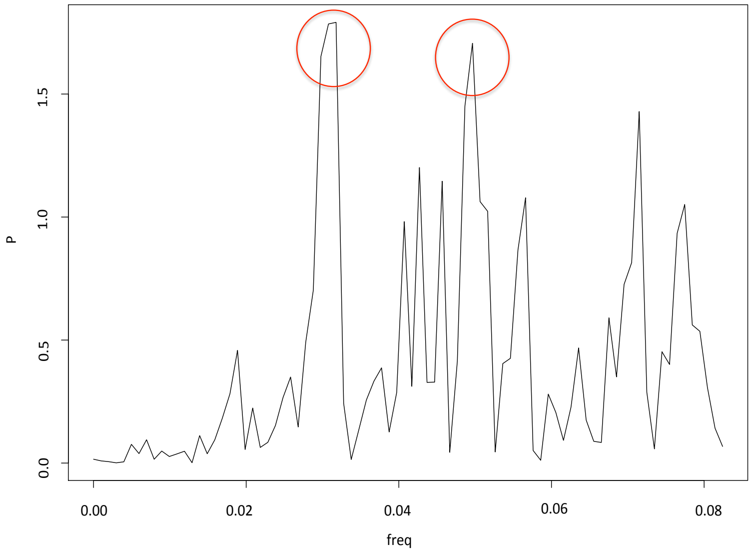

Figure 38. Periodogram (plot of power versus frequency) displaying the power spectral analysis of perchlorate at WAIS Divide, which indicates several peak occur around frequencies of 0.035 and 0.05 (circled in red) - equivalent to 28 months and 20 months, respectively.

5.5.2 Periodicity in Greenland perchlorate?

The Fast Fourier Transform was also applied the 300-year annual mean perchlorate time series from Summit, Greenland (Figure 39). The x-axis is frequency where 1/frequency is equal to number of years. Examination of the resultant periodogram indicates there are frequency peaks at approximately 0.38 and 0.45 (Figure 39), which are equivalent to 2.6 years and 2.2 years, respectively. This periodicity is somewhat similar to the periodicity in the WAIS Divide time series. However, as in the case of the WAIS Divide record, the scale of the y-axis indicates that the peaks in frequency are also indistinguishable from the noise. This suggests that perchlorate in Greenland does not have any significant periodicity or dominant frequency.

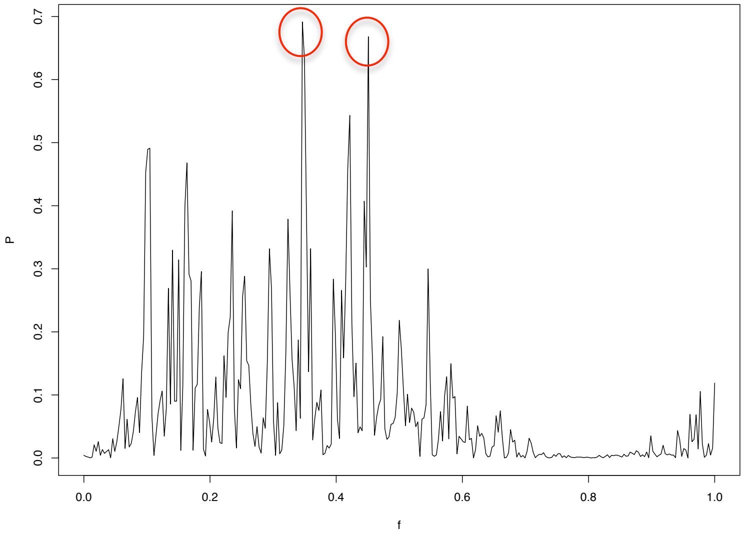

Figure 39. Periodogram of perchlorate at Summit, Greenland indicating several peaks occur around frequencies of 0.38 and 0.45 (circled in red), which would be equivalent to 2.6 years and 2.2 years, respectively. Data is from *Peterson* [2016].

5.7 Conclusion

Short-term variations of perchlorate in Antarctic snow do not appear to occur on a regular or consistent cycle or with any noticeable periodicity. There are oscillations (maxima and minima in concentration) throughout the 82-year record of perchlorate in WAIS Divide snow, and yet these maxima and minima do not appear to occur in a regular pattern or with consistent timing. It does appear that perchlorate concentrations may vary significantly from one year to the next. Variations in annual perchlorate concentrations may be a result of changes in production. The temperature in the stratosphere may have a direct impact on perchlorate production, where colder temperatures result in more chlorine activation, thus promoting perchlorate production. Sulfate aerosols that reach the stratosphere (likely from very large volcanic eruptions) may provide surfaces for chlorine activation, thus also enhancing the production of perchlorate. The variance of perchlorate in ice may also be influenced by changes in atmospheric transport of perchlorate from where it is produced in the stratosphere to its final deposition in snow. Fast Fourier Transform was utilized to separate the seasonal component and random noise from the overall trend. This analysis indicates that there is no underlying periodicity or seasonal pattern, and that the overall increasing trend appears to be the main factor influencing the observed data.

6. Conclusions and Future Work

6.1 Perchlorate in the environment

Perchlorate is ubiquitous in the environment and as such, human exposure to perchlorate is also widespread. Evaluating the impact or effectiveness of proposed regulation and remediation of perchlorate remains difficult. This is due to the lack of knowledge and understanding of the magnitude of atmospheric perchlorate source and its contribution to the current environmental perchlorate budget. Polar ice core records indicate that atmospheric perchlorate production is greater (by an order of magnitude) in the Antarctic than in the Arctic. Polar ice core records further indicate that global atmospheric perchlorate production has increased significantly over the latter half of the twentieth century, particularly since the 1980s.

Perchlorate concentrations in recent snow have most likely been indirectly influenced by increased stratospheric chlorine concentrations. Increases in stratospheric chlorine levels have enhanced the stratospheric production of perchlorate, resulting in an approximately threefold increase in perchlorate levels post-1980 when compared to pre-1980 levels. Increasing amounts of stratospheric chlorine throughout the 1980s and 1990s have been largely attributed to the emission of CFCs. Thus, human activities appear to be indirectly responsible for about two-thirds of the current environmental perchlorate. Yet, as stratospheric chlorine levels continue to decrease due to the regulation and phasing-out of CFCs and other chlorine compounds, perchlorate concentrations in polar snow are expected to decrease over the coming decades.

6.2 Factors that complicate the interpretation of ice core records of perchlorate

The potential exists for perchlorate to be used in future long-term (millennial-scale) ice core records as a proxy for past variations in atmospheric chemistry and climate. The ice core data suggest that perchlorate is produced in the stratosphere and then deposited to Earth's surface. However, proper interpretation of the perchlorate concentrations in polar snow and ice is complicated by several factors: vertical transport, deposition to the snow surface, and post-depositional changes within the snowpack. The ice core data suggest that dry deposition of perchlorate is significant at low accumulation sites whereas wet deposition dominates at locations with moderate to high accumulation. This is important as dry deposition can complicate ice core records of perchlorate in that changes in accumulation can dilute or enhance perchlorate concentrations even if atmospheric concentrations or the amount deposited remains unchanged. The overlapping ice core profiles from the South Pole indicate that perchlorate undergoes significant post-depositional loss of approximately 50% of the initial amount that was deposited. However, the overlapping ice core profiles from WAIS Divide indicate perchlorate is preserved without significant alteration at a location of moderate accumulation, and that post-depositional loss of perchlorate is confined to low accumulation sites. It is possible that perchlorate undergoes post-depositional loss within the polar snowpack at low accumulation sites where perchlorate remains in surface snow for an extended period of time. At sites with higher accumulation, perchlorate is buried at a sufficient rate so that it does not remain exposed in surface snow for an extended period of time, thus limiting the effects of the post-depositional loss process. The mechanism causing the post-depositional loss of perchlorate remains undetermined and a comprehensive understanding requires future work. It is evident, however, that perchlorate is preserved without significant alteration in the snowpack at moderately high accumulation sites such as the WAIS Divide site in Antarctica and many sites throughout the Arctic, thus allowing for viable ice core records of perchlorate that are uncomplicated by dry deposition and/or post-depositional loss that can be used to investigate the atmospheric production of perchlorate.

6.3 Key drivers of perchlorate production

It is apparent that the long-term (decadal) perchlorate trend is directly proportional to stratospheric chlorine levels and inversely related to total column ozone. It is likely that levels of activated chlorine heavily influence atmospheric perchlorate production. There are significantly more amounts of activated chlorine in the Antarctic than in the Arctic [*Solomon et al.*, 2014], which might explain why the perchlorate levels are an order of magnitude higher in the Antarctic than in the Arctic. If perchlorate production is directly related to levels of activated chlorine, then environmental conditions that influence activated chlorine likely also influence perchlorate production. Annual perchlorate concentrations are inversely correlated to stratospheric temperature – colder temperatures in the stratosphere result in more PSCs, leading to an increase in activated chlorine and, thus more perchlorate production. Additionally, there also appear to be increased levels of Antarctic perchlorate during years when stratospheric sulfate is elevated by very large volcanic eruptions. It may be that stratospheric H_2SO_4 aerosols from large volcanic eruptions also provide surface area for heterogeneous chlorine activation, and consequently, enhance perchlorate production.

6.4 Future Work

The perchlorate record in polar ice cores is expected to contain information about atmospheric chemistry due to the probable link between perchlorate and chlorine radicals and ozone. However, this work shows that ice core records of perchlorate can be complicated by several factors: post-depositional alterations of perchlorate concentration result in net loss in the top snow layers. Average loss of 52 ± 26% of initial concentration (Table 6) was observed in South Pole snow. It is worth noting that losses of 85-95% of initial concentration (Table 6) were observed between the years 1992-1995. It is expected that perchlorate production became enhanced during these years due to stratospheric sulfate aerosols emitted from the Mt. Pinatubo volcanic eruption. The reason for this unusually high loss remains unclear. Could it be that perchlorate deposited from volcanically enhanced production is more susceptible to post-depositional alteration than perchlorate deposited from typical perchlorate formation? Could a different loss mechanism or rate of loss be affecting the perchlorate deposited during these specific years? Alternatively, what if the amount of loss is not proportional to the initial concentration? Rather, loss leads to a fixed concentration despite what the starting concentration is. This may hint at loss mechanism. The amount of post-depositional loss needs to be studied at other low-accumulation sites to more accurately quantify loss as well as gain further understanding of the loss mechanism. Additionally, the unusually high degree of alteration of perchlorate concentration in South Pole snow during the years surrounding the Pinatubo eruption also need further investigation.

Stratospheric chlorine levels peaked in 1997 followed by a decrease of close to one per cent per year [*National Oceanic & Atmospheric Administration (NOAA)*, 2015; *Solomon et al.*, 2014; *von Clarmann*, 2013; *WMO/GAW Ozone Monitoring Community*, 2015]. Perchlorate concentrations in both the Arctic and Antarctic follow the same trend with very similar timing in peak concentrations in the late 1990s, and followed by a gradual decrease. Recent ground-based and satellite data [*Mahieu et al.*, 2014], however, show a recent and significant increase in HCl, the main stratospheric chlorine reservoir, that starts around 2007 in the lower stratosphere of the Northern Hemisphere and continues to present day (Figure 40) [*Mahieu et al.*, 2014; *Mahieu et al.*, 2015]. This trend anomaly is attributed to a slowdown in the Northern Hemisphere atmospheric circulation, occurring over several consecutive years, transporting HCl-enriched air from the upper stratosphere (7 hPa) to the lower stratosphere (46 hPa) [*Belleflamme et al.*, 2015; *Mahieu et al.*, 2014; *Mahieu et al.*, 2015]. It is expected that this recent HCl increase in the Northern Hemisphere lower stratosphere will likely lead to increase in active chlorine, and thus an increase in perchlorate production. It is not currently known if perchlorate production has increased in the Arctic in response to the increase in Northern Hemisphere stratospheric chlorine. This is because the record of Arctic perchlorate developed by *Peterson* [2016] covered the period 1700-2007. A more recent perchlorate profile from the Arctic covering the period from 2007 would allow for an investigation to study the response of perchlorate production to rapid changes in stratospheric chlorine.

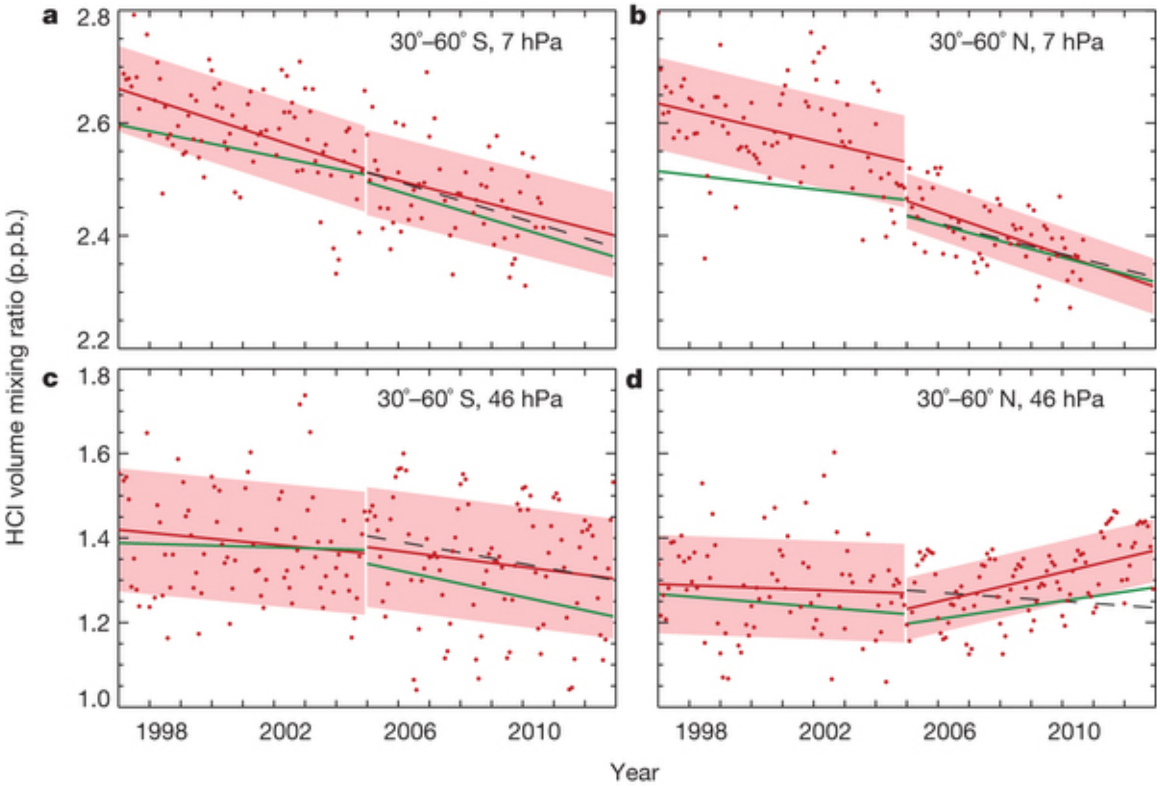

Figure 40. Stratospheric HCl data from satellite observations and SLIMCAT model runs for NH and SH mid-latitude lower (46 hPa) and upper stratosphere (7 hPa) monthly means are shown as red dots. Linear fits to the satellite data and SLIMCAT model runs are displayed as red and green lines, respectively, for periods before and after 2005. The dashed black line shows fits to the S2000 model run which assumes no change in circulation. An upward trend is observed in the Northern Hemisphere lower stratosphere (d) while HCl is decreasing in the southern and northern upper stratosphere (a, b). Figure from *Mahieu et al.* [2014].

In the Southern Hemisphere, it does not appear that there is a change in the overall decreasing trend in stratospheric HCl post-2007 (Figure 40). As such, Antarctic perchlorate continues to slowly decrease. This decreasing trend is observed in annual average perchlorate from the WDC13 core (Figure 41).

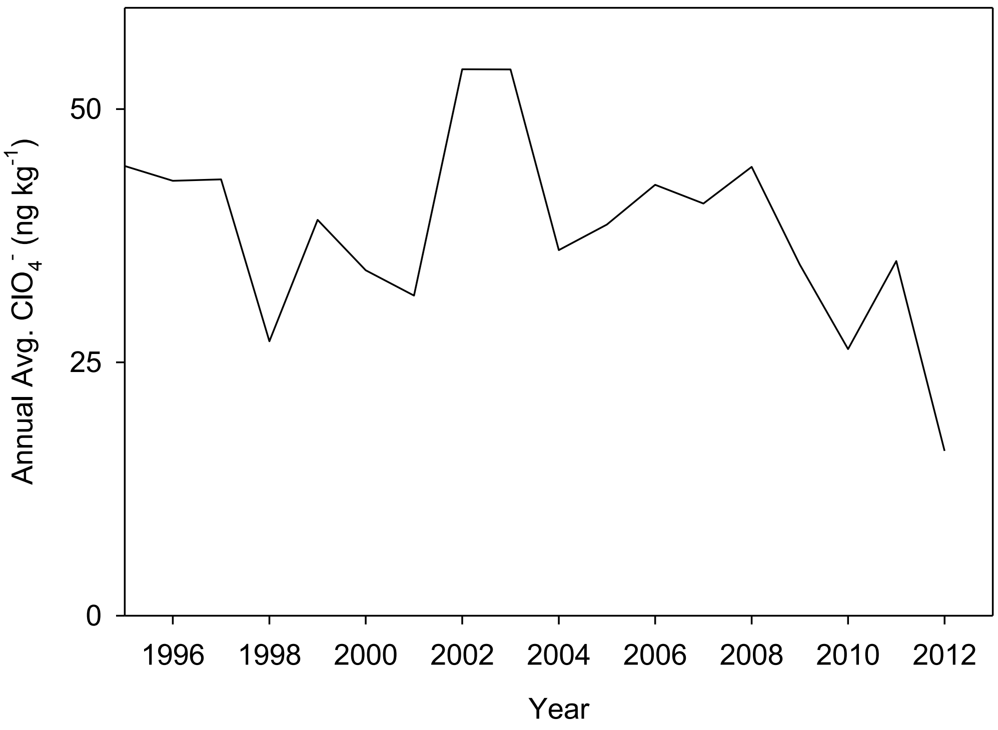

Figure 41. Annual average perchlorate concentrations from the WDC13 core display a decreasing trend since 2007, similar to the decreasing trend in HCl in the stratosphere of the Southern Hemisphere.

6.4.1 Perchlorate as a proxy

Due to its link stratospheric ozone, stratospheric chlorine chemistry has been studied intensely. It is recognized that three requirements exist for massive ozone loss in the stratosphere: (1) chlorine and bromine in the atmosphere, (2) cold temperatures and particle surfaces for heterogeneous chemistry, and (3) modest amounts of sunlight. These conditions and their respective seasons are shown schematically in Figure 42, which are all met in the unique environment of the Antarctic stratosphere. The polar vortex that forms each

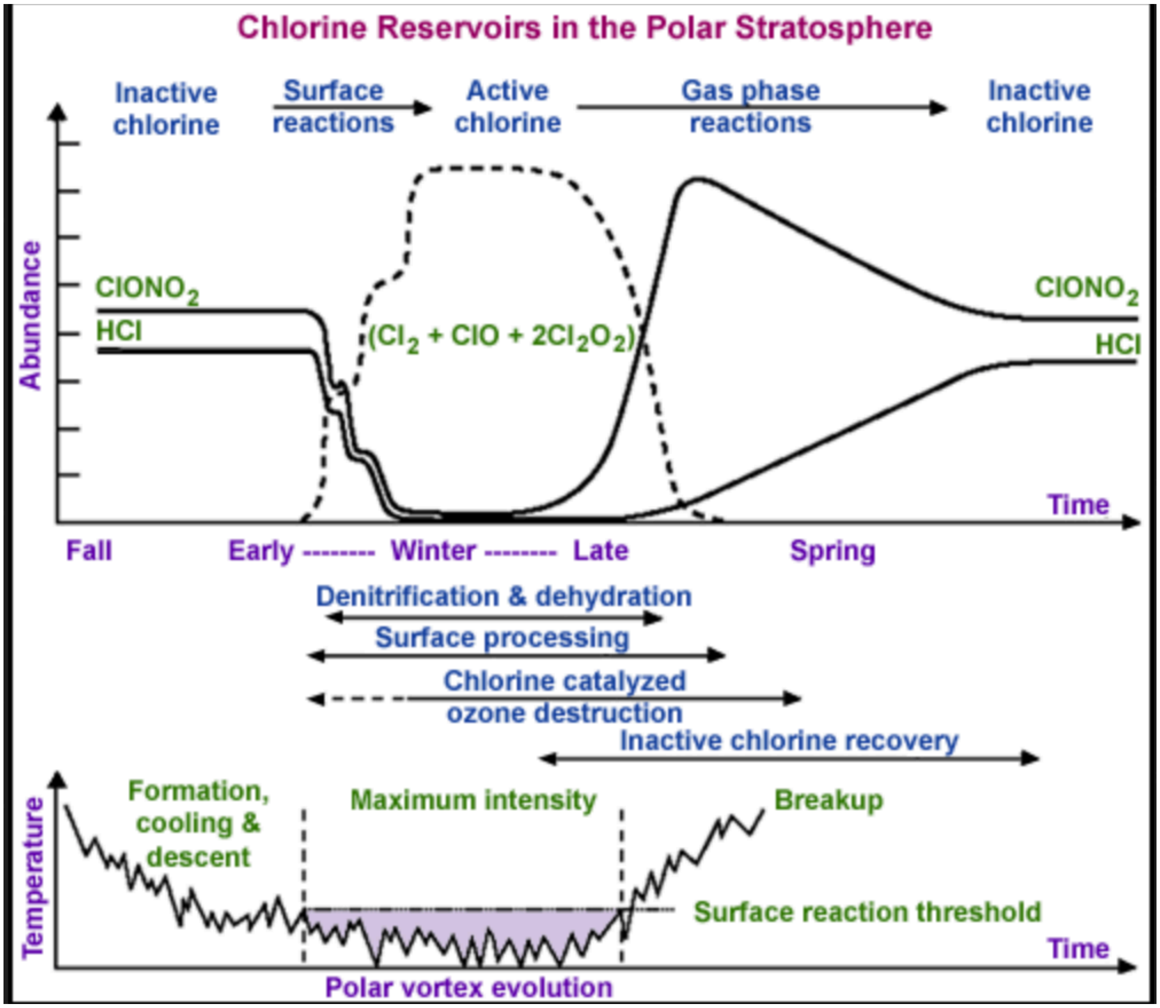

Figure 42. Schematic diagram of the chemistry that causes the ozone hole. During the cold, dark polar winter, PSCs form, and the reservoir chlorine compounds $ClONO_2$ and HCl react on their surfaces. With very little sunlight, the Cl_2 is photolyzed into Cl atoms that react with ozone. As the temperature increases in the late spring, the PSCs evaporate and the reservoir reactions slow down, resulting in increased $ClONO_2$ and HCl concentrations and replenishment of ozone. Figure from *WMO (World Meteorological Organization)* [2011].

winter above Antarctica is important for isolating the stratospheric air, which allows the air to become very cold during the winter and reduces the influx of ozone-rich air from the tropics. The low temperatures allow PSCs to form in the winter/ spring and thus support the heterogeneous chemistry to convert chlorine reservoir molecules into chlorine radicals (active chlorine) and sunlight is needed to drive the actual ozone-loss cycles. The PSCs also lead to denitrification, which prevents the active ClO from reforming inactive $ClONO_2$. At the altitude of PSCs, the ozone layer is completely destroyed. Only when the polar vortex breaks down in the late spring or early summer does ozone from lower latitudes fill in the hole. It is important to note that of the three requirements for ozone loss, the only one that has significantly changed since the 1950s is the amount of chlorine and bromine in the atmosphere. Thus, it is the increasing levels of these halogens that have caused the regular appearance of the Antarctic ozone hole. How does perchlorate formation fit into the stratospheric chlorine chemistry cycle?

Perchlorate data from ice cores has potential to be used as a proxy to assess past variations in atmospheric chemistry and climate. Long-term (millennial-scale) records of perchlorate can possibly be used to track the abundance of stratospheric chlorine and activated chlorine in the past; whereas, current measurements of perchlorate in precipitation may provide estimates of current stratospheric chlorine levels and activated chlorine levels. Additionally, as perchlorate levels are inversely related to ozone levels, perchlorate records also have the potential to be used as a proxy for ozone levels and ozone depletion events in the past as well as aid in assessment of the evolution and recovery of the Antarctic ozone hole. As the detailed pathway and key reactions involved in atmospheric perchlorate production are elucidated and identified with further research and studies, the relationships between perchlorate levels observed in polar snow and various atmospheric conditions (i.e., stratospheric chlorine, ozone, activated chlorine species, stratospheric temperature, etc.) will be better understood. And as these relationships become better understood, perchlorate’s use as a proxy for these conditions will also become stronger.

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