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Investigation of Natural Perchlorate Levels in Antarctic Snow in Relation to the Ozone Hole

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ABSTRACT

Snow samples collected from the West Antarctic Ice Sheet Divide in January 2013 were analyzed for perchlorate concentrations to determine a possible seasonal variation. These samples were dated for the years 2007 through 2012 using annual variations in sulfate concentration as determined by an ion chromatography (IC) method. Perchlorate concentrations in the samples were measured with an IC instrument paired with tandem mass spectrometry detection. The concentration data show that perchlorate reached an annual maximum concentration in the austral autumn seasons, assuming that snowfall was relatively constant throughout the course of each year. Comparison with published total column ozone density at the South Pole shows that the perchlorate annual maximum does not occur in the same seasons when ozone is at a minimum level.

INTRODUCTION

Perchlorate is a common naturally occurring anion found throughout the world. Although little research has been done on the specific sources of perchlorate in nature, research suggests that it forms primarily in the atmosphere. It has been suggested that perchlorate is formed in the atmosphere when chlorine species are oxidized by ozone[1]. This project has focused on this proposed formation by investigating how perchlorate concentrations relate to stratospheric ozone. Specifically, the project's focus was to determine if a seasonal relationship exists between perchlorate in Antarctic snow and stratospheric ozone over Antarctica, which is known to drop in the austral spring during the appearance of the ozone hole.

The Polar Regions have been a primary location for investigation of trends of naturally occurring chemical species due to the preservation of atmospheric content in snow. Dating of such ice samples can be completed for a depth of snow using knowledge of annual snow accumulation as well as seasonal variations of ions in snow. Sulfate, for example, is known to reach an annual maximum Antarctic concentration during the austral summer months of January to February[4]. Published research articles have utilized polar snow to measure perchlorate in Arctic Snow[1]; however, few have involved Antarctic snow, and none have investigated seasonal variation in perchlorate in relation to ozone. Some preliminary measurements of preserved snow and ice samples had shown perchlorate levels to increase around the late 1970s, when the ozone hole was known to begin forming. These measurements suggested a possible relationship between perchlorate and the ozone hole.

The original hypothesis of this study revolved around the idea that the depletion of stratospheric ozone over the Antarctic continent would allow additional ultra-violet (UV) light to pass through to the troposphere. This increased UV radiation would then lead to increased tropospheric ozone, as well as airborne chlorine radicals as reactants in perchlorate formation. By Le Châtlier's Principle, the addition of ozone and chlorine radicals should cause an increase in perchlorate concentration. To test this hypothesis, we created a seasonal timeline of perchlorate in Antarctic snow to determine in which season elevated levels occurred.

METHODS

In a 3-meter deep snow pit, 88 snow samples from West Antarctic Ice Sheet Divide (WAIS) (112.085 °W, 79.467 °S) were taken from the surface downward in 3 cm depth increments in January 2013. These snow samples were stored in sealed plastic cups and transported frozen to a laboratory for analysis. The snow was allowed to melt and then directly poured into clean autosampler vials which were then capped and analyzed by two separate sets of instrumentation.

Each sample was automatically injected and analyzed with an Ion Chromatography (IC) apparatus consisting of a Dionex IC600 system with a GP50 Gradient Pump, Dionex IonPac® AS11 3 x 250 mm column with CSRS300 2 mm suppressor, and ED50 Electrochemical Detector to detect sulfate concentrations at the part-per-billion (ppb) level. An eluent of 1.5 mmol NaOH was used at a flow rate of 0.60 mL/min. The area of the sulfate peak in the chromatogram was calibrated with a set of standard solutions to determine the sulfate concentration. The uncertainty of ion concentrations measured with this method is less than 10%.

Additionally, a method including a similar IC instrument system paired with a SCIEX QTRAP electrospray-ionization tandem mass spectrometry detector allowed for detection of perchlorate at concentrations down to the low or sub-part-per-trillion (ppt) level. This method was similar to that outlined by Jiang, et al.[2], with a precision of 10%.

RESULTS

The data of the snow samples are presented in Figure 1 against a plot of ozone density assuming snow depth and time are perfectly proportional. The gap in perchlorate at depth 224 cm corresponds to a sample of insufficient volume to successfully gather a perchlorate concentration.

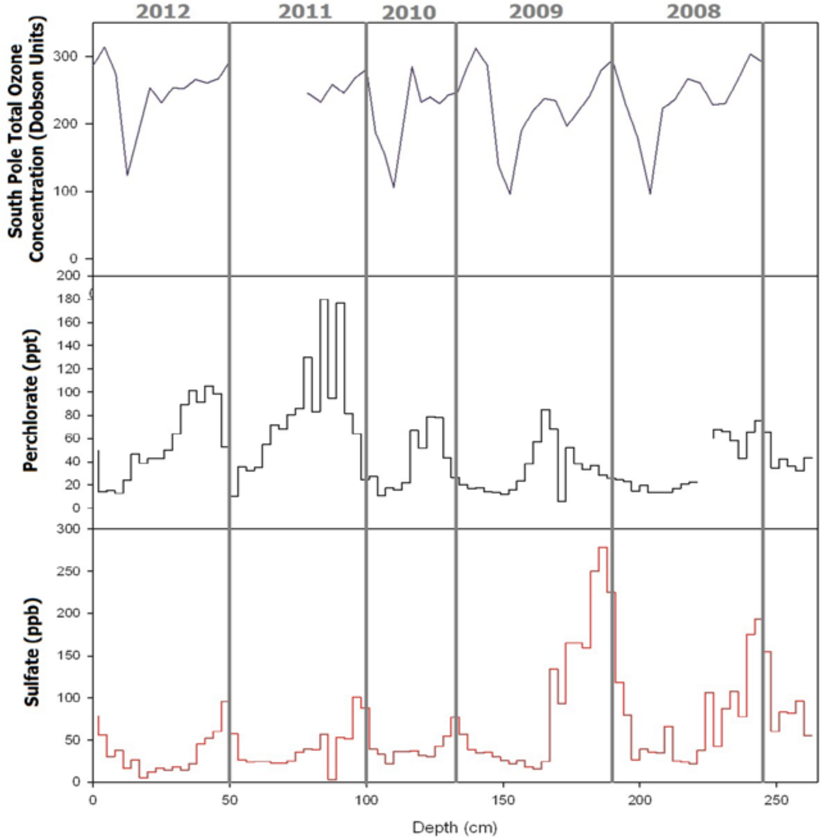

Figure 1: Measured Sulfate and Perchlorate Concentrations in Antarctic Snow Samples, and Published Total Ozone Levels[3]

The sulfate concentrations are used to mark the beginnings of each year as sulfate concentrations in Antarctica peak in the months of January and February[4]. According to the years as shown in Figure 1, it appears that perchlorate concentration reaches an annual maximum in the austral autumn, approximately the months of March and April. The lowest concentrations generally appear in the austral spring, approximately September and October, when the ozone hole is present. This is highlighted by the extreme dips in the total ozone density for this season as measured at the South Pole[3]. The collected data regarding the perchlorate concentrations shows such seasonal variation consistently for all of the years studied.

DISCUSSION

The results contradict our hypothesis in that perchlorate levels are at an annual minimum when the ozone hole is present. However, the consistency of seasonal variation in perchlorate concentration suggests there might still be a relationship between perchlorate levels and the ozone hole, although different than initially hypothesized. It is possible that the atmospheric production of perchlorate occurs primarily in the stratosphere rather than the troposphere. The decreased level of stratospheric ozone during the spring season could be a limiting factor in stratospheric perchlorate production during that season.

Extensive study on the creation of the ozone hole shows that the ozone is depleted during the austral spring because air temperature is low enough to allow formation of polar stratospheric clouds (PSCs) in the stratosphere during a period when daylight is present enough for a UV initiation of ozone depletion[5]. These PSCs act as a necessary factor in chlorine catalyst regeneration in that Cl_2 and HOCl can collect on them and return to chlorine radicals by UV photolyzing[5]. For the rest of the year, these PSCs are not present;

chlorine catalyst regeneration may not occur and thus ozone depletion is limited. It is possible that the formation of perchlorate occurs in the stratosphere alongside this chlorine catalyst regeneration reaction in such a way that they are competing. In one case, PSCs are present and allow for the chlorine catalysts to predominantly reform after ozone depletion. In the other case, PSCs are not present, and thus, perchlorate formation predominates and can be precipitated out of the atmosphere into snow. It has already been suggested that perchlorate acts as a natural sink for chlorine catalysts[1]; the data from this study reinforces this proposition.

In conclusion, the collected data establishes a seasonality in perchlorate concentrations. In comparison to total column ozone density, it appears that the presence of the ozone hole relates to decreased perchlorate concentrations. The data suggests that perchlorate production may be acting as a sink for stratospheric chlorine and thus competing with the chlorine catalytic depletion of ozone. Seasonal trends in Antarctic perchlorate concentration may be attributable to the presence of polar stratospheric clouds during the spring season.

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