



Presence of perchlorate in marine sediments from Antarctica during 2017–2020

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Abstract Perchlorate of natural origin is a persistent pollutant that affects thyroid function by inhibiting iodine uptake, and this pollutant is frequently detected in different ecosystems at concentrations that can harm human health. In this study, we measured the perchlorate concentrations in 3,000 marine sediment samples from January to March in 2017, 2018, 2019, and 2020 during the 3rd, 4th, 5th, and 6th Colombian Scientific Expeditions to Antarctica. The sampling zones were located at 15 different points on the South Shetland Islands and Antarctic Peninsula, and they were measured using a selective perchlorate electrode. The concentration data indicate that perchlorate reached a minimum concentration of 90 ppm on Horseshoe Island and a maximum concentration of 465 ppm on Deception Island, suggesting a spatial variation in perchlorate concentrations that can be attributed to the natural formation of this pollutant due to volcanic eruptions. Additionally, homogeneous distribution of perchlorate was not observed in Antarctica.

Keywords Selective electrode · Endocrine disruptor · Environmental fate · South Shetland Islands · Toxicology · Occurrence assessment

Introduction

Perchlorate (ClO_4^-) is a chemically stable anion and a powerful oxidant (Cao et al., 2019) that possesses a tetrahedral structure where a chlorine atom is surrounded by four oxygen atoms (Murray & Bolger, 2014; Wan et al., 2018). It affects thyroid function by inhibiting iodine uptake (Park et al., 2006; Pleus & Corey, 2018). This pollutant is of natural origin and can persist in the environment in a stable form for a long period of time (Acevedo-Barrios et al., 2018; Acevedo-Barrios et al., 2019a, b; Acevedo-Barrios et al., 2019a; Bardiya & Bae, 2011). Due to its high solubility, stability, and persistence, ClO_4^- can be found in all environmental matrices (Logan et al., 2001).

ClO_4^- can also be of anthropogenic origin. It is used in military and firework industries as an additive for explosives, and it can also be used as a fertiliser. The widespread use of ClO_4^- further explains the anthropogenic sources and thus ClO_4^- sources in the environment are of interest (Cao et al., 2019; Liao et al., 2020). Recent findings indicate the occurrence of natural formation in the atmosphere due to photochemical reaction pathways (Dasgupta et al., 2005; Kumarathilaka et al., 2016; Roberts, 2009; Trumpolt et al., 2005). Natural formations occur during storms (U.S. Food and Drug Administration, 2008), volcanic eruptions, and tectonic plate movements (Furdui et al., 2018; Simonaitis & Hecklen, 1975). Additionally, arid zones (Murray & Bolger, 2014; Vega et al., 2018) and hypersaline environments (Acevedo-Barrios et al.,

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2016, 2019a, b) have been reported as natural sources of ClO_4^- . This compound has been detected even in extreme and remote environments such as in Antarctica (Jackson et al., 2012; Kumarathilaka et al., 2016).

Although this compound was previously detected in Antarctica, not more than two extensive studies have been performed and published that further examine the presence of ClO_4^- in this remote location. The first study was performed by Kounaves et al. (2010), who reported the presence of ClO_4^- in soil and ice from Antarctic Dry Valleys at a concentration of 1100 $\mu\text{g}/\text{kg}$. The second study was performed by Jiang et al. (2016), who reported concentrations of approximately 33 and 351 ng/kg in samples collected from three Antarctic locations. They reported a trend of higher concentrations of ClO_4^- in recent Antarctic snow (post-1980) than in older snow. These results are similar to those obtained by Peterson et al. (2015a, 2015b), who reported that the ClO_4^- concentration in Arctic snow increased over time.

The Antarctic ClO_4^- occurrence and increasing concentration over time are presumably attributed to natural formation in the atmosphere and deposition onto the surface and into water bodies by precipitation (Cao et al., 2019; Jiang et al., 2013). ClO_4^- detection and distribution in Antarctica will aid in understanding its formation and its effects on the flora and fauna, exposed to environmental concentrations (Goleman et al., 2002). However, more data on the occurrence of this compound are required. Thus, the aim of this study was to measure ClO_4^- levels in the Antarctic marine sediments (Shetland Islands and Antarctic Peninsula) from 2017 to 2020 to better understand the occurrence of ClO_4^- in Antarctica.

Materials and methods

Sampling stations

A total of 3,000 sample points were selected from 15 different locations throughout the South Shetland Islands and Antarctic Peninsula to measure ClO_4^- concentration in situ without the need to transport the samples. The ClO_4^- concentrations in South Shetland Island were measured at several different locations, including the Livingston Islands, Byers Peninsula, Deception Island, King George Island,

and Half Moon Island. The ClO_4^- concentrations in the Antarctic Peninsula were measured from Cierva Point, Petermann Island, Goudier Island, Port Neko, Danco Island, Couvreville Island, Palmer Archipelago, Avian Island, Horseshoe Island, and Lagotellerie Island (Fig. 1, Table 1). Sampling was performed from January to March in 2017, 2018, 2019, and 2020. Additionally, parameters, such as pH (accuracy ± 0.2 units), salinity (accuracy ± 0.1 ppt), and temperature (accuracy ± 0.2 °C), were recorded in situ using a multiparameter YSI Pro1030 (Yellow Springs Instruments, Yellow Springs, USA).

Quantification of ClO_4^- concentrations in Antarctic marine sediments

ClO_4^- concentration measurements were performed using portable ion specific (ISE)/pH Meters and a Thermo Scientific Orion 93 selective ClO_4^- electrode (Thermo Fisher Scientific Inc., Beverly, MA) that functions as an electroanalytical sensor and is composed of a sensing module joined to an epoxy body. This sensing module contains a solution that is in contact with an organophilic membrane possessing a perchlorate-selective ion exchanger. Its potential reveals the activity of the ion ClO_4^- (Koryta, 1986; Thermo Fisher Scientific Inc., 2008).

The ability to measure the ion concentration depends on the potential generated when the electrode module is in contact with the solution containing the studied ions. This potential was described by the Nernst equation (Eq. 1), where E is the measured potential, E^0 is a constant, S is the electrode slope (approximately -56 mV per decade), and A is the ClO_4^- ion activity level in the solution (Thermo Fisher Scientific Inc., 2008).

$$E = E^0 + S \times \log (A) \quad (1)$$

Prior to use, the electrode was prepared by treating the module with distilled water and submerging it in a 100-parts-per-million-(ppm) preparation solution for 1 to 2 h (Thermo Fisher Scientific Inc., 2008). Calibration was performed using a series of standards prepared by serially diluting 1,000 ppm NaClO_4 to create three standards (1, 10 and 100 ppm). The electrodes exposed to the sample were directly measured for ClO_4^- . The concentration is determined by comparing samples to standards. The electrode was rinsed

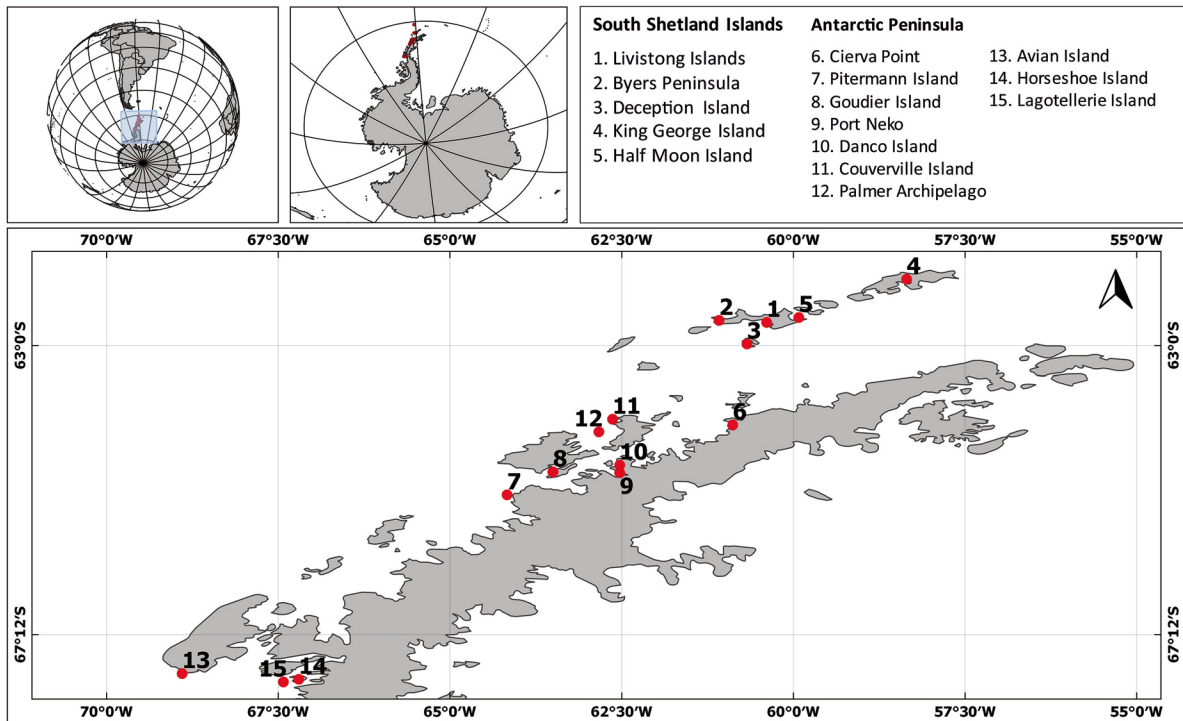


Fig. 1 Map of the area under study showing the fifteen sediment sampling sites in Antarctica. Sampling sites 1 to 5 are located in the South Shetland Islands, and sampling sites 6 to 15 are located in the Antarctica Peninsula

with distilled water between each measurement to prevent sample carryover, and each sample was analysed three times with $\pm 2\%$ error. A calibration curve was

constructed using solutions containing ClO_4^- at concentrations of 100, 1,000, and 10,000 ppm (Dimeski et al., 2010; Thermo Fisher Scientific Inc., 2008).

Table 1 Geographic locations of sampling sites in different parts of Antarctica

Sample number	Sampling site	Location	Latitude	Altitude
1	Livingston Islands	South Shetland Islands	62°39'46"S	60°23'20"W
2	Byers Peninsula	South Shetland Islands ASPA* N°126	62°38'00"S	61°05'00"W
3	Deception Island	South Shetland Islands	62°58'38"S	60°40'33"W
4	King George Island	South Shetland Islands	62°02'00"S	58°21'00"W
5	Half Moon Island	South Shetland Islands	62°35'30"S	59°55'15"W
6	Cierva Point	Antarctic Peninsula ASPA* N° 134	64°09'00"S	60°53'00"W
7	Petermann Island	Antarctic Peninsula	65°10'00"S	64°10'00"W
8	Goudier Island	Antarctic Peninsula	64°50'00"S	63°30'00"W
9	Port Neko	Antarctic Peninsula	64°50'41"S	62°31'48"W
10	Danco Island	Antarctic Peninsula	64°44'00"S	62°31'48"W
11	Couverville Island	Antarctic Peninsula	64°4'00"S	62°38'00"W
12	Palmer Archipelago	Antarctic Peninsula	64°15'00"S	62°50'00"W
13	Avian Island	Antarctic Peninsula ASPA* N°117	67°46'00"S	68°54'00"W
14	Horseshoe Island	Antarctic Peninsula	67°51'00"S	67°12'00"W
15	Lagotellerie Island	Antarctic Peninsula ASPA* N° 115	67°53'20"S	67°25'30"W

* ASPA: Antarctic specially protected area

Statistical analysis

Statistical analysis was performed based on an analysis of variance (ANOVA) with a significance level of 0.05 using the Statgraphics software (<https://www.statgraphics.com>). To obtain consistent and reliable results, site variations were investigated by measuring independent replicate samples. Additionally, a mean value assessment was performed using Tukey's test.

Results and discussion

ClO_4^- was present in all South Shetland Islands and Antarctic Peninsula sediment samples, thus indicating a wide occurrence of this compound. The ClO_4^- concentration varied significantly when each concentration was analysed according to sampling location ($P < 0.05$). The temperature ranged from 2.0 °C to 4.0 °C, pH varied from 8.0 to 8.7, and salinity ranged from 35.0 ‰ to 36.0 ‰.

The ClO_4^- concentrations in the 3,000 sediment samples measured from January to March in 2017, 2018, 2019, and 2020 ranged from 91.063 to 465.167 ppm (Table 2). In the Shetland Islands, the concentration reached 465.167 ppm, while that in the Antarctic Peninsula reached 250.833 ppm. These

values are higher than those reported by Kounaves et al. (2010), who measured ClO_4^- in soil from Antarctic Dry Valleys (0.031–0.630 ppm). Jiang et al. (2013) measured concentrations of 50.7 to 339 ng/L in snow and 0.6 to 16.9 ng/L in ice using coupled ion chromatography.

The occurrence of this inorganic anion species in Antarctica has been related to its natural origin in the atmosphere, and its presence in the landscape surface occurs through wet and dry deposition (Rajagopalan et al., 2009; Rao et al., 2007). There is not a certain pathway for atmospheric ClO_4^- origin; however, it is believed that ClO_4^- forms in the atmosphere when chlorine species are oxidised in reactions involving ozone (Catling et al., 2010; Crawford et al., 2017; Peterson et al., 2015a, 2015b).

In Antarctica, ClO_4^- can be formed when chlorine free radicals ($\text{Cl}\cdot$) and ozone (O_3) react in the stratosphere when an ozone hole is present in the austral spring (Jiang et al., 2021). Thus, a seasonal pattern of ClO_4^- was observed in the Antarctic continent due to the ozone hole formed during the late winter and spring when there is sunlight; however, by late December when temperatures in the stratosphere begin to rise, the ozone levels recover (Crawford et al., 2017; Solomon, 1999; Solomon et al., 2014). ClO_4^- levels reach higher concentrations during

Table 2 Concentrations of ClO_4^- in marine sediment samples measured from different sites in Antarctica

Sample number	Sampling site	Location	Total number of samples (<i>n</i>)	Mean concentration of ClO_4^- (ppm)	Standard deviation (SD)
1	Livingston Islands	South Shetland Islands	240	361.292	6.937
2	Byers Peninsula	South Shetland Islands ASPA N°126	160	123.813	7.637
3	Deception Island	South Shetland Islands	240	465.167	9.936
4	King George Island	South Shetland Islands	320	401.531	8.984
5	Half Moon Island	South Shetland Islands	240	203.708	9.374
6	Cierva Point	Antarctic Peninsula ASPA N° 134	240	131.667	7.635
7	Petermann Island	Antarctic Peninsula	160	165.250	9.774
8	Goudier Island	Antarctic Peninsula	160	172.500	7.354
9	Port Neko	Antarctic Peninsula	160	167.000	8.745
10	Danco Island	Antarctic Peninsula	160	181.000	8.845
11	Couvertville Island	Antarctic Peninsula	200	141.650	9.837
12	Palmer Archipelago	Antarctic Peninsula	240	250.833	10.714
13	Avian Island	Antarctic Peninsula ASPA N°117	160	111.000	8.482
14	Horseshoe Island	Antarctic Peninsula	160	91.063	10.069
15	Lagotellerie Island	Antarctic Peninsula ASPA N° 115	160	102.875	8.195

autumn, and the lowest concentrations occur during winter and spring (Crawford et al., 2017). According to Jiang et al. (2021), ClO_4^- forms during September and October in the stratosphere, and it then moves to the boundary layers during the next several months, where it reaches higher concentrations in March and the lowest concentration in December.

In our study, ClO_4^- concentration measurements were performed during the summer and autumn from 2017 to 2020. We observed an increase in the mean ClO_4^- concentration from 2017 to 2019 at each sampling point (Fig. 2). This trend was also reported by Jiang et al. (2013), where ClO_4^- levels in ice sheets located in West Antarctica increased since the 1970s and were associated with a natural origin in the stratosphere. In other parts of the world, there are reports of increasing ClO_4^- concentrations over time; however, this is due to the increased stratospheric chlorine levels caused by emissions of anthropogenic volatile chlorine compounds, and this has been reported in the Miaoergou glacier of East Asia since 1980 (Du et al., 2019). Likewise, increased anthropogenic contributions associated with ClO_4^- have been reported in Greenland, the High Arctic of Canada, and the ice cores of North America (Cole-Dai et al., 2018; Furdui et al., 2018; Peterson et al., 2015a, 2015b; Rao et al., 2012).

In contrast, our study recorded a reduction in ClO_4^- concentration at all sampling points in 2020 (Fig. 2). This lower ClO_4^- concentration is related to the extreme climatologic events that occurred in the spring of 2019, when a sudden stratospheric warming curtailed the development of the ozone hole (Klekociuk et al., 2021; Wargan et al., 2020). This unusual event in 2019 was compared to small ozone holes that formed in the Southern Hemisphere during the 1980s and broke the record set by the sudden stratospheric warming that occurred in 2002 (Shen et al., 2020a, 2020b). When the stratospheric temperature increases, the formation of polar stratospheric clouds is suppressed, and this slows catalytic chemical reactions such as chlorine regeneration (Crawford et al., 2015; Shen et al., 2020a). Therefore, ClO_4^- formation can decrease under stratospheric heating events, as the presence of chlorine free radicals ($\text{Cl}\cdot$) that allow for ClO_4^- formation is reduced.

When the ClO_4^- concentrations were analysed according to location, the results revealed that the highest concentration was observed on Deception Island (maximum value: 465.167 ppm) (Fig. 3), and this higher ClO_4^- concentration than at other sampling locations was attributed to the active volcano on the island. Volcanic eruptions are a source of natural ClO_4^- (Cao et al., 2019; Furdui et al., 2018; Muniz

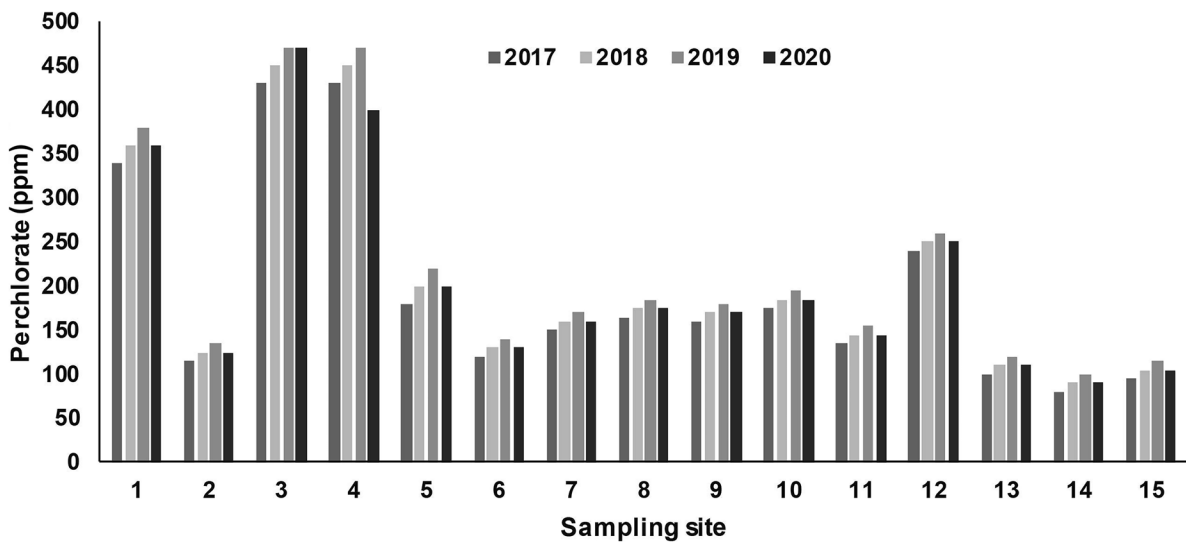


Fig. 2 Distribution of ClO_4^- concentrations in sediments from the South Shetland Islands and the Antarctic Peninsula from 2017 to 2020. Significant differences in mean concentrations ($P < 0.05$)

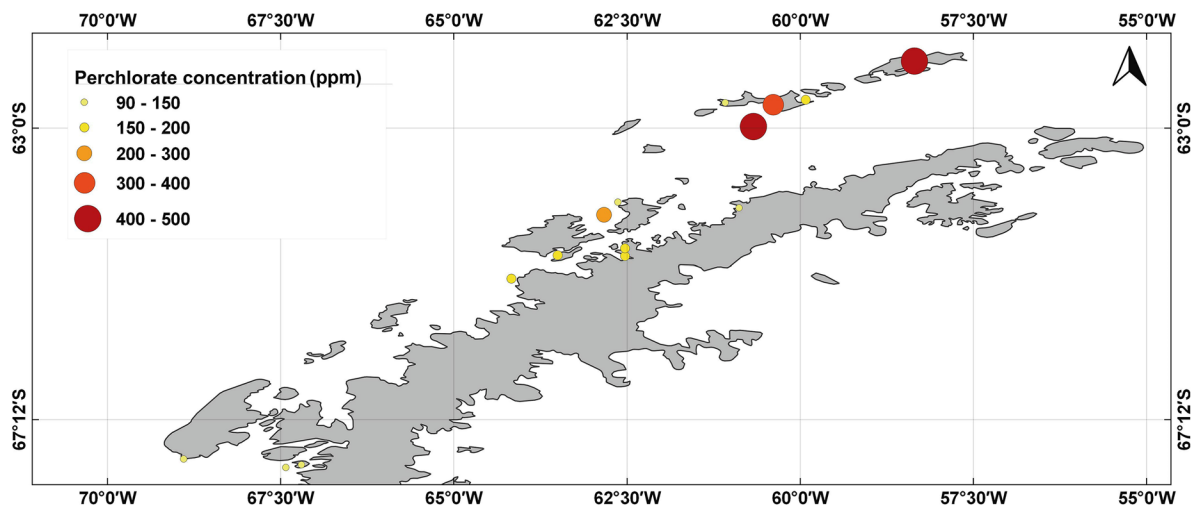


Fig. 3 Bubble map indicating the spatial ClO_4^- concentration distribution in the South Shetland Islands and the Antarctic Peninsula. Small yellow dots represent low concentrations, and large red dots represent high concentrations

et al., 2018; Peterson, 2016; Simonaitis & Hecklen, 1975), as volcanic aerosols promote the formation of chlorine radicals and ClO_4^- intermediates (Kennedy, 2020). ClO_4^- occurrences have been linked to volcanic eruptions. Furdai and Tomassini (2010) observed an atmospheric increase in ClO_4^- concentration in the Arctic that was attributed to volcanic eruptions that caused periods that exhibited higher levels of sulphate deposition. Cole-Dai et al. (2018) reported that the ClO_4^- depositions in the ice sheets of Agassiz (Nunavut, Canada) increased during volcanic eruptions that occurred during 1980–2001. From an ice core from Summit Station in Greenland, Gibson and Shea (2019) reported that a temporary but significant increase in the amount of ClO_4^- in the atmosphere was caused by the Huaynaputina eruption.

The lowest concentration was observed in Horse-shoe Island (91.063 ppm), and this was followed by Avian Island and Lagotellerie Island (mean concentrations of 111 and 102.875 ppm, respectively), farther from Deception Island. These low concentration could be explained by the distance from volcanic islands and based on the knowledge that terrestrial ClO_4^- is not transported efficiently over long distances (Jiang et al., 2021). Conversely, although we believe that the measured concentrations of ClO_4^- in this study result from natural sources due to

atmospheric deposition and volcanic eruptions in certain areas such as Deception Island, it is of interest to determine if there are possible anthropogenic sources of ClO_4^- on this continent. To differentiate the types of sources, further ClO_4^- source assessment based on isotopic analysis is required.

ClO_4^- levels measured in Antarctica could present a risk to resident biota based on the effects on animals such as amphibian metamorphosis at environmental ClO_4^- concentrations of 200–500 ppm (Goleman et al., 2002). Crane et al. (2005) studied environmental ClO_4^- effects in *Pimephales promelas* fishes and reported impaired development and thyroid dysfunction at 10 and 100 ppm and also poor pigmentation and lack of scales with a significantly lower wet weight. However, extensive studies are required to determine the effects of ClO_4^- on Antarctic biota. The use of ion-selective electrodes to assess the occurrence of compounds represents a good strategy for assessing remote environments such as Antarctica where mobility and sample transportation could be an issue. Although ion-selective electrodes have been previously used in Antarctica (Sands et al., 1998; Xie & Sun, 2008), to the best of our knowledge, this is the first study to use an ion-selective electrode to detect the ClO_4^- levels in this continent.

Conclusions

This study provides updated information on ClO_4^- concentrations at different points in the southern Shetland Islands and the Antarctic Peninsula. In situ measurements were performed using a selective electrode. Increased ClO_4^- concentration was observed during 2017–2019 time period. However, a decrease in concentration was observed in 2020, and this was attributed to a sudden stratospheric warming event. Spatial variation was observed in ClO_4^- concentrations based on this anion species reaching a minimum concentration of 90.063 ppm on Horseshoe Island and a maximum concentration of 465.167 ppm on Deception Island, and these variations may be due to a possible volcanic contribution to ClO_4^- formation. This study contributes to the literature by expanding the knowledge regarding ClO_4^- occurrence in Antarctica, and our results will help to identify ClO_4^- distribution patterns in this continent.

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Data availability Not applicable.

Code availability The analyses were performed using Statistics software.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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