



# Perchlorate in antarctica, origin, effects, treatments, environmental fate, and astrobiological perspectives: a review

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## Abstract

Perchlorate ( $\text{ClO}_4^-$ ), which is a powerful endocrine disruptor affecting iodine fixation in the thyroid gland in humans and in biota, is a pollutant of natural and anthropogenic origin. For this reason, this pollutant must be eliminated from the ecosystems. It has been found in extreme environments such as Antarctica.  $\text{ClO}_4^-$  reduction can be achieved with physicochemical treatments in small concentrations and through bacterial degradation. This is a cost-effective method, easy to implement, which makes it a viable method for the removal of perchlorate contamination in ecosystems. This review provides an updated discussion of reducing perchlorate contamination; that includes different perspectives of investigations related to its origin, use, effects on living beings; as well as the technologies used to eliminate this pollutant from the environment; its environmental fate in strategic ecosystems such as Antarctica in particular and astrobiological perspectives.

**Keywords** Antarctica peninsula · Environmental pollutant · Environmental fate · Emerging pollutants · Extreme environments · Toxicity

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## Introduction

Perchlorate ( $\text{ClO}_4^-$ ), an inorganic compound of chlorine, is present in all ecosystems. It is, both, highly toxic and persistent, and it has strong kinetic stability. Its source can be either natural or anthropogenic. The anthropogenic origin of the pollutant is mainly related to its use in the manufacture of  $\text{ClO}_4^-$  salts used in rocket fuel, fireworks, ammunition, and flares. It forms naturally in the atmosphere during storms, through reactions between common chlorine species (chlorides) and ozone ( $\text{O}_3$ ) (Jiang et al. 2021).  $\text{ClO}_4^-$  is also formed in volcanic eruptions. It is present in hypersaline environments, deserts, and Antarctica (Acevedo-Barrios et al. 2022a, b).

$\text{ClO}_4^-$  is easily transferred to groundwater and surface water due to its high solubility, and this compound is considered a pollutant due to its negative effects on human health when ingested in low concentrations (24.5  $\mu\text{g/L}$  drinking water) (Jiang et al. 2021).  $\text{ClO}_4^-$  has been found in foods such as vegetables, cereals, and fruits. Similarly, traces of this pollutant are found in human tissues and in breast milk. The negative health impacts include its ability to act as a potent endocrine disruptor by inhibiting iodine fixation in



the thyroid gland, which regulates metabolism in adults, and the growth and development of infants (Li et al. 2022).

$\text{ClO}_4^-$  is found in remote ecosystems, such as Antarctica, due to atmospheric depositions (Acevedo-Barrios et al. 2022a), and on the Martian surface. The presence of  $\text{ClO}_4^-$  in Antarctica has been reported in two points on the South Shetland Islands, and in nine points on the Antarctic peninsula (Acevedo-Barrios et al. 2022a, b).

The presence of humans in Antarctica in recent years has been increasing; research, transportation, and tourism activities have promoted the establishment of stations and transfer systems that could become considerable sources of contamination (Kounaves et al. 2010b). Thus, it is important to increase research and studies related to the presence of perchlorate in Antarctica, to monitor its incidence and possible environmental impacts (Acevedo-Barrios et al. 2022a, 2023).

This review provides an updated discussion of reducing perchlorate contamination; that includes different perspectives of investigations related to its origin, use, and effects on living beings; as well as the technologies used to eliminate this pollutant from the environment; its environmental fate in strategic ecosystems such as Antarctica, in particular, and astrobiological perspectives. This research was carried out in Antarctica, from January 2021 to August 2023

## Materials and methodology

Academic texts were compiled and reviewed, using “Antarctica”, “Astrobiology”, “Perchlorate”, and “perchlorate toxicity” as keywords. Search criteria included combinations of keywords in article titles, abstracts, or texts. The title and abstract of each publication were examined to determine if the topic was relevant to this review. Additionally, this information was used to analyze the presence of this contaminant in Antarctica, as described in this research.

## Origin and uses of $\text{ClO}_4^-$

$\text{ClO}_4^-$  is a chemically stable ion, with toxic effects on humans and biota. It is found in different environmental matrixes (Pleus and Corey 2018), and it is characterized by its persistence in ecosystems (Bardiya and Bae 2011). It has a stable anion in its chemical structure, which is considered as highly oxidizing, surrounded by four oxygen atoms (Murray and Bolger 2014), bringing it a great fugacity that allows it to travel over long distances (Cao et al. 2019).

This pollutant originates, naturally, due to volcanic eruptions and atmospheric processes, and anthropogenically, due to industrial and aerospace activities. Fireworks are one of the largest sources of perchlorate pollution in the

environment. This is because fireworks contain a variety of chemicals, such as potassium nitrate, potassium chloride, potassium perchlorate or ammonium perchlorate, carbon, sulfur, manganese, sodium, nitrate, strontium, aluminum, titanate barium, and iron oxalate powder (Wu et al. 2011). In addition to this, a large part of the perchlorate contamination found in groundwater and surface water is associated with military, aerospace, and explosives use, among others (Murray and Bolger 2014; Kumarathilaka et al. 2016).

Electronic waste is considered the type of waste with the greatest flow of exponential growth, and it is related to perchlorate contamination (Eguchi et al. 2014; Parvez et al. 2021). Perchlorate is found in polyvinyl chloride (PVC) and in lithium-ion batteries as a doping material (Interstate Technology Regulatory Council 2005). Therefore, residents and workers at e-waste recycling sites are likely to be exposed to the contaminant. Furthermore, this strong oxidant is used as a cleaning agent during the production of LCD displays (Her et al. 2011).

Ammonium, lithium, magnesium, and potassium perchlorate are used to manufacture herbicides and automobile air bag inflators. The latter has been used in medicine, mainly between 1950 and 1960, to treat hyperthyroidism (Murray and Bolger 2014).

Similarly, perchlorate has been used in the manufacture of dyes, lubricants, rubber, and matches (Interstate Technology Regulatory Council 2005). Likewise, other anthropogenic sources have been identified such as: foundries, flares, drying and etching agents, gunpowder, batteries (Wang et al. 2014), chlorine-based disinfectants, bleaches, cleaners and chemicals for swimming pool chlorination, electronic tubes, paints, enamels, fertilizers, nuclear reactors, and other materials for commercial uses (Maffini et al. 2016; Kumarathilaka et al. 2016). Perchlorate has also been implemented as a growth promoter and thyrostatic drug to increase mass in livestock (Gholamian et al. 2011).

## Natural origin

Chlorate ( $\text{ClO}_3^-$ ) and Perchlorate ( $\text{ClO}_4^-$ ) are two oxyhalides. These compounds are formed in the atmosphere through the reaction of chlorite ( $\text{ClO}_2^-$ ), mediated by  $\text{O}_3$ , and, possibly, UV during photochemical processes, or through electrical activity during thunderstorms. (Dasgupta et al. 2005). They can acting as alternative electron acceptors, supporting a range of microbial metabolic processes (Coates and Achenbach 2006).

After being formed in the stratosphere,  $\text{ClO}_4^-$  has two ways to enter the soil: wet or dry deposition. In wet deposition, it dissolves in moisture droplets and is brought down to the ground through precipitation. Once on the ground, it can be deposited into the soil. However, because it has a high solubility and low sorption properties, it can easily

enter surface water or groundwater sources (Rao et al. 2010). Dry deposition, which can occur through eolian dust, atmospheric aerosols, and gases, is also a possibility. These processes may be responsible for the presence of trace amounts of perchlorate in various environments (Vega et al. 2018).

The high mobility of  $\text{ClO}_4^-$  can lead to its accumulation in ecosystems, due to its chemical stability under normal environmental conditions. (Brown and Gu 2006). High concentrations of natural  $\text{ClO}_4^-$  are found in specific ecosystems with arid, hyper-arid, and semi-arid soil conditions. Likewise, it can be found in nitrate deposits in the Atacama Desert in Chile, with concentrations of  $1000 \text{ mg kg}^{-1}$  of  $\text{ClO}_4^-$  (Jackson et al. 2015), as well as in hypersaline environments, volcanic eruptions, and Antarctic soils (Acevedo-Barrios and Olivero-Verbel 2021; Acevedo-Barrios et al. 2022a).

Perchlorate salts present in soils can dissolve and be transported by water which can be used for human consumption, irrigation of crops, or in industrial processes. Consequently, perchlorate originating from a single source can affect various human exposure pathways, leading to an increased intake of  $\text{ClO}_4^-$  perchlorate (Murray and Bolger 2014).

The high mobility of perchlorate in water and soil has led to the establishment of regulations to ensure safe levels in drinking water. For instance, the State of California establishes that the maximum level of  $\text{ClO}_4^-$  allowed is  $6 \text{ }\mu\text{g/L}$ , the same level set by the Canadian Environmental Protection Act (Srinivasan and Sorial 2009). On the other hand, in 2009, the US EPA set a recommended value of  $15 \text{ }\mu\text{g}\cdot\text{L}^{-1}$  for drinking water (USEPA 2008, 2009).

Studies on natural sources of  $\text{ClO}_4^-$  that focus on different environmental matrixes have been limited; however,

the currently available information allows for proposing different methods for its reduction (Jiang et al. 2021).

However, in the case of Antarctica, the problem could be even greater, since there are several areas with the presence of natural perchlorate (Acevedo-Barrios et al. 2022a), due to the high mobility in water, and because it is used through desalination processes, and for cleaning work on ships and bases; and, in the case of freshwater lakes for human consumption, they must be analyzed for perchlorate. But perchlorate is not one of the aspects considered in water quality evaluations (Dean et al. 2004), and it must be taken into account within the regulations, recognizing its teratogenic potential (Acevedo-Barrios et al. 2018).

$\text{ClO}_4^-$  is distributed in ecosystems through runoff, and it accumulates in food (Murray and Bolger 2014). Processed products like beverages may contain small concentrations of perchloride. Studies show that plants accumulate perchlorate, primarily in the leaves, up to two orders of magnitude of available perchlorate in irrigation water or soil. The fruits of these plants can also accumulate perchlorate, in lower concentrations (Calderón et al. 2017; Estrada et al. 2017). Therefore, crops can accumulate perchlorate if they are irrigated with contaminated water, if they are grown in contaminated agricultural soils, or if fertilizers containing perchlorate are used (Vega et al. 2018).

$\text{ClO}_4^-$  is also present in milk, sauces, instant mixes, meats, fish, tea, sodas, plants, and tobacco products (Andrew Jackson et al. 2005; Zhang et al. 2010; Lee et al. 2012). Another common route of exposure is through domestic inhalation (Kumarathilaka et al. 2016). The estimated daily intake concentrations of  $\text{ClO}_4^-$  are shown in Table 1.

**Table 1** Concentrations of ( $\text{ClO}_4^-$ ) present in different sources

Source of ingestion	( $\text{ClO}_4^-$ ) concentration ( $\mu\text{g/Kg}$ )	References
Rice	0.38 – 3.23	Kim et al. (2014); Kumarathilaka et al. (2016)
Spinach (USA)	$133 \pm 24.9$	Wang et al. (2009); Kumarathilaka et al. (2016)
Green grapes (Chile)	$45.5 \pm 13.3$	Wang et al. (2009); Kumarathilaka et al. (2016)
Romaine lettuce (USA)	$29.1 \pm 10.5$	Wang et al. (2009); Kumarathilaka et al. (2016)
Guatemalan melons	$156 \pm 232$	Wang et al. (2009); Kumarathilaka et al. (2016)
Water drop ( <i>Oenantho stolonifere</i> DC)	20.7	Yang and Her (2011); Kumarathilaka et al. (2016)
Spinach (South Korea)	39.9	Lee et al. (2012); Kumarathilaka et al. (2016)
Bean sprouts ( <i>Glycine Max L Merr</i> ) (South Korea)	35.2	Yang and Her (2011); Kumarathilaka et al. (2016)
Ham and sausage (South Korea)	7.31	Lee et al. (2012); Kumarathilaka et al. (2016)
Instant noodles (South Korea)	7.58	Lee et al. (2012); Kumarathilaka et al. (2016)
Fish, meat, and drinks (South Korea)	<2	Lee et al. (2012); Kumarathilaka et al. (2016)
Wheat (USA)	982–3924	Sanchez-Hernandez (2006); Kumarathilaka et al. (2016)
Fresh milk (USA)	1.7–6.4	Kirk et al. (2003); Kumarathilaka et al. (2016)
Chicken eggs	$7.16 \pm 1.99$	Blount et al. (2008); Kumarathilaka et al. (2016)
Infant milk powder	1.49–33.3	Her et al. (2010); Kumarathilaka et al. (2016)



## Atmospheric origin

Atmospheric production of  $\text{ClO}_4^-$  is a known process expressed with the  $\text{Cl} + 2\text{O}_3 \rightarrow \text{ClO}_4^-$  reaction, and this photochemical reaction occurs between chlorine and atmospheric ozone (Trumpolt et al. 2005).

## Desert environments

The extreme conditions present in this ecosystem, located at the south pole, range from low temperatures and high salinity, which lead to the natural formation of  $\text{ClO}_4^-$  (Calderon et al. 2014). This pollutant is found in the soil and ice of the Antarctic continent at concentrations as high as 1,100  $\mu\text{g}/\text{Kg}$  (Kounaves et al. 2010b; Jiang et al. 2013; Acevedo-Barrios and Olivero-Verbel 2021). The Antarctic ecosystem is considered to be a hypersaline environment, and the source of natural  $\text{ClO}_4^-$  is the result of atmospheric depositions. This source increases according to the decrease in precipitations, making its permanence in the ecosystem's indefinite (Acevedo-Barrios et al. 2018). It presents favorable conditions for the development and growth of native bacteria capable of reducing the pollutant due to its extreme conditions. In the desert valleys of Antarctica,  $\text{ClO}_4^-$  concentrations are between 91 and 465 ppm, as reported by Acevedo-Barrios et al. 2022a; 2023; 2024.

The accumulation of  $\text{ClO}_4^-$  in arid regions is mainly due to the absence of rain and aerobic conditions, which prevent its reduction by bacteria that can use it as an electron acceptor under anaerobic conditions. Microbial reduction of  $\text{ClO}_4^-$  occurs via the  $\text{ClO}_4^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_2^- \rightarrow \text{Cl}^- + \text{O}_2$  biochemical reaction. Perchlorate reducing organisms can use a wide range of electron donors, and they can be found in various natural settings. These organisms are usually facultatively anaerobic or microaerophilic (Coates and Achenbach 2004). Under relevant environmental conditions,  $\text{ClO}_4^-$  is highly conserved and is not transformed by known abiotic processes in toxic environments due to its high solubility.  $\text{ClO}_3^-$ , on the other hand, has received less research attention than  $\text{ClO}_4^-$ , mainly due to challenges in analyzing environmental samples with low concentrations (Jackson et al. 2012).

## Antarctic ecosystem

The presence of  $\text{ClO}_4^-$  has been detected in small amounts across all continents, including in Arctic and Antarctic ice sheets, indicating its widespread occurrence in a natural environment (Jiang et al. 2021). The atmosphere deposits environmental pollutants in snow, glaciers, and polar ice caps, which makes it possible to measure the records of the presence of compound environmental contaminants in Antarctica (Du et al. 2019). In polar regions such as Antarctica,

Greenland, the Canadian Arctic, North America, and East Asia, increasing  $\text{ClO}_4^-$  concentrations have been reported since 1980. Jiang et al. (2016) observed a strong positive correlation between effective stratospheric chlorine equivalent and  $\text{ClO}_4^-$  in Antarctic snow, suggesting that increased stratospheric chlorine may have caused the increase in  $\text{ClO}_4^-$ . Meanwhile, Cole-Dai et al. (2018) suggest that the increase since 1980 is likely due to increased atmospheric  $\text{ClO}_4^-$  production, possibly associated with emissions from anthropogenic sources of  $\text{ClO}_4^-$  into the atmosphere in recent years.

Moreover, significant correlations between  $\text{Cl}^-$  and  $\text{ClO}_4^-$  fluxes and concentrations in a shallow ice core from Agassiz Ice Cap suggest that  $\text{ClO}_4^-$  was predominantly formed from tropospheric  $\text{Cl}^-$  during the 1940–1959 period (Furdui et al. 2018). This increase could be attributed to the emissions of compounds such as methyl chloroform, which is capable of being converted into inorganic species and may contribute to the formation of  $\text{ClO}_4^-$  in the stratosphere (Brown and Gu 2006).

The presence of  $\text{ClO}_4^-$  is mainly of natural origin, since there are few interactions with human populations in Antarctic snow (Acevedo-Barrios and Olivero-Verbel 2021; Acevedo-Barrios et al. 2022a, b; 2023, 2024). Perchlorate in this region has progressively increased since the 1970s. This trend could be the result of the elevation of atmospheric chlorine levels caused by anthropogenic chlorine emissions (Jiang et al. 2016), because this pollutant is formed when free radicals ( $\text{Cl}^\cdot$ ) and ozone ( $\text{O}_3$ ) react in the stratosphere due to the presence of the ozone hole during the austral summer (Jiang et al. 2021).  $\text{ClO}_4^-$  has been found on the Antarctic continent through the ozone hole in late summers due to sunlight, and its concentrations increase in late December when temperatures rise (Crawford et al. 2017). Concentrations of  $104.3 \pm 33.3$  ng/kg of perchlorate have been found in the superficial snow caps of Eastern Antarctica, and this private area presents apparently high concentrations in areas with low accumulation rates (Jiang et al. 2020).

## Mars

Antarctica has been highlighted as one of the most suitable places to study surface processes on Mars (Wynn-Williams and Edwards 2000). In Antarctica, three specific areas have been identified as Mars analog sites (Martins et al. 2017). The McMurdo Dry Valleys, which are recognized as the coldest and driest places on planet Earth, with average temperatures of  $-30$  °C in winter and  $-15$  °C in summer. Likewise, abundant presence of microorganisms has been documented in the permafrost and rocks of this region (Friedmann 1982; Gilichinsky et al. 2007). Since the time of the Viking missions, these valleys have been considered the closest climatic analogues to Martian conditions.



The other two Antarctic analogues are the Victoria Land Mountains and Lake Vostok. In the case of Victoria Land, it shares similarities with McMurdo due to the presence of dry valleys, but its higher altitude has favored the existence of microorganisms resistant even to the intense UV radiation present in Antarctica (Meeßen et al. 2015). Lake Vostok has been categorized as an analogue of Enceladus or Europa, due to the presence of microorganisms in a lake covered by a layer of ice several kilometers thick (Shtarkman et al. 2013).

However, an intriguing aspect that deserves attention in the study of astrobiological analogues is the presence of perchlorates on Mars (Kounaves et al. 2010a). Interestingly, perchlorates have also been found in Antarctic marine sediments, with a higher concentration recorded on Deception Island, possibly related to volcanic contributions to the natural formation of perchlorate in Antarctica (Acevedo-Barrios et al. 2022a, b). This connection could be related to the presence of perchlorates on Mars (Kounaves et al. 2014).

The Phoenix Mars lander detected perchlorate anions in amounts close to 0.5% by weight on the Martian surface (Hecht et al. 2009; Kounaves et al. 2010b). The Mars Science Laboratory, using Sample Analysis at Mars, has also detected perchlorate (Archer et al. 2013). Another relevant feature of Mars is the presence of large permafrost layers, which are covered by regolith layers comparable to terrestrial gelisols (Certini et al. 2020).

Having terrestrial perchlorate as an analog has led to some hypotheses suggesting that Martian perchlorate is formed from the oxidizing chemistry of a dry environment. The oxidizing power is in the atmosphere (Hunten 1979). On the other hand, cosmic ray action can produce superoxide ( $O_2^-$ ) free radicals (Yen et al. 2000). Chlorine would be of volcanic origin during intense volcanism on Mars (Hartmann and Neukum 2001). Furthermore, due to the red planet's cold and dry environment, perchlorate would have accumulated on the surface due to photochemical reactions (Kounaves et al. 2010b). These perchlorates represent a fundamental point of convergence between astrobiology and Antarctica as an analog ecosystem of Mars.

### Anthropogenic origin

Perchlorate, with its high oxidation potential, has been synthesized for use in various applications, including rocket fuels, explosives, fireworks, airbags, ammunition, and signal flares. This has resulted in its use in military industries, pyrotechnics, and in the manufacture of fertilizers for agricultural use (Cao et al. 2019). The effects of this pollutant is directly proportional to its concentration from anthropogenic sources, where concentrations of 0.1–35.0  $\mu\text{g/L}$  in fresh water (Blount et al. 2010), 0.1–22.1  $\mu\text{g/L}$  in groundwater, 0.0–2,300  $\mu\text{g/L}$  in surface water (Wu et al. 2010), and 1.0–13  $\mu\text{g/kg}$  in soil (Jackson et al. 2010) can be found. The

presence of  $\text{ClO}_4^-$  in groundwater is considered to be due to runoff via sand or soil.

A considerable percentage of  $\text{ClO}_4^-$  in surface water comes from the military industry (Cao et al. 2019). In the same way, the aerospace industry (Murray and Bolger 2014; Kumarathilaka et al. 2016) contributes large concentrations of  $\text{ClO}_4^-$  to ecosystems with rocket launches, where the heat generated causes all of the  $\text{ClO}_4^-$  to be used in the reaction. Furthermore, various studies report the presence of  $\text{ClO}_4^-$  residues from fireworks in surface and underground water (Backus et al. 2005).

The anthropogenic factor could be linked to the use of household detergents in Antarctica, taking into account that the expeditions are carried out on ships or at scientific bases in different countries. Hypochlorite solutions are characterized by having traces of  $\text{ClO}_4^-$  (Aranda-Rodriguez et al. 2017).

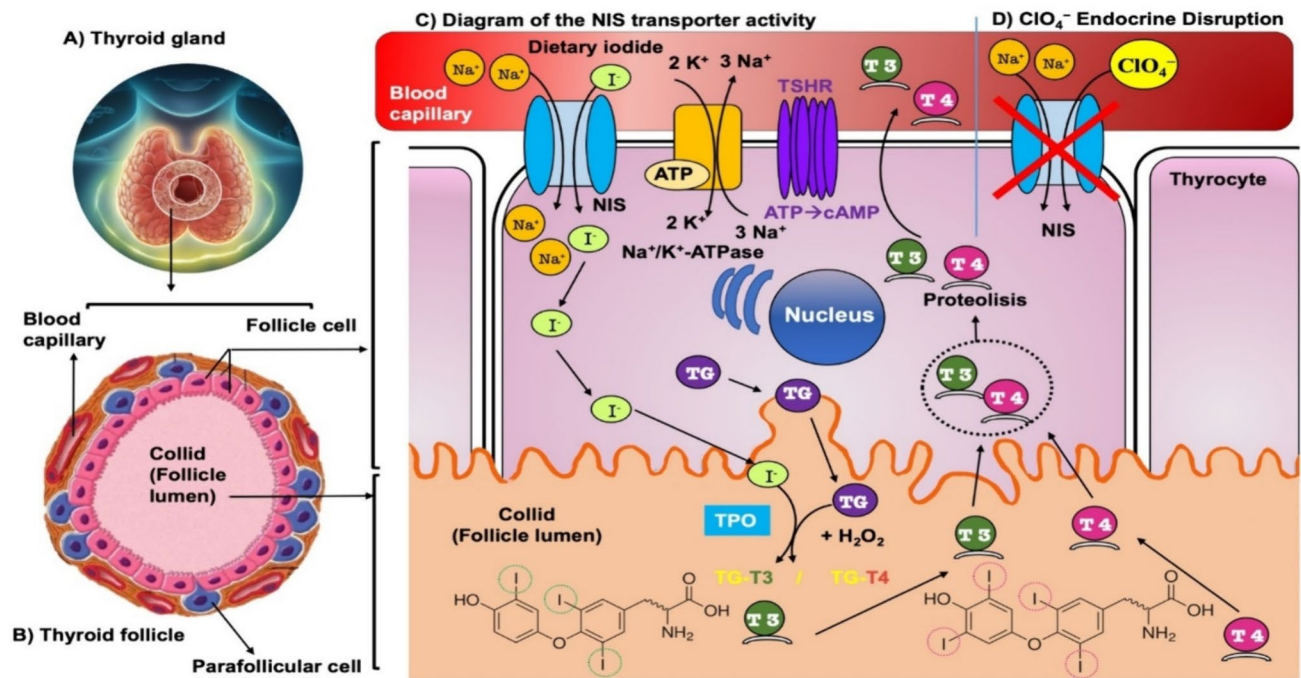
### Effects of $\text{ClO}_4^-$ on the environment and on health

The extensive application of  $\text{ClO}_4^-$  in human activities has distributed it in aquatic and terrestrial ecosystems, and in the food chain (Li et al. 2022). Since it is an emerging pollutant, the information available on its impact on the environment is scarce. Therefore, it is necessary to carry out more studies to determine its effects on biota, considering that its toxicity varies depending on the species (Acevedo-Barrios and Olivero-Verbel 2021).

$\text{ClO}_4^-$  has generated interest among investigators for being a potent endocrine disruptor (Acevedo-Barrios and Olivero-Verbel 2021) that affects thyroid gland function (Li et al. 2022). For instance, the thyroid gland in humans (represented in Fig. 1a) produces two main forms of “iodothyronines”: thyroxine (3,5,3',5'-tetra-iodo-L-thyronine, T4) and triiodothyronine (3,5,3'-tri-iodo-L-thyronine, T3) (Koibuchi 2018). These hormones are necessary for both adult physiology and appropriate development. Together with distributor proteins (transthyretin and thyroxine binding-protein), these two forms of thyroid hormone circulate in the bloodstream (Zoeller 2021). Then, they are transported to target cells, where they will play a key role in the development and functional maintenance of many organs (Koibuchi and Chin 2000).

Thyroid follicles, which are made up of a layer of follicular epithelial cells (sometimes referred to as thyroid follicular cells or thyrocytes) encircling a follicular lumen, are the special structure within the thyroid gland where thyroid hormone is generated (Fig. 1b). The production of thyroid hormone in the follicular lumen, rather than within the follicular epithelial cells, is a noteworthy characteristic of the





**Fig. 1** (a) Synthesis of thyroid hormones T<sub>3</sub> (triiodothyronine) and T<sub>4</sub> (thyroxine). **a** Thyroid gland in humans, **b** Thyroid follicle, **c** The accumulation of I<sup>-</sup> is mediated by the Na<sup>+</sup>/I<sup>-</sup> symporter (NIS), driven by the Na<sup>+</sup> gradient produced by the Na<sup>+</sup>/K<sup>+</sup> ATPase. When I<sup>-</sup> effluxes towards the colloid, thyroid peroxidase (TPO) catalyzes the

organization of I<sup>-</sup> on the thyroglobulin (TG) molecule. The thyroid hormones are released into the bloodstream after the iodinated-TG is proteolyzed following endocytosis. **d** Endocrine disruption associated with ClO<sub>4</sub><sup>-</sup> in thyrocytes. This compound inhibits the uptake of iodine, thereby blocking its entry into thyroid follicular cells

thyroid hormone synthetic pathway. Outside the cell, no additional hormone is generated (Koibuchi 2018).

The synthesis of T<sub>4</sub> and T<sub>3</sub> occurs in the follicular cell. Iodide is actively transported into the thyroid follicular cells via the sodium (Na<sup>+</sup>)/iodide (I<sup>-</sup>) symporter (NIS) located at the basolateral membrane (Dohán et al. 2003). NIS-mediated I<sup>-</sup> uptake in the thyroid is the initial step in the production of the iodine-containing thyroid hormones, which are crucial in the early stage of life for suitable Central Nervous System (CNS) formation, with an electrogenic stoichiometry of 2 Na<sup>+</sup> per I<sup>-</sup>. The electrochemical gradient that is required for the iodide transport is produced by the sodium–potassium (Na<sup>+</sup>/K<sup>+</sup>) ATPase. After reaching the apical membrane, pendrin, an anion exchanger, and maybe anoctamin, allow for iodide to be released into the follicular lumen (Wémeau and Kopp 2017). Thyroperoxidase (TPO) oxidizes iodide in the follicular lumen when Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) is present (Ohye and Sugawara 2010).

Thyroglobulin (TG) primarily forms the colloid in the follicular lumen. Firstly, there is an organization step in which TPO iodinates certain tyrosyl residues on TG to create mono- and diiodotyrosines (MIT, DIT; respectively). TPO, then, couples the iodotyrosines to form T<sub>4</sub> and T<sub>3</sub>. Thyroid hormones are released into the bloodstream, at least in part, through the thyroid hormone-transporting channel MCT8, after TG is internalized by pinocytosis from the follicular

lumen into the follicular cell (Visser et al. 2011). T<sub>4</sub> makes up over 80% of the hormone released, whereas T<sub>3</sub> makes up 20%. The liberated iodide is then recycled back into the follicular lumen for the creation of thyroid hormones (Moreno et al. 2008) (Fig. 1c).

The presence of ClO<sub>4</sub><sup>-</sup> can cause disruption of the thyroid gland, since this compound can obstruct or compete with iodine for transport through NIS into the thyroid; effectively blocking iodine from entering the thyroid follicular cells through circulation. This may inhibit the thyroid's ability to absorb iodine and lower the production of thyroid hormones, both of which have been related to hypothyroidism in organism (Kirk 2006). Iodide transport is inhibited at low ClO<sub>4</sub><sup>-</sup> concentrations by altering the stoichiometry of iodide transfer, which reduces the driving force (Kumar et al. 2023).

Electrophysiological analyses showed that perchlorate ions attach to a sodium symporter allosteric region that is non-transport, hindering the binding of Na<sup>+</sup>/I<sup>-</sup> ions (Llorente-Esteban et al. 2020) (Fig. 1d). In addition to the thyroid tissues, the cerebrovascular plexus, eyes, lactate, and salivary glands all have sodium/iodide symporters. NIS is also found in the heart, kidneys, and lungs in trace levels (Dohán et al. 2007). These tissues, in contrast to the thyroid, do not metabolize iodine; instead, it is reabsorbed into the bloodstream, milk, and saliva (Spitzweg et al. 1999). Other effects



associated with perchlorate in humans and other species will be detailed further below.

## Effects on human health

Human beings intake contaminated water and food allowing  $\text{ClO}_4^-$  to enter into the digestive system; this is the main route of  $\text{ClO}_4^-$  exposure (Ali et al. 2021). It can also enter the respiratory system if it is inhaled from dust contaminated with  $\text{ClO}_4^-$  (Li et al. 2022). After it enters the body, it is absorbed by the digestive system and sent to the bloodstream, where it inhibits the fixation of iodine in the thyroid gland. Changes in this process hinder what causes hypothyroidism (Li et al. 2022). Numerous studies have investigated the association between exposure to  $\text{ClO}_4^-$  in the environment and alterations in the production of T3, T4, and TSH thyroid hormones. In addition,  $\text{ClO}_4^-$  increases the risk of cardiovascular diseases; it also affects the nervous, reproductive, and immune systems (Pleus and Corey 2018).  $\text{ClO}_4^-$  is a neurotoxic capable of inducing teratogenesis in pregnant women.

The presence of  $\text{ClO}_4^-$  has been detected in adult and infant biological samples such as urine, saliva, breast milk, maternal blood, and in the umbilical cord (Pleus and Corey 2018; Ali et al. 2021; Li et al. 2022).

$\text{ClO}_4^-$  can induce teratogenesis during the first trimester of pregnancy (Acevedo-Barrios et al. 2018; Acevedo-Barrios and Olivero-Verbel 2021). High concentrations of  $\text{ClO}_4^-$  can affect the metabolism, development, and reproduction of unborn babies, as it causes a decrease in the transfer of thyroid hormones from the placenta to the fetus (Ali et al. 2021). Damage to the DNA of testicular tissues occurs in men, which leads to a reduction in testicular spermatogenesis (Ali et al. 2021). It can damage the skeletal system and the central nervous system of newborns and children, leading to learning problems, intellectual deficiencies, and physical disabilities (Ye et al. 2012; Acevedo-Barrios and Olivero-Verbel 2021).

## Effects on the biota

$\text{ClO}_4^-$  enters living beings through trophic transfer, passing from soil to higher organisms through plants, due to the application of chlorine-based fertilizers or irrigation water contaminated with  $\text{ClO}_4^-$  (Constantinou et al. 2019). The majority of vascular plants are able to rapidly absorb and accumulate  $\text{ClO}_4^-$  in their plant tissues, mainly in their leaves, affecting their normal development and growth (Acevedo-Barrios and Olivero-Verbel 2021; Oze et al. 2021).

Furthermore,  $\text{ClO}_4^-$  reduces the plant's leaf area and levels of dry shoot biomass, directly due to its toxicity, or indirectly by modifying the release and/or availability of soil nutrients (Oze et al. 2021). A study by He et al. (2013) found

that  $\text{ClO}_4^-$  affects the root systems and the chlorophyll content of the *Acorus calamus*, *Canna indica*, *Thalia dealbata*, and *Eichhornia crassipes* species (He et al. 2013). It can also alter the biomass ratio in different organs of *Alternanthera philoxeroides*, thus increasing its proportion in the stem, and decreasing it in the leaf (Xie et al. 2009).

Potassium perchlorate ( $\text{KClO}_4^-$ ), on the other hand, affects the bioluminescence of the *Vibrio fischeri* bacterium, alters the homeostasis of the *Pseudokirchneriella subcapitata* algae, and can cause endocrine disruption in the *Daphnia magna* crustacean. In the *Eisenia fetida* earthworm, it causes severe weight loss, alterations in the central nervous system, teratogenesis, and mucus production (Acevedo-Barrios et al. 2018). In pregnant female rats,  $\text{ClO}_4^-$  causes hypothyroidism, and, in male rats, it causes DNA damage and reduced sperm production (Yu et al. 2019). It decreases the number of spawned eggs in the *Oryzias latipes* fish, and it causes functional hermaphroditism in *Gasterosteus aculeatus* females. The effects in fish, in general, include affectation of the normal development of their lateral plates, decrease in swimming, reduction in pigmentation, and slow growth rates (Acevedo-Barrios and Olivero-Verbel 2021).

Concentrations ( $1.6 \pm 1.1 \mu\text{g}/\text{kg}$ ) of  $\text{ClO}_4^-$  have been found on the Fildes Peninsula in Antarctica. This peninsula has high levels of wildlife activity, especially colonies of penguins, skuas, and seals (Jiang et al. 2021). The presence of this pollutant has also been determined in seawater, algae, and Antarctic fish, considering that they function as food for wildlife. They could have the pollutant in their body (Jiang et al. 2021). However, to date, there are no studies on the effect of  $\text{ClO}_4^-$  on Antarctic fauna (Acevedo-Barrios and Olivero-Verbel 2021). Table 2 outlines the effects associated with some organisms.

## Physicochemical methods to determine the origin of $\text{ClO}_4^-$

The determination of the origin of  $\text{ClO}_4^-$  is associated with the sources of exposure; therefore, the methods to identify  $\text{ClO}_4^-$  show whether it is present in the sample to be evaluated. The origin is studied by evaluating the possible exposure to this pollutant, which can be present both in food and in drinking water, as well as in other environmental matrixes (Dong et al. 2019).

## Selective $\text{ClO}_4^-$ electrode

An ion-selective membrane (ISM) is used for this technique, which contains the ionophore responsible for the selectivity of the electrode (Itterheimová et al. 2022). One of the most frequently used ionophores is Dodecabenzylymbambusuril (Bn12BU[6]), because it binds very strongly to the ion



**Table 2** Effects associated with some organisms

Mechanism	Target in cell	Concentration	Organisms	Effect	References
Reduction in thyroid hormone synthesis	Thyroid Gland	100 mg/L, $\text{KClO}_4^-$	<i>Gasterosteus aculeatus</i> (Sticklebacks)	Increase in early ovarian follicles in females and advanced spermatogenic stages in males	Petersen et al. (2015)
Reduction in thyroid hormone synthesis	Embryonic cells	10 $\mu\text{g/L}$ , $\text{KClO}_4^-$	<i>Oryzias latipes</i> (Medaka fish)	Delayed hatching, lower rate heartbeat, inhibited primordial germ cells migration and increased larval developmental deformities	Reh et al. (2022)
Reduction in thyroid hormone synthesis	Thyroid Gland	14 mg/L, $\text{NaClO}_4^-$	<i>Lithobates sylvaticus</i> (wood frog)	Chemical interference with the synthesis of thyroid hormone	Bulaeva et al. (2015)
Oxidation	Liver	30 mg/L, $\text{NaClO}_4^-$	<i>Gasterosteus aculeatus</i> (Sticklebacks)	Non-alcoholic fatty liver disease	Minicozzi et al. (2019)
Reduction in thyroid hormone synthesis	Skeletal development	250 $\mu\text{g/L}$ $\text{NaClO}_4^-$	<i>Rana chensinensis</i> tadpoles	Histological damage to the femur and tibia-fibula and inhibited the hindlimb length	Li et al. (2023)

$\text{ClO}_4^-$  ion [stability constant  $\sim 10^{10}$  /M], due to the good ratios between the size of the ion and the receptor cavity (Itterheimová et al. 2022). The electrode is rinsed with distilled water before use and calibrated depending on the quantities to be measured in ppm. Likewise, it is rinsed between measurements, to avoid dragging and contamination of the samples (Acevedo-Barrios et al. 2022a, b).

### Liquid chromatography tandem mass spectrometry (LC–MS/MS)

This technique has an analytical power that combines chromatography— either liquid or gas—as a separation method, and mass spectrometry as a method of detection, identification, and quantification of compounds. MS is characterized by being highly sensitive; it uses the ionization and separation of molecules, and it records the ions produced in a vacuum system. MS has also been used for the quantification of trace amounts of  $\text{ClO}_4^-$  in aqueous matrixes: in human urine and saliva samples, in food, soil, and water. (Kannan et al. 2009; Kumarathilaka et al. 2016).

### UHPLC-Q-orbitrap HRMS (ultra high-performance LC-Q-orbitrap high resolution mass spectrometry) method

This method has been used for the nutritional investigation of the quality of goat's milk contaminated with sodium perchlorate ( $\text{NaClO}_4^-$ ). This untargeted metabolomics and proteomics method based on UHPLC-Q-Orbitrap HRMS

for metabolic pathways and biological processes involved in animal enzymes is used to study the composition and concentrations of the metabolite molecules, with the aim of determining the presence of the pollutant. Furthermore, statistical methods are used to analyze the samples, where the significant metabolites become discriminated by a sample treatment process, in such a way that the amount of milk contaminated with  $\text{NaClO}_4^-$  can be determined (Jia et al. 2022).

### Technologies for the remediation of $\text{ClO}_4^-$

$\text{ClO}_4^-$  is not easily degradable in the environment; therefore, its use in fertilizers, irrigation, and water treatment allows leads to its persistence in food and drinking water (Xie et al. 2018). Over the years, several important technologies have been introduced to remove or reduce  $\text{ClO}_4^-$  in water and soil (Ye et al. 2012). These methods include filtration by membrane, biodegradation, chemical reduction, electrochemical reduction, bioelectrochemical reduction, and ion exchange (IX) (Ye et al. 2012).  $\text{ClO}_4^-$  remediation technologies are classified into four groups: Physical–chemical treatments, chemical treatments, integrated or combined technologies, and biological treatments (Ye et al. 2012; Xie et al. 2018; Acevedo-Barrios and Olivero-Verbel 2021).

Halophilic bacteria isolated from hypersaline soils have the Perchlorate reductase and Superoxide chlorite enzymes. The perchlorate reductase enzyme is responsible for reducing perchlorate to chlorate, and chlorate to chlorite, while





the superoxide chlorite enzyme reduces chlorite to  $\text{Cl}^-$  and molecular oxygen. Figure 2 describes the perchlorate degradation pathway (Acevedo-Barríos et al. 2019, 2022b). The biological reduction of perchlorate is regulated by environmental factors such as pH, temperature, salt concentration, presence of metabolic inhibitors or electron acceptors, nutritional conditions, and contact time; also due to physiological factors, such as type and physiological age of the bacteria, concentration of cellular biomass, and mutations (Ting et al. 2008; Acevedo-Barríos and Olivero-Verbel 2021). Phenotypic characterization studies have shown that perchlorate-reducing bacteria exhibit a wide range of metabolic capabilities and can thrive in diverse and extreme conditions. Although these technologies are effective, it is necessary to continue carrying out studies that allow for improving the reduction and complete elimination of  $\text{ClO}_4^-$  in ecosystems (Ye et al. 2012).

## Physicochemical methods

These are the most widely used technologies for the elimination of  $\text{ClO}_4^-$ . They include treatments such as activated carbon, membrane filtration, ion exchange (IX), precipitation, and chemical and electrochemical reduction (Ye et al. 2012; Xie et al. 2018). When using these methods, it must be considered that, although physicochemical treatments have advantages such as low cost, easy operation, and high treatment efficiency, they have the disadvantage of being non-selective. They can generate regenerative brines or reject streams with high concentrations of  $\text{ClO}_4^-$  that can affect the effectiveness of the process (Xie et al. 2018; Acevedo-Barríos and Olivero-Verbel 2021).

## Activated carbon

Powdered or granulated activated carbon is the oldest and most widely used adsorbent (Xie et al. 2018). Its adsorption

mechanism is based on surface complexation and electrostatic forces (Ye et al. 2012). The capacity of activated carbon to adsorb  $\text{ClO}_4^-$  is limited by the nature of the material, the pH of the contaminated water, and other inorganic/organic components with which it comes into contact, thus greatly affecting the chemistry of the surface and the porous structure of the adsorbent (Ye et al. 2012; Xie et al. 2018). The high efficiency of activated carbon is due to the presence of oxygenated functional groups such as: carboxylic, lactonic, and phenolic (Ye et al. 2012; Acevedo-Barríos and Olivero-Verbel 2021). In addition, its simplicity of operation, profitability, and regenerative nature of the adsorbents (Baimenov et al. 2020), which can be of various types (cellulose nanofibers, biocarbon, carbon nanotubes, modified activated carbon, among others) (Shahrokhi-Shahraki et al. 2021). It is important to mention that of the adsorbents, activated carbon has distinctive characteristics (high pore volume and large surface area) that make it a valuable adsorbent for the removal of many contaminants, such as heavy metals (Shahrokhi-Shahraki et al. 2021), it also increases the efficiency in the absorption of perchlorate and other types of endocrine disrupting contaminants (Shahrokhi-Shahraki et al. 2021).

$\text{ClO}_4^-$  is a typical anion, and it is considered to be an emerging contaminant. Among the strategies for its removal from the environment, especially from water, is the use of activated carbon, which can be modified with various functional groups. In research carried out on the adsorption of  $\text{ClO}_4^-$  on raw and oxidized carbon nanotubes, to elucidate the affinity mechanism of these with anionic contaminants, it was demonstrated that the adsorption of  $\text{ClO}_4^-$  was promoted by oxidized double-walled carbon nanotubes (DWCNT), due to the introduction of more oxygen-containing functional groups, which served as additional adsorption sites, thus, the adsorption mechanism of  $\text{ClO}_4^-$  depends on the pH and on the adsorbent (mainly on the oxygen- and nitrogen-containing groups) (Fang and Chen 2012).

Other studies suggest that the adsorption of  $\text{ClO}_4^-$  occurs, at least partially, through specific interactions of  $\text{ClO}_4^-$  with surface functional groups, so that specific chemical interactions between these, in combination with electrostatic forces, are the main mechanism for the adsorption of  $\text{ClO}_4^-$  on activated carbon (Mahmudov and Huang 2010). Furthermore, it has been shown that treating granular activated carbon with acids can improve its  $\text{ClO}_4^-$  removal capacity in water. Several studies have examined the characteristics of acid-treated granular activated carbons, which have made it possible to define the effects of various adsorption parameters on their efficiency, taking into account contact time, the initial concentration of  $\text{ClO}_4^-$ , the pH of the solution, temperature, and the presence of coexisting anions on its efficiency (Krishnan G. et al. 2017). These findings highlight the importance of different functional groups in activated carbon in elucidating

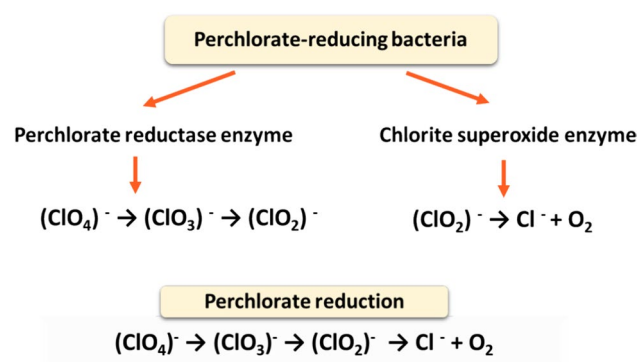


Fig. 2 Biological reduction route of perchlorate



the adsorption mechanisms of environmental pollutants (Mahmudov and Huang 2010; Byrne et al. 2014; Yao et al. 2017).

## Membrane filtration

Membrane filtration one of the most widely used methods—it can be divided into reverse osmosis (RO), which is based on the use of a semipermeable filtering membrane that generates this phenomenon in order to retain all the total dissolved solids TDS existing in the water; purified water collection and storage tanks; ultrafiltration (UF) and nanofiltration (NF), techniques activated through the use of pressure, in which solutes of different molecular weights are separated from the solution (Muñi et al. 2005); and, finally, electrodialysis, a separation process that uses selective ionic membranes, enabling the separation of charged species present in an electrolyte solution by applying an electric current in a direction perpendicular to the membranes (Mier López et al. 2004; Ye et al. 2012; Xie et al. 2018; Hu et al. 2021).

In RO, NF, and UL, the  $\text{ClO}_4^-$  is selectively eliminated through a membrane, and, in the case of electrodialysis, the ions that are dissolved in water move to both ends of the polymeric membrane, while they are under the effect of an electric field (Hu et al. 2021). The diffusion of this pollutant by any of the membrane filtration methods increases with decreasing pH, mainly because the charge on the membrane surface increases its negativity, which in turn increases the electrostatic repulsion dynamics that occur between  $\text{ClO}_4^-$  and these electronegative membranes (Ye et al. 2012). Therefore, the optimum pH to carry out the reduction or elimination of  $\text{ClO}_4^-$  is 4.3, with which it is possible to obtain removal results of approximately 92% with adsorbent doses and  $\text{ClO}_4^-$  concentrations of 0.8 g/L and 10 mg/L, respectively (Hu et al. 2021). Reverse osmosis treatment is essential to eliminate chlorates and perchlorates in water for food use, which guarantees the absence of salts. However, to improve the effectiveness of this technology, it is necessary to pre-treat the water that includes filtration, ultrafiltration, dosing system, using a filter with a diameter of less than 5 microns (Eisenberg and Middlebrooks 2013); which will improve the percentage reduction of perchlorate in the treated water (Ye et al. 2012).

## Ion exchange

One of the most widely used technologies for the removal of  $\text{ClO}_4^-$  in drinking water is ion exchange (IX), which is one of the most effective technologies when working with small amounts (Xie et al. 2018). The method is based on anion exchanges that are achieved through the loading of an immobilized functional group (Ye et al. 2012). The efficient removal of the pollutant with this method is affected

by factors such as cation exchange capacity, regeneration capacity, and stability, apart from the choice of resin (Hu et al. 2021). Conventional resins, such as IRA-900, have a slow removal rate. On the other hand, if highly selective resins are used, this removal/reduction rate is increased, and the advantage is that the chemistry of the water is not changed by adding nutrients or chemical compounds during the treatment process (Ye et al. 2012).

Additionally, conventional resins are usually composed of a polymer matrix to which a large number of polar radicals, acids, or bases have been attached, while highly selective resins can be chelating resins or hybrid technologies (Hu et al. 2021). Conventional ones may have a larger particle size, while highly selective resins may have a more homogeneous structure with only micropores within the sites. This can influence the kinetics and operating capacity of the resins (Alexandratos 2009). Therefore, conventional resins are more suitable for general applications, while highly selective resins are more specialized and can adapt to different types of water and wastewater (Ye et al. 2012).

## Precipitation

Several analytical chemistry techniques have been used for reduction of the  $\text{ClO}_4^-$  anion with large organic cations. Among them, we find the use of tetraphenylarsonium chloride combined with conductimetry, potentiometry, and gravimetry, for which it became an important method for the preparation of various porous oxide materials, with good results (Lu et al. 2013). However, the  $\text{ClO}_4^-$  present in aqueous solutions is reduced because, in this technique, concentrating it in others has disadvantages, such as an increase in costs due to the implementation of filters, the production of moisture and sludge, and an increase in waste in need of disposal (Acevedo-Barrios and Olivero-Verbel 2021).

## Chemical reduction

Metals, such as iron, are used for this method. At high temperatures and pressures, and an acidic pH, they can reduce considerable concentrations of  $\text{ClO}_4^-$  to chloride. Titanium and transition metals, such as molybdenum, ruthenium, and vanadium, are used in the same way. Chemical reduction poses a problem because no typical reducer is capable of reducing  $\text{ClO}_4^-$  up to typical environmental concentrations, the reduction reaction is slow, and the implementation of this technique is limited by economic and technical factors (Acevedo-Barrios and Olivero-Verbel 2021).

## Electrochemical reduction

Electrochemical reduction reactions can be conducted without catalysts (Ye et al. 2012), where the  $\text{ClO}_4^-$  ions that

are dissolved in acidic aqueous solutions are reduced to  $\text{Cl}^-$  ions. The preferred materials for electrodes are ruthenium, tungsten, iridium, platinum, rhodium, technetium, and rhenium (Acevedo-Barrios and Olivero-Verbel 2021). The main disadvantage of this technology is electrode erosion (Ye et al. 2012), in addition, the reactions require large surfaces and are very slow, apart from being affected by the presence of other substances in the solution (Acevedo-Barrios and Olivero-Verbel 2021).

## Biological treatment of $\text{ClO}_4^-$

Biodegradation is possible because native soil and groundwater bacteria have special enzymes that can lower the activation energy required for the biological reduction of  $\text{ClO}_4^-$  (Ye et al. 2012; Song et al. 2017). This pollutant manages to be microbiologically reduced to chloride ( $\text{Cl}^-$ ) under anaerobic conditions, because its high reduction potential ( $E^\circ = 1.287 \text{ V}$ ) makes it a good electron acceptor (Ye et al. 2012; Acevedo-Barrios et al. 2022b).

The key factors to conduct bioremediation or biodegradation of the soil are the absence of oxygen, the presence of an electron donor, an optimal pH value ( $\sim 7$ ), and, when an unsaturated zone is to be remedied, enough liquid content to promote the growth of bacteria (Xie et al. 2018). However, these conditions are difficult to maintain in deep unsaturated zones or when performing in situ soil remediation. These techniques include phytoremediation, which involves the use of plants and trees to accumulate and remove perchlorate from groundwater and soils (Sijimol et al. 2015), where  $\text{ClO}_4^-$  is degraded through its absorption and accumulation in plants and microorganisms in their rhizosphere (Xie et al. 2018).

The cost required to implement these technologies is relatively low, and they are suitable for treating large-scale wastewater and soil areas highly contaminated with  $\text{ClO}_4^-$ . However, the bioremediation rate is relatively slow, the metabolic products of microorganisms can lead to secondary contamination, and, to be used in drinking water treatment, they must have very strict operating conditions and a somewhat long operating cycle, without considering the health

effects associated with these microorganisms (Ye et al. 2012; Xie et al. 2018).

## Antarctic $\text{ClO}_4^-$ Reducing Bacteria

$\text{ClO}_4^-$  can be present in various environmental matrixes thanks to its high solubility and stability (Acevedo-Barrios et al. 2022a, b). In arid and semi-arid areas, such as Antarctica or the desert of Atacama in Chile (Jackson et al. 2015), traces of the pollutant can be found in soils and their sediments, or in surface and groundwaters (Jia et al. 2022). The presence of  $\text{ClO}_4^-$  in marine sediments, seawater, Antarctic soil, and other areas, has allowed and increased the growth of bacteria that can naturally tolerate and degrade this pollutant (Acevedo-Barrios et al. 2022b).

### Characteristics of the Bacteria

These bacteria with the potential to reduce  $\text{ClO}_4^-$  are anaerobic or facultative microaerophilic. They are phylogenetically diverse, and the most detected class is Betaproteobacteria; Gammaproteobacteria, Deltaproteobacteria, Alphaproteobacteria (Acevedo-Barrios and Olivero-Verbel 2021), and Psychobacteria, as can be seen in Table 3 (Acevedo-Barrios et al. 2022b). The bacteria collected from Deception Island can grow in heterotrophic aerobic conditions at  $4^\circ\text{C}$ , and presented positive catalase and negative oxidase activity, apart from having positive reactions for N-acetylglucosaminidase and nitrate reduction capacity (Acevedo-Barrios et al. 2022b).

### Habitat of the Bacteria

The habitat of these microorganisms is extreme, with limited bacterial diversity. They have high salt concentrations, low nutrient availability, and a variable ionic composition (González Díaz and Mira Peinado 2021). Reducing perchlorate bacteria can grow in different ecosystems, including extreme conditions, such as hypersaline and hyperthermophilic soils, saline lakes, and even hot springs (Acevedo-Barrios et al. 2022b). They develop in environments with neutral pH, and one of their energy sources is yeast, which

**Table 3** Bacteria isolated from Antarctica

Bacterium	Molecular identification	From	Morphology
UTB-113	<i>P. cryohalolentis</i>	Deception Island	Cocccobacilli shaped
UTB-114	<i>P. urativorans</i>	Deception Island	Rod shaped
UTB-154	<i>I. loihiensis</i>	Horseshoe Island	Rod shaped
UTB-156	<i>I. loihiensis</i>	Horseshoe Island	Rod shaped
UTB-160	<i>P. nivimaris</i>	Half Moon Island	Cocccobacilli shaped
UTB-161	<i>S. aquimarina</i>	Half Moon Island	Rod shaped
UTB-162	<i>P. lactis</i>	Half Moon Island	Rod shaped



stimulates their growth. Their nutrition is variable due to their presence in different ecosystems, and the temperature zones in which they can develop are mesophilic and thermophilic (González Díaz and Mira Peinado 2021; Acevedo-Barrios et al. 2022b).

### Metabolism of the *Bacteria*

These microorganisms use two enzymes that can lower the activation energy required to reduce  $\text{ClO}_4^-$  (Acevedo-Barrios et al. 2019), making it a valuable electron acceptor for different types of bacteria. The mechanism used by these microorganisms to reduce the concentration of the pollutant depends on its reduction to chlorite ( $\text{ClO}_2^-$ ) in the bacterial periplasm (Melnik and Coates 2015). Using the perchlorate reductase enzyme that reduces perchlorate to chlorate and chlorate to chlorite, then using the chlorite superoxide enzyme (Acevedo-Barrios et al. 2019), it is dismutated from chlorite to chloride and molecular oxygen. This biogenic oxygen produced as an intermediate is not released, but it is rather reduced by the microorganism itself (Melnik and Coates 2015). The biological reduction route of perchlorate can be seen in Fig. 2 (Acevedo-Barrios et al. 2022b).

The main application of these extremophilic bacteria is for biotransformation, and, with this method, the  $\text{ClO}_4^-$  is reduced in a less toxic way and helps with the sanitation of environments contaminated with it. With this method, the “*in-situ*” and “*ex-situ*” bioremediation of ecosystems are carried out, and, in this sense, it can be used to treat unsaturated areas and soils (Acevedo-Barrios and Olivero-Verbel 2021).

### Integrated or combined technologies

The combinations of different technologies provide greater flexibility and degradation efficiency during the reduction or elimination of  $\text{ClO}_4^-$  (Xie et al. 2018). An example of these integrated techniques is the chemical reduction of  $\text{ClO}_4^-$  using  $\text{H}_2$  by heterogeneous catalysis, combined with activated carbon powder, which has good adsorption capacity and is used as a support medium (Ye et al. 2012). This technique requires further research before being applied because it is in the exploration stage (Xie et al. 2018).

### Environmental fate

The course of  $\text{ClO}_4^-$  is directly associated with its source, and it is understood that this would be a factor of variability when identifying its environmental destination. Stable isotope techniques ( $^{180}/^{160}$  and  $^{170}/^{160}$ ;  $^{32}\text{Cl}/^{35}\text{Cl}$ ) help identify natural  $\text{ClO}_4^-$  and anthropogenic  $\text{ClO}_4^-$  (Kumarathilaka et al. 2016).

Most of the natural sources of  $\text{ClO}_4^-$  are found in arid and desert areas on Earth, which is related to the fact that the mobilization of groundwater is restricted by the net infiltration of precipitation in these environments, together with a higher percentage of evapotranspiration, which results in a greater accumulation of  $\text{ClO}_4^-$ . An example of this is the Atacama Desert in Chile, which is also known as one of the largest sources of nitrate, where electrostatic discharges with oxidants such as ozone  $\text{O}_3$ , electrostatic discharges, and gas–solid reactions with oxidants followed by dry deposition led to the presence of  $\text{ClO}_4^-$  in this ecosystem, as cited in Kumarathilaka et al. (2016). This same scheme is also suggested for other arid zones.

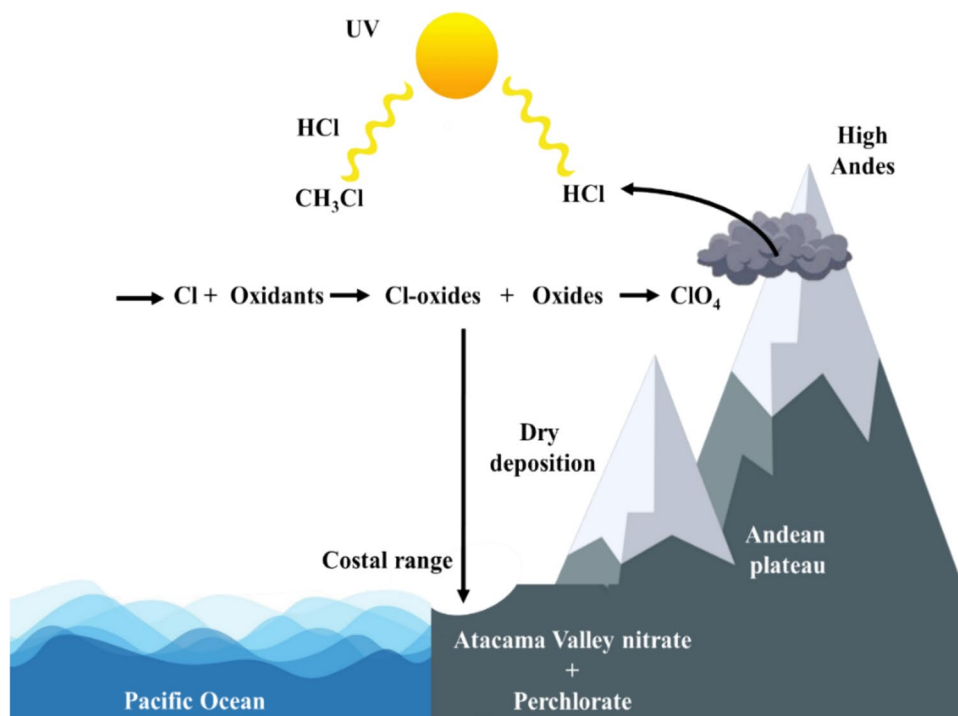
The atmospheric concentration of perchlorate and chlorate found in Antarctic lakes is 1,100  $\mu\text{g}/\text{kg}$ , and perchlorate salts have been reported in kelp forests and Antarctica (Kounaves et al. 2010b; Kumarathilaka et al. 2016). Furthermore, the concentration of perchlorate in different ecosystems is associated with anthropogenic sources, which causes the environmental fate to vary or be different from the perchlorate cycle shown in Fig. 3. In the cycle of  $\text{ClO}_4^-$  formation through the atmospheric photochemistry in the Atacama Desert, the difference is mainly in the origin of the source, which changes the environmental fate cycle of  $\text{ClO}_4^-$  (Fig. 4).

### Astrobiological perspectives

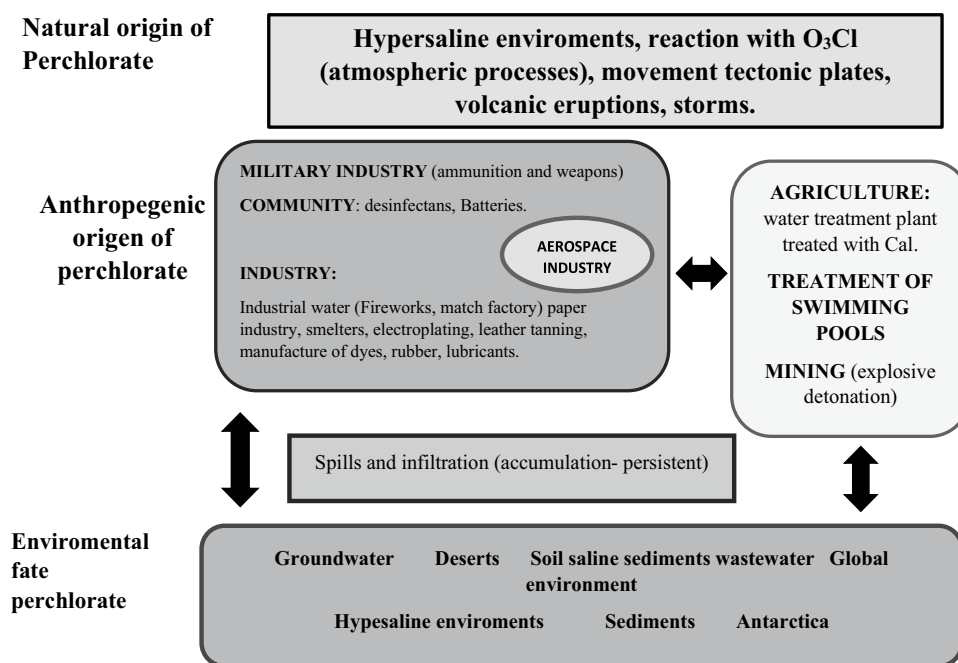
The presence of perchlorates, possible liquid water, low temperatures, and the ability of some terrestrial microorganisms that resist these conditions make Mars a potentially habitable planet (Schirmack et al. 2015). Considering that various Antarctic organisms, such as *Halorubrum lacusprofundi*, are tolerant to perchlorate, being inhibited only at higher concentrations than those detected on Mars, then, the development of organisms similar to this haloarchaea in the Martian environment would be possible (Laye and DasSarma 2018).

Haloarchaea are relevant extremophiles in astrobiology, as they survive in different planetary environments and are critical to detecting life in situ. Their study addresses the origin of life, biochemical capabilities, and pigments as possible biosignatures. Investigation of these extremophiles in laboratories, and by future space telescopes, could provide valuable answers on the existence of life in the universe (DasSarma et al. 2020). In addition, research on other perchlorate-reducing microorganisms, such as *Azospirillum brasilense* USD2, provides insights into Mars's terraforming and future astronauts' well-being (Sunilkumar and Lal 2021). These findings open new questions on the habitability of other planets and life in the universe, particularly considering that the presence of perchlorates can form cryo-brins,

**Fig. 3** Cycle of  $\text{ClO}_4^-$  formation through the atmospheric photochemistry in the Atacama Desert



**Fig. 4** Environmental fate and formation of  $\text{ClO}_4^-$  in the environment and its areas of use



making water able to remain liquid due to the presence of salts (Cottin et al. 2017).

The incidence of cosmic rays on the Martian surface, with the presence of perchlorates, could release oxygen ( $\text{O}_2$ ) (Quinn et al. 2013). Reaching, in calcium and magnesium perchlorate brines, even levels close to those

currently found in Earth's oceans, being the possible concentration of  $\text{O}_2$  on Mars, today, higher than the one that was present in the great moment of oxidation and allowed aerobic life on Earth. Perchlorate is an opportunity for the potential habitability of aerobic life on Mars (Stamenković et al. 2018).

## Conclusion

$\text{ClO}_4^-$  is a toxic pollutant for humans, biota, and the environment, found in different ecosystems, and its origin can be anthropogenic or natural (Acevedo-Barrios et al. 2022a). Because of its high solubility, its presence in groundwater or surface water classifies it as a pollutant of increasing relevance (Cao et al. 2019). Its main effect on health is its potential as an endocrine disruptor, since it attacks the thyroid cells (Ali et al. 2021). It is imperative to continue delving into the mechanism of endocrine disruption at the molecular level of  $\text{ClO}_4^-$  and its toxicity in other unstudied biological models.

There are many types of technologies for reducing  $\text{ClO}_4^-$ , which are classified into four groups: Physical–chemical treatments, chemical treatments, integrated or combined technologies, and biological treatments (Ye et al. 2012; Xie et al. 2018; Acevedo-Barrios and Olivero-Verbel 2021). The four groups (physical–chemical treatments, chemical treatments, integrated or combined technologies, and biological treatments) can be effectively combined to treat perchlorate pollution in Antarctica and worldwide; generating hybrid technologies, to obtain a balance between their cost and efficiency (Fang and Naidu 2023).

However, biological methods are the most promising, because it does not generate waste that could be environmentally dangerous, and, therefore, do not generate cost overruns (Acevedo-Barrios and Olivero-Verbel 2021). The extremophile bacteria used in this method belong to the Betaproteobacteria, Gammaproteobacteria, Deltaproteobacteria, Alphaproteobacteria, and Psychobacteria classes (Acevedo-Barrios and Olivero-Verbel 2021; Acevedo-Barrios et al. 2022b).

Within environmental fate specifications, it has been determined that it can vary according to the perchlorate's sources of origin, which can be natural or anthropogenic (even combined). Likewise, this pollutant has a natural environmental fate regulated by the photochemical formation of the atmosphere and an anthropogenic environmental fate, because of industrial and domestic activities.

In conclusion, Antarctica is an excellent ecosystem to isolate perchlorate-reducing bacteria, which may also have great astrobiological potential. However, studies and existing bibliographic information are limited, so it is necessary to conduct more research to elucidate the biological reduction mechanisms of this pollutant in strategic ecosystems such as Antarctica (Acevedo-Barrios et al. 2022b). Research points to the development of new technologies to eliminate perchlorate contamination from ecosystems, which requires the combination of various technologies with ionic exchange and bioremediation, to remove perchlorate from the environment (Acevedo-Barrios and Olivero-Verbel 2021).

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## Declarations

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