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Perchlorate as an emerging contaminant in soil, water and food

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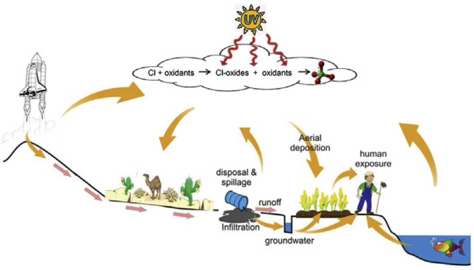
H I G H L I G H T S

- Perchlorate is a naturally occurring and man-made chemical substance.
- Specific analytical methods detect perchlorate in the environment.
- RfD for perchlorate exposure is set at 0.7 $\mu g\ kg^{-1}$ body weight/day.
- Perchlorate detected in food, soil and water exceeding USEPA RfD.
- Physico-chemical and biological methods look promising way to remove perchlorate.

G R A P H I C A L   A B S T R A C T



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A B S T R A C T

Perchlorate (ClO_4^-) is a strong oxidizer and has gained significant attention due to its reactivity, occurrence, and persistence in surface water, groundwater, soil and food. Stable isotope techniques (i.e., ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) and $^{37}Cl/^{35}Cl$) facilitate the differentiation of naturally occurring perchlorate from anthropogenic perchlorate. At high enough concentrations, perchlorate can inhibit proper function of the thyroid gland. Dietary reference dose (RfD) for perchlorate exposure from both food and water is set at 0.7 $\mu g\ kg^{-1}$ body weight/day which translates to a drinking water level of 24.5 $\mu g\ L^{-1}$. Chromatographic techniques (i.e., ion chromatography and liquid chromatography mass spectrometry) can be successfully used to detect trace level of perchlorate in environmental samples. Perchlorate can be effectively removed by wide variety of remediation techniques such as bio-reduction, chemical reduction, adsorption, membrane filtration, ion exchange and electro-reduction. Bio-reduction is appropriate for large scale treatment plants whereas ion exchange is suitable for removing trace level of perchlorate in aqueous medium. The environmental occurrence of perchlorate, toxicity, analytical techniques, removal technologies are presented.

1. Introduction

Perchlorate (ClO_4^-) is an inorganic anion and strong oxidizer capable of contaminating water and soils when solid salts of ammonium (NH_4^+), potassium (K^+), magnesium (Mg^{2+}) and sodium (Na^+) perchlorate and perchloric acid ($HClO_4$) dissolve in water (Duncan et al., 2005; Motzer, 2001; Smith et al., 2004). The strong oxidizing character of perchlorate is a result of chlorine having a maximal +7 oxidation state. Perchlorate is highly soluble and capable of mobilizing in aquatic environments. Kinetically, perchlorate is relatively stable under ambient conditions, potentially related to the tetrahedral arrangement of oxygen restricting

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reductants from interacting with the central chlorine atom (Ye et al., 2012). As a result, perchlorate may persist for many years, possibly decades, under typical surface water and groundwater conditions (Sturchio et al., 2014).

United States Environmental Protection Agency (USEPA) placed perchlorate on its contaminant candidate list (CCL) in 1998 (EPA, 2014). Putting a chemical on the CCL means that the chemical should be evaluated to determine whether it should be considered a major environmental contaminant requiring regulation. In this sense, studies following its inclusion have primarily focused on the identification of perchlorate sources, improving analytical techniques, assessing its health impacts and forwarding remediation techniques and strategies. Over the past decade, the identification and measurement of perchlorate in the environment has improved, especially in the micromolar range, where investigations assessing perchlorate in soil and groundwater have steadily increased (Wagner et al., 2006; Wendelken et al., 2006). Many countries including the USA, Canada, China, South Korea and India have detected perchlorate from nanogram to milligram level in water, soil and food (Her et al., 2011; Kannan et al., 2009; Poghosyan et al., 2014; Wilkin et al., 2007; Ye et al., 2013). Due to the persistent behavior of the perchlorate, many studies have focused on determining the fate of perchlorate in the environment.

In this overview, we (*a*) discuss sources of perchlorate in water, soil and food, (*b*) provide a summary of anthropogenic and geogenic perchlorate sources and their respective concentrations, (*c*) summarize the potential impact of perchlorate on living organisms, (*d*) review methods for detecting and measuring perchlorate and (*e*) elucidate current remediation strategies. Several technical terms may frequently used throughout the manuscript for describing perchlorate in the environment hence we have defined them here. A synthetic substance is a substance made by chemical synthesis, especially to imitate a natural product. Natural means a something existing in or derived from nature, not made or caused by humankind. Anthropogenic defines as environmental pollution and pollutants originating in human activity whereas non-anthropogenic means environmental pollution and pollutants originating in naturally.

2. Sources of perchlorate

Perchlorate is an anthropogenic and naturally occurring chemical substance. As it well known, recent development in stable isotope techniques facilitates the differentiation of naturally occurring perchlorate from anthropogenic perchlorate. By assessing triple-oxygen isotope ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$), Bao and Gu (2004) demonstrated that perchlorate from Atacama Desert soil possessed isotopic signatures distinctly different from the commercially produced samples. It appears that when a perchlorate oxyanion is formed its oxygen will not be exchanged under typical environmental conditions. As a result, the perchlorate anion maintains the oxygen isotopic signature of its source and, therefore, can be traced. Additionally, $^{37}Cl/^{35}Cl$ fractionation can be used to distinguish the unique origin of the natural perchlorate from the anthropogenic perchlorate. A study by Böhlke et al. (2005), successfully utilized stable isotope analysis ($^{37}Cl/^{35}Cl$ and $^{18}O/^{17}O/^{16}O$) to differentiate the natural sources of perchlorate from the synthetic perchlorate. Based on similar approaches, nonanthropogenic perchlorate occurrences have been identified in many places throughout the world.

Most natural perchlorate occurrences are confined to arid and semiarid environments on Earth (Rajagopalan et al., 2006; Rao et al., 2007). In such environments, mobilization of perchlorate to groundwater is restricted by the net infiltration from precipitation. In addition, higher evapotranspiration rate in those environments leads to higher accumulation of perchlorate compared to other places in the world (Albright et al., 2008). Table 1 shows several locations of geogenic perchlorate and their respective concentrations. The Atacama Desert in Chile is well known for its nitrate deposits, as well as one of the largest natural sources of perchlorate in the world. Photochemical reactions with oxidants such as O_3, electrostatic discharge and gas–solid reactions with oxidants followed by dry deposition are potential mechanisms responsible for generating perchlorate in the Atacama (Catling et al., 2010; Michalski et al., 2004). Fertilizer mined from ores and brines in the Chilean deposits have been exported throughout the world for over a century. Perchlorate ranging from 0.03 to 0.1% and 6.3% nitrate are commonly present in these fertilizers (Duncan et al., 2005). In addition to the Chilean deposits, (a) New Mexico and Canadian potash, (b) Searles Lake, California, evaporative deposits, (c) Bolivian playa crusts, (c) West Texas and New Mexico surface deposits in semi-arid regions originating from atmospheric deposition and (d) marine deposits in the Mission Valley Formation, California, are other recognized terrestrial deposits of perchlorate present in significant concentrations (Duncan et al., 2005). Additionally, perchlorate can be present in precipitation because it can be formed naturally by atmospheric processes. The exact mechanism for the production of perchlorate is unknown. It suggests that chloride, probably in the form of sodium chloride from the ocean or land-based chloride aerosol blown in from atmosphere, expose to high concentration of ozone. Consequently, photochemical reactions between chloride and ozone make perchlorate in the atmosphere (Trumpolt et al., 2005). Additionally, another theory suggests that lighting involves in the production of perchlorate atmospherically (Dasgupta et al., 2005). Following the atmospheric production, perchlorate returns to the earth's surface via deposition. A study by Dasgupta et al. (2005) demonstrated that perchlorate was present in many rain and snow samples in southern high plains (Texas Panhandle). Recently, considerable amounts of perchlorate (10–340 ng L^{-1}) has been detected in Antarctic snow and ice potentially related to atmospheric deposition (Jiang et al., 2013). Fig. 1 shows identified geogenic pechlorate occurrences in the world so far. In contrast to geogenic sources, perchlorate may be released and/or introduced into the environment at an even greater extent due to anthropogenic activities.

Anthropogenic sources of environmental perchlorate contamination results from the heavy use of perchlorate-containing products. As a result of its strong oxidative properties, perchlorates were used for explosives and propellants extensively since World War II. In the USA, about 90% of ammonium perchlorate synthesized is used for the military purposes (Duncan et al., 2005). Solid rocket fuels, signal flares, colored and white smoke generators, artillery traces, incendiary delays and railway torpedoes are a few examples pertaining to military sources of perchlorates (Backus et al., 2005; Wilkin et al., 2007). Additionally, a wide range of industrial applications produces and uses perchlorates. Gas drying agents, lubricating oils, tanning, finished leather, electronic tubes, fabric fixes, dyes, cloud seeding, electroplating, aluminum refining, signal and road flares, rubber manufacture, paint and enamel production, cattle feeds and magnesium batteries are some of the industrial applications of perchlorates (Backus et al., 2005; Cheng et al., 2004; Dean et al., 2004). As it well known, perchlorate from rocket fuel production facilities in Henderson, Nevada contaminated Lake Mead and the Colorado River and the water imported to California from the Colorado River. This big anthropogenic occurrence of perchlorate contamination led to perchlorate being put on the USEPA CCL (EPA, 2014). Table 2 provides several examples related to the anthropogenic distribution of perchlorate and their respective concentrations.

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