Isotopic Tracing of Perchlorate Sources in the Environment

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Perchlorate (ClO₄⁻) is an emerging persistent pollutant that is ubiquitous in the environment at trace concentrations. Perchlorate ingestion poses a risk to human health because it interferes with thyroidal hormone production. The identification of perchlorate sources in groundwater is a primary concern. Chlorine and multi-oxygen isotopic tracing of perchlorate (δ³⁷Cl, ³⁶Cl/Cl, δ¹⁸O, and Δ¹⁷O) can provide a unique tool for identifying the origin and transport of perchlorate in groundwater. Along with the kinetic fractionation of chlorine and oxygen isotopes, the Δ¹⁷O value, ³⁶Cl/Cl ratio, and ε¹⁸O/ε³⁷Cl (the fractionation coefficient of oxygen and chlorine isotopes) are constant, potentially indicating the biodegradation of perchlorate, without disguising its source information. Therefore, comprehensive characterization of stable chlorine and poly-oxygen isotopes is expected to provide direct evidence for identifying the source of perchlorate in groundwater. However, further studies are needed to increase the amount of isotopic data of different perchlorate sources, to make the end-member model available to broader regions. It is critically important to understand the range of values and differences of isotopes among natural perchlorate sources and the perchlorate formation mechanisms.

1. Introduction

Groundwater is an important water resource, which is of strategic significance to the sustainable development of a country and its people. It has become a hot issue to use water resources rationally, to ensure continued quality and availability, to meet economic and social developmental needs [1]. In some areas, groundwater is an important (or the only) source of drinking water, and water safety issues directly affect residents’ health and quality of life [2]. With the rapid development in recent decades of China’s economy, groundwater hydrochemistry is affected by natural factors, such as geology, geography, and climate change, and increasingly by anthropogenic inputs [3], making the situation of water shortage severe in China. Groundwater pollution is hard to be found and difficult to reverse; thus, the effective prevention and control of groundwater pollution should first be based on “prevention.” That is, identifying the source of the pollutants in groundwater and determining their migration and transformation paths in groundwater are the primary concerns that should be considered to solve groundwater pollution.

Perchlorate (ClO₄⁻) is typically a persistent environmental pollutant, attracting extensive attention for research on its environmental pollution status, ecotoxicological effect, pollution control, and remediation [4–7]. Trace amounts of ClO₄⁻ can interfere with the normal function of the thyroid, leading to a series of developmental and metabolic diseases in the human body, especially in women of childbearing age and infants [8]. Currently, ClO₄⁻ widely exists in different environmental media, such as rivers, lakes, groundwater, soil, and sediment [9–11], and is widely found in food, making its way into humans at a fast rate [12–14]; it can be detected in body fluids (such as breast milk, saliva, blood, and urine) [15,16], constituting a serious threat to human health. In 2008, the US Environmental Protection Agency (EPA) listed ClO₄⁻ as a level 1 monitoring indicator and recommended a safe reference dose of 0.7 μg/kg/day.
exposure to humans, which is likely to be without an appreciable risk of adverse effects. The US EPA in February 2011 officially listed ClO$_4^-$ for regulation under the Safe Drinking Water Act; hence, perchlorate has become an important research topic.

Perchlorate originates from both natural and human sources. Natural perchlorate has been attributed to the earlier use of Chilean nitrate as fertilizer and atmospheric origin. Because perchlorate is a strong and stable oxidant and a strong acid, it is widely used in aerospace, military, and industrial fields, such as in rocket solid fuel, fireworks manufacturing, ammunition equipment, electroplating, desiccants, and oxidants (Table 1). The sources of perchlorate in groundwater vary; the pollution paths are complex and varied and are often affected by the widespread effects of physics, chemistry, and biology. Isotope technology is used to explore the source of material, related migration, and transformation laws at the “atomic” scale, having many unique advantages compared with the content measurement approach at the “molecular” scale. The comprehensive characteristics of the contents of stable chlorine and oxygen isotopes along with the radioactive isotope $^{36}$Cl of perchlorate provide an important analytical tool for tracing the source of perchlorate and its migration and transformation in the environment.

China is a large traditional country of fireworks manufacturing and consumption. As the direct products of chemical plants (oxidants and additives of the perchlorate) are widely distributed throughout the country, the potential of perchlorate environmental pollution problems cannot be ignored. A recent investigation shows that 86% of 300 water samples from 13 provinces and cities in China had ClO$_4^-$ detected in them [17]. The concentration of ClO$_4^-$ detected in the blood of adults in Nanchang is more than 10 times higher than that reported in the United States [12]. However, studies on the pollution of ClO$_4^-$ in China have just begun, and the source analysis of ClO$_4^-$ in groundwater has not been reported. Given the present situation of environmental pollution of perchlorate, this paper summarizes and discusses perchlorate isotope testing technology and its application in tracing the source of ClO$_4^-$ in groundwater, providing a reference for effective prevention and control of ClO$_4^-$ pollution in groundwater in China.

2. Environmental Pollution

Status of Perchlorate

The United States was the first country to find perchlorate pollution, and existing research has mainly focused on its water pollution; thus far, ClO$_4^-$ has been detected in 44 states [18]. The EPA recommended that the concentration of perchlorate in drinking water be less than 15 μg/L [19]. The Safe Drinking Water Act (SDWA) allows States to establish drinking water standards that are more stringent than EPA’s national standards. California’s latest concentration standard for perchlorate in drinking water is 6 μg/L [18], and Massachusetts’s standard is 2 μg/L [19]. In 2008, the US EPA recommended a safe intake of 0.7 μg/kg/day for the human body. ClO$_4^-$ was detected in high amounts in the southwest of the United States, including California, Arizona, the highlands of Texas, the East Coast between New Jersey and Long Island, and Massachusetts. In 2008, the US EPA published the test results of 3,865 public water supply samples collected from 2001 to 2005, and the average content value of ClO$_4^-$ was 4–420 μg/L [20]. Recently, apart from the United States, other countries have begun to investigate the concentration of ClO$_4^-$ in water. The concentration of ClO$_4^-$ was 340–2,300 μg/L in the upstream and tributary (Usui River) of the Tone River in Japan. Moreover, different concentrations of ClO$_4^-$ were detected in tap water from the Tone River, and a part of the water sample concentration exceeded 10 μg/L [21]. The concentration of ClO$_4^-$ in the Nakdong River in South Korea is as high as 60 μg/L, and the concentration in drinking water is as high as 35 μg/L [10]. The average concentration of groundwater samples from six states of India is 1.0 μg/L, wherein samples greater than 1.0 μg/L were obtained from central industrial cities [22]. North Korea tested 520 tap water samples from more than 100 areas. The concentration of ClO$_4^-$ was <1.0–6.1 μg/L, and 80% of the samples exceeded the concentration limit in drinking water [23]. The relevance ratio of ClO$_4^-$ in German groundwater samples is 100%, and the concentration is 0.79–2.38 μg/L [24] (Table 2).

In the past 10 years, China has also investigated perchlorate environmental pollution. The results show that the environmental pollution problem of perchlorate has been widespread in China, and research on the prevention and control of ClO$_4^-$ pollution in groundwater is imminent. Liu et al. reported the ClO$_4^-$ concentration in factory water and source water of three water plants in Beijing. The results showed that 67% of the samples, with detectable ClO$_4^-$, were obtained from water plants that used groundwater as their water source. The concentration of ClO$_4^-$ in the source water reached 30.7 μg/L [25–27]. In a recent water survey, covering 13 provinces or autonomous regions in China (including tap water, groundwater, surface water, and bottled water), the detection rate of ClO$_4^-$ is up to 86%, with a concentration of 0.02–54.4 μg/L, where the average concentration of groundwater was the highest, 3.04 μg/L [17]. Severe ClO$_4^-$ pollution exists in Liuyang City, Hunan Province; their fireworks production accounts for more than 60% of that of the world. High concentrations of ClO$_4^-$ are detected in the river water, bottom mud, soil, and groundwater [11, 17], among which ClO$_4^-$ is detected in groundwater, whose concentration is as high as 22.14 μg/L. ClO$_4^-$ was also detected in rice and milk samples from 26 cities in China, with concentrations ranging from 0.16 to 4.88 μg/kg and 0.30 to 9.1 μg/L, respectively [27]. Furthermore, the results of 131 blood samples from donors in Nanchang showed that the concentration of ClO$_4^-$ in human blood of different age groups (0.4–90 year) was as high as 10.5 μg/L, with an average value of 2.68 μg/L [16].

3. Perchlorate Chlorine and Oxygen Isotope Testing Technology

3.1. Isotope Characterization. Chlorine (Cl) and oxygen (O) in perchlorate (ClO$_4^-$) have multiple isotopes in nature. There are mainly two stable isotopes of Cl on the earth’s
δ\text{isotope} \text{is} \text{usually} \text{expressed} \text{by} \text{the} \text{and} \text{0.20\%} [29], \text{respectively}. \text{The} \text{composition} \text{of} \text{a} \text{stable} \text{isotope} \text{is} \text{usually} \text{expressed} \text{by} \text{the} \text{δ17O} \text{and} \text{δ18O} \text{value, that is}, \text{δ17O} \text{and} \text{δ18O} \text{is} \text{typically} \text{used} \text{to} \text{characterize} \text{17O} \text{and} \text{18O} \text{based} \text{on} \text{the} \text{above} \text{method} [30], \text{and} \text{this} \text{method} \text{has} \text{been} \text{further} \text{adapted} \text{and} \text{developed} [29, 34–36]. \text{These} \text{methods} \text{require} \text{the} \text{analysis} \text{sample} \text{to} \text{be} \text{high-purity} \text{perchlorates, such as KClO4, RbClO4, or CsClO4.} \text{The} \text{δ36Cl} \text{content} \text{is} \text{usually} \text{expressed} \text{as} \text{δ36Cl/Cl}, \text{which} \text{is} \text{the} \text{ratio} \text{of} \text{the} \text{atoms}.

### 3.2. Testing Technology of Perchlorate Chlorine and Oxygen Isotopes.

Research on the sources of perchlorate, geochemical behavior, and isotope kinetic fractionation effect in environmental media is still in its initial stages. The high-precision test method of stable isotope ratio provides the necessary technical support for the mechanism and application of perchlorate environmental pollution. The high-precision stable isotope data of perchlorate (δ18O, Δ17O, and δ37Cl) are usually measured using a gas stable isotope ratio mass spectrometer, and the analysis gases are CO, O2, and CH3Cl [30–32]. Ader et al. and Sturchio et al. first established a test method for the δ37Cl value of perchlorate [14, 30–32]. Bao and Gu reported a test method for the simultaneous determination of δ18O and δ17O and the preparation of O2 via high-temperature pyrolysis of perchlorate [33]. Furthermore, Böhlke et al. successively reported the preparation of CO via high-temperature carbon reduction of perchlorate, an online measurement δ18O value test method [31]. Sturchio et al. established a test method for the simultaneous analysis of δ37Cl, δ18O, and δ17O based on the above method [30], and this method has been further adapted and developed [29, 34–36]. These methods require the analysis sample to be high-purity perchlorates, such as KClO4, RbClO4, or CsClO4. The δ36Cl content is usually determined using an accelerator mass spectrometer (AMS). This article summarizes the current mature testing techniques for perchlorate chlorine and oxygen isotopes.

#### 3.2.1. Oxygen Isotopes.

The oxygen isotope composition of perchlorate can usually be determined using two isotope ratio mass spectrometry (IRMS), namely the CO-TC/EA-IRMS high-temperature carbon reduction online continuous flow method, which determines the δ18O value and O2-DI-IRMS pyrolysis; this off-line two-stage method measures the δ17O value and δ18O values simultaneously [31, 32, 34, 35].

The principle of the CO-TC/EA-IRMS high-temperature carbon reduction online continuous flow method can be summarized as follows. Perchlorate (such as CsClO4) and glassy carbon in a reduction reaction in a high-temperature cracking furnace at 1,325–1,400°C generate CO. After purging pure He carrier gas, CO goes through a gas chromatographic column equipped with a 5 Å molecular sieve for purification. Then, it enters the IRMS in a continuous flow mode and is received by a Faraday cup with m/z of 28 and 30 to determine the δ18O value. For high-purity ClO4− reagents and samples, the yield of O(CO) was usually 100 ± 2%, and the test accuracy of δ18O was ±0.3‰ [31, 32, 35, 37]. This method can be used to rapidly and efficiently perform an online test of the perchlorate δ18O value, which is especially suitable for batch tests.

### Table 2: The global pollution situation of perchlorate.

| Area          | Sample concentration (µg/L) | Drinking water concentration (µg/L) |
|---------------|-----------------------------|-----------------------------------|
| EPA recommend | 4–420 (public water)        | 15                                |
| USA           | 340–3000 (river water)      | 10                                |
| Japan         | 60 (river water)            | 35                                |
| South Korea   | 1.0 (groundwater)           | 35                                |
| North Korea   | <1.0–6.1 µg/L (tap water)   | <1.0–6.1 µg/L                     |
| Germany       | 0.79–2.38 (groundwater)     |                                   |

### Table 1: Applications of perchlorate.

| Application field         | Raw material                                                                 |
|---------------------------|-------------------------------------------------------------------------------|
| Rocket solid fuel         | NH4ClO4, LiClO4, NO2ClO4, NOClO4, N2H2ClO4, (NH4)2N2H6(ClO4)4               |
| Fireworks manufacturing   | KClO4, HClO4, HClO4, HClO4, Mg(ClO4)2                                          |
| Electroplating            |                                                                               |
| Oxidant                   |                                                                               |
| Desiccant                 |                                                                               |
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| Fireworks manufacturing   | KClO4, HClO4, HClO4, HClO4, Mg(ClO4)2                                          |
| Electroplating            |                                                                               |
| Oxidant                   |                                                                               |
| Desiccant                 |                                                                               |
For some special samples, it is necessary to measure the $\delta^{18}O$ and $\delta^{37}Cl$ values of perchlorate simultaneously; therefore, O$_2$ must be used as the mass spectrometry gas. Perchlorate is vacuum cracked into O$_2$ at 600–650°C using the two-stage method outside the pyrolysis line of O$_2$-DI-IRMS; the reaction formula is CsClO$_4$ $\rightarrow$ CsCl + O$_2$. This cracking reaction can be carried out in a sealed quartz tube or Pyrex heat-resistant glass tube. Then, the produced O$_2$ enters the IRMS in a two-way mode after purification and is received by the Faraday cups with m/z of 32, 33, and 34 to simultaneously determine the $\delta^{18}O$ and $\delta^{17}O$ values [31, 32, 37]. For high-purity ClO$_4^-$ reagents and samples, the yield of O(O$_2$) is usually 100 ± 5%, and the test accuracy of $\Delta^{17}O$ is ±0.1‰.

3.2.2. Chlorine Isotopes. The perchlorate stable chlorine isotope composition ($\delta^{37}Cl$) was determined using the IRMS method, and the radioisotope content ({$^{36}Cl}$/Cl) was determined via the AMS method.

To determine the $\delta^{37}Cl$ value of perchlorate, first, the perchlorate was vacuum decomposed to produce chloride at 600–650°C. The chloride was dissolved in deionized water, and Cl was precipitated as AgCl by adding AgNO$_3$, which reacted with the excess CH$_3$I in a sealed glass tube at 300°C for 2 h to produce CH$_3$Cl. The CH$_3$Cl purified cryogenically by gas chromatography enters IRMS with continuous flow or dual-inlet mode and is measured at m/z of 50 and 52. The accuracy of the $\delta^{37}Cl$ analysis was ±0.2‰ [31, 32, 35, 37].

To determine the {$^{36}Cl}$/Cl content, the same steps as above are used to convert the perchlorate to AgCl precipitate; then, the AgCl precipitate is dissolved in a dilute ammonia (NH$_4$OH) solution. The AgCl precipitate is prepared again for the AMS measurement using Cl$^-$, which is purified via anion chromatography or cation exchange chromatography. Typically, seawater is used as a reference substance, and its $^{36}Cl$/Cl = 0.5 × 10 −15.

3.2.3. Collection and Preparation of ClO$_4^-$ Samples in Groundwater. The IRMS measurement usually requires a sample amount of at least 0.2 mg ClO$_4^-$; thus, an effective sample preparation method is needed to achieve the isotope test of trace environmental ClO$_4^-$.$^-$ The most successful and widely used collection and extraction method is based on a highly efficient ClO$_4^-$ selective bifunctional anion-exchange (Figure 1) resin [29, 31, 33, 34, 38]. The principle is that the resin is loaded with numerous exchangeable anions. ClO$_4^-$ replaces the anions on the resin and is adsorbed on the resin because of the difference in the concentration of the two ions in the (Figure 1) resin when water flows through the resin [39]. This anionic resin can efficiently and selectively adsorb ClO$_4^-$ and release ClO$_4^-$ under the elution of a mixed solution of 1 M FeCl$_3$ and 4 M HCl. The resin can be reused after activation [39]. The collection and preparation of ClO$_4^-$ samples in groundwater is generally divided into two steps: ClO$_4^-$ adsorption and elution. In the actual sampling process, the water sample usually passes through the filter device to remove interfering ions such as Cl$^-$, SO$_4^{2-}$, NO$_3^-$, and humus, to avoid affecting the adsorption effect of ClO$_4^-$.$^-$ The treated water then passes through the A530 E type at a flow rate of 17 BV/min resin column, comprising bifunctional anion-exchange resin (20–30 mesh). When the entire water sample passes through the resin column, most of the ClO$_4^-$ is adsorbed on the resin and needs to be eluted to prepare the sample. First, a 4–5 BV of 4 mol/L HCl solution or deionized water is passed through the resin column to wash off other adsorbed ions and unadsorbed ClO$_4^-$. Subsequently, a mixed solution of 1 mol/L FeCl$_3$ and 4 mol/L HCl is prepared; the solution is passed through the resin column at a flow rate of 0.06–0.13 cm/min. NaOH is added to the obtained eluent and centrifuged to obtain the supernatant. CsCl is added to the supernatant, heated, and evaporated to obtain CsClO$_4$ precipitation, which is prepared for mass spectrometry tests after purification [29, 40].

4. Isotope Tracing of Chlorine and Oxygen from Perchlorate

4.1. Isotopic Composition Characteristics of Perchlorate from Different Sources. Perchlorates from different sources have characteristic isotopic composition values related to their formation mechanism; perfecting and establishing an end-member model of their sources is a necessary basis for the application of isotope technology to trace the source. The existing natural origin and synthetic perchlorate isotope data show that the comprehensive characteristics of chlorine and oxygen isotopes of perchlorate are expected to provide direct evidence for identifying the source of perchlorate in groundwater.

4.1.1. Synthetic Perchlorate. Synthetic perchlorate is usually produced by the electrolytic oxidation of NaCl. The perchlorate production process largely depends on the content of the raw material Cl, while the electrolyzed water provides an O source for the synthesis of perchlorate. Since 2001, American scholars have analyzed the isotopic composition of various perchlorate reagents (used in laboratories, industry, and military) and products (used in road blasting, fireworks, pesticides, bleaching agents, and propellants). According to reported data [14, 31, 33, 34, 42], the synthetic perchlorate $\delta^{37}Cl$ value is −3.1% to +2.3‰; the $\delta^{18}O$ value is −24.8‰ to −12.5‰; the $\Delta^{17}O$ value is 0.0 ± 0.1‰; the ratio of $^{36}Cl$/Cl is ≤2.5 × 10 −15 − 40 × 10 −15; and the average value of $\delta^{37}Cl$ of synthetic perchlorate is about +0.6‰, which is similar to the $\delta^{37}Cl$ value of raw material, NaCl (0.0 ± 10−15) 0.9‰) [43]. A similar value indicates that there is almost no fractionation of chlorine isotopes during the process of synthesizing perchlorate by electrolytic oxidation. The $\delta^{18}O$ value has a larger range of variation, which may be related to the isotope composition of the water source used in the perchlorate production process and oxygen isotope fractionation [32]. Preliminary studies have shown that ClO$_4^-$ produced by the disproportionation reaction of commercial bleach (NaOCl) solution has an abnormally high $\delta^{37}Cl$ value (+14.0‰) [42]. Therefore, the isotopic composition of perchlorate is not only related to the isotopic composition of its raw materials but may also be affected by its production process.
4.1.2. Perchlorate of Natural Origin. It has been reported that perchlorate of natural origin is mainly distributed in the Atacama Desert in northern Chile and in the arid region of the southwestern United States. However, there are regions (such as the southern high plains and eastern New Mexico) where there is no clear historical or current evidence of the presence of rocket fuel or Chilean fertilizer sources. In these regions, perchlorate has been attributed to meteoric ClO$_4^-$ that accumulated in the unsaturated zone, with subsequent flushing to groundwater by the advent of the irrigation [44, 45]. They have distinctly different isotopic compositions from synthetic perchlorates, and the isotopic compositions in the two regions have their own characteristics.

The Chilean saltpeter in the Atacama Desert is the most typical naturally occurring mineral that is rich in ClO$_4^-$. However, owing to the differences in sampling locations and detection methods, the mass content of ClO$_4^-$ reported in the literature is not the same, ranging from 0.03% to 3.6% [46–48]. Chilean saltpeter is an important raw material for fertilizers, and the total amount of Chilean saltpeter (imported by the United States and widely used in agriculture decades ago) has reached millions of tons [49]. It was an important potential source of ClO$_4^-$ in groundwater (but now with the development of processing the percentage of perchlorate in Chilean fertilizers has been reduced). Bao and Gu first reported the oxygen isotopic composition of ClO$_4^-$ in Chilean saltpeter; that is, the $\delta^{18}O$ value ranged from $-24.8\%$ to $-4.5\%$, and the $\Delta^{17}O$ value ranged from $+4.2\%$ to $+9.6\%$ [47]. Furthermore, some scholars have successively expanded their oxygen isotope data [31, 32, 34], where the $\delta^{18}O$ value ranged from $-9.3\%$ to $-2.2\%$, and the $\Delta^{17}O$ value ranged $+7.9\%$ to $+18.4\%$. The large positive $^{17}O$ anomaly of ClO$_4^-$ in Chilean saltpeter may be the result of the photochemical interaction of atmospheric Cl and O$_3$, indicating that ClO$_4^-$ in natural minerals originated from the atmosphere, and was deposited and preserved in an arid climate with strong evaporation. The $\delta^{37}Cl$ value of ClO$_4^-$ in Chilean saltpeter ranges from $-14.5\%$ to $-11.8\%$ [31, 32, 34], and the ratio of $^{36}Cl/Cl$ is $22 \times 10^{-15} - 590 \times 10^{-15}$ [42].

Figure 1: Sample collection device [41] (the left picture is the device used in the lab by authors).
Natural perchlorate is widely distributed throughout the arid and semiarid regions of the world, such as the southwestern United States, the southern high plains of United States, and Chile [48, 50]. Perchlorate is widely distributed on the earth, but the deep research has regional limitations. The scientists have collected samples for stable isotope analysis in the earth, but the deep research has regional limitations. The arid and semiarid regions of the world, such as the southwestern United States, Long Island in New York, and San Bernardino Basin in California are three typical ClO4−-contaminated aquifers. The isotopic composition of ClO4− (δ37Cl, δ18O, and Δ17O) in groundwater in the three regions was plotted on the end-member model diagram of the isotopic composition of ClO4− from different sources (as shown in Figure 4). The comprehensive characteristics of Cl and poly-oxygen

4.1.3. Comparison of Isotopic Composition of Perchlorate from Different Sources. Based on the known isotope data of perchlorate, the relation chart of δ37Cl versus δ18O, Δ17O, and δ37Cl/δ18O in the sodium nitrate deposit in ore deposits ranges from +2.9‰ to +26.1‰, respectively; meanwhile, the DV area is an unsaturated zone. The δ18O, Δ17O, and δ37Cl values of ClO4− in the sodium nitrate deposit in ore deposits ranges from +2.9‰ to +26.1‰, +8.6‰ to +18.4‰, and -3.1‰ to -0.8‰, respectively. The 36Cl/Cl ratio of ClO4− in arid southwestern United States is 3,130 × 10−15 – 28,800 × 10−15 [42].

4.2. Fractionation Characteristics of Isotopes during the Biodegradation of Perchlorate. The biodegradation of ClO4− is a multi-stage reaction catalyzed by reductase [52, 53], which can be divided into three steps: ClO4− → ClO3− → ClO2− → Cl + O2. The biodegradation of ClO4− is often accompanied by the fractionation of stable chlorine and oxygen isotopes. Previous laboratory and field studies have conducted experiments for preliminary research on the degree and characteristics of fractionation. Coleman et al. [54] and Sturchio et al. [30] used Azospira suillum bacteria to conduct liquid culture medium experiments, to determine the dynamic fractionation effect of Cl isotopes, wherein acetate was the electron donor and ClO4− was the only electron acceptor. By conducting two separate culture fluid experiments (ClO4− complete degradation time is about 90 min), Coleman et al. obtained δ37Cl values of -15.8 ± 0.4‰ and -14.8 ± 1.3‰ at 37°C. By performing the culture solution experiment, which has different degradation rates (ClO4− complete degradation time is 18 days and 5.5 h). Sturchio et al. obtained δ37Cl values at 22°C of -16.6‰ and -12.9‰, respectively. Ader et al. [55] obtained a more accurate δ37Cl value (-14.98 ± 0.15‰) based on the statistical analysis of experimental data (reported by Coleman et al.). Additionally, Sturchio et al. [53] performed further experiments using two different strains (A. suillum JPLRND and Dechlorospirillum sp. FBR2) to degrade ClO4− in liquid culture at 22°C and 10°C, respectively, and simultaneously determined the fractionation effect of Cl and O. The values of δ37Cl and δ18O were -13.2 ± 0.5‰ and -33.1 ± 1.2‰, respectively, and the value of e18O/e37Cl of the remaining proportion of ClO4− is always constant (2.50 ± 0.04). Sturchio et al. also used 18O-rich heavy oxygen water to test whether oxygen isotope exchange occurred between ClO4− and H2O during the biodegradation process. The experimental results did not show the occurrence of an oxygen isotope exchange reaction [53]. This indicated that biodegradation did not change the Δ17O value of ClO4−. The push-pull field experiment of in situ aquifers conducted by Hatzinger et al. [36] showed that the δ37Cl and δ18O values are only 0.3–0.4 times that of the indoor experiment, whereas the e18O/e37Cl ratio (2.63) is consistent with the measured value of the indoor experiment. Therefore, the consistency of the e18O/e37Cl ratio between the indoor and in situ experiments in the field provides a possibility for stable chlorine and oxygen isotopes being able to indicate the biodegradation of perchlorate without concealing its source information. In Figure 3, the set of parallel dashed lines with arrows indicates the changing trend of the δ37Cl and Δ17O values of ClO4− during the biodegradation of ClO4−. The concentration of ClO4− (remaining fraction F) can be used to inversely calculate the isotope composition before biodegradation.

4.3. Application Examples of Isotope Tracer of ClO4− in Groundwater. Investigating and determining the isotopic composition of different sources of ClO4− provide necessary data support for establishing the end-member model of the isotope characteristic value of different sources of ClO4−. The isotope kinetic fractionation characteristics of ClO4− biodegradation provide a theoretical basis for tracing the source of ClO4− in environmental media. The Chino Basin in California, Long Island in New York, and San Bernardino Basin in California are three typical ClO4−-contaminated aquifers. The isotopic composition of ClO4− (δ37Cl, δ18O, and Δ17O) in groundwater in the three regions was plotted on the end-member model diagram of the isotopic composition of ClO4− from different sources (as shown in Figure 4). The comprehensive characteristics of Cl and poly-oxygen
Figure 2: $\delta^{37}\text{Cl} \,(‰) \text{ versus } \delta^{18}\text{O} \,(‰)$ values (upper diagram) and $\Delta^{17}\text{O} \,(‰)$ versus $\delta^{18}\text{O} \,(‰)$ values (middle diagram) for samples of synthetic $\text{ClO}_4^-$, Atacama $\text{ClO}_4^-$, and southwest $\text{ClO}_4^-$. Southwest $\text{ClO}_4^-$ is subdivided into southern SHP and DV [31, 32, 34]. $^{36}\text{Cl}/\text{Cl}$ versus $\delta^{37}\text{Cl} \,(‰)$ values (bottom diagram) for samples of synthetic $\text{ClO}_4^-$, Atacama $\text{ClO}_4^-$, and Southwest $\text{ClO}_4^-$. The colored points represent the isotope value of some analytical reagents and firework samples measured by the authors (purple points: $\text{KClO}_4$, $\text{CsClO}_4$, $\text{NaClO}_4$, $\text{RbClO}_4$, and $\text{Mg(ClO}_4\text{)}_2$ and blue points: firework samples).

Figure 3: Schematic relation between characteristic $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ values (per mil) of synthetic and natural perchlorate samples during biodegradation processes [53].
isotopes in the groundwater of the three regions indicated that the main source of ClO\textsuperscript{4}\textsuperscript{-} in the groundwater of the Chino Basin in California was Chilean saltpeter from the Atacama Desert, which is used as agricultural fertilizer [56]. The source of ClO\textsuperscript{4}\textsuperscript{-} in the groundwater of Long Island in New York was Chilean saltpeter from the Atacama Desert and synthetic ClO\textsuperscript{4}\textsuperscript{-} [57]. The source of ClO\textsuperscript{4}\textsuperscript{-} in the groundwater in the San Bernardino Basin of California is Chilean saltpeter from the Atacama Desert and synthetic ClO\textsuperscript{4}\textsuperscript{-} from the rocket test site; some areas are a mix of the two pollution plumes [58].

5. Conclusion and Outlook

Perchlorates from different sources have different isotopic characteristic values (\(\delta^{18}O\), \(\Delta^{17}O\), \(\delta^{37}Cl\), and \(^{36}Cl/Cl\)) and are related to their formation mechanisms. The \(^{17}O\) abnormal signal can be preserved for thousands or even millions of years in arid environments. Even if the biodegradation of perchlorate occurs under some specific conditions, along with the kinetic fractionation of chlorine and oxygen isotopes, its \(\Delta^{17}O\) value or \(^{36}Cl/Cl\) ratio will not change. Moreover, \(\epsilon^{18}O/\epsilon^{37}Cl\) (the fractionation coefficient of oxygen and chlorine isotopes) is constant, potentially revealing the biodegradation of perchlorate without disguising its source information. Therefore, the comprehensive characteristics of stable chlorine and poly-oxygen isotopes are expected to provide direct evidence for identifying the source of perchlorate in groundwater. However, further studies are needed to qualitatively identify and quantitatively evaluate perchlorate pollution sources.

1. The key problem in applying multi-isotope technology to identify the source of perchlorate in groundwater is to effectively distinguish the characteristic values of the end-member isotopes of different sources of perchlorate. Current research achievements are mainly limited to the United States and Chile and have apparent geographic limitations. The effective analysis of the source of perchlorate in polluted aquifers in different regions needs to be enriched by the isotope characteristic values and end-member model.

2. Nonmass fractionation of oxygen isotopes (\(\Delta^{17}O > 0\)) is a unique feature of natural perchlorate, which can effectively distinguish between natural sources of perchlorate and synthetic pollution sources. The isotopic composition characteristics of natural perchlorate show apparent differences in different regions and environments. To characterize its isotopic composition characteristics on a global scale and reveal the formation mechanism, it is necessary to analyze and study more representative samples from different regions.

3. Perchlorate pollution in groundwater is mostly caused by natural sources, and some are caused by human activities [59]. Natural and synthetic perchlorates have significantly different isotope characteristic values. Natural perchlorate isotope characteristic values have apparent geographic limitations (limited to the United States and Chile), so the more important research is to supplement the isotope signatures from other regions. At this stage, there is still considerable uncertainty in the distinction between synthetic perchlorate pollution sources. The perchlorate products produced by the same production process have similar chlorine isotope compositions; however, oxygen isotope compositions are quite different, which may be related to the water source used in the production process. Research on the isotope composition of synthetic perchlorate, its production process, and other influencing factors can provide a theoretical basis for effectively distinguishing the synthetic pollution sources of perchlorate.

Data Availability

The data used to support this study are from previous studies and experiments.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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