

Review

Review on Zinc Isotopes in River Systems: Distribution and Application

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Abstract: Zinc (Zn) is an essential trace element widely present in rivers and plays a crucial role in ecosystems. Human activities have led to the extensive migration and dissemination of Zn in the environment. When the accumulation of Zn in rivers reaches excessive levels, it transforms into a potentially harmful contaminant. Consequently, tracing Zn's origin by its isotope ratios ($\delta^{66}\text{Zn}$) from natural and anthropogenic sources is essential for the management of and safeguarding against river pollution and comprehending Zn behavior in rivers as well. This review presents the advancements in Zn isotope research in river environments, including a summary of Zn isotope measurement, the distribution and controlling factors (mineral adsorption, precipitation, and biological effects) of Zn isotopes, and the applications of Zn isotopes in rivers. The median $\delta^{66}\text{Zn}$ values for uncontaminated river water and suspended particulate matter (SPM) were 0.37‰ and 0.22‰, respectively, close to the bulk silicate Earth (BSE) value of $0.28 \pm 0.05\text{‰}$. With respect to the contaminated river, $\delta^{66}\text{Zn}$ falls within -0.73‰ to 1.77‰ , with it being heavily influenced by anthropogenic sources, such as the electroplating and metal processing industries. Apart from contamination identification, this review summarizes the river material exchange process and the $\delta^{66}\text{Zn}$ values of rainwater (-0.2‰ ~ 0.38‰), groundwater (-0.13‰ ~ 1.4‰), lake water (-0.66‰ ~ 0.21‰), and seawater (-1.1‰ ~ 0.9‰), which facilitates a holistic understanding of the Zn cycle and isotope fractionation in the river system. In conclusion, Zn isotopes are an effective tool for tracing pollution sources and Zn migration processes, with enormous unexplored potential. Therefore, this review finally summarizes some challenges and future directions in current research on Zn isotopes.



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1. Introduction

Amid rapid economic expansion and population upsurge, significant industrial and agricultural activities have culminated in the emission of heavy metals into the environment [1]. Under favorable meteorological conditions, precipitation commonly washes away deposits and particles laden with heavy metals, forming runoff into rivers [2,3]. River systems play a pivotal role in sustaining human life and diverse ecosystems. Currently, river water quality is profoundly threatened by the escalating industrialization and urbanization of global river basins [2]. Hence, the environmental issues related to rivers have received augmented consideration since the beginning of the 21st century. Zn is one of the most common heavy metals in the environment; it can be present as a solute, as SPM, and as sediments in rivers [4,5]. Ecosystems and the environments related to human health are susceptible to potential harm due to the ongoing accumulation of Zn in the surroundings. Nevertheless, a diverse range of human activities has contributed to the buildup of Zn in river systems. For example, the discharge of industrial and household waste into rivers is a significant factor [2,6]. Prolonged mining and metallurgical operations

have generated significant amounts of heavy metal-enriched waste and byproducts, which eventually transfer into river water and cause pollution of the water [7–9]. The excessive accumulation of Zn can negatively impact both the function and structure of plants. Furthermore, Zn is crucial for human health as it is involved in a multitude of physiological processes, including immune function, DNA synthesis, and cell growth [2]. Especially in young children, Zn deficiency results in stunted growth and increased vulnerability to diseases such as diarrhea, pneumonia, and malaria, leading to an estimated 800,000 premature deaths annually [10]. Therefore, controlling Zn concentrations in surface water has become an urgent priority for environmental and public health considerations.

Zn has five stable isotopes in nature, including ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , and ^{70}Zn , with natural abundances of 49.2%, 27.8%, 4.0%, 18.4%, and 0.6%, respectively [11]. Currently, $\delta^{66}\text{Zn}$ is commonly used as the target in research because ^{64}Zn and ^{66}Zn have a relatively high abundance, resulting in more accurate measurements, typically close to 0.10‰ [3]. The study of Zn isotopes can be traced back to 1957; Blix et al. [12] used thermal ionization mass spectrometry (TIMS) to determine the $\delta^{66}\text{Zn}$ in 18 samples. However, due to the limitations of the instrumental analysis precision (approximately 0.1‰), no Zn isotopic fractionation was observed [12]. Thus, the issue of testing precision severely constrained the application of Zn isotopes. With the development of novel instruments and analytical techniques over the past few decades, more precise isotope measurements using TIMS have become possible (generally better than 0.001‰) [13]. Nonetheless, a key potential advantage of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) when compared with TIMS is that mass discrimination is potentially more easily dealt with [14]. Maréchal et al. [15] first utilized MC-ICP-MS to analyze the $\delta^{66}\text{Zn}$ of samples such as those of silicate rocks, Cu and Zn ores, and sediments. The analytical precision achieved was better than 0.05‰, satisfying the testing accuracy requirements for most samples [15]. The high-precision measurements provided by MC-ICP-MS has laid the foundation for the application of Zn isotopes in research fields such as biogeochemistry [16–18], astrochemistry [19,20], ore deposit geochemistry [21], life sciences [22,23], and environmental geochemistry [4,24].

This review aims to provide an overview of the recent research on Zn isotopes in river environments, offering insights into a relatively novel isotope system in geochemistry. The review first summarizes the latest sample preparation procedures and mass spectrometry techniques, necessary for the achievement of the precision and accuracy required to detect the subtle variations in Zn isotopic ratios in natural systems. Subsequently, it delves into the impact of mineral adsorption, precipitation, and biological effects on Zn isotopic fractionation in rivers. The focus is on the application of Zn isotopes in identifying pollution sources in rivers. Zn isotope tracing techniques can effectively pinpoint the origins and transformation processes of pollutants in the environment, quantifying the relative contributions of various pollution sources. Through a comprehensive understanding of the research on Zn isotopes in river systems, this review aspires to provide vital scientific support for the improved protection of water resources and the preservation of ecosystem health. The research in this field is expected to aid in the endeavor to more effectively manage and mitigate the adverse effects of Zn pollution on river environments.

2. Zn Isotope Measuring

2.1. Sample Pretreatment

Interference from metallic impurities in the environment must be minimized during sample pretreatment [25]. Specifically, pretreatment of samples of Zn should be conducted in a Class 1000 (ISO Class 6) clean laboratory equipped with a Class 100 (ISO Class 5) laminar flow exhaust hood [26], and the laboratory should maintain a positive pressure to prevent the entry of unpurified air from the external environment. The concentrated HNO_3 and HF used should be obtained through sub-boiling distillation or double distillation [27,28]. The instruments used (such as PFA digestion vessels, pipette tips, tubes, and chromatography columns) should undergo rigorous acid washing and rinsing with

ultrapure water. Sample digestion includes both solid samples and liquid samples. Different samples require distinct digestion methods (Table 1) [29,30]. For common solid samples, it is usually necessary to add concentrated HNO_3 to oxidize the metal ions and some of the organic matter. If the sample has a high content of SiO_2 and organic matter, HF and HClO_4 can be added separately [24,27]. Water samples should be filtered prior to processing to remove insoluble impurities, such as suspended solids, and then concentrated before analysis. Methods of concentrating and purifying Zn include distillation, solvent extraction, co-precipitation, and ion exchange chromatography [31,32]. The distillation methods require a long time and may cause high blank values. The solvent extraction method is simple and easy to operate, but the addition of hydrophilic chelating agents may interfere with the testing of ^{64}Zn . The co-precipitation method involves the addition of ammonia into the sample, resulting in the formation of magnesium hydroxide precipitate; then, ion exchange chromatography is employed to effectively separate the Zn [33]. However, the incomplete removal of $^{24}\text{Mg}^{40}\text{Ar}$ cluster ions may interfere with the determination of ^{64}Zn . Ion exchange chromatography is used to enrich Zn in a large number of water samples using anionic exchange resin, followed by elution with concentrated acid. Various digestion methods can be employed to attain thorough digestion, depending upon the specific environmental samples and the Zn content.

Table 1. Digestion methods for different samples.

Sample Types	Digestion Methods	References
Straw, grain, and paddy soil	15 N HNO_3 , 30% H_2O_2 , 28 N HF , and 0.1 N HCl	[29]
Mun River Basin soil	3:1 Concentrated HNO_3 and concentrated HF and 3:1 concentrated HNO_3 and HCl	[27]
Aquatic plants, mussels, sludge, etc.	Concentrated HNO_3 , HF , and HClO_4 (4:5:1)	[30]
Silicate rocks	6:2:1 Concentrated HF : HNO_3 : HClO_4	[15]
Sedimentary rocks	16 N HNO_3 and concentrated HF and 12N HCl	[15]
Diatom cells	5% HNO_3 and 5% H_2O_2	[34]
Seine River SPM and sediment	16 N HNO_3 and 27 N HF	[5]
River water	Filtering, steamed dry, concentrated HNO_3	[24,35,36]

2.2. Chemical Separation and Purification

To avoid interference from matrix ions (Cu, Fe, and Ni) in the isotope analysis of Zn, the purification and separation of the Zn elements in all of the samples must be conducted before testing [37]. Currently, the most common method for purification is ion exchange chromatography. The principle of element separation and purification is based on the ion exchange reactions between the sample and the resin. The resin adsorbs the ions present in the sample, and the subsequent elution is performed using eluents that exploit variations in the binding capacities between the resin and the different ions. This sequential elution process enables the separation of distinct elements [27,38,39]. Typically, achieving a recovery rate of approximately 100% for Zn is crucial to determine the completion of the purification process [27,38,40]. Maréchal et al. [15] first achieved the purification and separation of Fe-Cu-Zn in solid samples using anion exchange resin (AG MP-1). Chen et al. [41] developed a dual resin column method for concentrating and purifying Zn, where cation exchange resin Chelex-100 was used for the Zn concentration in water samples, followed by anion exchange resin AG-1 X4 for Zn separation and purification. Among them, AG MP-1 is widely used due to its satisfactory recovery rate [15,38].

2.3. Mass Spectrometry

$\delta^{66}\text{Zn}$ is usually expressed as a deviation δ in parts per thousand (‰) of the sample isotopic ratio (e.g., $^{66}\text{Zn}/^{64}\text{Zn}$) relative to the isotopic ratio of the standard (Equation (1)):

$$\delta^{66}\text{Zn} = \left(\frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{standard}}} - 1 \right) \times 10^3 \quad (1)$$

where $(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}$ and $(^{66}\text{Zn}/^{64}\text{Zn})_{\text{standard}}$ represent the isotopic ratios of ^{66}Zn to ^{64}Zn in the sample and standard, respectively. The JMC 3-0749L standard developed by the University of Lyon, France, and the IRMM-3702 standard of the European Reference Materials Research Institute are commonly used to determine the $\delta^{66}\text{Zn}$ values. Other standards used include SRM NIST 683, IMC 12053, PCIGR-1, and Imperial [15,42,43]. In this study, JMC 3-0749L was used as the standard.

Obvious mass discrimination effects may occur in the measurement of $\delta^{66}\text{Zn}$ by MC-ICP-MS by both the external sample introduction system and the ionization and ion transmission processes within the plasma and mass spectrometer [5,37,44]. The most commonly used techniques to correct this mass bias are the standard-sample bracketing (SSB), the elemental external standard (EES), and the double spike (DS) methods. The SSB method assumes that the mass bias of a sample can be rectified by referencing the mass bias of the standards measured both before and following the sample analysis. This method assumes that there is an instrument to maintain a consistent operational state, and it demands alignment between the sample's matrix and that of the standard. The major advantage of the SSB method is the ease of operation, but it is time-consuming and requires high instrument stability [38,45,46]. In EES-based analysis, the mass bias can be rectified by utilizing the measured isotopic ratios of a separate element that is measured concurrently with the element under investigation. The chosen element is assumed to behave similarly to the element of interest in terms of mass bias; therefore, it usually has a similar mass number to the element of interest [15,47]. In the DS method, the procedure entails combining the sample with a DS solution that includes two artificially enriched isotope spikes. This is particularly relevant when the element of interest comprises three or more isotopes and the ratios of these spikes are known or precisely determined [48]. This approach proves particularly effective for samples characterized by intricate matrices or low concentrations of the target element. The DS method offers two notable advantages: firstly, it enables the correction of both instrumental mass bias and isotopic fractionations during chemical purification, even if this necessitates trading off some recovery for improved purification; secondly, it eliminates the necessity to achieve matrix parity between standards and samples. Nonetheless, there are some disadvantages, like the high cost of the DS method and the need for additional calibration [16,32].

3. Distribution of Zn Isotopes and the Controlling Factors

3.1. Zn Isotope Compositions in Water Systems

Zn is one of the major elements in natural aquatic systems, and its migration and transformation play a crucial role in the global Zn cycle. Currently, research on the Zn isotope compositions in natural aquatic systems mainly focuses on seawater and river water, with little research on rainwater and groundwater. Nevertheless, we can still outline the profile of the Zn isotope compositions in natural aquatic systems (Figure 1). It mainly includes the following parts:

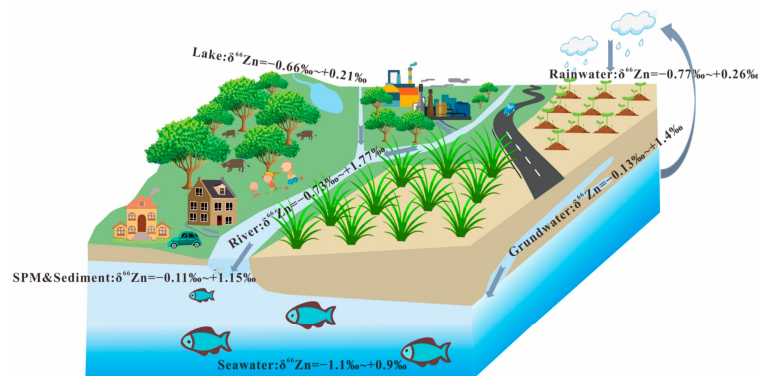


Figure 1. Isotope composition of Zn in surface water and the Zn circulation system [3,5,24,28,31,35,36,38,49–53].

3.1.1. Rivers

The dissolved $\delta^{66}\text{Zn}$ in rivers ranges from -0.73‰ to 1.77‰ , with an average value of 0.24‰ [5,24,35,36]. In rivers predominantly unaltered by human influence, soluble Zn concentrations typically range from 1 to $2\text{ }\mu\text{g}\cdot\text{L}^{-1}$ [2]. The variation in the $\delta^{66}\text{Zn}$ in solution in rivers with little human impact ($[\text{Zn}]_{\text{dissolved}} \leq 2\text{ }\mu\text{g}\cdot\text{L}^{-1}$) was relatively minor, with values between 0.23 and 0.55‰ ($n = 41$, IQR) and a median value of $+0.37\text{‰}$, which is close to the BSE value ($+0.28 \pm 0.05\text{‰}$, 2σ) (Figure 2) [2,4,50,54]. This review primarily compiles the Zn isotope compositions of river waters from relatively significant basins, including the Seine River in France ($\delta^{66}\text{Zn} = 0.07\text{‰}\sim 0.58\text{‰}$) [4], the Erren River in Taiwan ($\delta^{66}\text{Zn} = -0.73\text{‰}\sim 1.77\text{‰}$) [35], the Rio Grande River ($\delta^{66}\text{Zn} = -0.57\text{‰}\sim 0.41\text{‰}$) [36], the Calisto River ($\delta^{66}\text{Zn} = 0.37\text{‰}\sim 0.88\text{‰}$) [50], the Nile River ($\delta^{66}\text{Zn} = 0.04\text{‰}\sim 0.31\text{‰}$) [50], the Yangtze River ($\delta^{66}\text{Zn} = 0.37\text{‰}\sim 0.83\text{‰}$) [50], the Amazon River ($\delta^{66}\text{Zn} = 0.12\text{‰}\sim 0.61\text{‰}$) [50], the Tocantins River ($\delta^{66}\text{Zn} = -0.12\text{‰}\sim 0.18\text{‰}$) [50], and the Central European Elbe River ($\delta^{66}\text{Zn} = -0.21\text{‰}\sim 0.75\text{‰}$) (Figure 2) [24].

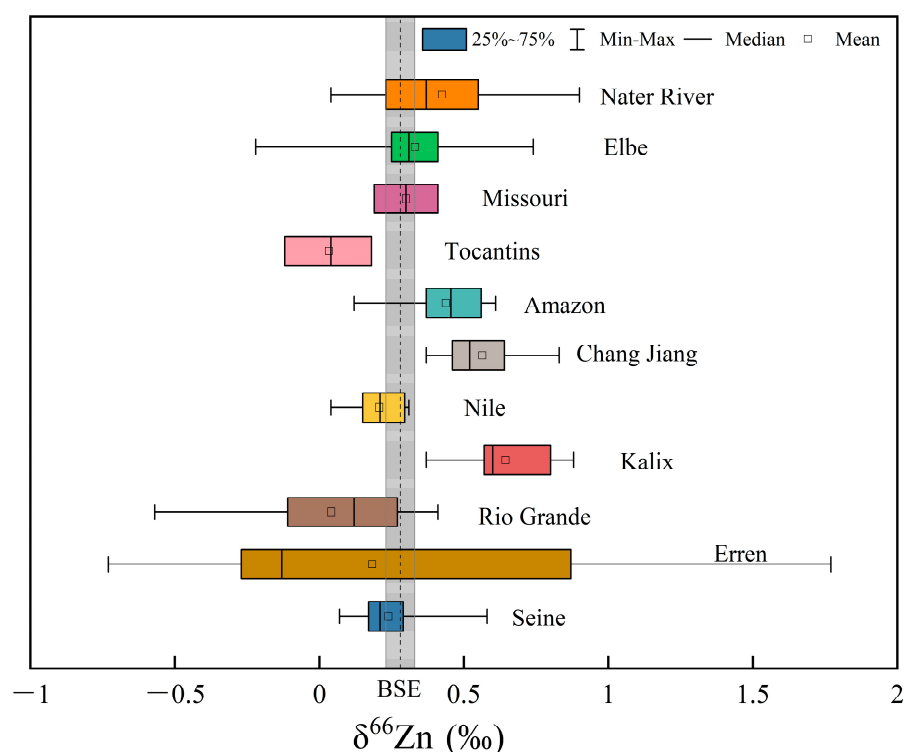


Figure 2. Composition of Zn isotopes in rivers [4,24,35,36,50].

The SPM and sediment in rivers are crucial indicators for studying river systems. However, there is relatively limited research using $\delta^{66}\text{Zn}$ for SPM and sediments in rivers. The majority of the sediments and SPM collected from the rivers with little human influence ($[\text{Zn}]_{\text{particulate}} \leq 200\text{ mg}\cdot\text{kg}^{-1}$) exhibit a range of $\delta^{66}\text{Zn}$ from $+0.2$ to $+0.35\text{‰}$ ($n = 28$, IQR). The median value of $+0.22\text{‰}$ closely approximates the BSE value ($+0.28 \pm 0.05\text{‰}$, 2σ) (Figure 3) [2,5,6,54]. The earliest studies at the Scheldt River estuary revealed that the $\delta^{66}\text{Zn}$ values of the SPM samples ranged from 0.21‰ to 1.13‰ (Figure 3) [55]. In the Seine River Basin, the $\delta^{66}\text{Zn}$ values of the SPM in the rivers ranged from 0.08‰ to 0.27‰ , while the $\delta^{66}\text{Zn}$ values of the sediment samples ranged from 0.18‰ to 0.30‰ (Figure 3) [24]. At the mouth of the Sepetiba Bay River, the $\delta^{66}\text{Zn}$ values of the sediment samples ranged from 0.30‰ to 1.15‰ , while the $\delta^{66}\text{Zn}$ values of the SPM in the river ranged from 0.83‰ to 0.88‰ (Figure 3) [6]. The SPM in the Zhujiang River Basin exhibited $\delta^{66}\text{Zn}$ values ranging from -0.11‰ to 0.41‰ (Figure 3) [38]. Additionally, the $\delta^{66}\text{Zn}$ values of the SPM and surface sediments in the South Paraíba River and Guandu River ranged from 0.12‰ to 0.34‰ (Figure 3) [28].

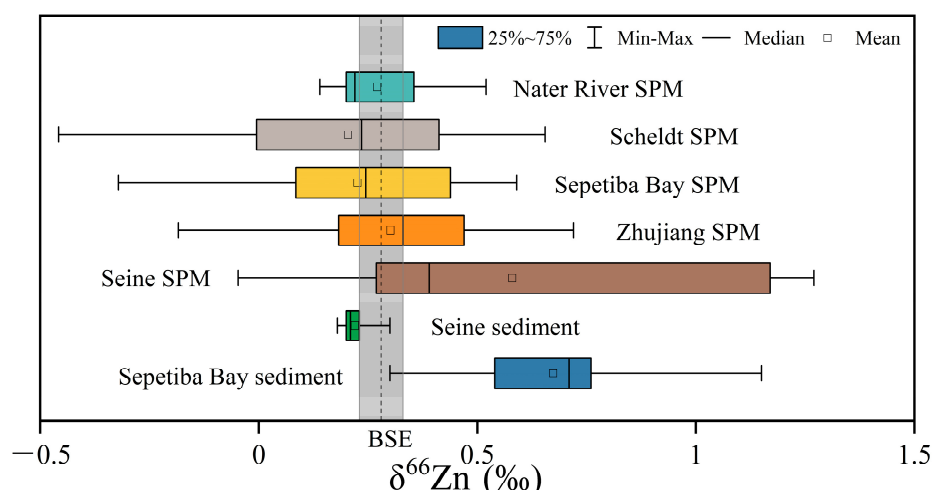


Figure 3. Composition of Zn isotopes in the river SPM and sediment [5,6,24,28,38,55].

3.1.2. Seawater

Seawater serves as the ultimate convergence point for rivers. In the North Atlantic Ocean, the $\delta^{66}\text{Zn}$ values ranged from -1.1‰ to 0.9‰ , with the greatest variations occurring in surface waters between 0 and 100 m (Figure 4) [31]. In waters between 100 and 1000 m, the $\delta^{66}\text{Zn}$ values ranged from -0.6‰ to 0.6‰ , while below 1000 m, the $\delta^{66}\text{Zn}$ values became relatively uniform, averaging at $0.45\text{‰} \pm 0.24\text{‰}$. Overall, as one moves deeper into the ocean, $\delta^{66}\text{Zn}$ tends to increase [49]. In the northeast Pacific, the $\delta^{66}\text{Zn}$ values were reported as $-0.15 \pm 0.06\text{‰}$ at 25 m and $-0.05 \pm 0.09\text{‰}$ at 100 m. Below 500 m, the $\delta^{66}\text{Zn}$ values ranged from 0.45‰ to 0.56‰ (Figure 4), showing a similar increasing trend to that of the North Atlantic Ocean (Figure 4) [56]. A study of Zn isotopes in the Southern Ocean indicated that the $\delta^{66}\text{Zn}$ values ranged from 0.07‰ to 0.80‰ above a depth of 50 m. The primary cause of the variation was the organic complexation of Zn by diatoms, followed by the uptake of Zn by phytoplankton cells. By combining the data from different regions, it was found that the $\delta^{66}\text{Zn}$ values below 1000 m were similar in the Southern Ocean, North Pacific, and North Atlantic, with an average value of $0.53 \pm 0.14\text{‰}$ (Figure 4) [31].

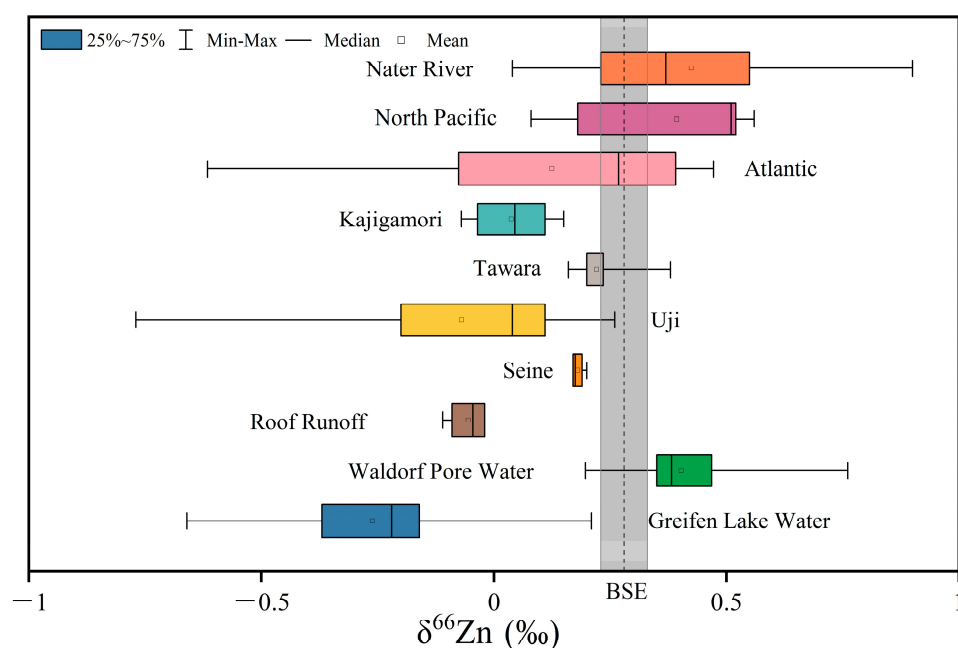


Figure 4. Composition of Zn isotopes in seawater, rainwater, porewater, and groundwater [5,31,36,49,51–53,56,57].

3.1.3. Rainwater, Pore Water, and Groundwater

In addition to seawater and river water, the influences of rainwater, lakes, pore water, and groundwater are also considered when studying the $\delta^{66}\text{Zn}$ in rivers [36,53,57]. For instance, in the downstream groundwater of the Riou Mort-Lot River, the $\delta^{66}\text{Zn}$ values ranged from 1.18‰ to 1.4‰ (Figure 4) [57]. Similarly, in the Rio Grande Basin in the United States, groundwater samples affected by mineralization processes exhibited $\delta^{66}\text{Zn}$ values ranging from −0.13‰ to 0.12‰ (Figure 4) [36]. Furthermore, in the Ward Fork Mining District of the Colorado Rocky Mountains, the surface water in the area had $\delta^{66}\text{Zn}$ values ranging from 0.14‰ to 0.37‰, while the pore water at the bottom of waste rock piles had $\delta^{66}\text{Zn}$ values of 0.19‰ to 0.27‰. The study revealed that the pore water and surface water were likely influenced by tailings, with $\delta^{66}\text{Zn}$ ranging from 0.18‰ to 1.49‰ (Figure 4) [53]. Chen et al. [5], in a study on the sources of Zn isotopes in the Seine River, found that rainwater samples from Paris exhibited $\delta^{66}\text{Zn}$ ranges from 0.18‰ to 0.20‰ (Figure 4). Rainwater in the rural areas of southern France showed $\delta^{66}\text{Zn}$ values of 0‰ to 0.15‰, while the urban areas had $\delta^{66}\text{Zn}$ values of −0.2‰ to −0.1‰ [3]. Research conducted by Kyoto University in Japan on rainwater from rooftops and Kakeyama in Uji City revealed $\delta^{66}\text{Zn}$ values ranging from 0.16‰ to 0.38‰ (Figure 4) [51]. Peel et al. [52] investigated the $\delta^{66}\text{Zn}$ of Lake Greifen in Switzerland, where the $\delta^{66}\text{Zn}$ values ranged from −0.66‰ to 0.21‰ (Figure 4). Samples collected in the summer exhibited lower $\delta^{66}\text{Zn}$ values (−0.66‰~−0.44‰), while those collected in May and October were relatively enriched in heavier Zn isotopes. This seasonal variation suggests a correlation with the seasonal uptake by biota [52].

3.2. Factors Controlling Zn Isotopes' Fractionation

Zn isotopic fractionation processes and mechanisms are crucial for exploring the global cycle of Zn. In recent years, some scholars have conducted experimental studies on Zn isotopic fractionation in different processes and have gained a basic understanding of the factors affecting Zn isotopic fractionation. Stable isotopic fractionation describes the difference in the distribution of isotopes between two different phases (*a* and *b*); it is expressed as [10,27]:

$$\Delta^{66}\text{Zn}_{a-b} = \delta^{66}\text{Zn}_a - \delta^{66}\text{Zn}_b \quad (2)$$

The fractionation of Zn isotopes in rivers is a complex process controlled by multiple factors. Research efforts need to comprehensively consider these factors to gain a more comprehensive understanding of the dynamic processes of Zn isotopes in rivers. Building on previous advancements in this field, this review introduces the impacts of mineral adsorption, precipitation, and biological processes on Zn isotopic fractionation.

3.2.1. Mineral Adsorption

The adsorption of minerals in environmental processes mainly affects Zn isotopes. The degree of Zn isotopic fractionation during the adsorption processes on the surfaces of certain minerals ranges from −0.28‰ to 2.74‰ (Figure 5) [58–60]. Previous studies have demonstrated that metal ions in aqueous solutions can be adsorbed onto mineral surfaces through various mechanisms, forming complex adsorption on the mineral lattice [59,61,62]. These adsorption mechanisms depend on the properties of the ligands and the solution conditions; ligand properties are primarily determined by coordination number and bond energy, while solution conditions include ionic strength (IS) and pH.

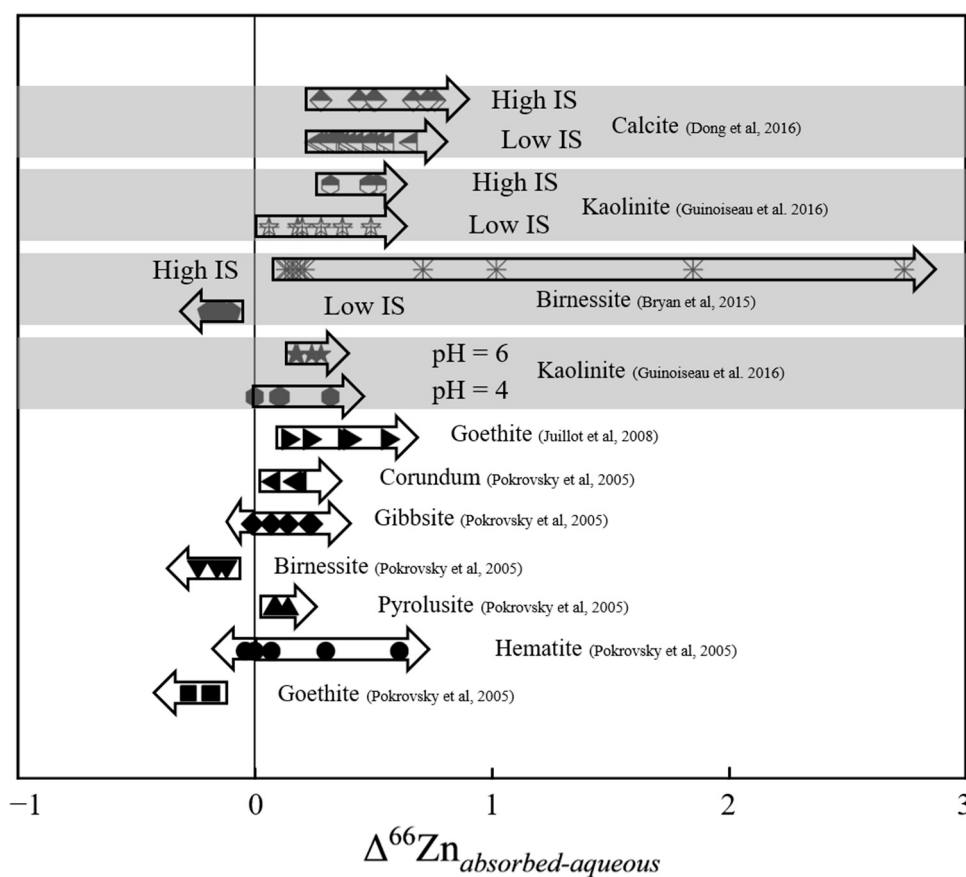


Figure 5. The principal processes inducing Zn isotopic fractionation in minerals. The length of the arrows indicates the range of observed $\Delta^{66}\text{Zn}$ values, serving as an approximate indication of the extent of Zn isotopic fractionation [58,63–66].

Pokrovsky et al. [63] investigated the fractionation of Zn isotopes during mineral adsorption processes. Their findings indicated that goethite and birnessite surfaces tend to enrich lighter Zn isotopes, while pyrolusite, corundum, hematite, and gibbsite surfaces tend to enrich heavier Zn isotopes (Figure 5), and the fractionation values influenced by the adsorption on most mineral surfaces were less than 0.2‰ [63]. Subsequent studies revealed that Zn typically exists in aqueous solutions as octahedral complexes $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, with an average Zn–O distance of 2.08–2.10 Å [62]. The distances around 2.06–2.07 Å are usually reported for Zn in octahedral coordination in the solid phase, while distances of 1.95–1.98 Å were reported for Zn tetrahedral coordination on the surface sites [62]. The surface positions of Zn in tetrahedral coordination have a Zn–O distance of 1.95–1.98 Å. Recently, extended X-ray absorption fine structure (EXAFS) has been used to study the crystal structures of several different mineral systems [64], including $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-FeO}$ [64,67,68]. In the $\gamma\text{-Al}_2\text{O}_3$ system, the enrichment of heavier Zn isotopes adsorbed on aluminum oxide ($\Delta^{66}\text{Zn}_{\text{adsorbed-aqueous}} = 0.47 \pm 0.03\text{‰}$) was explained by the presence of tetrahedral structures, which had shorter Zn–O bond lengths (1.96 Å) compared to Zn in water (2.06 Å) [68]. Similarly, in the $\gamma\text{-FeO}$ system, Zn adsorption on ferrihydrite surfaces led to Zn isotopic fractionation ($\Delta^{66}\text{Zn}_{\text{adsorbed-aqueous}}$ of approximately 0.52‰). The Zn–O bond length on the ferrihydrite surface was 1.96 Å, and all of its adsorbed Zn existed in tetrahedral structure coordination. The Zn–O bond length in hematite was 2.06 Å and was in the form of octahedral adsorption of lighter Zn isotopes in solution [64,67]. This finding was consistent with the work of Little et al. [50], who used EXAFS to report the tetrahedral coordination of Zn^{2+} and Mn^{2+} in marine manganese crusts, which exhibited relatively heavier isotope signatures compared to those of seawater.

The properties of the solution can also affect the fractionation of Zn isotopes [65,66]. In high IS conditions, the adsorption of Zn^{2+} on minerals such as birnessite led to strong enrichment of heavier Zn isotopes, while in low IS conditions, the fractionation degree gradually decreased to 0.2‰ [65]. Therefore, the Zn isotopic ratio gradually decreased as the IS decreased, and this was mainly attributed to the formation of tetrahedral Zn complexes on the mineral surface in high IS and low surface charge density conditions [65]. As the surface coverage area increased, the surface began to form octahedral Zn complexes, resulting in an increase in the proportion of Zn bound in octahedral coordination and a decrease in the fractionation amplitude [65]. Similar fractionation processes have been observed in calcite and clay minerals. For example, in calcite, the average values of $\Delta^{66}\text{Zn}_{\text{adsorbed-solution}}$ were $0.41 \pm 0.18\text{‰}$ and $0.73 \pm 0.08\text{‰}$ in low and high IS systems, respectively (Figure 5) [66]. In the adsorption of Zn on clay minerals, the degree of Zn isotopic fractionation increased with the increasing IS and pH. The range of the $\Delta^{66}\text{Zn}_{\text{adsorbed-solution}}$ of the clay minerals was $0.06\text{‰} \sim 0.49\text{‰}$ in low IS and $0.32\text{‰} \sim 0.52\text{‰}$ in high IS conditions (Figure 5) [58].

3.2.2. Precipitation

Besides adsorption, the mineral precipitation process also affects Zn isotopic fractionation. Samples of hydrozincite formed by biologically driven processes from the Rio Nalaculi River in southwestern Sardinia consistently exhibited $\delta^{66}\text{Zn}$ values that were approximately 0.35‰ higher than the solution, indicating that the continuous precipitation of hydrozincite in the river enriched it in heavier Zn isotopes, which explained the gradual decrease in $\delta^{66}\text{Zn}$ values downstream [69]. In another experiment, it was also observed that both hydrozincite and phosphozincite preferentially enriched heavier Zn isotopes during their precipitation. Conversely, in the precipitation of sphalerite, the $\delta^{66}\text{Zn}$ values in the solution gradually increased [70], and this could be attributed to the different coordination environments of Zn with sulfur atoms in sphalerite compared to oxygen atoms, because the Zn-S bond length was longer [70]. Similar findings concerning Zn isotopic fractionation during sphalerite precipitation under sulfate-reducing conditions were also arrived at by Jamieson-Hanes et al. [71]. The co-precipitation study of Zn with calcite revealed that Zn^{2+} attached to surface growth sites in a tetrahedral configuration that was enriched with heavier Zn isotopes in the initial stage of calcite formation [72]. Following the incorporation of Zn into the crystal lattice and the substitution of Ca^{2+} , its coordination number increased to six. After this transition to a coordination number of six, the initially adsorbed heavier Zn isotopes became integrated into the lattice, and no further isotopic fractionation occurred. The Zn isotopic fractionation value ($\Delta^{66}\text{Zn}_{\text{calcite-aqueous}}$) between the precipitate phase and the solution phase was determined to be $0.58 \pm 0.05\text{‰}$ [72].

3.2.3. Biological Effects

Biological processes have been found to induce Zn isotopic fractionation. During biological activity, lighter Zn isotopes are preferentially absorbed, and heavier Zn isotopes are preferentially adsorbed. The biological absorption process is regulated by seasonal variations. Studies have found that, particularly during the summer, when biological activity is high and there is an increase in phytoplankton production, there is relatively higher enrichment of light Zn isotopes compared to other seasons [52,73]. In a study of Zn isotopic fractionation during the adsorption and absorption processes of marine and freshwater diatoms, it was discovered that diatoms preferentially interacted with heavier Zn isotopes ($\Delta^{66}\text{Zn}_{\text{cell-aqueous}}$ values of 0.35‰ and 0.27‰, respectively) [34]. The reason for isotopic fractionation during biota adsorption might have been attributed to changes in the coordination number of Zn when interacting with diatoms. In the solution, Zn^{2+} formed complexes with water molecules with a coordination number of six, such as $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ [34]. However, when Zn formed complexes with carboxyl groups, amino groups, and silanol groups inside or on the surface of cells, the coordination number became four, resulting in shorter Zn-O bond lengths and increased bond energies [34]. Similarly, the adsorption process of heavier Zn isotopes by marine diatoms (*Thalassiosira oceanica*)

has been observed during oceanic studies. The $\delta^{66}\text{Zn}$ in unwashed cells (-0.05‰ to 0.38‰) was higher than that in the media, while the $\delta^{66}\text{Zn}$ of washed cells (-0.80‰ to -0.16‰) was lower than that in the media [74]. The range of $\delta^{66}\text{Zn}$ obtained from the mixture of oxalic acid and oxalate–ethylenediamine–tetraacetic acid used for cell washing was 0.09‰ to 0.52‰ , indicating the adsorption of heavier Zn isotopes by the cells. This isotope effect could result from the preferential retention of the heavier Zn isotopes to a lower affinity transport binding site or a more rapid translocation of lighter Zn isotopes across the cell membrane [74]. In an experiment on bacterial surface complex adsorption, the equilibrium fractionation of $\Delta^{66}\text{Zn}_{\text{bacterial-aqueous}}$ was approximately 0.5‰ , indicating the preferential adsorption of heavier Zn isotopes onto bacteria [69]. A similar observation of the preferential adsorption of heavier Zn isotopes onto bacterial surfaces was made in another bacterial adsorption experiment. The isotopic fractionation of Zn is influenced by the type of bacteria and their growth cycle [75]. John et al. [76] conducted indoor cultivation experiments to study the enrichment of Zn isotopes by marine diatom *dunaliella tertiolecta*. Degradation experiments revealed the adsorption of heavy Zn isotopes onto *Dunaliella tertiolecta*. The adsorption mechanism is likely akin to that observed in *Skeletonema costatum* and primarily involves coordination with organic carboxylate moieties [63,76]. The diatoms preferentially absorb lighter Zn isotopes in the media ($\Delta^{66}\text{Zn}_{\text{plankton-media}} = -0.76 \pm 0.02\text{‰}$), which explains the enrichment of heavier Zn isotopes in surface seawater [76]. Similarly, experiments culturing diatoms in Zn solutions confirmed the preferential absorption of lighter Zn isotopes during the absorption process by planktonic algae [77].

4. Application of Zn Isotopes to Source Identification in Rivers

Isotope tracing is one effective method to trace the sources and evolution of pollutants by utilizing the changes in isotopic ratios [28]. The fundamental principle of isotope tracing is based on the fact that different sources of pollution release substances with specific $\delta^{66}\text{Zn}$ ranges. The origin and migration pathways of pollutants can be determined through the analysis of $\delta^{66}\text{Zn}$ isotopes in river water or sediment [38,62]. However, the isotopic compositions of pollutants from different sources need to remain relatively stable during the tracer process across different physical, chemical, and biological processes. The stability of isotopes from different sources determines the accuracy of source analysis. This is the advantage of isotope tracing technology compared to traditional tracing techniques based on elemental composition, chemical composition, or rare earth element composition [4,5]. The determination of pollution end-members is often based on the linear mixing figure of $\delta^{66}\text{Zn}$ and the enrichment factor of Zn, as well as the similar figure of the Ca/Zn, Cl/Zn, Al/Zn, U/Zn, Si/Zn, K/Zn, and Sc/Zn ratios. After determining the pollution end-members, the contribution ratios of Zn from each end-member can be calculated using isotope mixing models [4,5,24,28,38]. In the review by Wiederhold et al., there was a comprehensive summary of isotope mixing model calculation formulas [78]. When studying Zn isotopes in river systems, it is essential to discuss the different components present in the rivers, including dissolved substances, SPM, and sediments. These components provide crucial insights into the sources, transformations, and distribution of Zn isotopes within the river system, along with their potential implications for the ecosystem.

The Seine River is a classic example of a river polluted by heavy metals. The study on Zn isotopes in the Seine River in France showed significant variations in $\delta^{66}\text{Zn}$ values (0.07‰ to 0.58‰) [4]. The $\delta^{66}\text{Zn}$ value was 0.58‰ at the source of the Seine River and 0.07‰ at the estuary, indicating a decreasing trend of isotopic ratios along the river. A comparison of the $\delta^{66}\text{Zn}$ sources, such as Zn in residential Zn roofs (-0.02‰ to -0.07‰), Zn in wastewater from sewage treatment plants (-0.03‰ to 0.08‰), and Zn in fertilizers (0.19‰ to 0.42‰), with the $\delta^{66}\text{Zn}$ values in the Seine River suggested that a significant portion of the dissolved Zn in sewage treatment plants may have originated from Zn roofs [4]. Thus, Zn roofs were the main anthropogenic source, and by using mole ratios and a mixing equation with $\delta^{66}\text{Zn}$ values, the average contribution of the roof runoff was estimated to be 70% [4]. Similarly, the Erren River in Taiwan, which is heavily influenced

by anthropogenic activities, exhibited a wide range of $\delta^{66}\text{Zn}$ values (-0.73‰ ~ 1.77‰) [35]. The $\delta^{66}\text{Zn}$ in the Erren River was significant compared to that of other rivers worldwide. The Zn isotope indicated that the major anthropogenic sources in the Erren River were wastewaters from the electroplating and metal processing industries, while natural sources were associated with weathering processes. Additionally, it was challenging to assess the impact of agricultural activities on dissolved Zn in the Erren River due to the lack of distinct $\delta^{66}\text{Zn}$ in Taiwanese fertilizers. However, agricultural wastewater was considered a potential source [35]. In addition to anthropogenic pollution sources, Zn isotopes can also be successfully used to trace natural sources. In part of the Rio Grande, the upstream $\delta^{66}\text{Zn}$ values in the river ranged from -0.2‰ to 0.41‰ , while the tributaries exhibited $\delta^{66}\text{Zn}$ values of -0.6‰ to 0.2‰ [36]. Through the analysis of the $\delta^{66}\text{Zn}$ in the sampled river waters and comparisons with the results from other rivers, the researchers concluded that the influences of bedrock geology, weathering processes, and anthropogenic activities, as well as those of groundwater and surface water on the Zn isotopes in the studied river system, were relatively limited [36]. During the investigation of biogeochemical fractionation processes, the researchers observed that $\delta^{66}\text{Zn}$ increases as pH decreases within the range of 7 to 8.5 [36]. Previous research indicated that the most rapid changes in adsorption on environmental surfaces with pH occur in numerous minerals and solid organic materials. The lower $\delta^{66}\text{Zn}$ values were found downstream, leading the researchers to attribute this phenomenon to the preferential adsorption of heavier Zn isotopes onto suspended sediments and organic matter carried by the rivers [36]. In certain environmentally intricate river systems, the application of Zn isotopes may be constrained. The Zn isotopes in the Central European Elbe River are influenced not only by anthropogenic factors but also by natural fractionation processes [24]. Therefore, it was necessary to further exclude the effects of natural processes when using $\delta^{66}\text{Zn}$ to trace anthropogenic Zn discharge from pollution sources [24]. This also presents challenges in clearly tracing anthropogenic Zn emissions in large river systems.

In addition to river water, sediment and SPM in rivers are also employed for tracing sources of river pollution. The first study on SPM and sediments in rivers was conducted at the Scheldt River estuary [55]. Based on previous research data, it was speculated that the $\delta^{66}\text{Zn}$ of the SPM and sediments in the Scheldt River estuary was influenced by either natural fractionation processes or anthropogenic inputs [55]. The headwater sample of the Aube River exhibited a higher $\delta^{66}\text{Zn}$ value, while the upstream $\delta^{66}\text{Zn}$ values of the Seine River were lower than those of the Aube River. This difference was primarily due to the influence of canalization pipes [24]. After mixing with the Aube River, the $\delta^{66}\text{Zn}$ of the SPM in the Seine River decreased downstream, reaching its lowest value at the river mouth. Therefore, this was considered to be the result of the combined influence of natural and anthropogenic sources. The SPM within the Seine River originates from a combination of natural particles mobilized by erosion processes with anthropogenic particles that were depleted in heavier isotopes [5]. The research findings indicated that the primary sources of anthropogenic particles were wastewater treatment plants and combined sewer overflows [5]. At the Sepetiba Bay river mouth, the $\delta^{66}\text{Zn}$ in the sediments could be explained by a mixing model, including three end-members: terrestrial background ($+0.28 \pm 0.12\text{‰}$, 2σ), marine ($+0.45 \pm 0.03\text{‰}$, 2σ), and predominantly anthropogenic ($+0.86 \pm 0.15\text{‰}$, 2σ) sources, with the anthropogenic source being mainly attributed to electroplating waste [6]. In the study of the Zhujiang River, it was indicated that anthropogenic sources contributed significantly to the Zn content in the SPM of the Pearl River, with an average contribution rate of 30.2%, while natural sources contributed an average of 69.2%. Therefore, the Zn content in the SPM in the Pearl River Basin is controlled by both natural and human factors [38]. Similarly, the South Paraíba River and Guandu River in the industrial region of Brazil are also rivers controlled by both natural and anthropogenic sources [28]. Through the analysis of Zn sources and mixing processes, it was concluded that $\delta^{66}\text{Zn}$ is mainly controlled by a combination of rock-derived material ($\delta^{66}\text{Zn} \approx 0.30\text{‰}$) and multiple anthropogenic sources ($\delta^{66}\text{Zn} \approx 0.15\text{‰}$) [28].

5. Conclusions and Perspectives

In this review, the fractionation of Zn isotopes in surface water, including both the dissolved and the particulate phases arising from interactions involving minerals or biological processes and aqueous solutions, was considered. Whether it is via mineral adsorption or precipitation, Zn isotopic fractionation in solution is influenced by a combination of mineral characteristics and solution conditions. Notably, the same mineral may exhibit differing fractionation behaviors in solutions with varying pH or ionic strength (e.g., birnessite). During biological effect processes, lighter Zn isotopes tend to be preferentially absorbed, while heavier ones are preferentially adsorbed by organisms. This review provides a comprehensive overview of the current state of the application of Zn isotopes in river studies. $\delta^{66}\text{Zn}$ predominantly exhibits a notable range in rivers, varying from -0.73‰ to 1.77‰ . Overall, the isotope composition of Zn in rivers tends to be heavier compared to that of other surface waters. When unaffected by human activity, the $\delta^{66}\text{Zn}$ values in river water range from $+0.23$ to $+0.55\text{‰}$, with a median value of 0.37‰ . The $\delta^{66}\text{Zn}$ values in the SPM and sediments span from $+0.2$ to $+0.35\text{‰}$, with a median of 0.22‰ . These values closely align with the BSE value of $+0.28 \pm 0.05\text{‰}$. By comparing these findings with those of the previous research data, it becomes evident that anthropogenic sources are the primary contributors to Zn pollution in rivers. Moreover, it is worth noting that the factors influencing $\delta^{66}\text{Zn}$ in certain rivers are intricate, and achieving precise results solely based on Zn isotope data presents a formidable challenge.

There are several limitations associated with Zn isotope analysis. The complex laboratory techniques and expensive equipment required for sample preparation, purification, and separation make the analysis process cumbersome. Additionally, the results are influenced by various factors, such as sample pretreatment and matrix effects, which require corrections to obtain accurate results. Moreover, the availability of a sufficient amount of Zn in the sample and the requirement for $\delta^{66}\text{Zn}$ variation within the analysis range can limit the applicability of Zn isotope analysis in certain samples. Despite these limitations, the application of Zn isotope analysis in river tracing has achieved certain results, along with the challenges and limitations. Future directions for Zn isotope technology may include the following:

- (1) Future research can focus on improving Zn isotope analysis methods to enhance analysis efficiency, accuracy, and stability while reducing costs and workload.
- (2) Single isotopes often only identify certain important sources while neglecting other potential pollution sources. Combining the isotope analysis of other elements such as lead and Cu enables multi-element isotope tracing, providing a more comprehensive understanding of pollution sources and processes.
- (3) Further studies on the mechanism of Zn isotopic fractionation between minerals are required. This research can provide accurate information for understanding pollution sources in rivers.
- (4) The current research on the seasonal variations of Zn isotopes in rivers is limited. Establishing comprehensive databases through long-term monitoring of Zn isotopes can reveal seasonal and interannual variations in river systems, particularly in the regulation of biological and mineral processes by seasonal changes in Zn isotopes, deepening our understanding of the impact of human activities on river environments.

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