

Article

Geochemical and Seasonal Characteristics of Dissolved Iron Isotopes in the Mun River, Northeast Thailand

Xuhuan Xiao, Guilin Han , Jie Zeng , Man Liu  and Xiaoqiang Li 

Institute of Earth Sciences, China University of Geosciences (Beijing), Beijing 100083, China; xiaoxuhuan@email.cugb.edu.cn (X.X.); zengjie@cugb.edu.cn (J.Z.); lman@cugb.edu.cn (M.L.); xiaoqli@cugb.edu.cn (X.L.)

* Correspondence: hanguilin@cugb.edu.cn; Tel.: +86-10-8232-3536

Abstract: Dissolved iron (Fe) isotopes in river water have a pivotal role in understanding the Fe cycle in the surficial environment. A total of 13 samples of river water were collected from the Mun River to analyze the Fe isotopes and their controlling factors in river water, such as dissolved organic carbon (DOC) and different supply sources. The results showed that dissolved Fe (DFe) concentrations ranged from 21.49 $\mu\text{g/L}$ to 232.34 $\mu\text{g/L}$ in the dry season and ranged from 10.48 $\mu\text{g/L}$ to 135.27 $\mu\text{g/L}$ in the wet season, which might be ascribed to the dilution effect. The $\delta^{56}\text{Fe}$ of the dry season (-0.34 to 0.57‰ , with an average 0.09‰) was lower than that of the wet season (-0.15 to 0.48‰ , with an average 0.14‰). Combined with the $\delta^{56}\text{Fe}$ and DFe/DAI ratios, the end-members of DFe were identified, including rock weathering (high $\delta^{56}\text{Fe}$ and low DFe/DAI ratio), anthropogenic inputs (high $\delta^{56}\text{Fe}$ and high DFe/DAI ratio) and groundwater inputs (low $\delta^{56}\text{Fe}$ and low DFe/DAI ratio). The relationship between $\delta^{56}\text{Fe}$ and DOC concentrations suggested that the chelation of organic matter with heavy Fe isotopes was one of the important sources of heavy Fe isotopes in river water.

Keywords: dissolved Fe; Fe isotopes; seasonal variation; Mun River; Northeast Thailand



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1. Introduction

Iron (Fe) is abundant in the continental crust [1,2] and is an essential trace element for biology [3,4]. In freshwater systems, the availability of Fe is also an important factor for the survival of cyanobacterial [5]. Moreover, Fe might be important to climate change by influencing biological productivity and carbon sequestration rates [6–8]. Rivers are important channels for the continent to transport Fe to the ocean, and the filtrable Fe ($<0.45 \mu\text{m}$) from riverine flux to the marine is approximately 140 Gg/yr [9]. Fe occurs as Fe(0), Fe(II) and Fe(III), and Fe's valence state mainly depends on environmental conditions [10]. The most stable state is the oxidation state, Fe(III), because the atmosphere is mainly in an oxidizing state [11]. Combined with the redox chemistry of Fe and the abundance of this element in the river, further investigation of Fe in rivers is crucial to understanding continental erosional/weathering mechanisms [12,13].

In modern oxidizing Earth surface conditions, continental weathering preferentially releases light Fe isotope compositions, which is transported in rivers to marine areas [14–17]. According to the study on the Seine River, dissolved Fe is derived from anthropogenic inputs ($\delta^{56}\text{Fe} = -0.60\text{‰}$) and natural inputs ($\delta^{56}\text{Fe} > 0.00\text{‰}$) [18]. Based on the study of estuaries, particulate Fe sources were determined by Fe isotopes [19]. Hence, Fe isotopes can be used to trace Fe sources in hydrologic environments. Because of the strong complexation capacity of Fe, Fe(III) organic complexation is an important form of Fe [20]. The coordination bond Fe-O-C of the organic Fe complex is stronger than the Fe-O-Fe bond of Fe hydroxide, and the enrichment of heavy Fe isotopes in the Fe(III) organic complex is stronger than that of Fe oxyhydroxides [21,22]. In addition, the dissolved Fe isotope compositions have seasonal variations in the rivers. In the Amazon River Basin, the Fe isotope compositions of bulk water

vary little throughout the year [12], but the Fe isotope compositions of particulate matter in organic-rich rivers show seasonal effects [23–25]. Hence, the results may be canceled out by the variations in the dissolved Fe isotopes' compositions. The dissolved Fe isotope compositions in small organic-rich streams change significantly with time in the Arctic and subarctic regions [26].

The dissolved Fe and its isotopes in the Mun River (MR) were investigated in this study. The MR has important significance to the ecosystems of the Mekong River Basin, which is the largest tributary on the right bank of Mekong River [27], because local industrial development and intensive agricultural activities may bring environmental issues in the MR [28–30]. In addition, the seasonal variation and the influence of organic matter on dissolved Fe isotopes are unclear in the MR. The aims of this study are to explore (1) the seasonal characteristics and comparison of Fe isotopes in the dry and wet seasons of the MR, (2) the sources of dissolved Fe and (3) the influence of dissolved organic carbon (DOC) concentrations on Fe isotopes.

2. Materials and Methods

2.1. Study Region

The Mun River Basin (MRB) ($14^{\circ}00'–16^{\circ}00' \text{ N}$, $101^{\circ}30'–105^{\circ}30' \text{ E}$) is located on the Korat Plateau, Northeast Thailand (Figure 1). According to Akter and Babel [31], the MR is divided into upper ($101^{\circ}30'–102^{\circ}30' \text{ E}$), middle ($102^{\circ}30'–104^{\circ}30' \text{ E}$) and lower ($104^{\circ}30'–105^{\circ}30' \text{ E}$) reaches. The total length of the MR is 673 km, with a landmass of 82,000 km² [32]. The MRB has a tropical savannah climate, which is mainly controlled by the southwest monsoon (March to October) and the northeast monsoon (October to February) [33,34]. The average annual temperature is 24–30 °C, and the perennial temperature is no less than 18 °C. During the dry season, the rainfall variation is 40 to 120 mm. On the contrary, the rainfall in the wet season is from 800 mm to 1800 mm [35]. The average annual precipitation in MRB is 1300 to 1500 mm [36]. Thailand has a large population and its economy depends on agriculture. The main type of land use is arable land [37], most of which is paddy fields [38,39]. The main rock types of the MRB are clastic rocks and clastic rocks with evaporite, and sporadic igneous rocks existed only in the southern of the MRB [37].

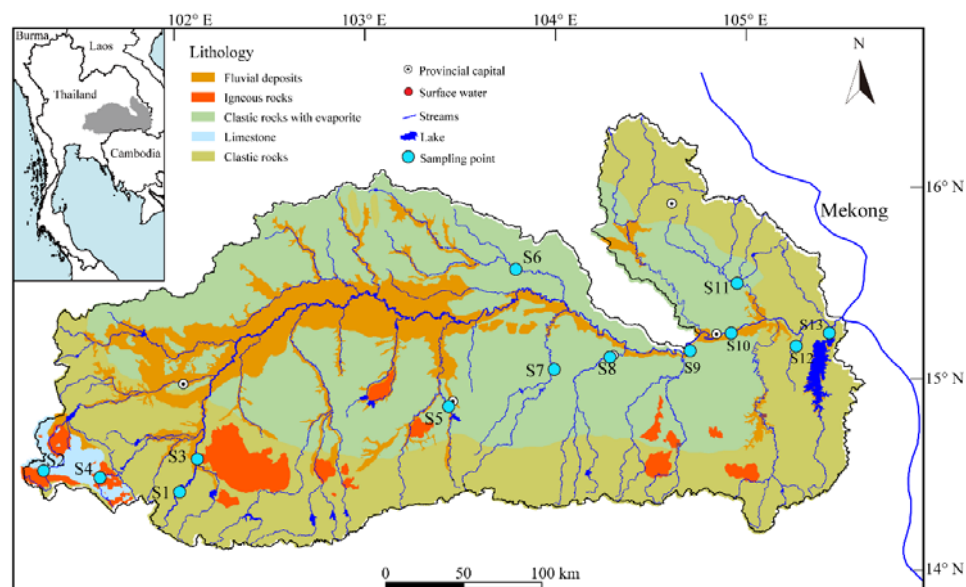


Figure 1. The sampling sites and the different rock types of the Mun River Basin, adapted from Li, Han, Liu, Song, Zhang, Yang and Liu [37].

2.2. Sampling and Analytical Methods

2.2.1. Field Sampling

In March 2018 (dry season), 13 samples were collected at a depth of approximately 10 cm in the MR [29]. The samples in the wet season (August 2017) were analyzed in a

previous study [40]. Among them, four sampling sites were located in the upper stream (S1, S2, S3 and S4), four sampling sites were in the middle stream (S5, S6, S7 and S8) and five samples were collected in the lower stream (S9, S10, S11, S12 and S13). Water samples were collected by LDPE bottles, which were retouched three times with the water samples at the sampling point. After that, the samples were filtered by 0.22 μm cellulose acetate filter membrane and were then collected in pre-cleaned HDPE bottles [41]. In order to prevent metal cations from adhering to the inner wall of the bottle, it is necessary to acidify the water samples with ultrapure concentrated nitric acid (HNO_3) to $\text{pH} < 2$. Before analysis, they were stored in a dark refrigerator.

2.2.2. Water Parameter and Elemental Analysis

The pH and dissolved oxygen (DO) were determined by a YSI multi-parameter before filtration, according to previous studies [26,28,35]. The concentrations of Fe and aluminum (Al) were measured by ICP-MS (Elan 9000, Perkin Elmer Optima, Waltham, MA, USA) in the Institute of Geographic Sciences and Nature Resources Research, Chinese Academy of Sciences (CAS). The standard reference (GSB 04-1767-2004) was used for quality control and method validation. The uncertainty was below 0.7%, and the percentage recoveries ranged from 97.21% to 109.80%.

2.3. Iron Isotope Analyses

2.3.1. Pretreatment of Iron

The iron isotope pretreatment was conducted in a class 100 fume hood in a class 1000 metal-free ultra clean laboratory at the Surficial Environment and Hydrological Geochemistry Laboratory (SEHGL), China University of Geosciences Beijing (CUGB). In this study, the reagents (HNO_3 and HCl , BVIII grade) were purchased from the Beijing Institute of Chemical Reagents. The experimental labware was cleaned with double distilled ultrapure acid and ultrapure water (18.2 $\text{M}\Omega\cdot\text{cm}$, Pall, New York, NY, USA) [42]. For Fe separation, the AG MP-1M resin (1.6 mL, 100–200 mesh, Bio-Rad, Hercules, CA, USA) was filled in the polypropylene column to obtain an anion-exchange chromatography. The column was cleaned three times with 10 mL 0.5N HNO_3 and 2 mL water. After this, 5 mL 7N HCl + 0.001% H_2O_2 and 5 mL water were used to further clean the column alternately. Then, 2 mL 7N HCl + 0.001% H_2O_2 was used to complete the acidification of the resin. The sample loading amount was typically 25 μg Fe. According to Fe concentrations in the samples, a certain amount of the samples were taken into Teflon beakers and dried on the heating plate. After that, the residue was treated with 1 mL concentrated HNO_3 to remove organic matter. Finally, the solutions were dried at 80 $^\circ\text{C}$ and re-dissolved three times in 7 N HCl + 0.001% H_2O_2 before separation. Following this, 1 mL solution (sample which had been dried and re-dissolved) was loaded onto the column until it was fully absorbed by the resin. The 40 mL 7N HCl + 0.001% H_2O_2 were used to eliminate the interference of the matrix. After that, 20 mL 2N HCl + 0.001% H_2O_2 were used to elute the eluent of Fe, which was collected with a 30 mL Teflon container. All samples were purified twice to separate Fe from the matrix completely. After purification process, the Teflon container containing the eluent of Fe was evaporated on the heating plate (80 $^\circ\text{C}$) until they were moist. In order to convert HCl medium into HNO_3 medium, concentrated HNO_3 (0.1 mL) was added into all samples; then, they were evaporated until dry (repeated three times) [43]. Afterwards, the purified Fe was re-dissolved in 2% HNO_3 solution to be analyzed on the instrument. The specific experimental details can be found in our previous studies [40,44].

2.3.2. Mass Spectrometry Analysis

The Fe isotope compositions were completed on MC-ICP-MS (Nu Plasma III) at the SEHGL. Before Fe isotopes analysis, the Fe concentration in solution was calculated through the intensity of ion beams to ensure that the loss of Fe was less than 1% in the chemical separation and purification. The average Fe content of the procedural blank was < 10 ng. During the analysis, the wet plasma method was used to measure the Fe isotopes

value. In order to eliminate the interference of spectral peaks of other plasmas, such as $^{40}\text{Ar}^{14}\text{N}$ to ^{54}Fe , $^{40}\text{Ar}^{16}\text{O}$ to ^{56}Fe and $^{40}\text{Ar}^{16}\text{O}^1\text{H}$ to ^{57}Fe , medium-resolution mode was adopted. In addition, the potential interference of ^{54}Cr still existed, the interference of $^{40}\text{Ar}^{12}\text{C}^+$ was eliminated by measuring the left shoulder of $^{52}\text{Cr}^+$ spectral peak to monitor the interference of $^{54}\text{Cr}^+$. In order to redress the error caused by the instrument itself, the “standard-sample bracketing” (SSB) was used for the analysis of Fe isotopes. In addition, the analysis results were affected by the concentration effect, so the standard-sample concentrations matched within 5% to reduce the effect. IRMM-014 was used in this analysis as the standard, which is a metallic Fe standard distributed by the IRMM (Institute for Reference Materials and Methods). For specific details of Fe isotope measurement, refer to our previous research [40,44].

In this study, all the $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ values obtained followed the theoretical mass-dependent fractionation line, so only the $\delta^{56}\text{Fe}$ were discussed. $\delta^{56}\text{Fe}$ was defined by micrometer deviation relative to the Fe standard IRMM-014, as the following relationship:

$$\delta^{56}\text{Fe} = [({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}} / ({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}} - 1] \times 1000$$

The long-term external reproducibility of Fe isotopes analysis was better than 0.07‰. The $\delta^{56}\text{Fe}_{\text{IRMM-014}}$ of reference standard BCR-2 was 0.08 ± 0.04 ‰ ($n = 2$), within the range reported in previous studies [40].

2.4. Software

The map of sampling sites and rock types of the MR was drawn by CorelDRAW 2021. Other figures were made by Adobe Illustrator 2015 and Origin 2018. In order to determine the influencing factors of dissolved Fe concentrations and Fe isotopes, all data were performed using SPSS 26.0 for Pearson correlation analysis, with two-tailed detection and the level of significance below 0.05.

3. Results and Discussion

3.1. Variations in Iron Concentrations in River Water

3.1.1. Temporal and Spatial Variations in pH, DO and DOC

The pH in the dry season ranged from 6.1 to 7.7, with an average of 7.0 [45], and the pH in the midstream (6.6) was lower than upstream (7.1) and downstream (7.1). The pH in the wet season varied from 6.4 to 7.7, with an average of 6.9 [29], and the pH in the midstream (6.6) was lower than upstream (7.4) and downstream (6.7). The DO in the dry season displayed a uniform variation of 3.3–10.3 mg/L, and the mean DO in the upstream, midstream and downstream showed no significant change, approximately 6.6 mg/L. The DO also displayed a uniform variation of 3.0–7.1 mg/L in the wet season, which was lower than that in the dry season. The DO in the upstream (5.8 mg/L) and downstream (5.3 mg/L) was higher than that in midstream (4.4 mg/L) (Figure 2). The DOC in the dry season varied from 5.7 to 12.6 mg/L (average 8.8 mg/L). In the dry season, The DOC in upstream (9.5 mg/L) was higher than that in the midstream (8.7 mg/L) and downstream (8.3 mg/L). The DOC varied from 1.7 to 35.8 mg/L in the wet season (average 12.5 mg/L). The DOC of the wet season in the upstream (3.5 mg/L) was lower than that in the midstream (14.6 mg/L) and downstream (18.1 mg/L). The rainfall in the wet season accounted for about 85% of the annual rainfall [34]. However, rainfall shows no dilution effects on the DOC because the DOC in the dry season was lower than that in the wet season. Intensive agricultural activities in the middle and lower reaches might increase DOC concentrations [29]. Furthermore, the increase in riverine DOC in the wet season might be ascribed to the vast humic substance from high rainfall in the forest area [40,46].

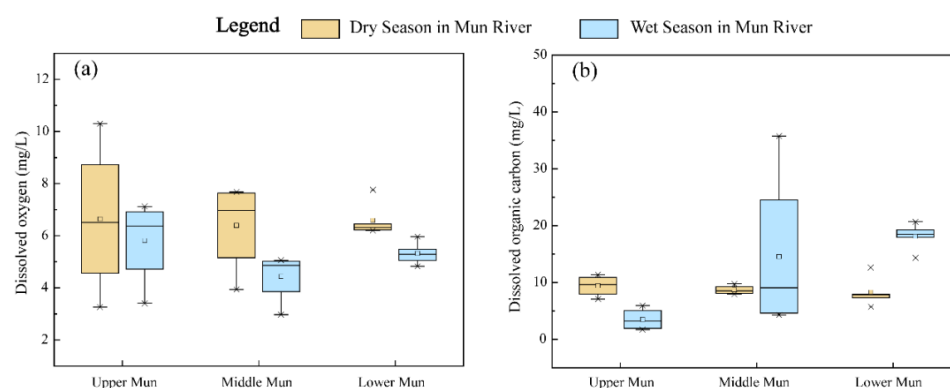


Figure 2. (a) Dissolved oxygen (DO) and (b) Dissolved organic carbon (DOC) in the upstream, midstream and downstream of Mun River (MR) during dry and wet season; data are from [29,45].

3.1.2. Variations in Dissolved Iron and Aluminum

The dissolved iron (DFe) concentration in the dry season varied from 21.49 to 232.34 $\mu\text{g/L}$ (Figure 3 and Table S1), with an average 94.70 $\mu\text{g/L}$. Compared with the Fe concentration of the marine area of 5.6 to 56 ng/L [18,47], the DFe concentration in MR was particularly high, and this may be related to anthropogenic input and rock weathering. The mean DFe concentrations in the dry season from the upstream to the downstream were 118.64, 67.09 and 97.64 $\mu\text{g/L}$. The DFe concentration in the middle reaches was the lowest. From upstream to downstream, there was a downward and then upward trend (Figure 3). The concentration of DFe during the wet season was from 10.48 to 135.27 $\mu\text{g/L}$ (mean concentration 36.54 $\mu\text{g/L}$). Compared with DFe concentration in the wet and dry seasons, the DFe concentration in the wet season was lower than that in the dry season. It indicated that DFe concentration was diluted by river water. The trend of DFe concentration in the wet season was opposite to that in the dry season. The DFe concentration in the midstream was highest in the wet season (Figure 3).

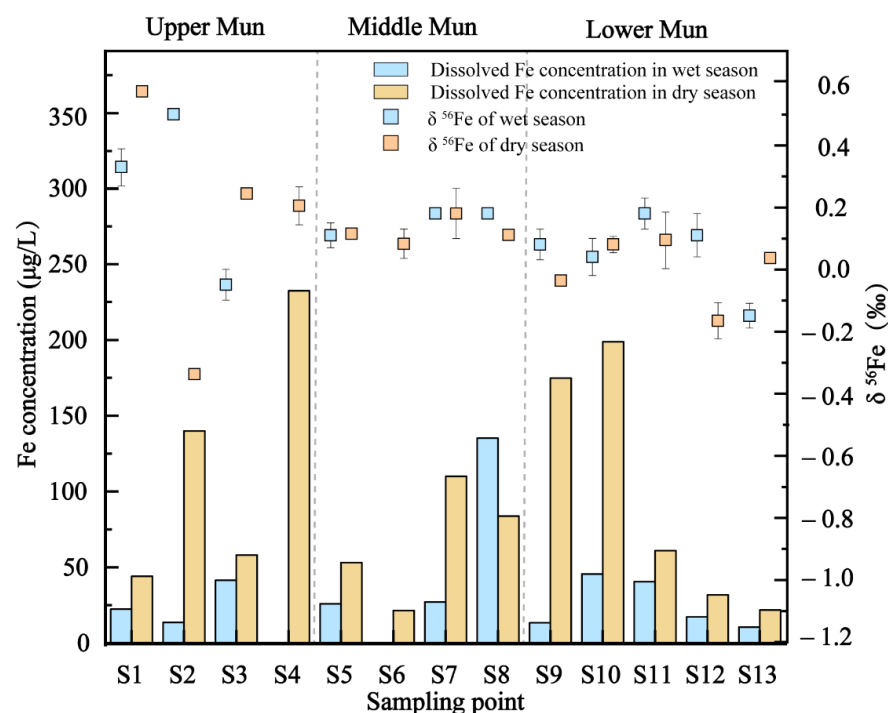


Figure 3. The concentration of dissolved Fe in MR during dry and wet seasons and the $\delta^{56}\text{Fe}$ of the dry and wet seasons. The $\delta^{56}\text{Fe}$ data of the wet season are from [40] and data of Fe concentration are from [30].

Aluminum is often used as a tracer due to its high content and relative immobility in the crust [48–50]. Based on the ratio of DFe/DAI, the dilution effect of DFe concentrations was eliminated. The concentration of dissolved aluminum (DAI) in the dry season varied from 1.77 to 167.42 $\mu\text{g/L}$ (average 41.97 $\mu\text{g/L}$). The average concentrations of DAI from the upstream to the downstream were 45.08, 44.69 and 20.26 $\mu\text{g/L}$. The DAI concentration in the wet season was 0–177.77 $\mu\text{g/L}$, with a mean of 44.05 $\mu\text{g/L}$ [30]. The average DAI concentrations from upstream to downstream were 2.84, 82.07 and 28.67 $\mu\text{g/L}$, which was highest in the middle reach. In the dry and wet seasons, the DAI concentrations showed a significant increase, which was probably attributed to humic-type colloids [51].

3.1.3. Influence Factors of DFe Concentration

The Fe in natural water was mainly soluble Fe (ionic Fe, Fe complexes and colloidal Fe) and insoluble Fe (suspended Fe, biological Fe and terrigenous clastic Fe). The solubility of Fe in water was affected by various factors (pH, DO, DOC, etc.) [52]. The relationship between dissolved aluminum (DAI) and dissolved Fe (DFe) concentrations (Figure 4a) ($r = 0.66$, $p < 0.05$ in the dry season and $r = 0.9$, $p < 0.01$ in the wet season) indicated that there was little correlation between DFe concentrations and DAI concentrations in the dry season and strong correlation between DFe concentrations and DAI concentrations in the wet season. In the dry season, there was an apparent correlation between DFe and DFe/DOC ($r = 0.95$, $p < 0.01$), but in the wet season, there was no correlation between DFe and DFe/DOC (Figure 4b). Therefore, the DOC concentrations were more associated with the DFe concentrations in the dry season than those in the wet season. In the dry season, the DFe concentrations correlated with Si/Al ratio in the MR (Figure 5), indicating higher DFe concentrations in congruent weathering systems and lower DFe concentrations in incongruent weathering systems. In incongruent weathering systems, the Fe may be fixed in secondary mineral phases.

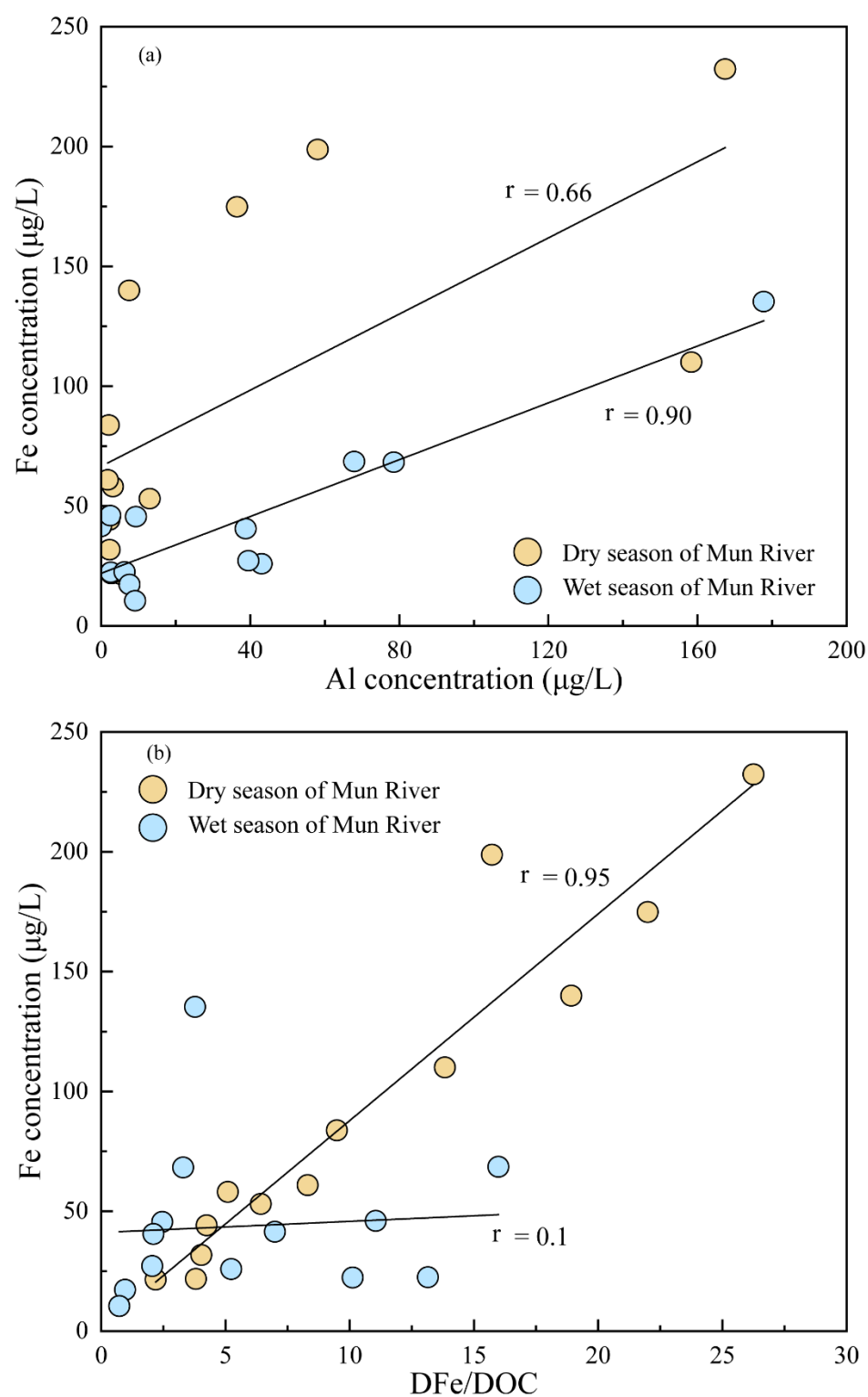


Figure 4. Fe concentrations (µg/L) versus (a) Al concentrations (µg/L) and (b) DFe/DOC ratio in MR water.

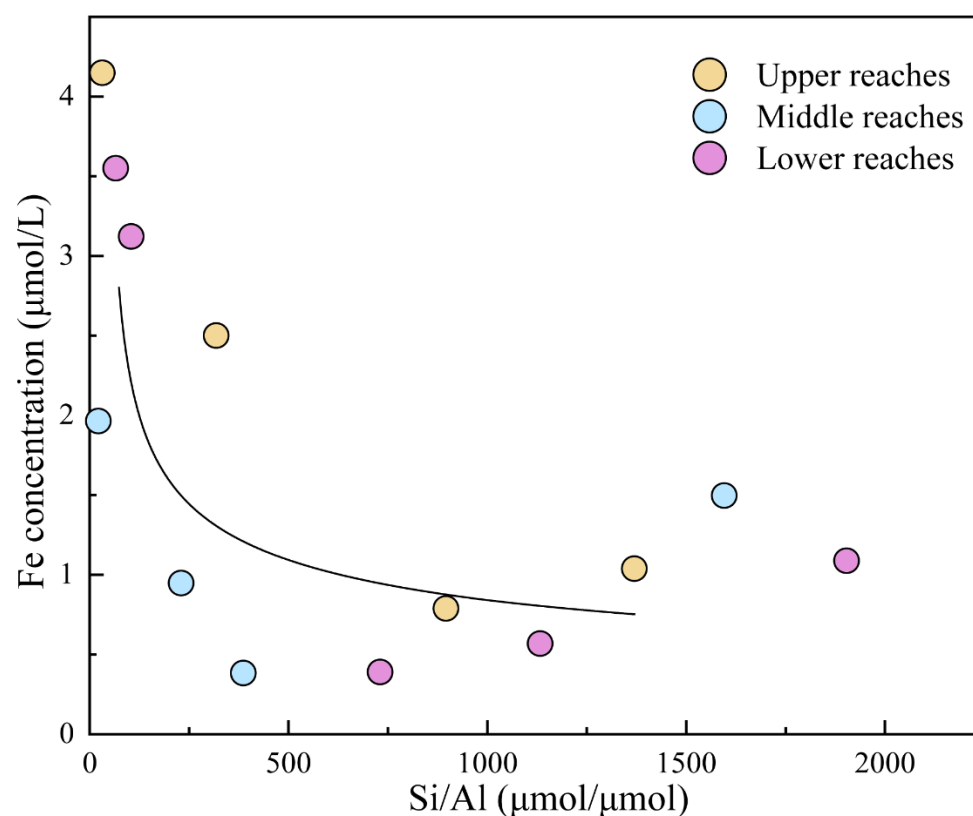


Figure 5. Fe concentration ($\mu\text{mol/L}$) versus Si/Al ratio ($\mu\text{mol}/\mu\text{mol}$) in MR water in the dry season. The data of Si are from [53].

3.2. Iron Isotope Compositions of River Water

3.2.1. Variation in Iron Isotopes

The $\delta^{56}\text{Fe}$ of MR varied from -0.34‰ to 0.57‰ (Table S1 and Figures 3 and 6), with an average of 0.09‰ . The average $\delta^{56}\text{Fe}$ of the upper, middle and lower reaches in the MR were 0.17‰ , 0.12‰ and 0.00‰ , respectively. The $\delta^{56}\text{Fe}$ in the continental crust was $0.06 \pm 0.03\text{‰}$ [54,55]. The $\delta^{56}\text{Fe}$ in sedimentary clastic rocks and igneous rocks were similar to the continental crust [19]. The bedrocks of the MRB are mainly clastic rocks and sporadic igneous rocks in the south of the MRB, and the $\delta^{56}\text{Fe}$ of the MR is consistent with that of bedrocks. Compared to Arctic rivers (e.g., Copper River, average $\delta^{56}\text{Fe} = -0.01\text{‰}$; Lena River, average $\delta^{56}\text{Fe} = -0.11\text{‰}$; and Ob' River, average $\delta^{56}\text{Fe} = -0.11\text{‰}$) (Figure 6) [26] and the tropical river (Amazon River, $\delta^{56}\text{Fe} = -0.17\text{‰}$) (Figure 6) [56], the $\delta^{56}\text{Fe}$ in the MR was higher. However, compared to the Negro River, an organic-rich river (average $\delta^{56}\text{Fe} = 0.28\text{‰}$), the $\delta^{56}\text{Fe}$ in the Mun River was lower.

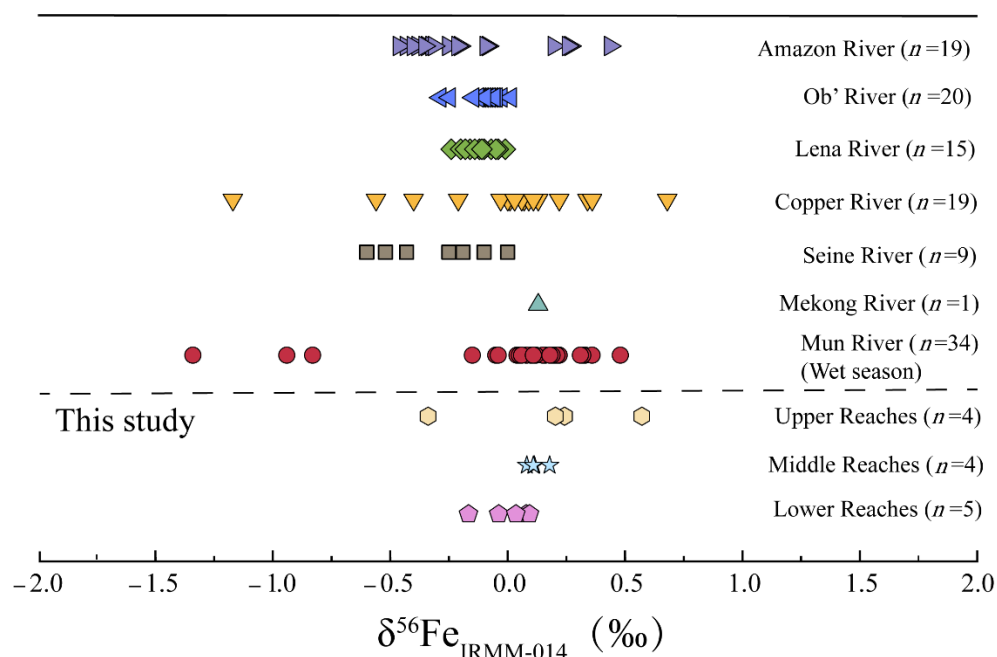


Figure 6. The $\delta^{56}\text{Fe}$ of MR and other world rivers. These data come from [16,24,38,54].

3.2.2. Seasonal Variation in the DFe Isotope

In the Arctic and sub-arctic regions, the DFe isotope of a small organic-rich river varied significantly with time (-1.7 – 1.6 ‰); in the wet season, low molecular weight organic colloids preferentially complexed heavy DFe isotopes, while light DFe isotopes were enriched in the dry season [26]. The $\delta^{56}\text{Fe}$ of the subglacial fluvial iron from the same site in Greenland varied slightly [57]. However, for a typical tropical river—such as the Mun River—the Fe isotope was different across different seasons. The average $\delta^{56}\text{Fe}$ of the MR in the dry season (0.09 ‰) was lower than that in the wet season (0.14 ‰) (Figure 3).

The main recharge source of the MR in the wet season was precipitation, and that in the dry season was groundwater [58]. A previous study reported $\delta^{56}\text{Fe}$ of atmospheric aerosols (0.08 – 0.12 ‰) [59], which were approximate to $\delta^{56}\text{Fe}$ of continental crust (0.06 ± 0.03 ‰). However, the Fe isotopes in groundwater were lighter than that in the continental crust [60,61]. Furthermore, the groundwater usually had low oxidation-reduction potential (ORP) and high concentrations of Fe (II) [61], which will slowly oxidize and settle, resulting in lighter dissolved Fe isotopes in river water and heavier Fe isotopes in suspended particulate matter (SPM) [16,23,24]. This process made the DFe isotopes of rivers lighter in the dry season. Therefore, precipitation and groundwater were the recharge sources of MR in the wet and dry seasons, respectively, resulting in the difference in the dissolved Fe isotopes in the MR.

3.2.3. The Source of Dissolved Fe

Dissolved Fe in river water had different sources, mainly including rock weathering, anthropogenic sources (agriculture and industry activities) and other potential sources (groundwater and precipitation, etc.) [59,62–64]. According to Han, Yang, Zeng and Zhao [40], the end-member of rock weathering had the highest Fe isotopes and a lower DFe/DAI ratio, the end-member of the anthropogenic source had a moderate Fe isotopes value ($\delta^{56}\text{Fe} > 0$) and the highest DFe/DAI ratio (anthropogenic input introduces extra Fe in river water) and the end-member of other potential sources had the lowest Fe isotopes value and a low DFe/DAI ratio (Chi River). However, in this study, only the end-members of rock weathering and anthropogenic inputs in Han, Yang, Zeng and Zhao [40] were used. Groundwater and precipitation were regarded as the third end-member. As mentioned above, the $\delta^{56}\text{Fe}$ of atmospheric aerosols was similar to that of the continental crust, so the end-member of precipitation was summarized as that of rock weathering. For the

end-member of groundwater, the $\delta^{56}\text{Fe}$ of groundwater of the basin whose lithology was mainly sandstone and Quaternary sediments was used to approximate (median $\delta^{56}\text{Fe} = -1.14\text{‰}$) [61]. For the DFe/DAI ratio in groundwater, the DFe and DAI concentrations in the groundwater in northeast Thailand were used (DFe/DAI = 10.74) [65]. In Figure 7, sample points in dry and wet seasons were near the end-member of rock weathering, indicating that the DFe mainly came from rock weathering. However, compared with the wet season, DFe in the dry season was more influenced by anthropogenic source. During the dry season, some samples in the midstream and downstream were obviously located between the end-members of natural sources and anthropogenic sources (Figure 7). The $\delta^{56}\text{Fe}$ of S2 was lowest in the dry season. This may be related to bedrock and external inputs. The bedrock of S2 was limestone, which had a low $\delta^{56}\text{Fe}$ (-0.95 – -0.21‰) [66]. The S2 was located in the forest area, where rivers in the forest took away the light Fe from the forest to reduce $\delta^{56}\text{Fe}$, and this process also increased the concentration of DFe in the river compared to natural rivers [67]. Therefore, the DFe of S2 may be mainly from forest and rock weathering. In general, in the dry season, the DFe of the upstream was mainly from rock weathering, while the DFe of the midstream and downstream was obviously influenced by anthropogenic activities.

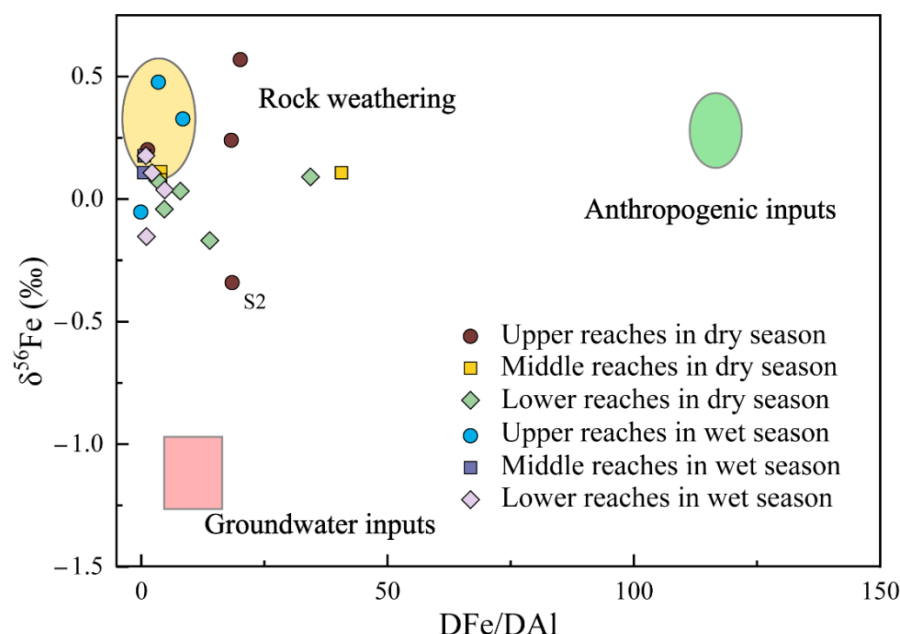


Figure 7. $\delta^{56}\text{Fe}$ versus DFe/DAI ratio in Mun River showing the source of dissolved Fe. The data of end-members of rock weathering and anthropogenic inputs are from [40] and those of end-member of groundwater inputs are from [61,65].

3.3. Influence of DOC on the DFe Isotopes

The Dfe isotopes were mainly affected by redox conditions, organic matter and biological activities. Experimental research showed that Fe^{3+} organic complexes were enriched with heavier Fe isotopes than Fe hydroxide or Fe^{2+} [21]. The study of Arctic rivers indicated that heavy Fe isotopes was enriched by the combination of Fe and organic ligands [26]. Ilina, Poitrasson, Lapitskiy, Alekhin, Viers and Pokrovsky [22] found that Dfe was more enriched heavy Fe isotopes than Fe of suspended particulate matter in the organic rich rivers. These finds were consistent with the quantum mechanical calculations, which suggested that the heavier isotope concentrates in the most tightly bound species [68]. The complexation of other metals with organic matter also proved this point [69,70].

In order to determine the influence of organic matter on DFe isotopes in rivers, the relationships between $\delta^{56}\text{Fe}$ and DOC concentrations of frigid rivers (Severnaya Dvina and Gulf of Alaska Basin) [26,67], a temperate river (Seine River) [18] and a tropical

river (Mun River) were compared. The strong positive correlation between $\delta^{56}\text{Fe}$ and DOC concentrations of the MR in the dry season suggested that the chelation of Fe and organic matter results in the enrichment of heavy Fe isotopes (Figure 8). A previous study showed that the DOC in the MR was influenced by human activities [29]; thus, the anthropogenic end-member of heavy Fe isotopes was carried by DOC in the MR. However, there was no correlation between the $\delta^{56}\text{Fe}$ and DOC concentrations of the MR in the wet season (Figure 8). It was possible that the uptake of plants caused the decomposition of organic matter in soil and then release light Fe isotopes to rivers [71]. As mentioned above, heavy precipitation will cause the increase in DOC concentration in the wet season (Section 3.1.1). The relationship between the $\delta^{56}\text{Fe}$ and DOC concentrations in boreal forested rivers and glacierized rivers also suggest that forested rivers may carry light Fe isotopes (Figure 8). For the Seine River, whose DOC concentrations were similar to the world riverine average (5.35 mg/L) [72], there was a strong positive correlation between $\delta^{56}\text{Fe}$ and DOC concentrations (Figure 8). The natural end-member of Fe had heavy Fe isotopes in the Seine River [18]; hence, according to the relationship between $\delta^{56}\text{Fe}$ and DOC concentrations, it can be determined that natural Fe was carried by organic matter. Similar to the above rivers, there was also a positive correlation between $\delta^{56}\text{Fe}$ and DOC concentrations in the organic-rich Severnaya Dvina (Figure 8). In summary, the chelation of organic matter with heavy Fe isotopes was one of the important sources of heavy Fe isotopes in river water in different climate zones.

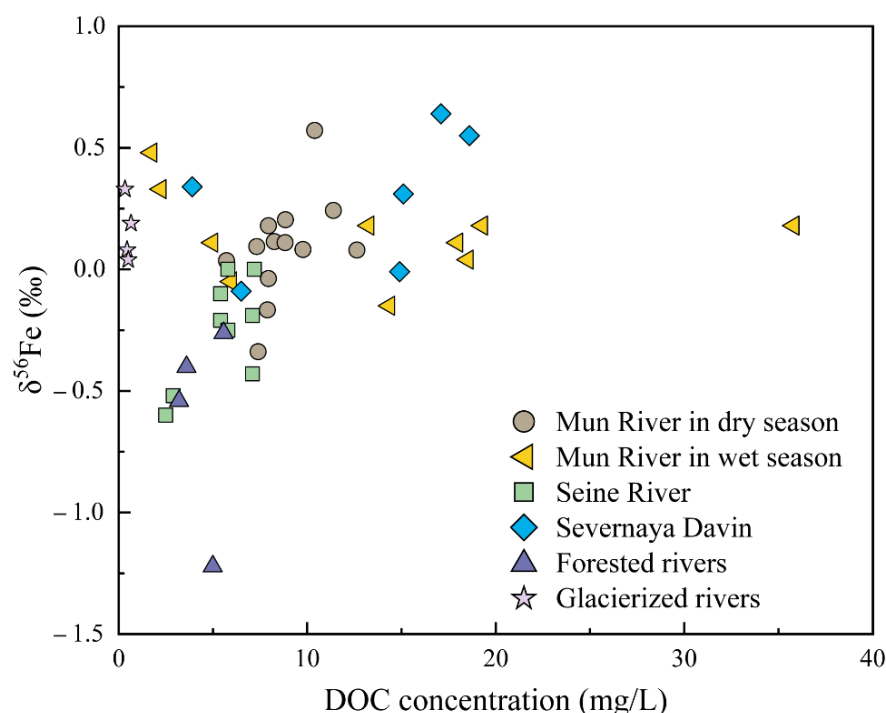


Figure 8. The relationship between Fe isotopes and DOC concentration in different climate zones. These data are from [16,24,38,63].

4. Conclusions

This study reported the DFe isotope compositions of the tropical river MR in the dry season. The $\delta^{56}\text{Fe}$ of the MR was similar to those of the continental upper crust. The $\delta^{56}\text{Fe}$ ranged from -0.34 to 0.57 ‰, and the average $\delta^{56}\text{Fe}$ of the upstream, midstream and downstream of the MR were 0.17 ‰, 0.12 ‰ and 0.00 ‰. From upstream to downstream, the $\delta^{56}\text{Fe}$ showed a downward trend as a whole. Compared with the $\delta^{56}\text{Fe}$ in the wet season of the MR, the $\delta^{56}\text{Fe}$ in the dry season was slightly lower than that in the wet season, which may be ascribed to the great influx of groundwater in the dry season. The $\delta^{56}\text{Fe}$ of groundwater was lower than that in the continental crust. In addition, the oxidation

and precipitation of Fe in groundwater will lead to the lightening of DFe isotopes in river water. The relationship between DAI and DFe concentrations suggested that there was little correlation between DFe concentrations and DAI concentrations in the dry season and a strong correlation between DFe concentrations and DAI concentrations in the wet season. According to the relationship between $\delta^{56}\text{Fe}$ and DFe/DAI ratio, the sources of DFe in MR were rock weathering, anthropogenic inputs and groundwater inputs. The DFe in upstream was mainly from rock weathering, and anthropogenic activities obviously influenced the DFe in the midstream and downstream. Furthermore, the relationship between the $\delta^{56}\text{Fe}$ and DOC concentrations of rivers in different climate zones showed that the heavy Fe isotopes were carried by organic matter.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14132038/s1>, Table S1: The data of DFe concentrations and DFe isotope compositions in the dry and wet seasons of the Mun River.

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