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Article

The Recycling Characteristics of Different Silicon Forms and Biogenic Silicon in the Surface Sediments of Dianchi Lake, Southwest China

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Abstract: Silicon (Si) is one of the main biogenic elements in the aquatic ecosystem of lakes, significantly affecting the primary productivity of lakes. Lake sediment is an important sink of Si, which exists in different Si forms and will be released and participate in the recycling of Si when the sediment environment changes. Compared to carbon (C), nitrogen (N) and phosphorus (P), the understanding of different Si forms in sediments and their biogeochemical cycling is currently insufficient. Dianchi Lake, a typical eutrophic lake in southwest China, was selected as an example, and the contents of different Si forms and biogenic silicon (BSi), as well as their correlations with total organic carbon (TOC), total nitrogen (TN), and chlorophyll a in the surface sediments, were systematically investigated to explore Si's recycling characteristics. The results showed that the coupling relationship of the four different Si forms in the surface sediments of Dianchi Lake was poor ($p > 0.05$), indicating that their sources were relatively independent. Moreover, their formation may be greatly influenced by the adsorption, fixation and redistribution of dissolved silicon by different lake substances. The contents of different Si forms in the surface sediments of Dianchi Lake were ranked as iron-manganese-oxide-bonded silicon (IMOF-Si) > organic sulfide-bonded silicon (OSF-Si) > ion-exchangeable silicon (IEF-Si) > carbonate-bound silicon (CF-Si). In particular, the contents of IMOF-Si and OSF-Si reached 2983.7~3434.7 mg/kg and 1067.6~1324.3 mg/kg, respectively, suggesting that the release and recycling of Si in surface sediments may be more sensitive to changes in redox conditions at the sediment–water interface, which become the main pathway for Si recycling, and the slow degradation of organic matter rich in OSF-Si may lead to long-term and continuous endogenous Si recycling. The low proportion (0.3~0.6%) and spatial differences of biogenic silicon (BSi) in the surface sediments of Dianchi Lake, as well as the poor correlation between BSi and TOC, TN, and chlorophyll a, indicated that the primary productivity of Dianchi Lake was still dominated by cyanobacteria and other algal blooms, while the relative abundance of siliceous organisms such as diatoms was low and closer to the central area of Dianchi Lake. Additionally, BSi may have a faster release capability relative to TOC and may participate in Si recycling.

Keywords: biogenic silicon; Dianchi Lake; different silicon forms; sediments; silicon recycling

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1. Introduction

Silicon (Si) is the second most abundant chemical element on Earth, the parent material element of soil, and the element that is the focus of the current research on global environmental change [1]. Like carbon (C), nitrogen (N) and phosphorus (P), Si is one of the most important biogenic elements and has a significant impact on the primary productivity of the water environment such as oceans and lakes [2,3]. For example, Si is an important component of the cell wall and bone structure of many aquatic organisms. Lake sediment is an important reservoir of Si. Usually, terrigenous Si is placed into the lake in the form of silicon-containing mineral weathering with runoff [4]. Part of the Si is deposited directly, and the other part is in the form of dissolved monosilicic acid, which can be absorbed and utilized by aquatic organisms (such as diatoms, phytoplankton (plants), etc.) [5]. The Si in the sediment exists as different Si phases or fractionations and can be mainly divided into two categories, according to whether it is active or not—valid silicon (Valid-Si) and nonvalid silicon (Nonvalid-Si). Nonvalid-Si comprises more than 90% inactive insoluble silicate minerals, which have little influence on the biogeochemical cycle of Si. On the other hand, Valid-Si, which accounts for a very small proportion, plays a crucial role in the biogeochemical cycle of Si in water environments [6–8]. Valid-Si in sediments includes different Si forms, which combine with different substances and have different biological availability for aquatic organisms. Especially when the environment of sediment changes, the different Si forms in Valid-Si have different sensitivity values and will be dissolved and released in different degrees, just like N and P, which can be absorbed and utilized by aquatic organisms and have a significant impact on the primary productivity of lake water ecosystem. In addition, biogenic silicon (BSi, also known as biological opal) in the sediment is mainly deposited by siliceous plankton (such as diatoms, radiolaria and sponges, etc.), which can comprehensively reflect the spatio-temporal change information of the siliceous biological productivity and play an indicator role in the eutrophication and algal evolution of the lake [9,10]. However, compared with the research studies on C, N and P in lakes, the current research on Si in lake environments is very scarce and even lacks some basic data. There are many deficiencies in the comprehensive understanding of the biogeochemical cycle of Si in lake ecosystems and the coupling relationship between different biogenic elements.

Dianchi Lake is the largest plateau freshwater lake in southwest China, and it is one of the most serious eutrophication lakes in China. Historically, Dianchi Lake was obviously polluted by urban domestic sewage, surrounding industrial, mining and agricultural non-point sources, and the water quality of the lake continued to deteriorate, with eutrophication being very serious [11]. For a long time, there have been a lot of studies on the pollution and control of N and P, the mechanism of burial and release of N and P in sediments and their effects on eutrophication and the cyanobacteria bloom outbreak in Dianchi Lake [12,13]. However, so far, the eutrophication problem in Dianchi Lake is still very prominent, and large-scale algal bloom events occur almost every year, which indicates that the understanding of the relationship between biogenic elements and eutrophication and the mechanism of algal bloom occurrence is not comprehensive. As one of the main biogenic elements, Si, like N and P, is also an important contributor to water nutrients, which may also have a deep impact on the primary productivity of Dianchi Lake, such as the growth and succession of algae [14]. However, until now, in the international community, apart from the preliminary research on the BSi deposition records of Dianchi Lake 10 years ago [15], there is almost no other basic information about the different chemical forms and biogeochemical cycle characteristics of Si in Dianchi Lake. In this study, for the first time, the spatial distribution characteristics of different Si forms and BSi, as well as their correlation with total organic carbon (TOC), total nitrogen (TN) and chlorophyll a, in the surface sediments of Dianchi Lake were analyzed. The filling of these basic information laid a foundation for exploring the sources, bioavailability and biogeochemical cycle characteristics of Si in the sediments of Dianchi Lake. It provides a scientific basis for further understanding of the coupling relationship between the cycle of different biogenic elements, eutrophication, primary productivity succession and lake ecosystem evolution in Dianchi Lake.

2. Materials and Methods

2.1. Sample Collection

In April 2019, six representative sites (S1~S6) in Dianchi Lake, southwest of China, were selected for collecting surface sediments (Figure 1). After the sediment samples were collected, they were quickly transported back to the laboratory in the dark and refrigerated. After a series of pre-treatments, such as freeze-drying, foreign matter removing, agate pear-grinding, and sifting (100 mesh), the samples were frozen and stored at −20 °C for later use.

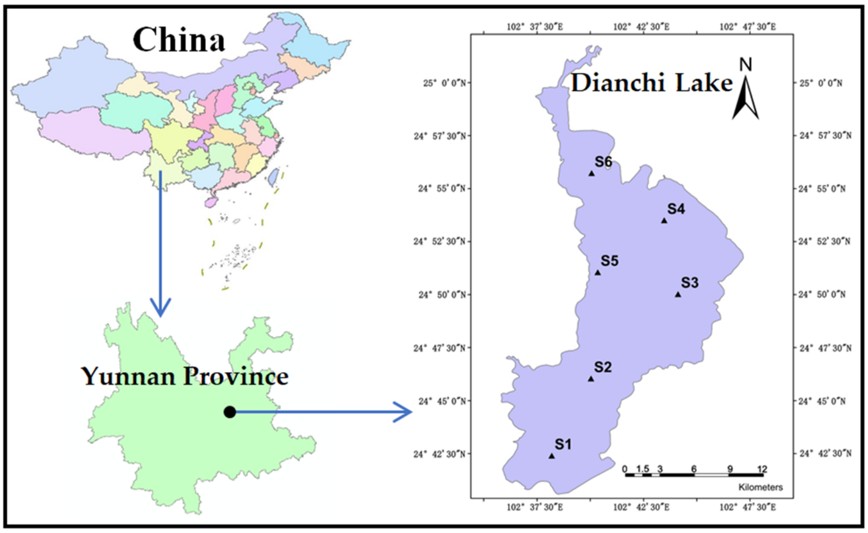

Figure 1. Sediment sample collection site in Dianchi Lake.

2.2. Sequential Extraction of Different Si Forms in Sediments

Valid-Si in sediments can be divided into ion-exchangeable silicon (IEF-Si), carbonate-bound silicon (CF-Si), iron-manganese-oxide-bonded silicon (IMOF-Si) and organic sulfide-bonded silicon (OSF-Si) based on the sequential extraction process of modified Tessier method [6,16,17]. The sequential extraction steps are summarized as follows (Figure 2): The 0.400 g sediment sample was accurately weighed and placed into a 50 mL plastic centrifuge tube, 20 mL 1 mol/L $MgCl_2$ solution was added, and then the sample continuously shaken at room temperature for 1 h. The supernate containing IEF-Si was obtained after centrifugation at 4000 r/min (for 15 min); 20 mL 1 mol/L NaAc-HAc solution was added to the centrifuged residue, which was continuously shaken at room temperature for 5 h. After centrifugation with 4000 r/min (for 15 min), the supernate containing CF-Si was obtained; 20 mL 0.04 mol/L NH_2OH-HCl-25% HAc solution was added to the centrifuged residue and extracted in a water bath at 96 °C for 5 h. After centrifugation at 4000 r/min (for 15 min), the supernate containing IMOF-Si was obtained; 2.5 mL 30% H_2O_2 solution and 1.5 mL 0.02 M HNO_3 solution were added to the centrifuged residue. After the reaction was mild, it was extracted in a water bath at 85 °C for 5 h. After cooling, 2.0 mL 3.2 mol/L NH_4Ac solution was added and then continuously shaken at room temperature for 30 min. After centrifugation at 4000 r/min (for 15 min), the supernate containing OSF-Si was obtained. (It is worth mentioning that glass containers were not used or the retention time of the solution in glass containers was minimized as much as possible to prevent the introduction of external Si during the sequential extraction process of different Si forms, the preparation of the extraction solution and the subsequent determination of Si content). All samples were set in three parallel.

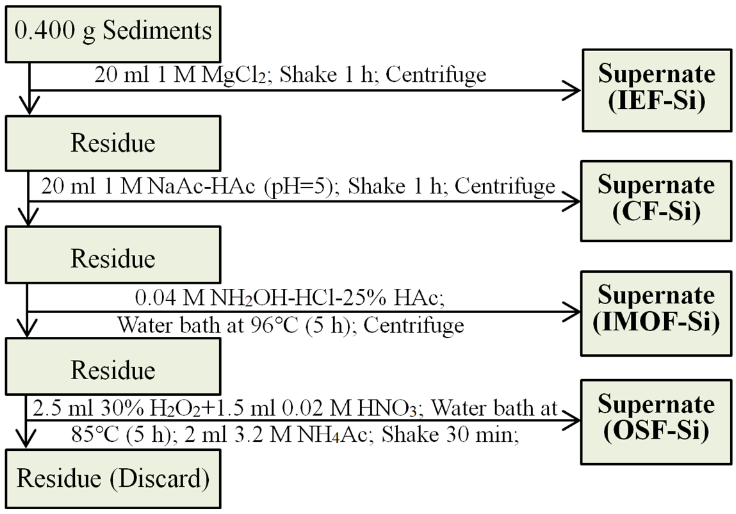

Figure 2. Sequential extraction steps of different silicon (Si) forms in sediments.

2.3. Extraction of BSi in Sediments

In total, 0.100 g sediment sample was accurately weighed and placed into a 50 mL plastic centrifuge tube, and 2.5 mL 10% H_2O_2 solution was added. After standing out for 30 min, 2.5 mL 1 mol/L HCl was added; then, ultrasonic oscillation was carried out for 30 min to effectively remove the carbonate and organic matter. Next, 10 mL pure water was added for washing the residue. After centrifugation at 4000 r/min for 15 min, the supernate was discarded, and the residue was freezing-dried. The, 20 mL 2 mol/L Na_2CO_3 solution was accurately added, ultrasonic oscillation was carried out for 30 min, and the solution was heated in a water bath at 85 °C, stirred at an interval of 2 h, and removed after 5 h. After centrifugation at 4000 r/min for 15 min, the supernate containing BSi was obtained (Figure 3) [15]. All samples were set in three parallel.

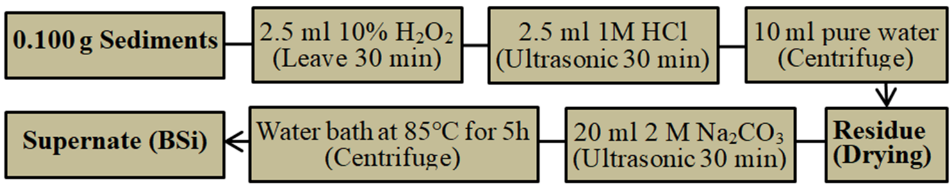

Figure 3. Extraction steps of biogenic silicon (BSi) in sediments.

The content of different Si forms and BSi in the supernate was determined at a wavelength of 812 nm with silicon-molybdenum blue spectrophotometry [18,19].

2.4. Determination of Chlorophyll a in Sediments

In total, 0.050 g sediment sample was accurately weighed and placed into a centrifuge tube, and 5 mL acetone–formaldehyde–water mixture (the three reagents in a volume ratio of 45:45:10) was added; placed into 0 °C ice–water mixture for ultrasonic extraction for 24 h; and quickly centrifuged at 4000 r/min for 10 min. Then, the supernate was taken directly for spectrophotometric determination of chlorophyll a content at wavelengths 649 nm and 665 nm, respectively. All samples were set in three parallel. (Note: Above experimental operation was conducted as far as possible from light, under dark conditions, to prevent the photolysis of chlorophyll *a*).

2.5. Data Statistics

Excel 2010, SPSS 2022 and Sigmaplot 10.0 were used in data sorting, statistics and plotting, respectively.

3. Results and Discussion

3.1. Content and Environmental Significance of Different Si Forms in Sediments

The different chemical forms of Si in the sediments reflect the differences of adsorption, fixation and co-precipitation of dissolved monosilicic acid by different substances in the lake. Due to the different binding and retention abilities of different substances relative to Si, the content of different chemical forms of Si is greatly different; however, on the other hand, different chemical forms of Si have different biological activities and can participate in the biogeochemical recycling of Si in the lake water ecosystem to different degrees. In general, the content of different Si forms in the surface sediments of Dianchi Lake varies greatly and is ranked as IMOF-Si > OSF-Si > IEF-Si > CF-Si (Figures 4–6), which exhibiting similar characteristics to previous reports on other lakes [6].

The IEF-Si content in the surface sediments of Dianchi Lake was generally low and ranged from 77.5 to 89.2 mg/kg, only accounting for 1.7~2.0% of Valid-Si. Moreover, there was no significant difference in IEF-Si content among the surface sediments at different sites in Dianchi Lake ($p > 0.05$) (Figures 4 and 5), which indicates that IEF-Si may be adsorbed by some active ions and sediment minerals, and regional spatial heterogeneity has little influence on it. Compared with the other three Si forms, IEF-Si has the highest biological activity and is the most sensitive to environmental reactions, such as wind and benthic bioturbation at the bottom of the lake, temperature and pH changes at the interface between sediment and water, etc. Therefore, it can easily be dissolved through direct dissolution or ion exchange, and it can then be released into the overlying water to be absorbed and utilized by plankton [6,20].

CF-Si in sediments mainly refers to silicon in the form of co-precipitation with carbonate, which can be easily re-released into the overlying water for biological absorption and utilization along with the carbonate dissolution in an acidic pH environment [21]. CF-Si content in the surface sediments of Dianchi Lake was between 50.1 and 94.2 mg/kg, only accounting for 1.1~2.0% of Valid-Si (Figures 4 and 5). CF-Si content of the surface sediments was the highest at the S1 site (94.2 mg/kg), followed by the S5 site (77.9 mg/kg). The surrounding areas near the S1 site and S5 site of the Dianchi Lake are rich in phosphate mineral resources (mainly carbonate phosphorite and silicate phosphorite) [22,23]. When these minerals are weathered, the carbonate drains gradually into the lake [24], making it more likely to form calcium carbonate and co-precipitate part of Si. It may also be the reason for the relatively high content of CF-Si among the surface sediments at these two sites in Dianchi Lake. The contents of CF-Si in surface sediments at other different sites of Dianchi Lake were very low, and the difference among them was small (<60.4 mg/kg). Additionally, the content of CF-Si in the surface sediments at the same site was the lowest compared with the other three Si forms.

IMOF-Si in sediments mainly refers to silicon combined with iron and manganese oxides. That is, under oxidation conditions, Fe^{2+} and Mn^{2+} in low-priced states can be oxidized to form iron and manganese oxides, which can continuously adsorb and co-deposit dissolved Si in the water. Therefore, IMOF-Si is sensitive to changes in redox conditions at the sediment–water interface at the bottom of lakes. In particular, under anaerobic reduction conditions, with the reduction of Fe^{3+} to Fe^{2+} and Mn^{4+} to Mn^{2+}, Si can be released synchronously with Fe and Mn to the overlying water [25]. IMOF-Si content in the surface sediments at different sites of Dianchi Lake ranged from 2983.7 to 3434.7 mg/kg, accounting for 68.2 to 73.9% of Valid-Si (Figures 4 and 5), which is significantly higher than that of the other three Si forms. Further, there was no significant difference in the contents of IMOF-Si in the surface sediments at different sites of Dianchi Lake. As the most abundant active silicon donor form in surface sediments, when the lake bottom is prone to hypoxia with the intensification of eutrophication,, along with the reduction and dissolution of iron and manganese oxides in the sediment, which can promote the release of IMOF-Si to participate in the Si recycling of water bodies and is the most important way for the release of silicon within sediment.

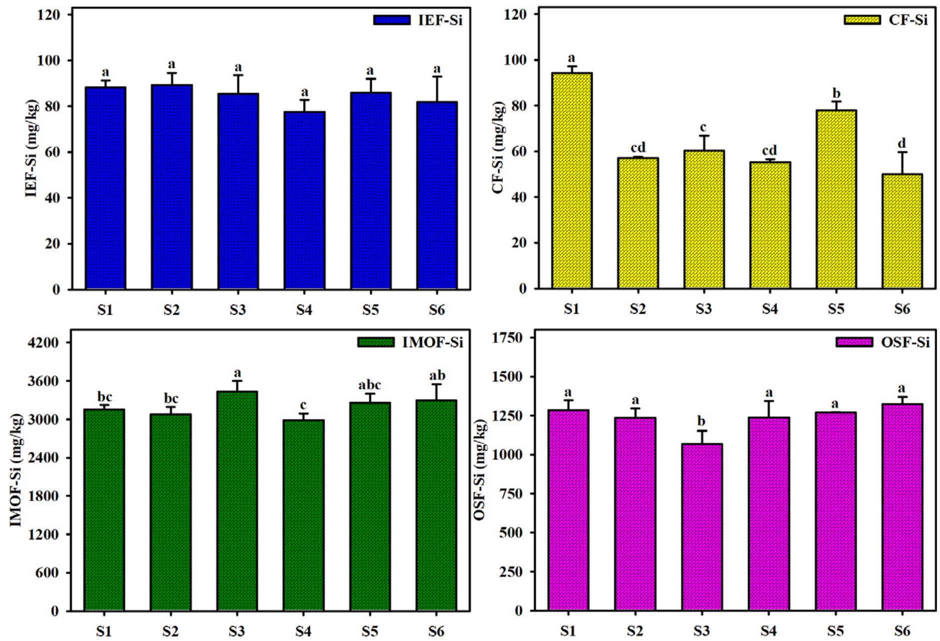

Figure 4. Contents of different Si forms in surface sediments of Dianchi Lake. (Note: The different letter indicated that there was significant difference in the contents of same Si form at different surface sediment site ($p < 0.05$)).

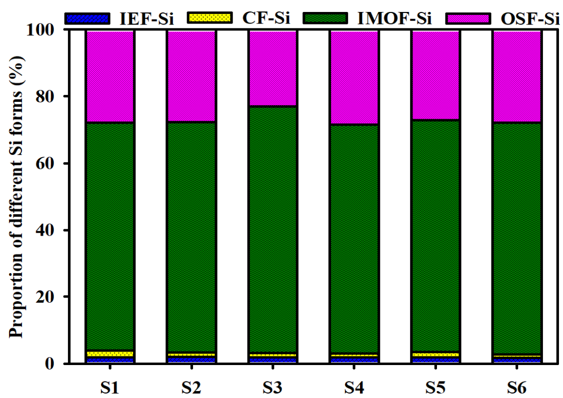

Figure 5. Proportion of different Si forms in surface sediments of Dianchi Lake.

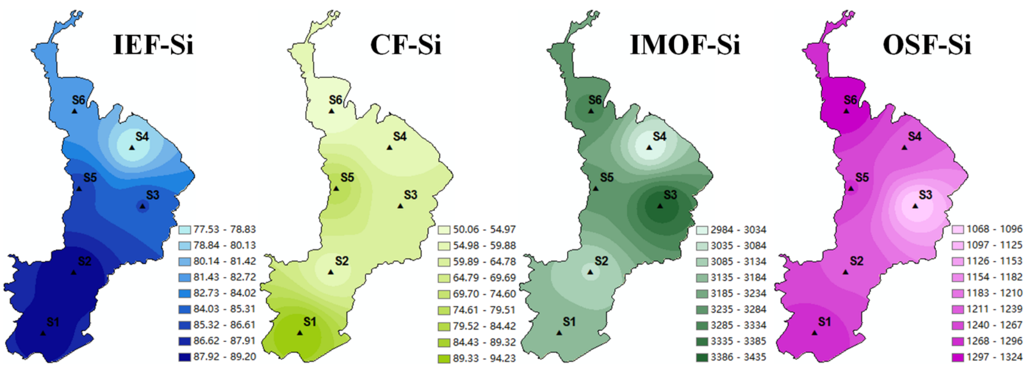

Figure 6. Spatial distribution of different Si forms in surface sediments of Dianchi Lake.

OSF-Si in sediments mainly refers to silicon combined with organic sulfide, which is relatively stable and has low bioavailability, and it cannot be easily activated and released in a short period of time [26]. However, OSF-Si is released slowly along with the degradation of organic matter in sediment. In the surface sediments of Dianchi Lake, OSF-Si content ranged from 1067.6 to 1324.3 mg/kg, accounting for 23.0 to 28.4% of Valid-Si (Figures 4 and 5). There is no significant difference in OSF-Si content in the surface sediments at other sites, except for the S3 site (with the lowest OSF-Si content of 1067.6 mg/kg in the surface sediment) of Dianchi Lake. In general, OSF-Si, as the second largest active silicon form in the surface sediments of Dianchi Lake, along with the degradation of organic matter in sediments, can be released to participate in the Si recycling of water bodies and may play an important role in the biogeochemical recycling of Si in the water ecosystem of Dianchi Lake in the long run.

In summary, it can be calculated that the content of Valid-Si in the surface sediments of Dianchi Lake ranged from 4352.9 to 4753.7 mg/kg and that in its content in the surface sediments at different sites of the whole lake shows relatively small difference (Figures 7 and 8). Four different Si forms of Valid-Si with different biological availability and environmental sensitivity, becoming the main internal silicon contributor, can participate in the Si recycling of lake water ecosystems to different degrees. The total amount of the most Bioactive-Si (which mainly contains IEF-Si and CF-Si) in the surface sediments ranged from 131.9 to 182.4 mg/kg, accounting for only 2.8 to 3.9% of Valid-Si (Figure 7). Moreover, the amount of Bioactive-Si in the surface sediments at the S1 and S5 sites was significantly higher than that at the other sites, mainly due to the significantly higher CF-Si content at the two sites (Figure 8). Although the amount of Bioactive-Si in the surface sediments of Dianchi Lake is very small in general, it has a crucial and important impact on the biogeochemical recycling and primary productivity of silicon in its lake water environment.

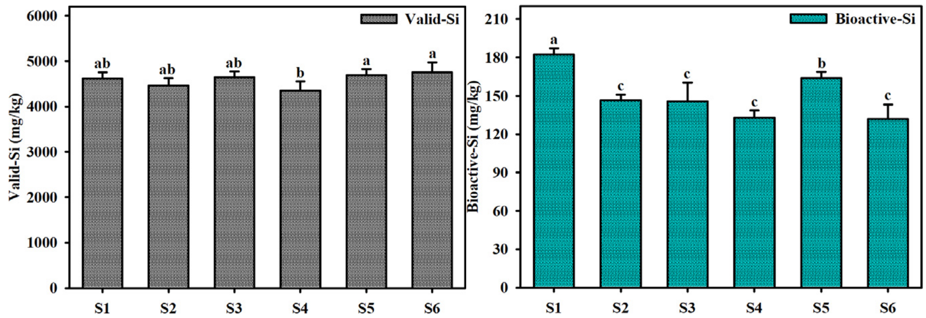

Figure 7. Contents of Valid-Si and Bioactive-Si in surface sediments of Dianchi Lake. (Note: The different letter indicated that there was significant difference in the contents of Valid-Si and Bioactive-Si at different surface sediment site, respectively. ($p < 0.05$)).

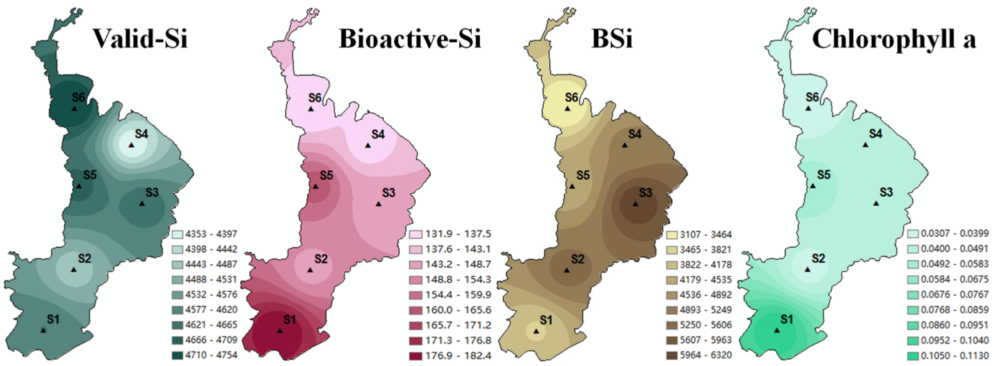

Figure 8. Spatial distribution of Valid-Si, Bioactive-Si, BSi and chlorophyll a in surface sediments of Dianchi Lake.

3.2. Indicator of BSi Contents, TOC/BSi (C/Si) and TN/BSi (N/Si) in Sediments

In natural water, silicon often exists in the form of dissolved monomer orthosilicate, which is an essential nutrient for the growth and reproduction of siliceous plankton. Dissolved silicon can be absorbed and assimilated by siliceous plankton, such as diatoms, radiolaria and spongium. After the death of these siliceous plankton, the diatom debris usually settles faster than other algae, the solubility of the diatom shell is relatively low, and it is continuously deposited to form biogenic silicon (BSi). Therefore, the significant difference between BSi and different chemical forms of silicon in sediments is that silicon with different chemical forms mainly reflects the state of silicon adsorbed and combined by different sediment substances, while BSi comes from the deposition of siliceous aquatic organisms, such as diatoms, which clearly indicates the occurrence of changes in the primary water productivity process.

The BSi content in the surface sediments of Dianchi Lake ranged from 3107.1 to 6319.9 mg/kg and had a certain spatial distribution difference (Figures 8 and 9). Overall, the BSi content in the sediments near the center of the lake (such as at the S2, S3, and S4 sites) was higher than that in the northern and southern areas near the lakeside (such as at the S1, S5, and S6 sites). To a certain extent, this indicated that there were spatial differences in the level of primary productivity (such as diatoms) in different regions of Dianchi Lake. It is worth noting that BSi at different surface sediments in Dianchi Lake accounted for 0.3~0.6%, with an average of 0.5%, which is relatively low. For example, the mean BSi content in the sediments of three non-eutrophication reservoirs in southwest China was 2.8%, 1.3%, and 1.8%, respectively [27]. Dianchi Lake is a typical eutrophic lake, and algal bloom events often occur there. The dominant species of algal bloom is cyanobacteria [28,29]. As different algae compete for growth, non-dominant diatoms are relatively unsuccessful and their abundance further decreases, which is one of the possible reasons for the low BSi content in the sediments of Dianchi Lake. However, BSi content in sediments can still be a clear indication of the spatial change and succession behavior of diatoms, and the sediment core samples can be used tp evaluate the historical succession of diatoms through the deposition records of BSi, providing references for the historical evolution of a lake environment [15]. Diatom sedimentation is generally fast, but the mineralization rate is relatively slow compared with nitrogen and phosphorus, which can easily lead to a lack of silicon in the water and an imbalance of silicon, nitrogen and phosphorus. Therefore, eutrophic algae, such as cyanobacteria, will gradually become the dominant species [30,31]. In addition, generally, finer particles in the sediments near the lake center are conducive to the accumulation of BSi, and the coarser and better permeable sediments near the lake shore are conducive to the dissolution and release of BSi in the sediments [32,33], which is consistent with the fact that BSi content in the lake center of Dianchi Lake is relatively higher than that in the areas near the lake shore in the north and the south.

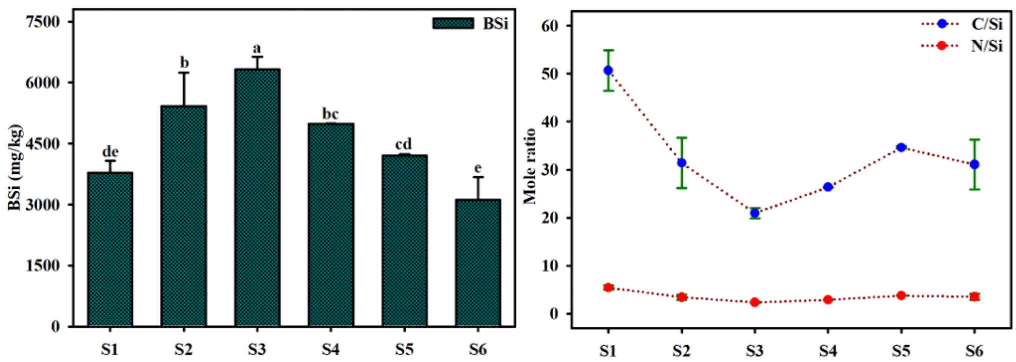

Figure 9. BSi content and its ratio to total organic carbon (TOC (C/Si)) and total nitrogen (TN (N/Si)) in surface sediments of Dianchi Lake. (Note: The different letter indicated that there was significant difference in the contents of BSi at different surface sediment site. ($p < 0.05$)).

Based on the TN (0.5~1.0%) and TOC (4.1~8.2%) data collected from the same batch of sediments by Jin [22], the C/Si atomic molar ratio of TOC to BSi in the Dianchi Lake surface sediments is between 20.9 and 50.7, and the N/Si atomic molar ratio of TN to BSi is between 2.5 and 5.2 (Figure 9). The atomic molar ratio of C/Si and N/Si at the middle S3 site is relatively low, while it is the highest at the S1 site in the south. Combined with the famous Redfield ratio (C/N/Si = 106:16:16, i.e., C/Si = 6.625; N/Si = 1) [34,35], both C/Si and N/Si in sediments were significantly higher than the Redfield values in this study, indicating that the dissolution and release rate of BSi in surface sediments may be higher than the degradation rate of organic matter, and it can preferentially participate in recycling. In addition, the pH of water in the Dianchi Lake is generally alkaline (pH~9), which may also promote the release and dissolution of BSi in surface sediments [36,37].

3.3. Correlation between Different Si Forms, BSi, TOC, TN and Chlorophyll a in Sediments

There is no significant correlation between the four different Si forms in the surface sediments of Dianchi Lake, indicating that the dissolved Si in water may exist or be adsorbed by different substances to co-precipitate and be redistributed relatively independently, while the direct coupling and sediment transport of terrigenous Si may have little influence (Table 1). IMOF-Si and CF-Si in surface sediments were significantly correlated with Valid-Si and Bioactive-Si, respectively (their correlation coefficients were 0.860 and 0.938, respectively; $p < 0.01$) (Table 1), indicating that the two had a decisive influence on the contents of Valid-Si and Bioactive-Si, respectively. This also shows that endogenous active Si release from surface sediments may be more sensitive to changes in redox conditions or pH at the sediment–water interface. The content of chlorophyll a in the surface sediments of Dianchi Lake ranged from 3.1×10^{-2} to 11.4×10^{-2} mg/g, and the content of chlorophyll a at the S1 site was significantly higher than that at the other sites (Figures 8 and 10). In the surface sediments of Dianchi Lake, CF-Si was significantly correlated with TOC, TN and chlorophyll a, respectively ($p < 0.01$), and TOC, TN and chlorophyll a were also significantly correlated with each other ($p < 0.01$) (Table 1). This indicates that there was homology and a coupling relationship between them. TOC is mainly derived from the deposition of organic matter, and the C/N atomic molar ratio of TOC to TN in the surface sediments of Dianchi Lake is between 8.9 and 9.4, indicating that the organic matter in the surface sediments is mainly algae-derived (rather than comprising terrestrial macroplants) [22,38]. In other words, the residual sedimentation of a large number of cyanobacteria with chlorophyll a in the water body of Dianchi Lake are the main contributors to the organic matter in its surface sediments. In addition, the formation of CF-Si may be related to the carbonate that co-precipitated Si directly into the sediment. Moreover, this very significant correlation indicates that the plankton in Dianchi Lake may also absorb water carbonates, making their biological skeleton contain both carbonates and silicates [39,40]. Therefore, the deposition of biological residue may become a key contributor to CF-Si. BSi is not correlated with TOC, TN and chlorophyll a, which also proved that Dianchi Lake, as a eutrophic lake, may have an insignificant impact on the contribution of siliceous biological residues, such as diatoms, to the organic matter in the sediments. On the other hand, this indicated that the dominant bloom algae, such as cyanobacteria, play a decisive role in the accumulation of organic matter in surface sediments. In addition, there was a significant negative correlation between OSF-Si and BSi ($R = -0.620$, $p < 0.01$). However, there was no significant correlation between OSF-Si and TOC, TN, or chlorophyll a (Table 1). The difference between biosilicon and silicone (BSi-(OSF-Si)) showed a good positive correlation with BSi ($R = 0.998$, $p < 0.01$) and a significant negative correlation with OSF-Si ($R = -0.670$, $p < 0.01$) (Figure 11). Since OSF-Si is generally considered to be an organosilicon form, these results indicated that OSF-Si in surface sediments may be mainly derived from the accumulation of residues of another class of siliceous organisms, which may be in obvious competition with diatoms (major contributors to BSi) for the uptake of silica in water bodies.

Table 1. Correlation of different Si forms, BSi, chlorophyll a, TOC and TN in surface sediments of Dianchi Lake.

	IEF-Si	CF-Si	IMOF-Si	OSF-Si	Valid-Si	Bioactive-Si	BSi	Chlorophyll a	TN	TOC
IEF-Si	1									
CF-Si	0.287	1								
IMOF-Si	0.137	−0.083	1							
OSF-Si	−0.115	0.175	−0.269	1						
Valid-Si	0.138	0.098	0.860 **	0.251	1					
Bioactive-Si	0.601	0.938 **	−0.020	0.105	0.132	1				
BSi	−0.024	−0.193	0.088	−0.620 **	−0.245	−0.170	1			
Chlorophyll a	0.102	0.850 **	−0.263	0.133	−0.131	0.746 **	−0.254	1		
TN	0.402	0.722 **	−0.265	−0.026	−0.204	0.748 **	0.168	0.644 **	1	
TOC	0.394	0.733 **	−0.280	0.001	−0.206	0.754 **	0.140	0.654 **	0.999 **	1

Note: "**" represents a significant correlation ($p < 0.01$, n = 18).

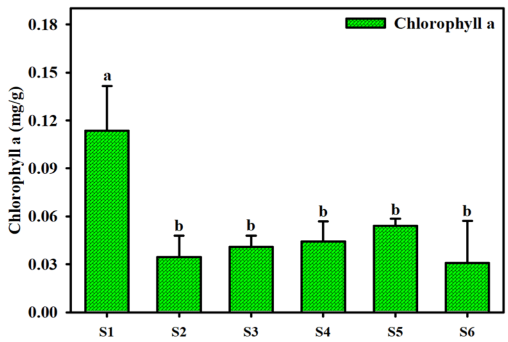

Figure 10. Chlorophyll a content in surface sediments of Dianchi Lake. (Note: The different letter indicated that there was significant difference in the contents of chlorophyll a at different surface sediment site. ($p < 0.05$)).

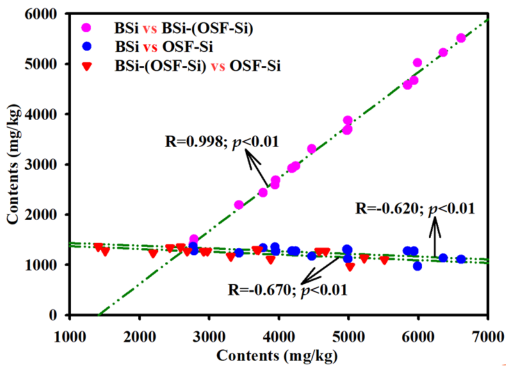

Figure 11. Correlation of BSi, OSF-Si and BSi-(OSF-Si) in surface sediments of Dianchi Lake.

4. Conclusions

(1) The coupling relationship between the four different Si forms in the surface sediments of Dianchi Lake was poor ($p > 0.05$), indicating that their sources were relatively independent and that their formation was more likely to be influenced by the adsorption, fixation and redistribution of dissolved silicon by different lake substances. Moreover, the influence of direct input and transport settlement of terrigenous silicon might be very small. The order of the relationship between the content of different Si forms in the surface sediments was IMF-Si > OSF-Si > IEF-Si > CF-Si.

(2) IMOF-Si (2983.7~3434.7 mg/kg) and CF-Si (50.1~94.2 mg/kg) in the surface sediments of Dianchi Lake had decisive effects on Valid-Si and Bioactive-Si, respectively. Furthermore, the release and recycling of sediment Si may be more sensitive to the redox conditions or pH changes at the sediment–water interface. In particular, the change of sediment redox conditions was the main method of silicon recycling in the

surface sediments of Dianchi Lake. In addition, the slow degradation of OSF-Si-rich organosilicones may lead to long-term and continuous internal silicon recycling.

(3) The low proportion (0.3~0.6%) and large spatial difference of BSi in the surface sediments of Dianchi Lake, as well as the poor correlation between BSi and TOC, TN and chlorophyll a, indicated that the primary productivity of Dianchi Lake was still dominated by bloom algae, such as cyanobacteria, while the relative abundance of siliceous organisms such as diatoms was low and closer to the lake center. However, BSi may have a faster dissolution and release ability than TOC to participate in silicon recycling within lake water ecosystems.

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