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Geochemical Cycle and Environmental Effects of Sulfur in Lakes

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Abstract. Sulfur is one of the main elements controlling the redox reactions in lakes. The nature of the geochemical cycle of sulfur is redox, which will have an important impact on the lake environment during its cycle. The paper discussed the the geochemical cycling mechanism of sulphur in lakes, control factors, and the various possible effects on the environment during the cyclic process. In the study of lake environment, the geochemical cycle of sulfur should be used rationally, for example, its positive effect should be used to improve the lake environment, and the adverse impact on the lake's ecological environment during the sulfur cycle should be reduced as much as possible.

1. Introduction

Sulfur is widely distributed in the earth's crust, mainly in the form of sulfide minerals, sulfate minerals, and sulfur. Sulfur, as one of the main elements of the proteins that make up living organisms, plays an important role in the structure and function of proteins. However, when the sulfur concentration is too high in some forms, it will be toxic to proteins. When sculpture is released into the environment through the combustion of fossil fuels, toxic and harmful gases sulfur dioxide will be released to pollute the air, and then enter the soil water body with the action of rainfall, resulting in the acidification of water bodies and soil, causing serious damage to the ecological environment [1]. Therefore, sulfur is often studied as a pollutant in environmental science.

As the most important aquatic ecosystem on the land, lakes have the functions of regulating floods, irrigating farmland, providing water resources, growing aquatic animals and plants, shipping, improving the ecological environment, and recreation and entertainment [2]. And its ecological environment has an important impact on the normal development of the region. China is rich in lake resources, there are many types of lakes distributed widely. Lakes play an important role in the development of society [3]. However, with the development of society, a large number of industrial and agricultural waste water and domestic sewage were discharged into lakes, and the awareness of environmental protection was weak, resulting in serious damage to the lake ecosystem [4]. In the world, a large number of lakes suffered from acid rain, eutrophication, and heavy metal pollution [5, 6, 7]. As one of the main elements controlling the redox reactions in lakes, sulfur is indispensable for the normal operation of lakes. First, sulfur is the main component of acid rain as a pollutant, to restore acidified lakes, we need to study the sulfur cycle. Secondly, the geochemical cycle of sulfur contains a series of physical, chemical, and biological processes in lake, especially the sedimentation and transformation of heavy metals. Thirdly, the sulfur cycle has a certain influence on the circulation of nutrients in lakes. Therefore, the sulfur cycle has become a hot issue in the study of lake ecological environment.

2. The Control Factors of Sulfur Cycle in Lakes

Sulfur enters the lake mainly in the form of sulfate. There are two main sources of sulfate in lakes, namely the formation of sulfate through the weathering of rock minerals in the basin and then enter lakes with the water, and the sulfur dioxide in the atmosphere enters the basin through atmospheric precipitation, then brought into the lake by the surface water system [8]. After sulphate enter the lake, they begin to participate in various geochemical cycles in the lake, including physical, chemical, and biological cycles, from one form to another.

The nature of the sulfur cycle in lakes is the redox reaction that takes place with the participation of microorganisms. The reduction of sulphate is considered to be the beginning of the sulfur cycle in the lake [9]. Under normal circumstances, the reduction of sculpture is carried out in an oxygen-deficient environment with the participation of anaerobic microorganisms. In anoxic water environments, sulfate is the electron acceptor of anaerobic microorganisms and is reduced to low-valent sulfur [10]. At the same time, other physical, chemical and biological effects, bio oxidation-reduction, dissolution-precipitation, adsorption-desorption, migration-transformation, diffusion-burial occur simultaneously. But the discovery of oxygen-resistant sulfate-reducing bacteria by Hardy and Hamilton in 1981, indicating the possibility of sulfate reduction in the presence of oxygen [11]. And then Zamana et al. discovered the presence of sulfur reduction in the oxide layer of lakes in Lake Doroninskoe, a soda-type lake in Russia, the content of hydrogen sulfide in the layer was inversely proportional to the content of oxygen, indicating that oxygen stilling restrict vulcanization to some extent(Fig 1) [12].

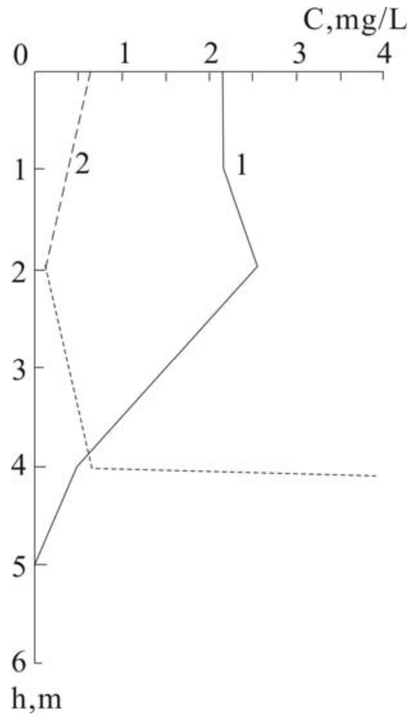

Figure 1. Distribution of (1) O2and (2) HS–in water at the central station of Lake Doroninskoeon August 2, 2006 (L. V. Zamana and S. V. Borzenko 2007).

In the reduction process of sulfur, the place where the reduction takes place is extremely important, so scholars have done a lot of related research. For most completely convective lakes, the sediment-water interface is the main site for sulfate reduction, and sculpture also deposit into the sedimentary reservoir at here [13]. The sediment-water interface is a special interface composed of water bodies and sediments. It is the main site for transport of materials. Because of the less oxygen, the low redox potential, and the existence of a large number of sulfur-reducing bacteria [14], the sediment-water interface become an excellent place for sulfur reduction.

However, in lakes with high salinity, because of the difference in salinity between the upper and lower layers, the density of the lower layer of water is relatively large, and the upper layer of water is relatively light, the water layer is perennially stratified. Such lakes are called meromictic lakes [15]. For meromictic lakes with chemocline, the sulfur cycle occurs mainly at the interface of the chemocline. There was a large amount of phototrophic bacteria (such as purple sulfur bacteria) and sulfate-reducing bacteria in the layer. In summer, phototrophic bacteria multiplied rapidly, polysulfides were produce by the reaction that hydrogen sulfide reacted with sulfur in the cells of bacteria, and the concentration of sulfides became low. After summer, the number of sulfur-reducing bacteria increased, and sulfates were reduced to sulphides. The carbon source consumed by sulfur-reducing bacteria in this layer was fixed by phototrophic bacteria [16].

The cycle of sulfur in meromictic lakes was affected by the seasons. Because of the effects of chemical and microbial redox caused by the season variation, different forms of sulfur appeared. The reduction of bacteria was greater than oxidation in the summer, large numbers of polysulfides were formed. In winter, the content of elemental sulfur was decreased, the content of thiosulfate was increased, and the content of oxygen was decreased (Fig 2) [17].

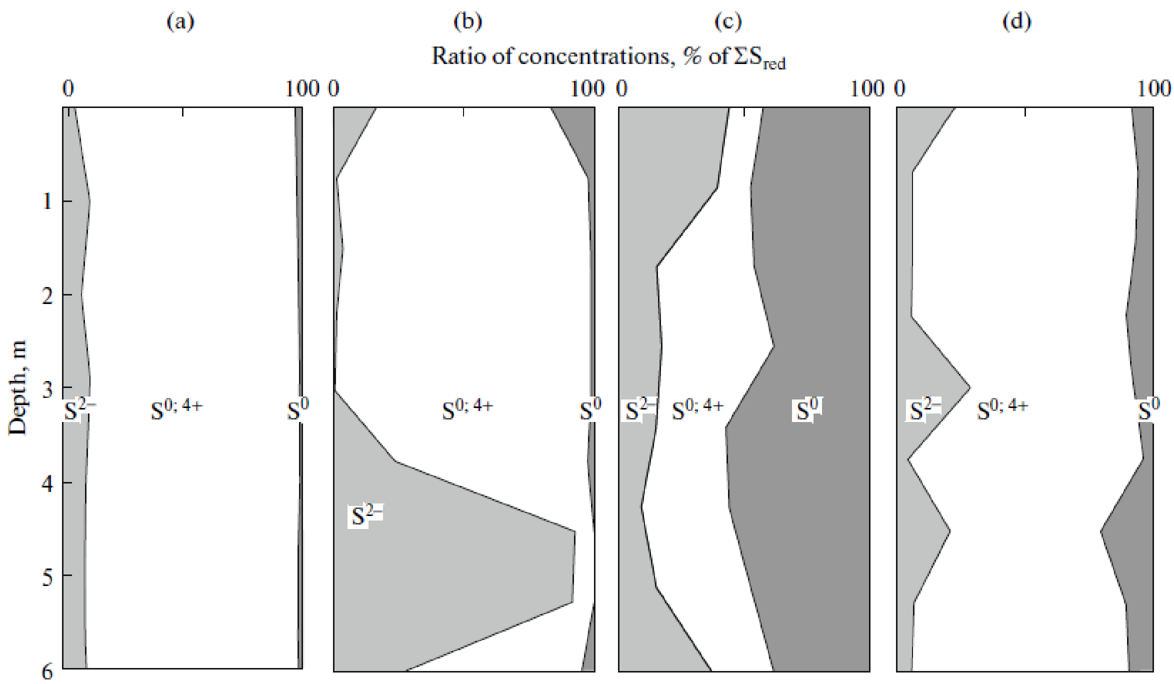

Figure 2. The ratio of reduced sulfur forms vertically in the water mass of Lake Doroninskoe: (a) March 2, 2007; (b) October 15, 2007; (c) February 28, 2008; (d) September 1, 2009. (L. V. Zamana and S. V. Borzenko 2011).

And the sulfur oxidation process is generally completed with the participation of sulfur-oxidizing bacteria. In this process, the reduced sulfur was oxidized to the high valence state, and provided the bacteria with the energy needed for growth [18]. Sulfur-oxidizing bacteria can be divided into phototrophic bacteria and chemotrophic bacteria. Phototrophic bacteria were distributed in anaerobic waters and chemotrophic bacteria were distributed in oxygenated waters. Therefore, the oxidation of sulfur could be carried out in both anoxic and aerobic environments.

3. The environmental effects of the sulfur geochemical cycle

The sulfur cycle in lakes is a complex geochemical process (Fig. 3) [19-20]. Sulfur is one of the main elements participating the material and energy cycle in the lake, and the geochemical cycle of it affects the lake waters, heavy metals in sediments, water nutrients element P, lake pH, organic matter, and a series of materials and energy transformation.

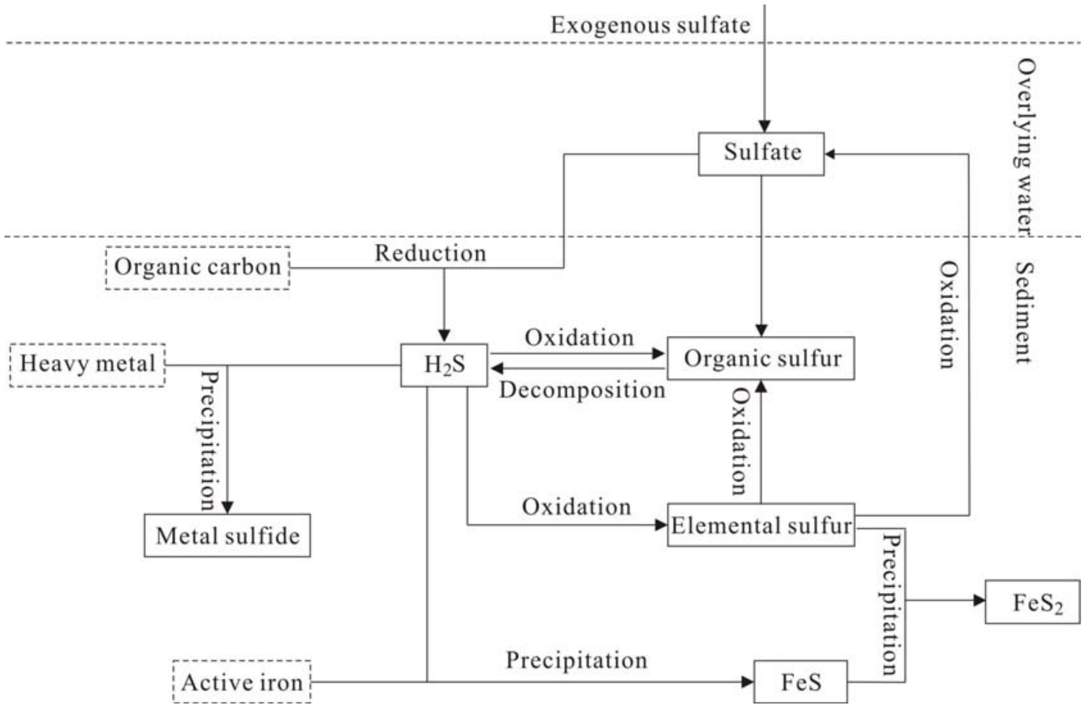

Figure 3. Schematic presentation of the sulphur cycle in lake sediments (Holmer and Stockholm, 2001; Xijie Yi, 2010).

First of all, as one of the pollution elements, sulfur may cause the increasing of sulfate content and the acidification of the water body when it entered the lake by rainfall and acid mine drainage. In the sulfur cycle, there are two types of sulfate removal in natural waters, ① reduced to organic sulfur compounds and deposited in sediment by biological assimilation absorption, ② under the action of sulfur reducing bacteria, reduced to the reduced sulfur and organic sulfur continuously and deposited. In addition, Berner believed that the sulfate reduction formula at the sedimentary interface was as follows (1), the sulfate reduction process continuously released HCO_3^- to the water, increasing the alkalinity of the water and restoring the pH of the water [21].

$$2FeOOH+ 6CH_2O+ 3SO_4^{2-}\rightarrow 6HCO_3^-+ FeS+ FeS_2+ 4H_2O \quad (1)$$

At the same time, sulfate degradation was accompanied by the mineralization of organic matter. Organic matter contained a large amount of nitrogen and phosphorus, under the action of SRB, some of the organic nitrogen and phosphorus that had been deposited could be converted into dissolved state and released into the water again. The reaction process was shown in Equation (2) [23]. Therefore, on the one hand, the sulfur cycle degrades the organic matter, and on the other hand, it increases the nutrient elements in the water and increases the possibility of eutrophication.

$$(CH_2O)\ 106\ (NH_3)16H_3PO_4+53SO_4^{2-}+14H^{+}\rightarrow 106HCO^{3-}+16NH^{4+}+HPO_4^{2-}+53H_2S \quad (2)$$

During the sulfate reduction process, the hydrogen sulfide formed could be further reacted with elemental sulfur to generate pyrite (FeS_2) and buried [23]. In addition, it could react with heavy metal ions to form insoluble heavy metal deposits and thus reduced heavy metal toxicity in lake water [24].

4. The Enlightenment of Sulfur Geochemical Cycle to Environmental Science

The sculpture cycle is a natural circulation phenomenon in lakes and has a positive effect on the lake's environment, such as reducing Lake PH, eliminating excess sulphates in lakes, and reducing the toxicity of heavy metals in waters and sediments. However, it could also cause negative effects, such as increasing the concentration of N and P in lakes and causing eutrophication. Therefore, the geochemical cycle of sulfur is an intricate process, in the science of lakes, we need to make rational use of the laws of the geochemical cycle of sulfur and actively guide them so as to greatly promote the process of the lake's ecological health in the course of its circulation, while minimizing the negative effects in the cycle as much as possible. To rationally use the mechanism of the sulfur cycle, human intervention is needed to achieve the purpose of improving the lake's ecological environment. For example, FeS has the ability to repair heavy metals in lake sediments. Li Haibo et al. (2017) had shown that the addition of FeS at 5% was the strongest for the repair of heavy metals, and increased its content did not increase the ability to repair heavy metals, instead, it would cause lake pollution [25]. The ratio of acidic volatile sulfur (AVS) and simultaneously extracted metals (SEM) could be used to evaluate the bioavailability and toxicity of heavy metals in lake sediments, when SEM/AVS<1, the AVS in sediments was sufficient to fix all SEM, and heavy metals were difficult to enter the aqueous phase and it was not biologically toxic. And when the SEM/AVS >1, the biological toxicity of heavy metals in sediments could not be ignored. Another study pointed out that, when ∑SEM/AVS was between 2.34 and 8.32, heavy metals might cause damage to large invertebrates, and when ∑SEM/AVS>9, it might be toxic to bentonic. Organisms [26].

References

[1] Hu Zhengyi, Xu Chengkai, Sulphur in soil and environmental quality, Beijing Science Press. (2002) 283 - 307.
[2] Ma Ronghua, Yang Guishan, Duan Hongtao, Jiang Jiahu, Wang Sumin, Feng Xuezhi, Li Ainong, Kong Fanxiang, Xue Bin, Wu Jinglu, Li Shijie, Quantities,area and spatial distribution of lakes in China. Science of China: Earth Science, 41 (2011) 394 - 401.
[3] Li Yuzhao,Liu Yong,Yan Xiaopin.Research on Evaluation Index System of Watershed Ecological Security Based on DPSIR Model .Acta Scientiarum Naturalium Universitatis Pekinensis. 48 (2012) 971 - 981.
[4] Ding Zhiyong, Pu Jia, Ji Lili.Abuduanwaili, Characteristics and Evaluation of Heavy Metal Pollution in Surface Sediments of Main Lakes in China, Environmental Engineering. 35 (2017) 136-141+102.
[5] Miao Hui, Shen Yi, Jiang Yu, Shi Huiyu, Zhang Yalei, Cai Yongjiu, Distribution of Nitrogen, Phosphorus and Organic Matter in Surface Sediments of Chaohu Lake and Their Pollution Assessment, Ecology and Environment. 12 (2017) 2120 - 2125.
[6] CAROHN C F, KUMAR PS, SARAVANAN A, et al., Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review, Joumal of environmental chemical engineering. 5 (2017) 2782 - 2799.
[7] Wang Zhongliang, Sulfur isotope tracer of sulphate source in karst lakes in southwest China, Chinese Society of Minerals and Minerals. The 11th Annual Conference of the Chinese Society of Mineralogy and Geochemistry. Chinese Society of Mineral Rock and Rock Geochemistry. 2 (2007).
[8] Mossmann J R Aplitl A, Curtis C D, et a1, Geochemistry of inorganic sulphur in organic-Rich sediments from the Peru Margin, Geohimica et Cosmochica Acta. 55 (1991) 3581 - 3595.

[9] Werner Eckert, Alexandra V Turchyn, Gilad Antler, and Alexey Kamyshny Jr, Annual sulfur cycle in a warm monomictic lake with sub-millimolar sulfate concentrations Nadav Knossow1, Barak Blonder1, Geochem Trans. 16 (2015).
[10] Yu Fenfang, Effect of exogenous sulfates on nutrients and heavy metals in the sediments of the ink lake in Wuhan, Huazhong Agricultural University, 2013.
[11] J. A. Hardy and W. A. Hamilton, Curr. Microbiol. 6, 259 (1981).
[12] L. V. Zamana and S. V. Borzenko, Hydrogen Sulfide and Other Reduced Forms of Sulfur in Oxic Waters of Lake Doroninskoe, Eastern Transbaikalia. Doklady Earth Sciences. 417 (2007) 1268 - 1271.
[13] Luo Shasha, Wan Guojiang, Study on the Mechanism of Geochemical Cycle of Sulfur in Lake Sediments, Sichuan Environment. (2000) 1-3.
[14] Wu Fengchang, Wu Guojiang, Huang Ronggui, Cai Yurong, Environmental Effects of Sulphate Heightening in Lake Water, Acta Scientiae Circumstantiae, (1998) 30 - 35.
[15] Wetzel, Robert G, Limnology: Lake and River Ecosystems (Third ed.), New York: Academic Press. (2001).
[16] Jörg Overmann J. Thomas Beatty, H. Roy Krause, Ken J. Hall, the sulfur cycle in the chemocline of a meromictic salt lake, Limnology and Oceanography. 41 (1996) 147 - 156.
[17] L. V. Zamana and S. V. Borzenko, Elemental Sulfur in the Brine of Lake Doroninskoe (Eastern Transbaikalia). Doklady Earth Sciences, 438 (2011), pp, 775 - 778.
[18] W. Eckert, Y. Z. Yacobi, and H. G, A Bloom of a Brown Phototrophic Sulfur Bacterium in Lake Kinneret: Hydrochemical Aspects, Truper Microb Ecol. 20 (1990) 273 - 282.
[19] Holmer M, Storkholm E, Sulphate reduction and suphur cycling in lake sediments: a review, Freshwater Biology. 46 (2001) 431 - 451.
[20] Yin Xijie, Zhou Huaiyang, Yang Qunhui, et al., Sulfate Reduction and Distribution of Different Forms of Sulfide in Coastal Sediments of Qi'ao Island, Pearl River Estuary. Chinese Journal of Oceanography. 32 (2010) 31 - 39.
[21] Berner R.A., New geochemical classification of sedimentary environ-ments, Sediment Petrology. 51 (1981) 359 - 365.
[22] Step Qingyun. Changes of dissolved oxygen in shallow lakes affect sediment P and N, Chinese Academy of Environmental Sciences, 2006.
[23] Luther G W, Pyrite synthesis via polysulfide compounds．Geochimica et Cosmochimica Acta. 55 (1991) 2839 - 2849.
[24] Lee J S, Lee J H, Influence of acid volatile sulfides and simultaneously extracted metals on the bioavailability and toxicity of a mixture of sediment—associated Cd, Ni, and Zn to polychaetes Neanthes arenaceodentata, Science of the Total Environment. 338 (2005) 229 - 241.
[25] Li Haibo, Cao Menghua, Wu Dingshan, Yang Lanfang, Fang Ding, Efficiency and Mechanism of Stabilization of Ferrous Sulfide to Remedy Heavy Metal Contaminated Lake Sediments, Techniques and Equipment for Environmental Pollution Control. 11 (2017) 3258 - 3263.
[26] Jia Zhenbang, Liang Tao, Lin Jianzhi, Lv Fengwei, Toxicity of Acid-Volatile Sulfide on Heavy Metals in River Sediments in Hong Kong, Acta Scientiarum Naturalium Universitatis Pekinensis. Z1 (1998) 247 - 254.