Archives of Environmental Sciences and Environmental Toxicology

Fang, et al. Arch Environ Sci Environ Toxicol 5: 134.

www.doi.org/10.29011/2688-948X.100134

www.gavinpublishers.com

Research Article

Modeling the Distribution of Copper Loading Using Water Quality Modeling and its Impact Factor Analysis

Jiawei Fang, Huan Tang, Jing Yuan*

Department of Civil Engineering, Tongling University, Tongling, China

***Corresponding author:** Jing Yuan, Department of Civil Engineering, Tongling University, Tongling, 244000, China

Citation: Fang J, Tang H, Yuan J (2022) Modeling the Distribution of Copper Loading Using Water Quality Modeling and its Impact Factor Analysis. Arch Environ Sci Environ Toxicol 5: 134. DOI: 10.29011/2688-948X.100134

Received Date: 31 March, 2022; **Accepted Date:** 8 April, 2022; **Published Date:** 12 April, 2022

Abstract

In this study, to trace the influence of copper pollution sources on sediments, the copper distribution in Lijiang River was studied with water quality model tools. In addition, the effects of velocity, sources, and hardness on the characteristic parameters of copper were investigated. The goal is to quantitatively reveal the space-time evolution law of copper in the surface sediments of Lijiang River during the period of over exploitation of the surrounding metal industry from 2005 to 2015 through model simulation, and to reveal the mechanism of its influence on the copper footprint. Assess the impact of potential causes, such as speed, resources, organic load, and hardness, and provide pollution prediction for critical areas and nature reserves that protect river ecosystems. The results show that the increase of copper pollution is due to the decrease of flow rate, increase of organic load, non-point source and increase of hardness.

Key words: Copper; Water quality model; Velocity; Ecosystems; Hardness

Introduction

Copper is the most important pollutant affecting water, soil, and air quality. The research of copper transportation in river is an important part of aquatic system research. Copper pollution reflects the current quality of the system and provides information on the impact of pollution sources. Copper's environmental problems lie in its environmental durability, potential bio toxicity, non-destructibility, non-biodegradability, and potential toxicity to organisms beyond a certain concentration [1-3]. It is estimated that natural decay of copper within a river channel is hard, the process lasts several hundred years [4]. Most copper released from human activities comes from disposal including industrial wastewater discharges, sewage wastewater, fossil fuel combustion and atmospheric deposition [3,5,6]. There are lots of copper's basic characteristics research. For example, Wan et al. checked the Bio sorption of copper and zinc by free algal biomass, and their effects of metals bio sorption on the growth and cellular structure isolated from rivers in Penang, Malaysia [7]. The results showed that copper and zinc were mainly adsorbed on the cell surface during the process of bio sorption. Others also found that copper could react with organic corrosive substances such as Cl-, and OH-, resulting in greater solubility in water, which made it released from the sediments again [8]. They found that the shape of copper would change with PH [9]. Zhang, et al. also found that copper did not seem to be biologically amplified by the nutrient levels of aquatic food, but it did accumulate in individual animals [10].

Moreover, copper concentrations in soil sediments have also been reported. However, the research in river have has been poorly studied. And those studies have focused on monitoring its pollution status. For instance, L Kalender and Çiçek Uçar used the pollution index to detect copper pollution in the sediments of tributaries of the Euphrates River in Turkey [11]; Mighanetara et al. study pollutant fluences from abandoned mines and diffusing source points in the Tamar River basin in the UK [12]. Houba examined the distribution of copper in the Nemunas River in Lithuania [13]. Kucuksezgin et al. studied the distribution of heavy metals such as copper in water, particulate matter, and sediments of the Gediz River in the eastern Aegean Sea [14]. Taking the upstream basin of Lake Baikal as an example, Thorslund et al. studied the impact of gold mining on monitoring heavy metal transport, especially copper transport, in rivers in sparse areas [15]. Yang et al. summarized the influence of aerosol copper on Marine phytoplankton and found that dissolved copper was widely distributed in the ocean, especially in the surface waters of the Mediterranean Sea, East China Sea and northeast Pacific Ocean [16]. David and Plumlee compared the concentration trends of dissolved copper in two rivers received from an inactive copper mine in Malique island, Philippines [9]. Wogu and Okaka did just a few pollution studies of Nigerian rivers: heavy metal concentrations in surface water in the Warri River Delta and found reduction sequences from surface water samples in the Warri River: Fe>Mn>Zn>Cu>Ni>V>Cr>Cd>Pb [17]. Stoyanova study the copper concentration in the soils of the Danube floodplain between the Timok and Vit rivers in north-western Bulgaria [18]; Xie et al. assess heavy metal contamination and did ecological risk in Poyang Lake area of China [19]. De Souza Machado et al. study the Metal fate and effects in estuaries by a detailed review of conceptual model for better understanding of toxicity [20]. Ciszewski and Grygar found that approximately 90% or more of copper load can be associated with sediment particles, the pathways of metals to the floodplain are essentially the same as those of suspended sediments [21].

At the same time, some scholars have also studied some factors affecting the migration and adsorption of copper in rivers [7,22,23]. Examples include pH., Ionic strength, river soil and pore structure, cation, and anion indices. Influence is the deep cause of copper in suspension to phase transformation (dissolved), become a biological during and after transported to the downstream areas affected by these factors [24]. Dissolved heavy metals, including copper, are believed to play a small role in the transfer process of metals to rivers [15]. For example, a decrease in pH in a downstream drainage system result in a much higher dissolution concentration farther downstream from the mining site than at the site [25]. Poot examines the effects of flow state and flooding on the availability of heavy metals in sediments and soil in dynamic river systems by analysing monitoring data [26]. Yuan et al. also studied the effect of velocity on partial discharge characteristics of moving metal particles [27]. Ciszewski and Grygar studies pollution factors controlling the source distribution of heavy metals in the bottom sediments of o River in southern Poland [21].

In addition, Lijiang River is the main source of urban water in Guilin, as well as the main source of industrial and agricultural water [10,28,29]. There are two main sources of copper pollution, the Wushan copper mine in the upper reaches of the Lijiang River and the hardware and cable factories in Guilin, both medium-sized enterprises. Copper content in the Lijiang River and its main tributary, Taohua River, exceeds the second-level national standard, especially due to metal pollution caused by large amounts of non-ferrous metal mining and agricultural activities. Therefore, the study of copper pollution in Lijiang River is worth to be carried out. At present, the research on copper in Lijiang River mainly focuses on Pollution investigation. For example, When Zhang et al. analysed the copper concentration, it could be inferred that the copper concentration was higher than the background value, as well as the potential ecological risk of copper to rivers [10]. Xue et al. evaluated the copper pollution and its serious impact on the surrounding ecosystem [30]. However, influencing mobility or adsorption of copper transport in Lijiang River using models has been poorly studied. In particular, the effects of flow rate, organic matter, and hardness on copper migration in rivers will also be discussed using models.

In conclusion, to reveal the influence mechanism of the copper transport footprint of Lijiang River, model generator was used to study the copper pollution of Lijiang River from 2005 to 2015, and the relationship between it and influencing factors such as velocity, point source or non-point source, hardness, etc. affecting the river deposition process was analysed.

Methodology

Study Area and Data

Lijiang River is ranked as one of the 15 best tourist rivers in the world by Cable News Network. It is the water source of Guilin, a world-famous river in southern China (Figure 1). It covers an area of about 500 kilometres and has a drainage area of 5,585 square kilometres, including manual removal of printer ink cartridges and unprotected removal, and open burning of power lines to recover copper. There are two main sources of copper, one is the Upstream of the Lijiang River Wushan copper mine, the other is the Guilin hardware factory and cable factory, are medium-sized enterprises. These toxic metals, especially those from copper plants, have caused many sudden river pollution accidents and seriously affected the surrounding ecosystem [30,31].

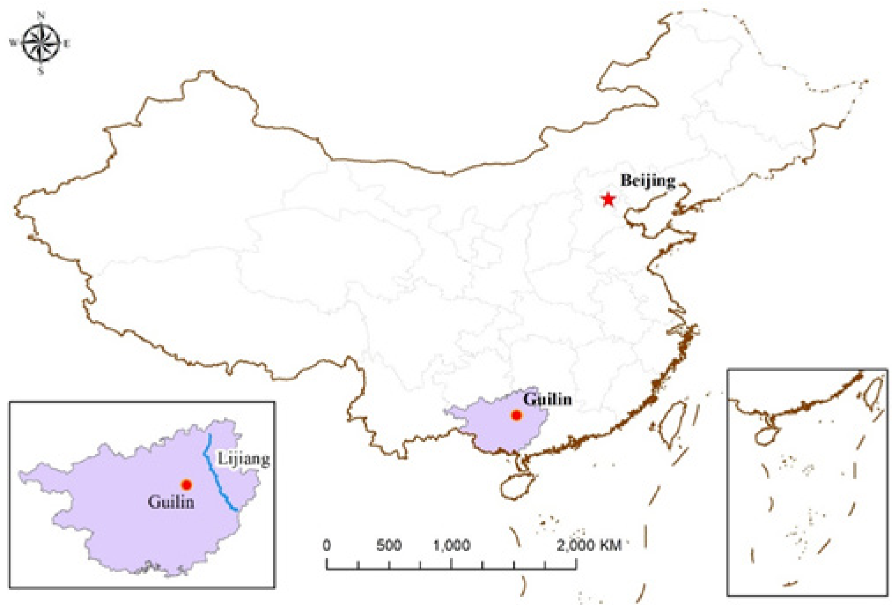


Figure 1: Satellite Map of the study area.

The detailed pollutions range of copper are listed in the following Table 1 and Figure 2, compared to the other typical rivers of the world.

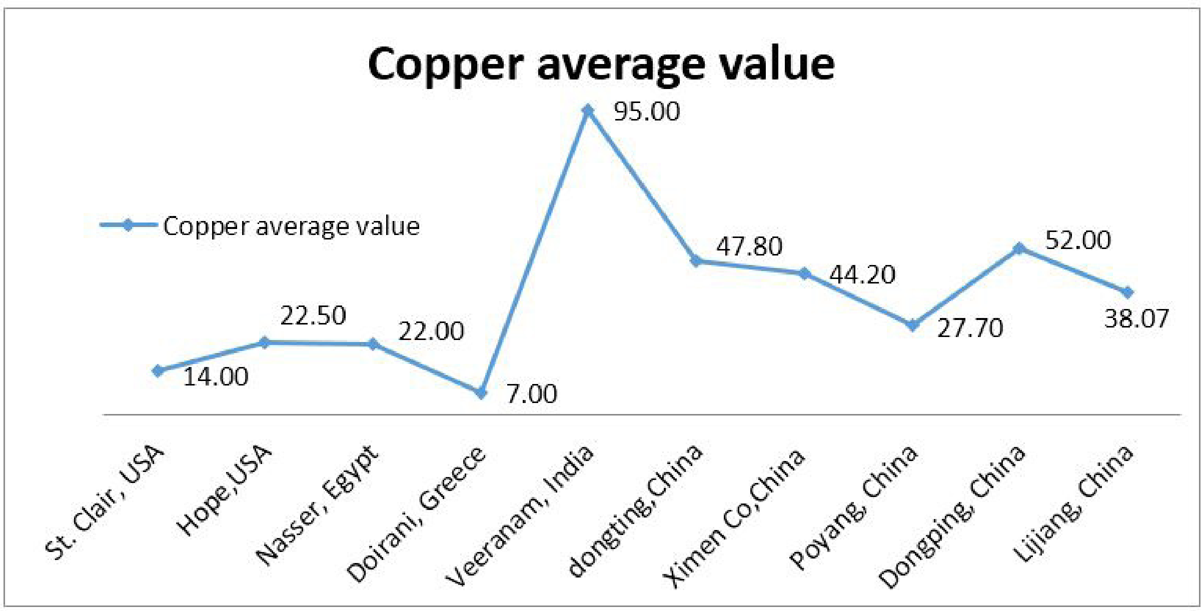


Figure 2: Average value comparison of copper in different water body.

In addition, water samples taken by Eastweek Magazine at the same location in the Lijiang River showed copper levels ranging from 21 to 56 mg/kg. To sum up, the Lijiang River is threatened by Guilin's rapid urbanization and industrialization, which has led to serious pollution, such as copper. The river has also given rise to competition for interests, including aquatic and wildlife, irrigation, water for livestock, drinking water supplies and recreation. It is also the final receiving body of water for wastewater generated in the region, which will increase future copper pollution. Therefore, it is of great significance to control the pollution of heavy metal copper in Lijiang River.

Variables	Temperature(°C)	Water depth(m)	Flow velocity(m/s)	Copper(mg/kg)
Minimum	15.99	0.056	0	21.01
Maximum	34.11	6.86	1.869	56.4
Mean	23.44	1.09	0.287	38.07
Standard Deviation (SD)	5.84	0.96	0.339	9.53

Table 1: The range of water quality (copper) in the Lijiang River (Average from 2005-2015).

Model and Equations

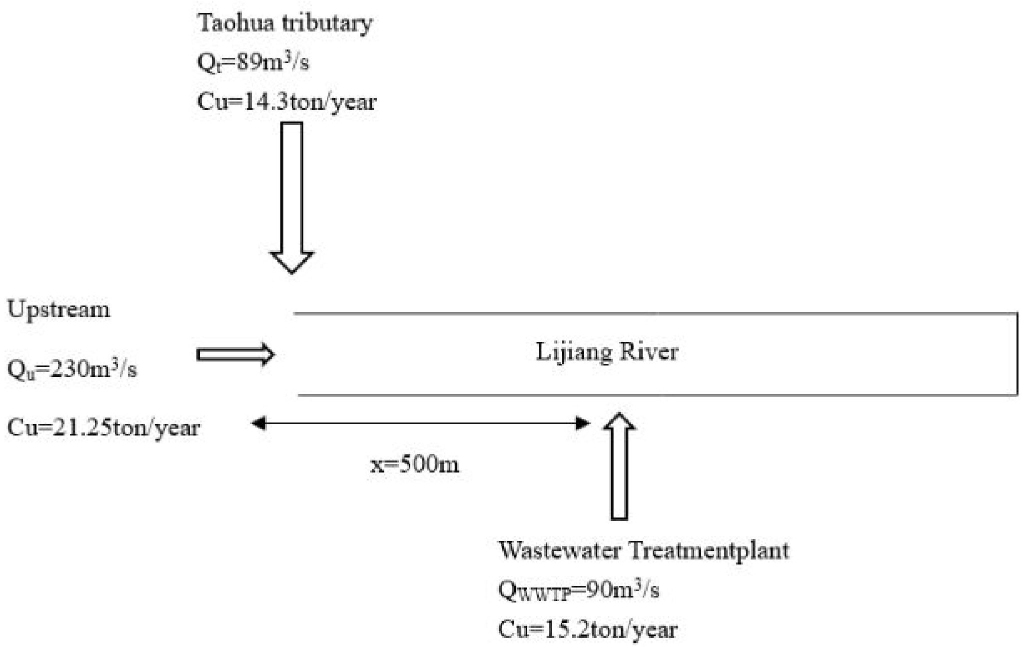


Figure 3: Cu's Concept model of Lijiang River in Model maker.

The point source model was established through model Maker (Figure 3). The point source model was established to simulate the copper transport situation of Lijiang River truly and accurately during the 10 years from 2005 to 2015. The total amount of metal copper is high due to contamination of copper plants with preservatives between 2005 and 2015. Heavy metals and suspended sediments indicate that these metals are granular and have no bioavailability, so point sources are the main consideration in this study.

Equations 1-2 is the model equation of copper transport in Lijiang River.

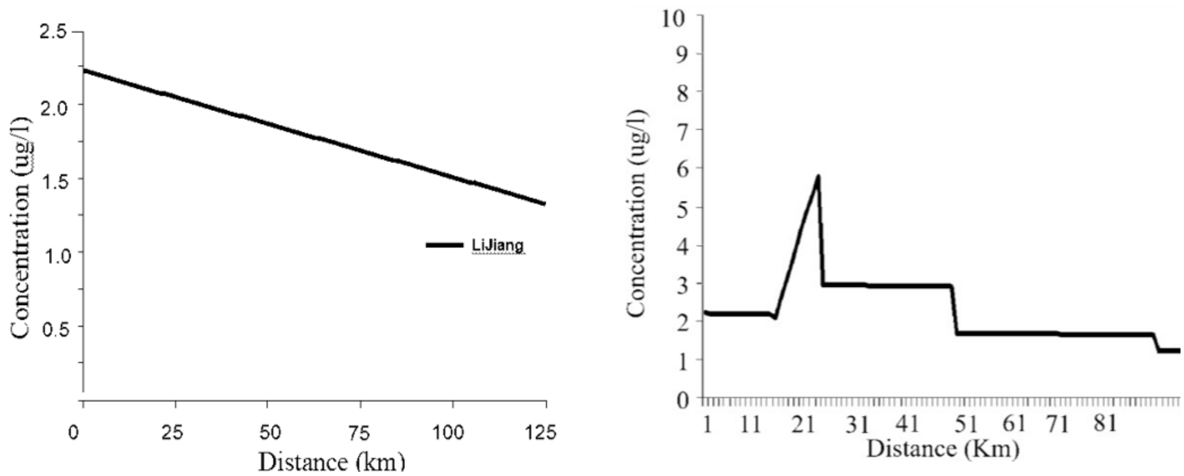
$$dC_T / dx = (-V_T /H) (C_T /U) \quad (1)$$

Where, C_T is the copper concentration at the outfall. U is the average water column velocity, Q is the volume of the river, H is the height change of the volume, and U is the sources' volume velocity. V_T is the decay rate of copper; here we use 0.2m/d. Among them, $H = 0.67Q^{0.26}$, and $U = 0.058Q^{0.53}$. After we solved Equation 1, it could be noted that Equation 2 will express copper's transport downstream of point source.

$$C_T = (W_T /Q) \exp [- (V_T /H) (x /U)] \quad (2)$$

Model Result

The non-point deficiency concentration of copper in Lijiang River is shown in Figure 4(a). The results show that the concentration of copper in Lijiang River decreases with the increase of distance. For the river reach dominated by point source of pollution, it is better to set up monitoring stations downstream of the location of pollution source. It can also be seen from Figure 4(a) that the concentration of copper decreases rapidly and continuously. At 25 Km downstream, the concentration was reduced to 2ug/ L, which reached China's second-level national standard. At 200 Km, the concentration of copper is reduced to 1ug/ L, a level 1 by the Chinese national standard. If point sources are included, the copper deficit is shown in Figure 4(b). The point source will make the concentration of copper increase sharply.



(a) Point source. (b) Non-point source.

Figure 4: Copper deficit of Lijiang River.

Effect Analysis

Normally, copper, and other heavy metals are discharged in both dissolved and solid phases. The proportion of discharge varies greatly due to lots of impact factors such as the nature of copper, the source of pollution, and the physical or chemical properties of the river (such as river velocity and hardness).

The effect of velocity to copper's concentration

First, the velocity of the Lijiang River affects the river deposition process. However, the main mechanism of river formation is deposition. In the sites with slower flow rate, deposition is higher and organic matter and clay content is higher, which in turn promotes the formation of hypoxia and the combination of copper and other metals. The variation of copper concentration in Lijiang River at different velocity is shown in Figure 5. When the velocity was 4 m/s, the copper concentration dropped sharply, while when the velocity was 0.2 m /s, the copper concentration in the downstream of Lijiang River changed little.

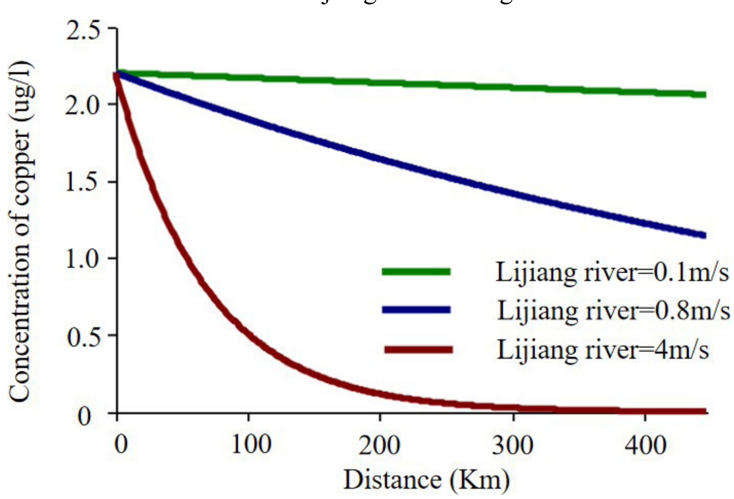


Figure 5: Comparing concentration of copper with different total velocity.

It can be seen from Figure 5 that the influence of velocity is related to seasonal flow change. The dissolved flux of copper in the period of small flow was higher than that in the period of large flow, indicating that attenuation occurred in the Lijiang River, such as adsorption particles or precipitation. The results are consistent with Zhou et al.' finding that aggregates formed by this deposition process have higher metal concentrations and higher settling velocity rates than discrete individual suspended particles [32].

The effect of non-point source

It can be seen from Figure 4(b) and Figure 6 that the influence of non-point sources on the concentration distribution is greater than that of the point sources themselves. The larger the non-point source, the greater the impact it will have relative to being a point source itself. The Lijiang River is widely distributed in the densely populated and industrially developed areas of the world, which is characterized by engineering structure that changes the river process. Therefore, the focus of this study is on artificially modified rivers, which are usually subject to a large amount of non-point source pollution.

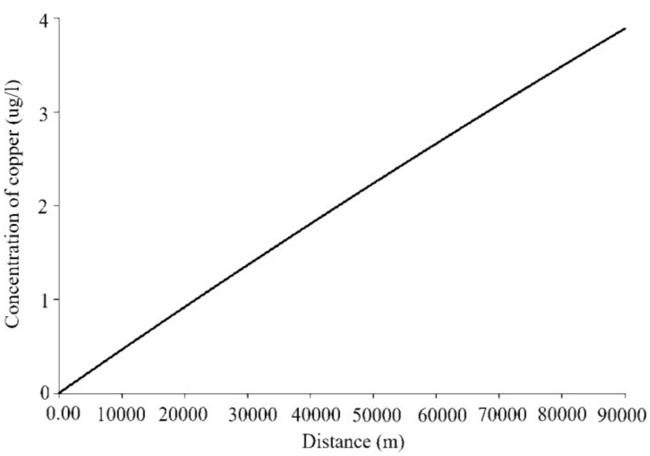


Figure 6: Distribution of copper with non-point source.

The effect of organic load

As shown in Figure 2, on ten years averagely, estimated up-stream copper load is 21.25 ton/per year, among them, from the Wastewater Treatment Plant (WWTP) copper load is 15.2 ton/per year (headwater inflow). The contribution to this load from headwater inflow estimated to be 99% or higher. This potential undefined local contribution appears to be important only for the winter and fall when the contribution from headwater inflow is relatively low. The more organic matter is accumulated, the more load is generated during summer and spring when headwater inflow is higher. Furthermore, reducing the inflow of organic pollutants by building public Wastewater Treatment Plant (WWTP) in each area of the Lijiang River will decrease the copper pollution.

Hardness

The standard for copper is usually based on the hardness level of water. According to Singleton [33], when the hardness is greater than 50mg /L $CaCO_3$, the maximum allowable copper concentration is calculated as: copper (µg/L) = [0.094 (hardness) +2]; The maximum mean criterion is: copper (µg/L) = [0.04 (average hardness)]. Therefore, using the relationship equations in Table 2, according to the sampling data from 2005 to 2015, the water hardness was determined to be 63.5mg/L, the maximum copper criterion for the measured water hardness of Lijiang River was 7.97 µg /L, and the maximum average was 2.54 µg/L. Both the maximum and average copper concentrations exceeded these criteria.

USEPA (1994) [34]/ Quebec (1990)/ Manitoba	chronic	$e^{0.9422*\ln(H)*1.464}$ µg/L
(Williamson 1998) [35]	acute	$e^{0.8545*\ln(H)*1.465}$ µg/L

Table 2: Relationship between chronic and acute toxicity values and its hardness.

As can be seen from Figure 7, the main chronic and acute toxicity values were obtained in water with $CaCO_3$ hardness between 50-300 mg/L. And it can be pointed out that the chronic guidelines are much lower than the acute guidelines, which means that the long-term guidelines should be more stringent than the acute guidelines at the same water hardness. And USEPA have less stringent guidelines for both acute and chronic copper toxicity test for the freshwater aquatic life. The higher the hardness, the higher the guidance value of copper for acute and chronic toxicity to aquatic organisms.

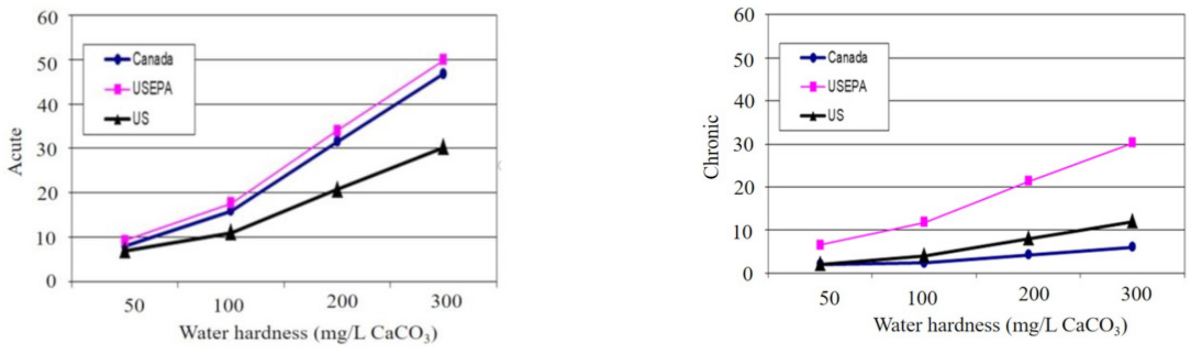


Figure 7: Comparison of freshwater aquatic life guidelines for copper (in ug/L) in different country.

Discussion

The existence of surrounding deposits and the expansion of mining activities played a key role in the accumulation of Cu in Lijiang River contribution from 2005 to 2015. The total copper output of Lijiang River is 21-56 mg/kg, while the average copper demand of the World Health Organization (WHO) from 2005 to 2015 is 0.0125 mg/kg [36]. To better reduce copper concentration, reduce copper emissions, reduce the source of copper pollution, and reduce copper pollution will be important. Therefore, clean production should be promoted in industries, especially those with high pollution. Such as hardware factory and cable factory, even the closure of hardware factory in Lijiang area is very necessary. Nevertheless, evaluating the copper mass balance on average seasonal basis does provide additional perspective on the possible extent of local, undefined non-point and point sources. Uncertainty about uncharacterized local loading contributions to total copper load is likely high given the inconsistencies and general lack of spatial detail in the downstream in-stream load pattern. Consider the influence factors, especially the influence of velocity, and divert water from other rivers to the Lijiang River to increase the velocity and flow rate of the Lijiang River. As the Lijiang River is a rain-fed river, its velocity in the dry season is less than 100 m^3/s, and its minimum velocity is only 38m^3/s. Therefore, if water is diverted to the Lijiang River, the velocity increases from 0.8 m^3/s to 1.0~1.2 m^3/s, then the concentration of copper decreases faster. For the hardness of copper, cadmium levels in the Lijiang River range from 0.01 to 0.033 mg/L, compared with WHO guidelines of 0.003 mg/L.

Conclusions

Based on field data, experiments and numerical simulation, the evolution of Lijiang River copper in recent 10 years is discussed. Over the past ten years, the annual copper concentration of Lijiang River has been 38.07 mg/kg. The estimated headwater contribution to this total exceeds 99% in all seasons except winter and fall when the Capital Region WWTP contributed 29% and 21%, respectively. In addition, a water quality model was used to evaluate the effects of velocity, water source, organic load, and hardness on the Lijiang River. The results show that copper pollution increases with the decrease of velocity and the decrease of the WWTP, also increase with the increase of non-point source and the increase of hardness. Therefore, the Lijiang River sediment is the main carrier of copper migration. The study can provide reference for the countermeasures of pollution control and sediment control in Lijiang River. Also, the study will provide pollution forecasts for important areas and nature reserves for the protection of river ecosystems.

Acknowledgments

This study was partially supported by Anhui Provincial Cultivate Excellent Innovation Plan.

References

1. Kosmidis D, Skordas K, Kelepertzis E, Panagiotaki P, Vafidis D (2015) Assessment of nutri- ents and heavy metals in the surface sediments of the artificially lake water reservoir Karla, Thessaly, Greece. Environ Earth Sci 73: 4483-4493.
2. Yang Y, Wang LF, Wang Y, Zhang W (2015) Geochemical speciation and pollution assessment of heavy metals in surface sediments from Nansi Lake, China. Environ Monit Assess 187: 261.
3. Pan B, Guan Q, Wang L, Guan W, Sun X et al. (2016) Distribution features and controls of heavy metals in surface sediments from the riverbed of the Ningxia-Inner Mongolian reaches, Yellow River, China. Chemosphere. 144: 29-42.
4. Moore JN, Langner HW (2012) Can a river heal itself? Natural attenuation of metal contamination in river sediment. Environ Sci Technol 46: 2616-2623.
5. Lin Q, Liu Ef, F, Zhang E, Li K (2016) Spatial distribution, contami- nation and ecological risk assessment of heavy metals in sur- face sediments of Erhai Lake, a large eutrophic plateau lake in southwest China. CATENA. 145:193-203.
6. Maolan W, Liu J, Lai J (2019) Metals Pollution and Ecological Risk Assessment of Sediments in thePoyang Lake, China, Bull. Environ. Contam. Toxicol. 102: 511-518.
7. Maznah WWO, Al-Fawwaz AT, Surif M (2012) Biosorption of copper and zinc by immobilised and free algal biomass, and the effects of metal biosorption on the growth and cellular structure of Chlorella sp. and Chlamydomonas sp. isolated from rivers in Penang, Malaysia. J Environ Sci (China) 24: 1386-1393.

8. Georgopoulos PG, Roy A, Yonone-Lioy MJ, Opiekun RE, Lioy PJ (2001) Environmental copper: Its dynamics and human exposure issues. J Toxicol EnviroN Heal - Part B Crit Rev 4: 341-394.

9. Primo C, David C, Plumlee G, (2006) Comparison of Dissolved Copper Concentration Trends in Two Rivers Receiving Ard from an Inactive Copper Mine (Marinduque Island, Philippines). J Am Soc Min Reclam 426-438.

10. Zhang Z, Mao J, Wang F, Pirajno F (2006) Native gold and native copper grains enclosed by olivine phenocrysts in a picrite lava of the Emeishan large province, SW China. Am Mineral 91: 1178-1183.

11. Kalender L, Çiçek Uçar S, (2013) Assessment of metal contamination in sediments in the tributaries of the Euphrates River, using pollution indices and the determination of the pollution source, Turkey. Geochemical Explor 134: 73-84.

12. Mighanetara K, Braungardt CB, Rieuwerts JS, Azizi F (2009) Contaminant fluxes from point and diffuse sources from abandoned mines in the River Tamar catchment, UK, J. Geochemical Explor. 100:116-124.

13. Houba C, Remade J (1982) Distribution of heavy metals in sediments of the River Vesdre (Belgium). Environ Technol Lett 3: 237-240.

14. Kucuksezgin F, Uluturhan E, Batki H (2008) Distribution of heavy metals in water, particulate matter and sediments of Gediz River (Eastern Aegean). Environ Monit Assess 141: 213-225.

15. Thorslund J, Jarsjö J, Chalov SR, Belozerova EV (2012) Gold mining impact on riverine heavy metal transport in a sparsely monitored region: The upper Lake Baikal Basin case. J Environ Monit 14: 2780-2792.

16. Yang T, Chen Y, Zhou S, Li H, Impact of copper on marine phytoplankton: A Review. Atmosphere (Basel) 10: 414.

17. Wogu MD, Okaka CE (2011) Journal of Biodiversity and Environmental Sciences (JBES) ISSN : 2220-6663 (Print) 2222-3045 (Online) Pollution studies on Nigerian rivers : heavy metals in surface water of warri river, Delta State. J Biodivers Environ Sci 1: 7-12.

18. Stoyanova V, Kotsev T, Zhelezov G, Sima M, Levei EA (2019) Copper concentration in the soils of the danube floodplain between the rivers Timok and Vit northwestern Bulgaria. Eur J Geogr 10: 134-149.

19. Xie Z, Jiang Y, Zhang H, Wang D, Qi S, et al. (2016) Assessing heavy metal contamination and ecological risk in Poyang Lake area, China. Environ Earth Sci 75: 549.

20. de Souza Machado AA, Spencer K, Kloas W, Toffolon M, Zarfl C (2016) Metal fate and effects in estuaries: A review and conceptual model for better understanding of toxicity. Sci Total Environ 541: 268-281.

21. Ciszewski D, Grygar TM (2016) A Review of Flood-Related Storage and Remobilization of Heavy Metal Pollutants in River Systems. Water Air Soil Pollut 227.

22. Rader KJ, Carbonaro RF, van Hullebusch ED, Baken S, Delbeke K (2019) The Fate of Copper Added to Surface Water: Field, Laboratory, and Modeling Studies. Environ Toxicol Chem 38: 1386-1399.

23. Karathanasis AD (1999) Subsurface Migration of Copper and Zinc Mediated by Soil Colloids. Soil Sci Soc Am J 63: 830-838.

24. Ciszewski D (1997) Source of pollution as a factor controlling distribution of heavy metals in bottom sediments of Chechlo River (South Poland). Environ Geol 29: 50-57.

25. Yang P, Mao R, Shao H (2009) An investigation on magnetic susceptibility of hazardous saline-alkaline soils from the contaminated Hai River Basin, China. J Hazard Mater 172: 494-497.

26. Poot A, Gillissen F, Koelmans AA (2007) Effects of flow regime and flooding on heavy metal availability in sediment and soil of a dynamic river system. Environ Pollut 148: 779-787.

27. Yuan W, Wang H, Fan L, Deng Y, Zeng Y (2020) Impact of wind on copper footprints in a large river-connected lake. Water Environ J 34: 586-596.

28. Xu D, Wang Y, Zhang R, Guo J, Zhang W, Yu K (2016) Distribution, speciation, environmental risk, and source identification of heavy metals in surface sediments from the karst aquatic environment of the Lijiang River, Southwest China. Environ Sci Pollut Res Int 23: 9122-9133.

29. Zhang D, Wang Y, Yu K, Li P, Zhang R, Xu Y (2014) Occurrence, distribution and sources of organochlorine pesticides (OCPs) in surface sediments from the lijiang river, a typical karst river of southwestern China, Bull. Environ Contam Toxicol 93: 580-585.

30. Xue B, Wang Y, Zhang D, Zhang J, Leng B, et al. (2013) Concentration, distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from Lijiang River, South China. Bull Environ Contam Toxicol 90: 446-450.

31. Pan L, Dai J, Yu C, Xie X, Wu Z (2019) Spatial-temporal Features of Nitrogen and Phosphorus Losses of Jingui River Watershed in the upstream of Lijiang River. IOP Conf Ser Earth Environ Sci 304.

32. Zhou Y, Zhang P, Zhang Y, Li J, Zhang T, et al. (2017) Total and settling velocity-fractionated pollution potential of sewer sediments in Jiaxing, China. Environ Sci Pollut Res Int 24: 23133-23143.

33. Singleton, HJ 1987. Water Quality Criteria for Copper. Technical Appendix. Resource Quality Section, Water Management Branch, Ministry of Environment and Parks, Province of British Columbia. 121p.

34. USEPA. U.S Environmental Protection Agency. (1994) Water Quality Standards Handbook: Second Edition. EPA-823-B-94-005a.

35. Williamson DA (1988) Rationale Document Supporting Revisions to Manitoba Surface Water Quality Objectives. Manitoba Environment and Workplace Safety and Health. Water Standards ans Studies Report No. 88-5.

36. WHO Guidelines for Drinking-water Quality.