



Sediment-copper distributions in hyper-concentrated turbulent solid-liquid system

YANG Jun^{1,*}, NI Jin-ren²

1. Department of Environmental Engineering, Beihang University, Beijing 100083, China. E-mail: yangjun@buaa.edu.cn

2. College of Environmental Sciences, Peking University, Key Laboratory for Water and Sediment Sciences, Ministry of Education, Beijing 100871, China

Received 23 January 2006; revised 10 March 2006; accepted 10 April 2006

Abstract

This study presents a special problem on vertical distribution for sediment and copper in hyper-concentrated turbulent solid-liquid system that is essentially different from the ordinary low-concentrated turbulent system. A resonance type turbulent simulation equipment is used for the experimental study in which a vertically uniform turbulent field of the mixture of loess and water is produced in a testing cylinder with a grille stirrer that moves up and down harmoniously with varying vibration frequencies. In order to compare the variations of the vertical profiles of sediment and copper in low- and hyper-concentrated solid-liquid system, different scenarios for input sediment content ranging from 5 to 800 kg/m³ was considered in the experimental studies. It was found that solids copper content increases with input sediment content, S_0 , and reaches its peak as S_0 goes to 10 kg/m³ and then decreases rapidly with increasing input sediment content. Such a behavior is possibly resulted from the joint effect of the specific adsorption of copper on loess, precipitation of carbonate and hydroxide of copper due to high carbonate content in the loess and the so-called "particulate concentration effect" due to the present of the sediment variation in water. The vertical sediment concentration distribution resulted from the uniform turbulence is generally uniform, but slight non-uniformity does occur as sediment concentration exceeds certain value. However, the vertical concentration distributions of soluble copper seem not to be affected much by the variation of sediment concentrations.

Key words: hyper-concentrated system; loess; copper; vertical sediment distribution

Introduction

Chinese rivers are noted for their high sediment concentrations. Thus, the hyper-concentrated flow in large rivers has been the main concern in China. For example, the recorded maximum sediment concentration in Yellow River is up to 1650 kg/m³ (Chien, 1989). Unlike ordinary turbulent flows with sediment concentration lower than 100 kg/m³, most of the physical, chemical and biological characteristics in hyper-concentrated flows will be essentially changed, which implies either the sediment transport or the pollutant migration and transformation processes may be quite different. In order to describe the different mechanisms of the specific flows, new explorations must be made both experimentally and theoretically.

Much effort has been made by hydraulic scientists on the investigations of hyper-concentrated systems, particularly on their formation causes, transport processes and the changes of the physical characteristics such as viscosity, settling velocity and flocculation. Static, kinematic and dynamic characteristics have been widely studied by the Chinese scientists (Chien, 1989) in the past decades. However, the previous studies on hyper-concentrated flows, to

a large extent, were related to the variations of physical characteristics rather than those of chemical and biological characteristics, which are of significance to the motion of pollutants.

On the other hand, most of the previous researches on the interactions between heavy metals and sediments have been carried out under the conditions of the low-concentrated solid-liquid systems such as those in rivers, lakes, sea and estuaries. Since 1970s, many geographical and environmental scientists have investigated the heavy metal contents on sediments in natural waters (Chen *et al.*, 1991; Zhang and Selinus, 1997). Meanwhile, improvements of analytical techniques for metal speciations have been made (Tessier *et al.*, 1979). Mechanisms of adsorption and transport-transformation process have been studied (Forstner, 1989) in terms of various models. Moreover, methods have been proposed for evaluating the ecological and health effects of metal speciations (Grahn and Hakanson, 1987).

Nevertheless, what are the chemical and biological behaviors in the hyper-concentrated systems? What kinds of essential changes will occur when a system transfers from lower to higher sediment concentrations? The previous studies can hardly give satisfactory answers, and new understandings are scarcely needed.

The present paper, initiated from series of fundamental experiments on vertical profiles for sediment and copper distributions in a cylinder, aims at gaining new understandings of the seldom reported field by focusing on the adsorption and diffusion characteristics in a hyper-concentrated turbulent system. This study is expected to be of great help to interpret the abnormal polluting processes in hyper-concentrated sediment-laden flows, which can not be explained by the ordinary theory applicable for the low-concentrated turbulent system.

1 Materials and methods

1.1 Apparatus

The apparatus employed in the experimental study was a self-designed resonance-type turbulent simulation system. The main body is a plexiglass cylinder of $\phi 24$ cm \times 50 cm as shown in Fig.1. A 9-layer grille stirrer was fixed in the cylinder with equal distance of 4 cm between any two neighboring layers. The grille stirrer is driven by direct current motor through an eccentric wheel. When the grille stirrer moves up and down harmoniously with varying vibration frequencies, the vertically uniform turbulent field will be generated in the mixture of loess and water in the cylinder. Eight sampling openings were arranged on the wall of the cylinder with different vertical distance (H) from the bottom, i.e. 4, 7, 10, 16, 28, 34, 40, and 46 cm, respectively.

1.2 Materials

The porous Malan loess was used for solid sediment material in the experiments. The soil was from the Middle

Yellow River where subject to serious erosion. Physically the loess is composed of >50% silt with diameters of 0.05–0.005 mm, 10%–35% clay particles with diameters smaller than 0.005 mm and of <5% fine sand with diameters greater than 0.1 mm. The loess is chemically composed of SiO₂, Al₂O₃, solid organic matter less than 1% and carbonate salt. The high content of carbonate may greatly affect its adsorption characteristic on the heavy metals ranged 10%–16%. The loess is marked by its pH value of 7.5–8.6 and its negative charge characteristics.

The remaining fine particles after grinding and sieving of loess are of diameters smaller than 0.076 mm. A stock copper solution (10000 mg/L) was prepared in distilled water with CuSO₄·5H₂O (A.R.). Distilled water was used to prepare all the solutions. All the laboratory glassware was pre-cleaned by soaking in 10% HNO₃.

1.3 Procedure and analysis methods

The experimental procedures include five steps. First, disperse the prepared loess into distilled water and activate the sediments for 24 h. Second, transfer completely the activated water-sediment mixture and add 1 L of the stock copper solution into a 20-L sized testing cylinder. Third, shake the water-sediment-copper mixture for 1.5 h at a constant vibration frequency. Fourth, take samples (50–100 ml) from the sampling openings and measure the final pH, temperature and total sampling volume. Finally, analyze the soluble and solids copper concentration. Input sediment contents in the experimental series were 5, 10, 40, 70, 100, 200, 400, 600, 800 kg/m³, respectively. The detailed experimental parameters are presented in Table 1. Analytical duplicate, method blanks and matrix spike samples were considered.

Samples of the equilibrated copper-sediment mixture post vibration were centrifuged to determine the soluble copper concentration. The supernatant was decanted into an ultra-filtration system and filtered through a 0.45- μ m membrane of cellulose acetate. The filtrate was analyzed for copper concentration by flame atomic absorption spectrophotometer (AAS, Hitachi Model 180-80).

The copper content of the solids was determined by re-suspending the solids in NaOAc/HOAc buffer solution (pH 5) made of 8 ml of 1 mol/L NaOAc + 5 drops of concn. HOAc per gram solid. The mixture was agitated using a reciprocating shaker for 6 h at room temperature (20 \pm 2°C). Copper content in the mixture was analyzed through the process of centrifuge, filtration, dilution and AAS.

Copper content could be determined by the sampling

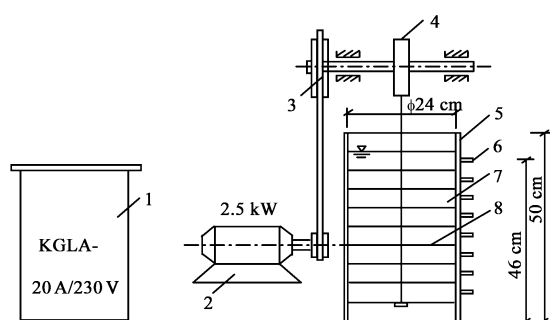


Fig. 1 Scheme of the resonance-type turbulent simulation system. (1) silicon controlled rectifier; (2) direct current motor; (3) belt pulley; (4) eccentric wheel; (5) plexiglass cylinder; (6) sampling openings; (7) solid-liquid mixture; (8) grille stirrer.

Table 1 Summary of experimental parameters

| Parameter | Input sediment content S_0 (kg/m ³) | | | | | | | | |
|---|---|------|------|------|------|------|------|------|------|
| | 5 | 10 | 40 | 70 | 100 | 200 | 400 | 600 | 800 |
| Initial Cu ²⁺ concentration (mg/L) | | | | | 500 | | | | |
| Average pH | 5.20 | 5.35 | 5.55 | 5.70 | 5.80 | 7.37 | 7.94 | 8.02 | 8.05 |
| Temperature (°C) | 20.4 | 20.5 | 22.0 | 21.8 | 22.1 | 22.0 | 21.2 | 22.0 | 19.7 |
| Vibration frequency (1/s) | 2.50 | 2.51 | 2.55 | 2.60 | 2.55 | 2.48 | 2.57 | 2.43 | 2.51 |
| Vibration intensity (cm/s) | 17.2 | 17.4 | 17.6 | 17.9 | 17.6 | 17.1 | 17.7 | 16.8 | 17.4 |
| Vibration time (h) | | | | | 1.5 | | | | |
| Depositing thickness (cm) | 0.1 | 0.3 | 0.5 | 0.7 | 1.1 | 1.6 | 2.5 | 5 | 7 |

copper concentration multiplied by the volume of the original sample, whereas solids copper content (mg/g) could be obtained from the copper content divided by the solids content.

2 Results and discussion

2.1 Relationships between main variables

The main variables in the present experiments include mean solid copper content, soluble copper concentration, pH and mean actual sediment concentration. Fig.2 describes the relationships between the variables, in which the x-axis denotes classification. The actual sediment concentration (S) is the measured content at different heights in the vertical, which is different from the input sediment content (S_0) at the beginning of the experiments. Under the uniform turbulent conditions, solid copper content increases when $S < 1 \text{ kg/m}^3$ and reaches its peak at $S = 1 \text{ kg/m}^3$, or when S_0 goes to 10 kg/m^3 . On the contrary, it drops rapidly with increasing S . These new findings on adsorption or sorption characteristics are quite different from those obtained in previous studies where the decreasing trend of solid copper content with increasing sediment concentration at negative exponent was often explained by the so-called "particle concentration effect". With the initial copper concentration of 500 mg/L , the experimental curve in Fig.2 indicates that the soluble copper concentration decreases rapidly as the actual sediment concentration (S) increases from 0.88 to 79.8 kg/m^3 , while the input sediment content is ranged from 5 kg/m^3 to 200 kg/m^3 . However, it decreases to $0.2\text{--}0.6 \text{ mg/L}$ as actual sediment concentration increases from 273 to 707 kg/m^3 , while larger input sediment content ranged $400\text{--}800 \text{ kg/m}^3$ is used. The experimental results showed greater sorption capacity of hyper-concentrated loess.

The adsorbed copper species on loess were determined by using revised Tessier's sequencing extract method (Tessier *et al.*, 1979). It is indicated that solids copper is comprised of $>93\%$ carbonate-bound, $2\%\text{--}4\%$

Fe/Mn-oxide-bound and $0.001\%\text{--}0.1\%$ exchangeable and organically bound, which is consistent with the monitored results of suspended sediments in the Yellow River (Yellow River Institute of Water Resource Protection, 1988). The high content of carbonate ($10\%\text{--}16\%$) and low organic matter ($<1\%$) in the original loess appear to play a key role in the above copper species distribution. The speciation of copper in sediment is related to their biogeochemical reactivity, which in turn is controlled by the local water and porous solid properties. Since the high content of carbonate-bound of copper is sensitive to solution acidity and easy to be re-dissolved when $\text{pH} < 5$, particular attention must be paid to prevent local acidic pollution which could lead to second pollution of heavy metal.

The adsorption kinetic analysis indicates that the time for attaining the adsorption equilibrium is normally less than 20 min . The adsorption of strongly hydrated copper on the loess belongs to specific adsorption that has been studied using IR, ESR, and XRD (Pickering, 1979), and could be explained by the surface complexation model. Moreover, blue-green precipitates were visually observed as the input sediment content increases accompanied by the rise of pH values in the mixture. The precipitate may be a mixture of $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ (azurite), $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (malachite) and $\text{Cu}(\text{OH})_2$, whose $\text{p}K_{\text{sp}}$ (negative logarithm of solubility product) are 21.53 , 21.51 and 19.66 , respectively. The precipitation or co-precipitation processes greatly depend on the pH value and the bicarbonate concentration in the solution. The pH value of most fresh waters is controlled by the concentration of dissolved carbon dioxide or bicarbonate in the solution. In the presence of bicarbonate, copper ions start to form $\text{Cu}(\text{OH})_2$ and carbonate precipitates at pH 5, and then over 80% of total copper ion transformed into precipitates at pH 7.5. It is recognized that there should be a steep rise of adsorption at pH values similar to the first $\text{p}K_{\text{h}}$ of the hydrated cation. The difficulty in distinguishing the precipitates from each other in the experiments is primarily due to the greater $\text{p}K_{\text{h}}$ (about 7.5) for copper than the pH for total precipitation (Pickering, 1979). Therefore, two processes exist in copper adsorption on the loess, one is specific adsorption and another is precipitation of carbonate and hydroxide. The chemical extract solution of HOAc-NaOAc buffer (pH 5) used in this study could dissolve and pick up at least the mixture of the above three precipitates.

The solids copper content reaches a peak when $S_0 = 10 \text{ kg/m}^3$. In principle, the critical input sediment content corresponding to the peak may depend on the properties of the loess and copper. For the present study, when $S = 0.88 \text{ kg/m}^3$ (or $S_0 = 5 \text{ kg/m}^3$), a specific adsorption played a main role in adsorption of copper on loess since the loess has little effect on the copper solution as pH value being 5.20. However, when the sediment concentration increases to 1.06 kg/m^3 (or $S_0 = 10 \text{ kg/m}^3$), the specific adsorption in addition to the precipitates of $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ formed by 500 mg/L copper ion and carbonate as well as $\text{Cu}(\text{OH})_2$ formed through hydrolysis at pH 5.35. In such a case, "particle concentration effect" does not remarkably affect the solids copper content owing

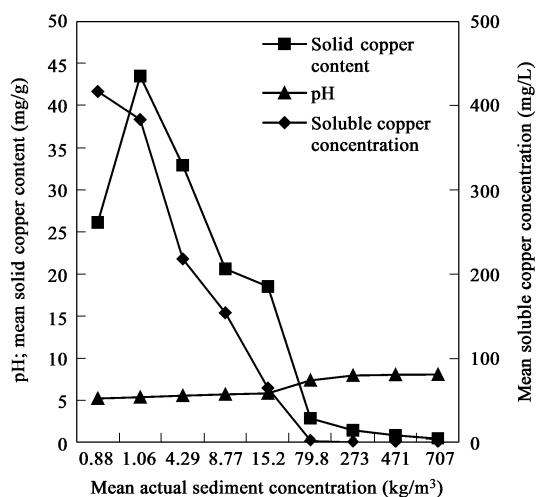


Fig. 2 Relationships between mean solid copper content, soluble copper concentration, pH and mean actual sediment concentration.

to the low sediment concentration. The dissolved carbonate and the slight increase of pH are resulted from high content of carbonate in the loess. When S further increases from 1.06 kg/m^3 , the precipitation effect becomes eminent and the “particle concentration effect” shadows its significance to the rapid decrease of solids copper content.

In summary, the mechanism of peak/maximum adsorption capacity of copper on the loess could be a joint effect of copper specific adsorption on loess, precipitation of carbonate and hydroxide of copper due to high content of carbonate in the loess and the “particle concentration effect”.

2.2 Vertical distributions of solid copper content

Comparisons of the vertical distributions of solid copper content were made (Fig.3) with varying input sediment contents while keeping the same uniform turbulent condition. There appeared certain fluctuation in the vertical distributions, which was also mentioned by some investigators (Xia and Song, 1983) but no available explanations at present.

2.3 Vertical distributions of actual sediment concentration

In Fig.4, comparisons of the vertical distributions of actual sediment concentration were given with varying input sediment contents. With the same intensity of turbulence, the actual sediment concentrations are distributed uniformly in the vertical when $S_0 < 100 \text{ kg/m}^3$, whereas the certain non-uniformity occurs when $S_0 > 200 \text{ kg/m}^3$ characterized by lower sediment concentration in the upper region and larger concentration in the bottom region in the vertical.

2.4 Vertical distributions of soluble copper concentration

Comparisons of the vertical distributions of soluble copper concentration were made with varying input sediment contents. Fig.5 shows that the distributions have similar characteristics as those of sediment concentration within the given range of input sediment content.

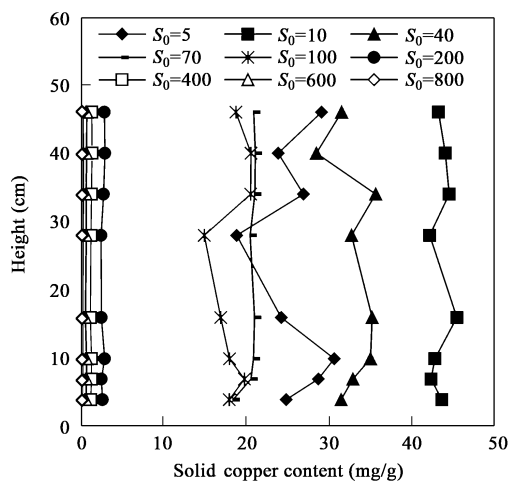


Fig. 3 Comparisons of the vertical distributions of solids copper content.

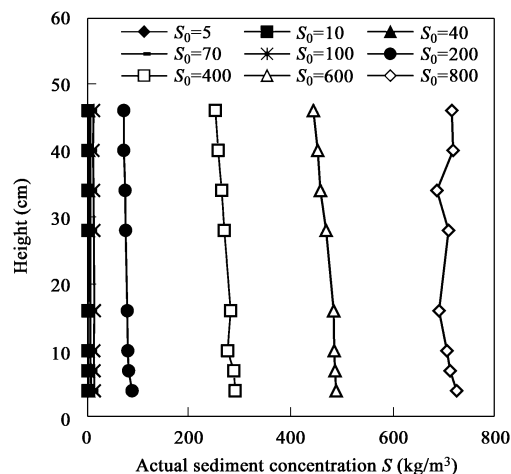


Fig. 4 Comparisons of the sediment vertical distributions.

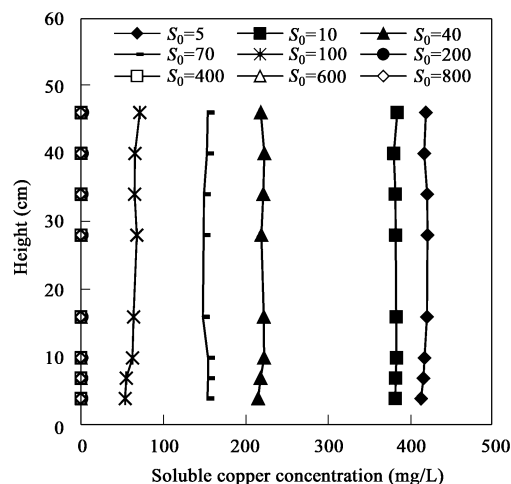


Fig. 5 Comparisons of the vertical distributions of soluble copper concentration.

3 Conclusions

The experimental studies were conducted in the hyper-concentrated turbulent solid-liquid system under the conditions of uniform turbulence with different scenarios of input sediment content ranging from 5 to 800 kg/m^3 . It was found that solids copper content reaches its maximum when the input sediment content goes to 10 kg/m^3 and then decreases rapidly with increasing input sediment content. This behavior is attributed to the joint effect of the specific adsorption of copper on loess, precipitation of carbonate and hydroxide of copper due to high carbonate content in the loess and the so-called “particulate concentration effect”.

The soluble copper concentration decreases rapidly while the input sediment content is increased from 5 to 200 kg/m^3 . However, it decreases to its minimum while input sediment content is ranged $400\text{--}800 \text{ kg/m}^3$. The experimental results showed greater sorption capacity of hyper-concentrated loess.

The vertical sediment concentration distribution resulted from the uniform turbulence is generally uniform. The vertical distributions of soluble copper concentration have

similar characteristics as those of sediment concentration within the given range of input sediment contents. The soluble copper concentration is primarily controlled by both the sorption and the diffusion characteristics of sediment and copper in the hyper-concentrated turbulent system.

References

- Chen J S, Cheng C Q, Wang F Y, 1991. Geographical tendency of geochemical characteristics and binding capacity of suspended matter from the five main rivers of east China for heavy metals[M]. In: Heavy metals in the environment (Vernet J. P., ed.). Amsterdam: Elseviers. 125–136.
- Chien N, 1989. Hyper-concentrated flow[M]. Beijing: Tsinghua University Press. 206.
- Forstner U, 1989. Contaminated sediments. Lecture notes in earth sciences[M]. Berlin: Springer-Verlag. 156.
- Grahn O, Hakanson L. 1987. Case studies of metal distribution and uptake in biota[M]. In: Speciation of metals in water, sediment and soil systems (Landner L., ed.). Berlin: Springer -Verlag. 127–144.
- Pickering W F, 1979. Copper retention by soil/sediment components[M]. In: Copper in the environment, Part I: Ecological cycling (Nriaga J. D., ed.). New York: John Wiley & Sons Inc. 225–229.
- Tessier A, Campbell P G C, Bisson M, 1979. Sequential extraction procedure for the speciation of particulate trace metals[J]. Anal Chem, 51: 844–851.
- Xia Z H, Song G P, 1983. Settling properties of sediments composed of cohesive and non-cohesive particles[C]. In: Proceedings of the 2nd International Workshop in Flow with Hyper-concentration of Sediment, Nanjing, China. 253–264.
- Yellow River Institute of Water Resource Protection, 1998. Sediment effect on the transport-transformation of heavy metals in the middle reaches of the Yellow River, 1988[R].
- Zhang C S, Selinus O, 1997. Spatial analyses for copper, lead and zinc contents in sediments of the Yangtze River Basin[J]. Sci Tot Environ, 204: 251–262.