

# The effect of ultrasonic algae inhibition on the concentration and state changes of heavy metals in sediments

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Received 24 Nov 2016

Accepted 5 Sep 2017

**ABSTRACT:** To evaluate the effect of ultrasound on the release of heavy metals in sediments during the ultrasonic algae inhibition and elimination process, low-frequency and low-power ultrasound at 35 kHz, 0.105 W/cm<sup>2</sup> was used to irradiate a simulated water body for 60 min. Water samples were extracted at 10 min intervals to detect the concentration changes of Cu, Zn, Pb, and Cr. Samples from the sediment surface and 10 cm below the surface were extracted to determine the changes of total amounts for the four heavy metals, as well as the corresponding concentration changes of exchangeable, carbonate binding, Fe–Mn binding, organic binding, and residue states. The test results showed that the concentrations of the four heavy metals in water increase rapidly during the first 20 min of ultrasonic treatment, decreasing thereafter. The concentrations approach a stable level after 50 min. The concentrations of all the four metals increased by over 80%. During the first 20 min of ultrasonic treatment, the release rates of Cu, Zn, Pb, and Cr at the sediment surface were 27%, 24%, 29%, and 29%, respectively, while the concentrations of the Fe–Mn binding state and exchangeable state decreased by 25% and 47%, 22% and 43%, 29% and 28%, and 29% and 29%, respectively. The release rate of the four heavy metals at 10 cm below the surface was 34%, 34%, 32%, and 39%, respectively. Meanwhile, the concentrations of the Fe–Mn binding state of Cu, Zn, and the Fe–Mn binding state and organic bonding state of Pb and Cr decreased significantly. After 50 min of ultrasonic treatment, the total amount of heavy metals and the five states approached a stable level. These findings suggest that ultrasonic treatment can accelerate the release of metal elements from sediments to the water body; thus the ultrasonic algae inhibition technology is not sufficiently safe and reliable, involving the risk of secondary pollution.

**KEYWORDS:** ultrasound, sediment of river and lake, heavy metal fraction, release

## INTRODUCTION

Cyanobacterial bloom has become an environmental issue worldwide, and the situation in China is emerging increasingly more serious. In particular, the problem of cyanobacteria bloom around the Taihu Lake has attracted global attention. The cyanobacteria bloom elimination and inhibition methods proposed are based on the emergency treatment concept, which can neither solve the problem of cyanobacteria bloom thoroughly nor eliminate the existing water pollution caused by cyanobacteria bloom. Considering the shortcomings of such methods, methods based on the prevention and control principles have been proposed. Since the beginning of 2000, the Japanese scholar

Nakano<sup>1</sup> and the Korean scholar Ahn<sup>2,3</sup> have published papers to explore the possible application of ultrasonic technology as a preventive treatment method to inhibit the outbreak of cyanobacteria bloom in natural water bodies. Subsequently, related research has been carried out step by step, and the ultrasonic algae inhibition technology has been further developed.

Over the past decade, most of the scholars in the related field focused on two major aspects, the parameter determination for ultrasonic algae inhibition and the effect of ultrasound on the physiologic system of algal cells. For instance, Joyce et al<sup>4</sup> reported that the optimal ultrasonic frequency for algae elimination is 580 kHz. Ma et al<sup>5</sup>, in accordance with the elimination rate of *Microcystis* and micro-

cystins, obtained an optimal frequency at 150 kHz. Tang<sup>6</sup> and Hao<sup>7</sup> applied high-frequency (1.7 MHz), low-intensity ( $0.6 \text{ W/cm}^2$ ) ultrasound and high-low frequency ultrasound (1.7 MHz, 20 kHz), respectively, to perform cyanobacteria inhibition test, and concluded that high-frequency ultrasound exhibits a better inhibition effect on cyanobacteria. Zhang et al<sup>8</sup> examined the changes occurred in cyanobacteria during ultrasonic treatment, and observed the optimal frequency at 200 kHz. In addition, some other scholars deemed 80 kHz as the optimal frequency for ultrasonic algae inhibition based on laboratory tests<sup>5, 9–11</sup>. Rajasekhar et al<sup>12</sup> suggested that the higher the ultrasonic power density, the better the inhibitory effect is. However, when the ultrasonic power exceeds a certain value, the inhibitory effect seems to approach a saturated level<sup>7</sup>. Lee et al<sup>13</sup> applied ultrasound to control cyanobacteria in the Senba Lake, and found that the ultrasound continuing for 3 s can settle 80% of algae cells and the ultrasound continuing for 30 s can settle almost all algal cells. With respect to the irradiation duration, most scholars deemed 5 min to be an optimal value<sup>7, 9, 12</sup>. The input mode of ultrasonic irradiation may also affect the algae elimination efficiency; the multi-frequency, low-dose irradiation mode can achieve a better inhibitory effect on the growth of algae<sup>2</sup>.

In practical applications, the ultrasonic technology has achieved satisfactory results in algae control. Nakano et al<sup>1</sup> constructed an ultrasonic integrated system by combining ultrasonic with jet flow, which was used to control cyanobacterial bloom in the Senba Lake; the outcomes indicated that the lake water quality is significantly improved. Ahn et al<sup>2, 3</sup> applied a device integrating ultrasonic with pump to deal with cyanobacteria in a eutrophic pond and the effect was significant. Ding et al<sup>14</sup> applied 20 kHz ultrasonic to control cyanobacterial bloom in the Taihu Lake and the algal density was successfully reduced from  $10^7/\text{ml}$  to  $10^5/\text{ml}$ . Fan et al<sup>15</sup> applied the ultrasonic technology to treat algal bloom in the Pengxi River of the Three Gorges Reservoir area, and the algal density is reduced from  $(1.10 \pm 0.02) \times 10^7/\text{ml}$  to  $(2.1 \pm 0.1) \times 10^5/\text{ml}$ . According to these results, ultrasonic treatment can inhibit the growth of algae, but the practical application of this process may lead to secondary pollution, such as the release of algal toxin and heavy metals into the sediment. Many studies have adopted the ultrasonic technology as a preprocessing method for determining heavy metals in environmental samples, and the outcomes were

satisfactory<sup>16, 17</sup>. Collasiol et al applied the process of “ultrasonic extraction-online flow injection-oxidation vapour atomic absorption spectrometry” directly to determine the Hg content in soil, river bed and marine sediment<sup>18</sup>. The validation using standard samples suggests a satisfactory result: compared with the traditional wet digestion method, the test results exhibit no significant difference. Ozkan et al<sup>19</sup> developed a method which uses ultrasonic technology to extract and analyse the Mn and Pb content in soil samples taken from the roadside. This method can be used to evaluate the vehicle exhaust pollution. The results indicate that, in a relatively short period, the ultrasonic extraction method can achieve a higher extraction rate compared with the traditional oscillation method.

It can be seen that ultrasonic treatment will release heavy metals from samples into the environment. Thus some scholars applied the ultrasonic technology to remove heavy metals from soil, sludge, and sediment. For example, He et al found that, compared with mechanical oscillation, ultrasonic treatment can intensify the release of Hg from  $\text{Al}_2\text{O}_3$ , a-HgS and PACS-2 sediments into the water<sup>20</sup>. In the presence of algae, the removal rate of  $\text{Hg}^{2+}$  of ultrasonic in 15 min is equivalent to the removal rate of  $\text{Hg}^{2+}$  after 60 min of mechanical oscillation<sup>21</sup>. Newman et al used flowing water to wash through the surface of soil substrate and performed ultrasonic irradiation for half an hour. The removal rate of Cu for the simulated soil pollution sample reached 40%; while under the same condition, the removal rate of the traditional oscillation method was only 6%<sup>22</sup>. The results of the study conducted by Chen et al showed that the precipitation rates of Cu, Zn, Ni, and Pb were 42%, 38%, 13%, and 15%, respectively, when ultrasonic treatment was performed for 30 min. The total precipitation rates were 53%, 45%, 24%, and 71%, respectively<sup>23</sup>.

According to the previous results, relatively low-frequency (20–200 kHz) and low-power ultrasonic is recommended in practical applications of algal control, and the irradiation duration should be generally no more than 5 min. Meanwhile, the batch-type, short-duration irradiation mode can achieve a better inhibitory effect. Although the ultrasonic technology has been applied to algal control and given satisfactory results, heavy metals in soil or sediment are released into the water. Furthermore, the effect of the ultrasonic algae inhibition method on the changes of the heavy metal five-state concentration in sediment is unknown. On

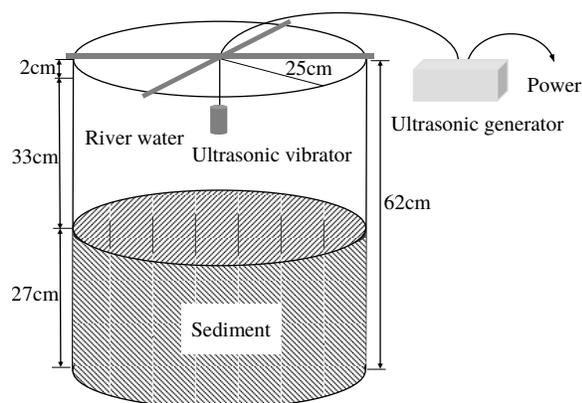


Fig. 1 Experimental equipment.

the basis of existing research findings, the present study applied low-frequency, low-power (35 kHz,  $0.105 \text{ W/cm}^2$ ) ultrasonic waves to irradiate a simulated water body, in order to examine the ultrasonic effect on heavy metals in sediments, as well as their concentrations of exchangeable, carbonate binding, Fe–Mn binding, organic binding, and residue states. The outcomes of this study will provide technical support for the practical applications of ultrasonic algae inhibition.

## MATERIALS AND METHODS

### Experimental apparatus

The experiment was conducted in a plastic barrel (diameter 59 cm, height 62 cm). The oscillator and generator of the ultrasonic generator used in the present test are separated and connected by wires. In the test, a cross bracket was placed in the centre of the bucket. The oscillator was placed at an appropriate position under the water, and then the wires were fixed at the centre of the cross. Then the ultrasonic generator was powered on for processing (Fig. 1). To simulate the actual environment, the sediments and water used in the experiment were extracted from a river in Yancheng city and stored in the barrel. The top of the ultrasonic vibrator was placed 5 cm above the water surface; the length of the vibrator was 10 cm; the diameter and the height of the barrel were 50 cm and 62 cm, respectively; the depth of the water sample was 33 cm, volume was  $0.065 \text{ m}^3$ ; the protection height was 2 cm and the sediment thickness was 27 cm. Considering the possibility that the background values of heavy metals in the sediments may be relatively low, appropriate amounts of Cu, Zn, Pb, and Cr nitrate solution were added into the water. Then a stick was

used to stir the sediments in order to mix the metal nitrate solution with the sediments and water well. After returning to static state, a self-made extractor was used to take samples from the sediment surface, 10 cm below the surface, and the water body for measurement.

During the generation of ultrasonic wave, the vibrator may produce some slight vibrations. As the bottom of the vibrator was about 18 cm above the sediment, such slight vibrations were unlikely to affect the sediment. A sampler similar to an injector was used to take water samples at the sampling depth gently and slowly. Thus neither the vibration nor the sampling process would stir the water sample. The sediment samples were taken by a self-made piston-type column sampler. Although the design of this sampler has been improved, a small amount of sediment can still drop from the bottom of the sampler during the lifting process. Hence it was necessary to raise the sampler out of the water surface as quickly as possible, and the depth of sediment sampling needs to be increased appropriately. After each time to sediment sampling, the position on the top of the barrel was recorded in order to ensure that the samples were not taken repeatedly from the same site.

### Instruments

Heavy metals are detected by an inductively coupled plasma emission spectrometer (ICP, Perkin Elmer). A total of 3 parallels are detected for each sample. The ultrasound generator used in the experiment is a Waterman ultrasonic algae eliminator manufactured by Water&Soil Management Associates (model 220, frequency 35 kHz, power  $0.105 \text{ W/cm}^2$ ). All test reagents were analytical reagents.

### Detection of heavy metal concentrations in water

To prepare the single-element standard solution, the corresponding metal salts (reference substance) were dissolved in water to obtain a  $1.00 \text{ mg/ml}$  standard stock solution. The acidity of the solution was maintained at 0.1 M or above. To prepare the single-element intermediate standard solution, Cu, Cr, or Zn were dissolved into the single-element standard stock solution prepared above to obtain  $0.10 \text{ mg/ml}$  solutions. Pb was prepared into  $0.50 \text{ mg/ml}$  solution. Certain amount of acid was supplied to maintain the acidity at 0.1 M or above.

To determination elements, the samples were filtered using a  $0.45 \mu\text{m}$  membrane immediately

after collection. The initial 50 ml of solution was discarded and 50 ml of the filtrate collected. We used (1+1)  $\text{HNO}_3$  to adjust the pH of the solution to  $\text{pH} < 2$ ;  $\text{HNO}_3$  was added into the wastewater until the concentration of  $\text{HNO}_3$  reached 1%.

To prepare the blank solution, the same volume of deionized water as the sample was used. Blank solution was prepared according to the same procedures. Sample determination was performed using two-point standardization for the preprocessed samples and the blank solution at the best instrument working parameters, in accordance with the instrument instructions. Then the interference was corrected after subtracting the background values<sup>24</sup>.

#### Detection of heavy metal concentrations in sediments

The samples were dried at room temperature, and plant residues, stones, and other debris were removed. After grinding using a 100-mesh nylon sieve to filter, the samples were packed into polyethylene bottles. Reserve samples were placed in a dryer. Non-metal tools were used for the mixing, crushing, grinding, and other necessary processes.

The  $\text{HNO}_3$ -perchloric acid-hydrofluoric acid system was used to fully decompose the samples. A 0.2 g (precision 0.0001 g) portion of a sample into a Teflon crucible/digestion tube and 5 ml of  $\text{HNO}_3$  was added into each sample and soaked overnight to preliminarily decompose the soil. Both blank and parallel samples were prepared for each batch. Then 5 ml of  $\text{HNO}_3$ , 5 ml of hydrofluoric acid, and 3 ml of perchloric acid were added to the samples during digestion. The samples were covered and placed into a fume cupboard for heating at  $180^\circ\text{C}$ . One hour later the cover was opened to remove the silicon. The crucible was shaken frequently during the heating process. When thick white smoke appeared, the sample was covered to let the black organic matter decompose. After the black organic matters has disappeared, the cover was opened to release the acid further. The heating was stopped after no more white smoke was generated and the samples became viscous. After cooling down, the samples were maintained at a constant volume of 25 ml and keep static for 24 h for measurement.

#### Detection of the various states of heavy metals

With respect to the analysis method for the five states of heavy metals in sediments, the five-step sequential extraction method proposed by Tessier et al<sup>25</sup> was used to extract the exchangeable, carbonate binding, Fe-Mn binding, organic binding,

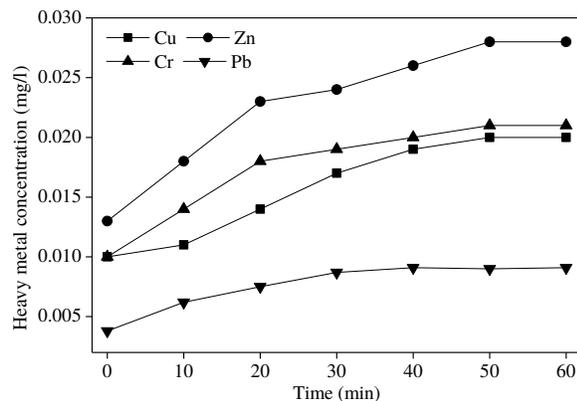


Fig. 2 The changes of heavy metal concentrations in water after ultrasonic treatment of different durations.

and residue states of heavy metals. Then ICP was used to determine the contents of various states for each heavy metal to analyse the distribution of each element state.

## RESULTS

#### The changes of heavy metal concentrations in water

The changes of heavy metal concentrations in water after 60 min of ultrasonic treatment are shown in Fig. 2. It can be seen that ultrasonic treatment increases the concentrations of Cu, Zn, Cr, and Pb in water. The concentrations of the four heavy metals increased rapidly during the first 20 min of ultrasonic treatment and then the increasing rate slowed down during 20–50 min. After 50 min of ultrasonic treatment, the concentrations approached a stable level. After 50 min of ultrasonic treatment, the concentration of Cu ion in water samples reached a peak value and became stable. At this point, the concentration of Cu ion was 2 mg/l, while the concentration of Cu ion in the water samples before ultrasonic treatment was 1 mg/l; thus the concentration of Cu ion doubled. After 50 min of ultrasonic treatment, the concentration of Zn ion in water samples reached a peak value and became stable. At this point, the concentration of Zn ion was 2.8 mg/l, while the concentration of Zn ion in water samples before ultrasonic treatment was 1.3 mg/l. Thus the concentration of Zn ion increased by 115%. After 40 min of ultrasonic treatment, the concentration of Cr ion in water samples reached a peak value and became stable. At this point of time, the concentration of Cr ion was 1.8 mg/l, while the concentration of Cr ion in water samples before ultrasonic treatment was

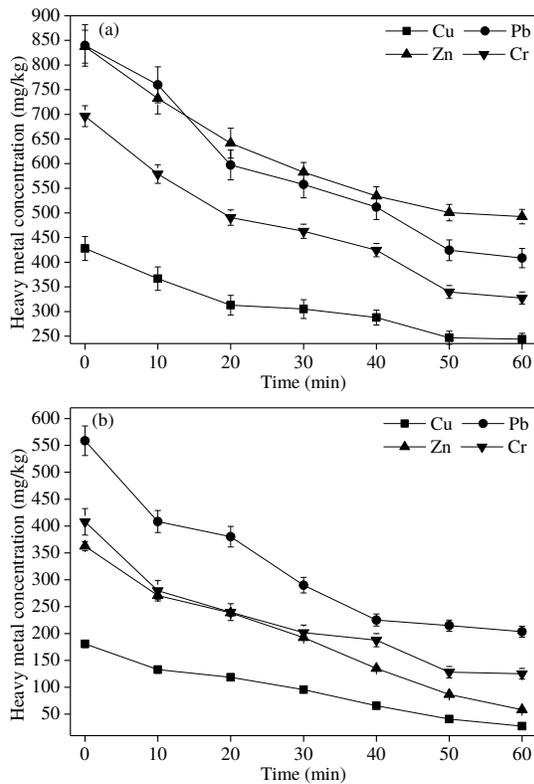


Fig. 3 The changes of concentrations of the four metals in sediment after ultrasonic treatment: (a) surface, (b) 10 cm below the surface.

1 mg/l. Thus the concentration of Cr ion increased by 80%. After 30 min for ultrasonic treatment, the concentration of Pb ion in water samples reached a peak value and became stable. At this point, the concentration of Pb ion was 0.87 mg/l, while the concentration of Pb ion in water samples before ultrasonic treatment was 0.38 mg/l. Thus the concentration of Pb ion increased by 129%. The effect of ultrasonic treatment varies for different heavy metals. The curve in Fig. 2 shows that ultrasonic treatment exhibits the most significant effect on the release of Zn, followed by Cr, while the effect on Pb is the least significant.

**The changes of the total amounts of heavy metals in sediments**

Fig. 3 shows that the four heavy metals in sediments are released rapidly during the first 20 min of ultrasonic treatment, and then the release rate slows down. At the point of 20 min, the release rate of Cu, Zn, Pb, and Cr at the sediment surface was 27%, 24%, 29%, and 29%, respectively, while the release rate at 10 cm below the surface was 34%, 34%,

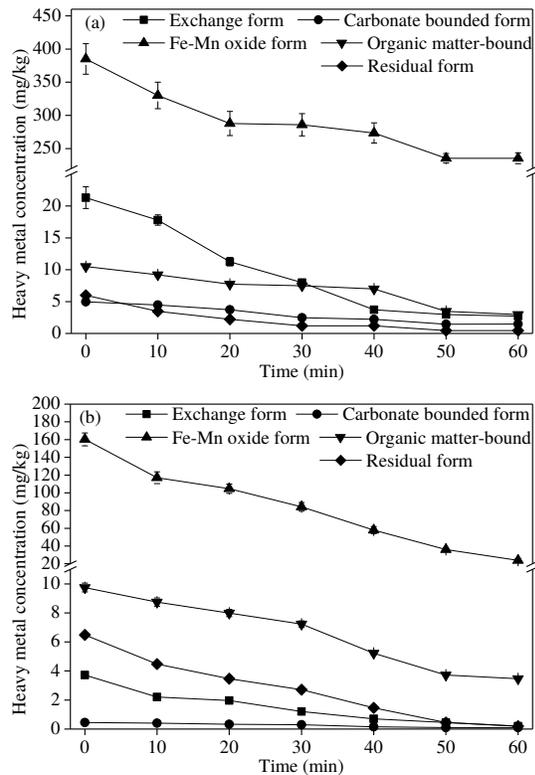
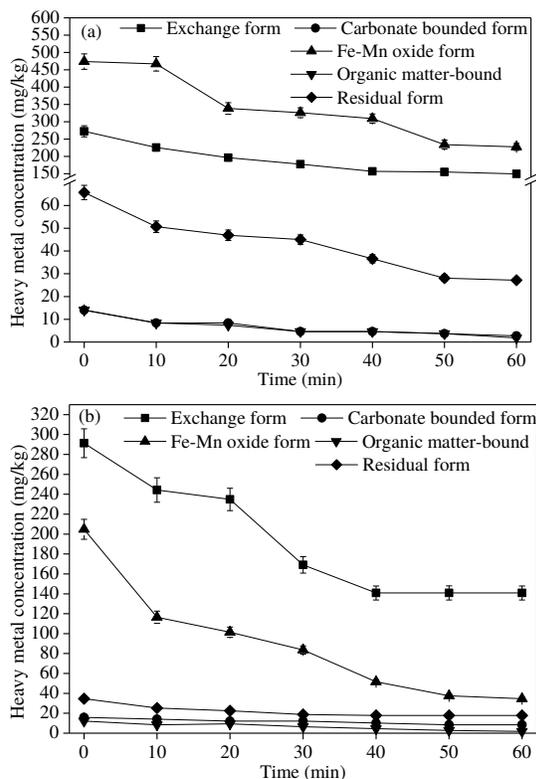


Fig. 4 The changes of concentrations of the five states of Cu in the sediment after ultrasonic treatment: (a) surface, (b) 10 cm below the surface.

32%, and 39%, respectively. After 50 min ultrasonic treatment has virtually no effect on the release of the four metals at the sediment surface; there was still some acceleration effect on the release of Cu and Zn at 10 cm below the sediment surface, but not on the release of Pb and Cr.

**The changes of the five states of heavy metals in sediment**

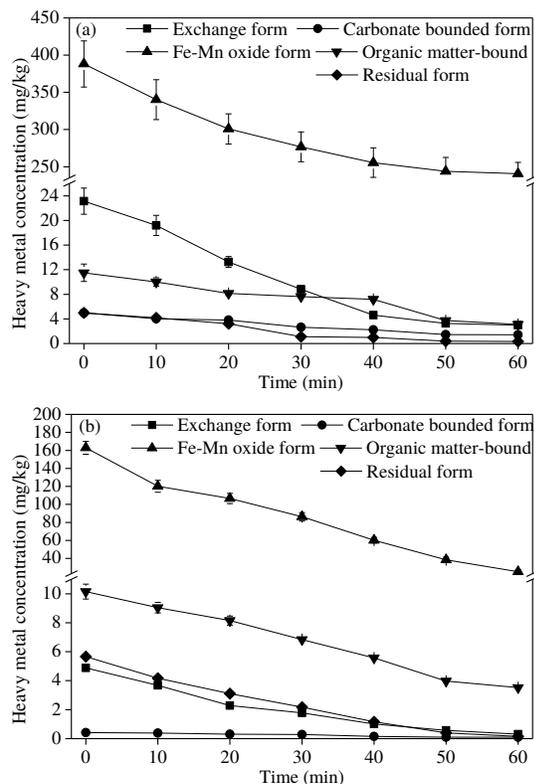
Fig. 4 to Fig. 7 present the changes of the concentrations of exchangeable, carbonate binding, Fe–Mn binding, organic binding, and residue states for Cu, Pb, Zn, and Cr after ultrasonic treatment. At the sediment surface, Cu, Zn, Pb, and Cr mainly exist in the forms of Fe–Mn binding state and exchangeable state, and these two states are most significantly impacted by ultrasonic treatment. Particularly, during the first 20 min, the concentrations of the two decrease rapidly; the concentrations of the Fe–Mn binding state and exchangeable state of the four metals decreased by 25% and 47%, 22% and 43%, 29% and 28%, and 29% and 29%, respectively. Ultrasonic treatment exhibits insignificant effect on



**Fig. 5** The changes of concentrations of the five states of Pb in the sediment after ultrasonic treatment: (a) surface, (b) 10 cm below the surface.

the organic binding, carbonate binding, and residue states of the four metals. In particular, there is no obvious change in the concentrations of organic binding state and carbonate binding state.

At 10 cm below the sediment surface, Cu and Zn mainly exist in forms of the Fe–Mn binding state and organic binding state, while Pb and Cr mainly exist in forms of the Fe–Mn binding state and exchangeable state. The ultrasonic effect on the four metals showed no regular pattern: the concentration of the Fe–Mn binding state of Cu decreases rapidly during the first 10 min; at the time point of 10 min, the concentration has been reduced by 27%. The concentrations of the Fe–Mn binding state and exchangeable state of Pb declined consistently during the first 40 min of ultrasonic treatment. At 40 min, the concentrations were reduced by 75% and 52%, respectively, and then the changes slowed down. The pattern of Zn was similar to that of Cu. At 10 min, the concentration of the Fe–Mn binding state of Zn was reduced by 26%. The concentration of the Fe–Mn binding state of Cr declined rapidly during the 0–10 min interval and

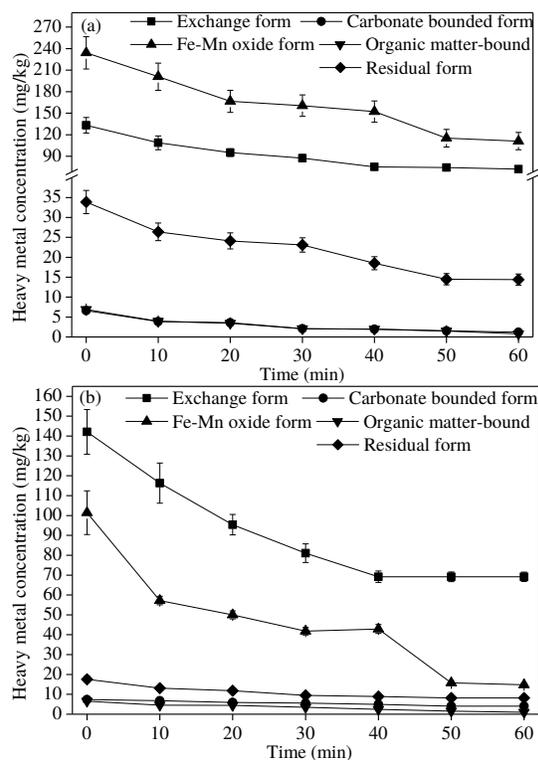


**Fig. 6** The changes of concentrations of the five states of Zn in the sediment after ultrasonic treatment: (a) surface, (b) 10 cm below the surface.

the 40–50 min interval, while during the 10–40 min interval and after 50 min, the concentration change was insignificant. At 10 min, the concentration of the Fe–Mn binding state of Cr was reduced by 44%. At 10 cm below the sediment surface, the concentrations of the carbonate binding state of Cu and Zn, as well as the concentrations of the carbonate binding state and organic binding state of Pb and Cr did not change significantly.

### DISCUSSION

The process of ultrasonic algae inhibition can accelerate the dissolution of heavy metals from sediments and therefore results in the risk of secondary pollution. Although this technology, which was developed over the past decade, has been shown to be an effective method for algal elimination and inhibition, its potential negative effects have rarely been investigated. The scholars in this field mainly focused on the inhibitory effect and related mechanisms. In the present study, low-frequency and low-power ultrasonic (35 kHz, 0.105 W/cm<sup>2</sup>) was used to irradiate the simulated water body.



**Fig. 7** The changes of concentrations of the five states of Cr in the sediment after ultrasonic treatment: (a) surface, (b) 10 cm below the surface.

By determining the concentration change of the four heavy metals in water and sediments, as well as the concentration changes in the exchangeable, carbonate binding, Fe–Mn binding, organic binding and residue states, this study confirms that the ultrasonic effect can accelerate the release of metal elements from the sediments. However, the present experiment was only performed on one type of ultrasonic wave (fixed power and frequency). Further studies need to be conducted to evaluate the effect of various combinations of frequencies and powers on the release of pollutants from sediments in the ultrasonic algal inhibition process. The experiment adopted a continuous timing mode, and the ultrasonic treatment continued for 60 min each time. Samples were taken at 10 min intervals. In comparison, the duration of ultrasonic treatment is usually shorter than 5 min in other studies. The present experiment did not investigate the effect of ultrasonic treatment on the release of heavy metals from sediments during the early stages (such as 30 s, 5 min). Thus the risk of heavy metal release at the early stage of ultrasonic treatment should be further

evaluated.

In the process of ultrasonic algae inhibition, the ultrasonic effect can accelerate the release of heavy metals from sediments into the water body, increasing the heavy metal concentrations in water. The longer the duration of ultrasonic treatment, the higher the amount of heavy metals released from the sediments, and thereby the higher the possibility of secondary pollution. During the first 20 min of ultrasonic treatment, the concentrations of Zn and Cr in water increased rapidly, and the ratio of increase reached 38% and 40%, respectively. The concentration of Pb increased rapidly during the first 10 min, while the concentration of Cu increased rapidly during the 10–40 min interval. After 50 min of ultrasonic treatment, the concentrations of the four heavy metals approached to a stable level. Peng et al<sup>26</sup> used ultrasonic at the frequency of 53 kHz, the power of 300 W to extract Cu, Fe, Zn, and Mn from soil; with 15 min of treatment, the standard recovery rate was 78–96%. Kazi et al<sup>27</sup> used ultrasonic to extract Cu, Cd, Cr, Pb, Ni, Zn, and other metal elements from the sludge of a sewage treatment plant. Compared with the BCR protocol (the Community Bureau of Reference, now the European Union Measurement and Testing Programme), the recovery rates of all metal elements were up to 95–100%, except that of Cu (92%). Maduro et al<sup>28</sup> extracted Pb and Cd elements from biological samples using ultrasound at a power of 63 W, the frequency of 22.5 kHz; with 5–10 min treatment, over 90% of the total metal elements were extracted from biological samples. Liu et al<sup>29</sup> used ultrasonic at the frequency of 40 kHz, the power of 250 W to extract Zn, Fe, Cu, and Mn elements from hairs, tea leaves, celery leaves, and celery stems. Their results showed that the optimal extraction time was 20–30 min and the recovery rate was 91%–16%. Wu et al<sup>30</sup> extracted K, Ca, Mg, B, Zn, P, Mn, and other elements from tobacco leaves with 40 min of ultrasonic treatment. Compared with the HNO<sub>3</sub>-perchloric acid extraction method, ultrasonic treatment achieves a better extraction effect on K, Ca, Mg, B, and Zn, but not on P and Mn. A possible explanation is that P and Mn exist in stable organic forms, which are difficult to disrupt.

According to the previous research findings and the results of this study, the metal extraction effect is quite satisfactory when the ultrasonic treatment is longer than 5 min. On the other hand, Liu et al obtained an optimal extraction time of 20–30 min. The present study confirms that the concentrations of the four heavy metals almost approaches to a

stable level after 50 min of ultrasonic treatment, which is slightly longer than the duration mentioned in previous work. The difference here is perhaps due to the choice of the extraction agents. This study used river water as the extraction agent, while others have used single acid (such as  $\text{HNO}_3$ ) or multiple acid solutions as the extraction agent. Metals have a higher solubility and dissolution rate in acid solution than in water, so the extraction time of acid solution is shorter. The changes of concentrations of the four metals are not consistent as at the sediment surface and 10 cm below the surface. At the surface, the concentrations decline rapidly during the first 20 min of ultrasonic treatment, while at 10 cm below the surface, the concentrations decline significantly during the first 10 min of ultrasonic treatment. For the liquid-solid system, the ultrasonic effect produces cavitation bubbles in the medium, as well as corrosion and local heating on the solid surface. The turbulence caused by micro jet can significantly improve the mass transfer process between the liquid medium and the solid surface<sup>31</sup>.

Out of the exchangeable, carbonate binding, Fe–Mn binding, organic binding, and residue states of the four heavy metals, the concentrations of the exchangeable state and carbonate binding state of Fe and Mn at the sediment surface changed greatly, while at 10 cm below the surface, the concentrations of the Fe–Mn binding state of Cu and Zn, as well as the Fe–Mn binding state and organic binding state of Pb and Cr declined significantly. The changes in concentration occurred during the first 20 min of ultrasonic treatment. Meng et al<sup>32</sup> used ultrasonic waves at the frequency of 42 kHz to extract Fe, Cu, and Pb elements from honeysuckle, and found the best extraction effect on Cu, followed by Pb, while the effect on Fe was the weakest. The extraction rate was irrelevant with the contents of elements in honeysuckle. The difference may be due to the state of various elements in the honeysuckle. The present study also shows that the concentrations of the five states of four metals change in different patterns as at the sediment surface and at 10 cm below the surface. This confirms the speculation of Meng et al<sup>32</sup>. Ultrasonic waves propagate differently at the sediment-water interface and in sediments, which is the root cause that leads to the different patterns of change of the four metals and five states at the sediment surface and 10 cm below the surface.

The experimental results suggest that the ultrasonic algae inhibition technology is not sufficiently

safe and reliable. While eliminating algae cells, ultrasonic technique can also generate a series of other mechanical, chemical, thermal, and biological effects.<sup>33,34</sup> Firstly, the mechanical effects includes micro jet, shock wave, and sound streaming caused by ultrasonic cavitation that can lead to the macro turbulence of liquid flow and high-speed collision of solid particles, which will in turn strengthen the eddy diffusion and promote the mass transfer effect. Secondly, the accompanied phenomena such as micro jet and impinging stream produced by ultrasonic cavitation can exert impact, peeling, and erosion effects on the liquid-liquid and liquid-solid interface, which will then update the interface status. Meanwhile, the accompanied activation effect can create an active surface. These two together will strengthen the mass transfer effect. Thirdly, the effect that promotes mass transfer is originated from the micro turbulence in the porous medium caused by micro jet and shock wave. It will strengthen the diffusion of substances within the pores. The combined action of these ultrasonic effects eventually accelerates the release of heavy metals from the sediment surface and sediments below the surface, which at the same time introduces the risk of secondary pollution. If the ultrasonic technology is applied to water sources, it may increase the contents of heavy metals in the raw tap water and thus increase the risk of drinking water safety. Hence the ultrasonic algae inhibition technology should be cautiously considered in practical applications in accordance with the specific use of water sources.

The study conducted by Lee et al<sup>13</sup> showed that ultrasonic waves applied for 3 s can kill 80% of algae cells, while applied for 30 s can lead to almost complete alga settlement. Some other scholars also concluded that the ultrasonic treatment can achieve good inhibitory effects on algal cells within 5 min of treatment<sup>7,9,12</sup>. Ample evidence can be found to prove the inhibitory effect of ultrasonic on algae within a short application time. Thus in practical applications, the duration of ultrasonic treatment should be controlled as short as possible, in order to limit the release of heavy metals from sediments into the water body. An optimal combination of ultrasonic parameters (frequency, power, and duration) should be able to achieve good inhibitory effect while reducing the risk of heavy metals release from sediments. Future studies with respect to the ultrasonic algae inhibition technology should focus on the determination of suitable ultrasonic parameters in order to control the release of heavy metals from sediments.

## CONCLUSIONS

Ultrasonic treatment can accelerate the release of heavy metals from sediments. The effect of ultrasonic is the most significant on the release of Pb, followed by Zn, Cu, and Cr. With the increase of ultrasonic treatment duration, the concentrations of Cu, Zn, Cr, and Pb in the water body reach the peak value and approach to a stable level at 45 min, 50 min, 30 min, and 35 min, respectively. The particular form of heavy metals in sediments can influence the release of metals to a certain extent. Ultrasonic exhibits a significant effect on the Fe–Mn binding state and exchangeable state of metals, while the effect on the carbonate binding, organic binding, and residual states is less significant. The ultrasonic algae inhibition technology is not perfectly safe and reliable. It involves the risk of increasing the concentration of heavy metals in the water body.

**Acknowledgements:** We gratefully acknowledge grant supported by Natural Science Foundation of China (3147 0507) and China Building Materials Industry Association technology innovation projects (2013-M5-2).

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