Sediment Re-Suspension and Release of Dissolved Heavy Metal Cu under Wave Actions

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Abstract. Located in the semi-enclosed Bohai Sea, the Yellow River subaqueous delta faces serious pollution by the heavy metal Cu in seabed sediments and is frequently subject to storm surges which further incur sediment re-suspension or even liquefaction, and cause Cu to be released back into seawater. This study performed an indoor wave flume experiment to simulate the release of Cu into overlying water under different hydrodynamic conditions in three phases: static diffusion, seabed non-liquefaction and re-suspension, and seabed liquefaction and re-suspension. As indicated by the results, the concentration distribution of Cu in overlying water was closely related to that of suspended sediment and had consistent change trends. Sediment liquefaction clearly promoted the release of Cu into overlying water, and the dissolved Cu concentrations in the overlying water during the seabed liquefaction and re-suspension phase were 18 times those in the static diffusion phase, and 11 times those in the seabed non-liquefaction and re-suspension phase. In addition, seabed liquefaction caused Cu in sediments to diffuse towards deeper levels, and the diffusion depth of was about half of liquefaction depth.

1. Introduction
Heavy metal pollution in the Yellow River subaqueous delta mainly comes from the exploitation, transport, and oil spills, and industrial pollution discharge from upstream watersheds [1]. When heavy metals entering the sea combine with suspended particles in water through adsorption and settle on seabed [2], sediments become major reservoirs for these pollutants. According to existing studies, the surface sediments in the Chengdao Oilfield area of the Yellow River estuary have a relatively high heavy metal Cu content [3, 4]. Sediments are constantly in material and energy exchange with overlying water. As hydrodynamic conditions change, heavy metal pollutants migrate from sediments to water by means of dissolution, desorption, and so on, posing both environmental hazards and ecological risks [5]. The heavy metal pollution of seawater in the Yellow River subaqueous delta...
region is caused by exogenous sewage discharge and endogenous heavy metal release, the latter of which is more difficult to control.

At present, laboratory simulation studies on sediment re-suspension mainly used annular water flumes [6, 7], particle entrainment simulator [8, 9], wave flumes [10] and other experimental equipment, focusing on the release of heavy metals during surface sediment re-suspension in lakes, rivers, estuaries, and other areas [11-13]. However, they rarely touch upon the release of heavy metals in marine sediments due to wave action and sediment liquefaction.

Using wave flume experiments, this paper simulated the re-suspension or even liquefaction of seabed sediments under different wave conditions, investigated the release and migration processes of the heavy metal Cu in sediments under different wave conditions, and offered a scientific basis for estimating Cu release amounts in sediments of the Yellow River subaqueous delta.

2. Materials and Methods

2.1. Study area
The soil sample used in this study was silty soil collected from the Diaokou lobe tidal flat of the Yellow River delta, as shown in Figure 1. In the Yellow River subaqueous delta, surface sediments are typically dominated by fine sediments, especially fine silty clay. The Yellow River delta silty seabed has some special properties, such as a high water content, high compressibility, liquefaction, and non-uniform consolidation. Waves in this region are mainly generated by local winds in the Bohai Sea area; they are less than 1.5 m in height under normal circumstances, but may reach as high as 5.8 m under extreme sea conditions. Under the influence of storm surge, the liquefaction extent of the seabed at water depths of 8-12 m may reach 4-6 m.

![Figure 1. Location of study area](image)

2.2. Experimental equipment and materials
The soil samples collected from the tidal flat were mainly composed of fine sand (29.3%), silt (61.9%), and clay (8.8%). To guarantee seabed homogeneity, silty soil was flattened and air-dried, and soil blocks were crushed and evenly mixed. After being screened using a 0.5 mm vibrating screen, the soil was used for seabed pavement. The overlying water used in this experiment was standard man-made seawater with a salinity of 35‰.

Figure 2 (a) shows the wave flume (4 m × 0.4 m × 1.0 m) used in this study. On the right side of the flume was a wave-making apparatus that pushed water back and forth to make waves. On the left side was a wave eliminator, which can reduce interference caused by wave reflections. There was also a capacitive water level meter (RBR, Canada) in the middle, used to collect wave heights and wave
periods. Turbidimeters (RBR, Canada) were placed at 5 cm and 20 cm above sediment to observe the change in suspended sediment concentrations. The entire system was under computer automated control. At the bottom center of the flume was a sediment groove (0.6 m × 0.4 m × 0.3 m), the right side of which was 1.6 m away from the wave-making board. A pore water pressure sensor was buried at a depth of 20 cm in the sediment to observe the change in pore water pressure. See sampling points, the turbidimeter, and pore water pressure sensor positions in Figure 2 (b).

![Figure 2. (a) Layout of the wave flume. (b) Layout of the sediment bed and sampling points](image)

2.3. Preparation and paving of experimental seabed
In this experiment, 623.7 g Cu (NO₃)₂·3H₂O was weighed and dissolved in 10 kg standard seawater to prepare the heavy metal solution. The solution was then mixed with 33.0 kg dry soil to prepare a uniform slurry with a water content of 32% (Cu/dry soil mass ratio = 4.99 mg·g⁻¹). To ensure that heavy metal Cu could reach a stable state, the prepared heavy metal-containing slurry was placed unmoving for 7 d before use (sealed and stored in darkness). The remaining soil was mixed with a suitable amount of standard seawater so that the water content of the mixture would be the same as that of the heavy metal-containing soil sample. First, the prepared slurry containing no heavy metal Cu was transferred to the bottom of the flume until slurry height reached 25 cm, and a 5 cm layer of Cu-containing slurry was paved over it, so the seabed sediments had a total thickness of 30 cm. After seabed pavement, standard seawater with a salinity of 35‰ was slowly added into the flume until water depth reached 50 cm.

2.4. Flume experimental process and parameters
The entire flume experiment was divided into three phases: static diffusion (phase I), 5 cm wave height (phase II), and 10 cm wave height (phase III).

In phase I, the overlying water was still and seabed sediments were in a static diffusion state for a duration of 40 h. Both phases II and III were under wave action and each wave height lasted for 180 min. In phase I, a self-designed water sampler was used to collect water samples at intervals of 8 h and a distance of 30 cm from the left side of the seabed at two sampling points, 5 cm and 20 cm above sediments (Figure 2 (b)). Three parallel samples were taken from each sampling point and all of them
were added with nitric acid and stored at a low temperature (4°C) for later use in determining the concentration of dissolved Cu in samples. The timing of phases II and III began with the stabilization of wave height. Water samples were taken once every 10 min in the first 60 min and once every 20 min in the last 120 min; the sampling positions and methods in phases II and III were the same as those in phase I. See experimental wave parameters and the experimental process in Table 1.

At the end of the experiment, a piston sampler was used to collect 24 cm columnar samples of sediments (set at 24 cm because after wave erosion and damage, the residual thickness of the seabed was 24 cm) at three sites: 10 cm, 30 cm, and 50 cm away from the left edge of the sediment groove. Then columnar samples were cut at intervals of 2 cm and three parallel samples were taken at each depth to measure the Cu content at different sediment depths.

| Test stage | Wave parameters | Duration | Sampling time |
|------------|-----------------|----------|---------------|
| Phases II  | -               | 40 h     | intervals of 8 h |
| Phases II  | 5.0             | 180 min  | once every 10 min in the first 60 min and once every 20 min in the last 120 min |
| Phases III | 10.0            | 180 min  |               |

2.5. Sample analysis
The concentration of heavy metal Cu was determined by the microwave digestion (HNO3-HClO4-HF) method. First, a 0.25 g sediment sample or a 25.0 mL water sample was added to a microwave digestion tank, followed by the addition of HF, HClO4, and HNO3. Then the digestion tank was properly sealed and placed in a microwave digestion tank. After digestion, the mixed solution was cooled down to room temperature and added into a 25.0 mL colorimetric tube through constant-volume sampling, and an inductively coupled plasma emission spectrometer (PE Optima 8000, American) was used to measure the heavy metal Cu content.

Turbidimeters were calibrated before the experiment. Suspended sediment solutions with concentrations of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g·L⁻¹ were prepared. Turbidimeters were then used to measure corresponding values of the solutions, and coefficients of correlation (R²) were 0.99 after calibration. The calibrated turbidimeters were used to measure the suspended sediment concentrations in overlying water during the experiment.

3. Results
In this study, the mean values of the three parallel samples taken at each sampling point were used as the heavy metal Cu concentrations in overlying water and sediments.

3.1. Variation characteristics of pore water pressure in seabed sediments
Figure 3 (a) shows the change trend of pore water pressure in seabed sediments under wave action with time. Under wave action at 5 cm wave height, pore water pressure rose rapidly but had a low vibration amplitude; only a few suspended particles were seen floating above sediments in this phase. In this phase, pore water pressure first increased, and then declined abruptly. The rate of pore water pressure increase incurred by water action was lower than the dissipation rate of the pore water pressure in sediment soil, so there was no obvious accumulation of pore water pressure. Under wave action at 10 cm wave height, pore water pressure rose rapidly to a peak value and had a high vibration amplitude. The rate of pore water pressure increase incurred by water action was higher than the dissipation rate of the pore water pressure in sediment soil, so this phase witnessed the liquefaction of seabed sediments into fluids oscillating from side to side with waves.
3.2. Content change characteristics of suspended sediment in overlying water

Figure 3 (b) shows the variation of suspended sediment concentrations in overlying water under continuous wave action. Clearly, the suspended sediment concentrations increased with wave height. At the 5 cm wave height phase, the suspended sediment concentrations fell within the range of 0.051-0.162 g·L⁻¹; at the 10 cm wave height phase, they ranged from 0.837-1.146 g·L⁻¹. That is, the concentration of suspended sediment under 10 cm height wave action increased by six to eight times compared to concentrations under 5 cm height wave action. The suspended sediment concentrations increased rapidly at the start of wave action, and they tended to be stable 20 to 30 min later. The change in concentrations of suspended sediment in the bottom layer (5 cm above sediments) was consistent with those in the middle layer (20 cm above sediments).

3.3. Concentration variation characteristics of dissolved Cu in overlying water

Figure 4 shows the concentration of dissolved Cu in overlying water in different phases. Clearly, in phase I, dissolved Cu concentrations in overlying water changed within the range of 0.45-0.67 mg·L⁻¹, and had a trend of first declining and then rising with time. In phase II, under wave action of 5 cm wave height, dissolved Cu concentrations in water changed within the range of 0.54-0.85 mg·L⁻¹, and first rose and then declined with time. In phase III, under wave action of 10 cm wave height, dissolved Cu concentrations in overlying water rose rapidly within a short period of time after wave application and had a steadily increasing trend after about 80 min. The dissolved Cu concentrations changed within the range of 0.54-9.02 mg·L⁻¹.
3.4. Content changes of heavy metal Cu in sediments

Sediment soil was liquefied under the action of 10 cm wave height and the erosion depth was around 6 cm. Thus, columnar sediments 24 cm in height below the eroded layer were collected for laboratory analysis.

Figure 5 shows the content distribution of Cu in sediments. In the horizontal direction, there were no significant concentration differences among the three sampling positions. With the change in depth, the content of Cu first rose and then declined, and the peak zone of Cu concentration occurred at 2-3 cm below the initial depth of the polluted layer. The Cu content in sediments changed within a range of 2.6-2,660 mg·kg⁻¹.

Figure 5. Cu concentration distribution in the sediment (Distance from the left edge of the sediment trough: a: 10 cm; b: 30 cm; c: 50 cm)
4. Discussion

4.1. Concentrations of heavy metal Cu in overlying water

In phase I, the initial phase of the experiment, the concentrations of dissolved Cu in water were relatively high (Figure 4 (a)), possibly because of surface sediment erosion due to the flow of water added into the flume. Eight hours later, dissolved Cu concentrations in water rose gradually. In this phase, the release of the Cu in sediments into overlying water followed the pathways as described: Due to the difference in dissolved Cu concentrations between the polluted layer paved on the sediment surface and overlying water, heavy metal Cu was released into overlying water via static diffusion. In addition, given that the reshaped sediments with relatively high water content would consolidate drainage, the heavy metal Cu in sediments was gradually discharged into overlying water with pore water during consolidation. The combined action of the two resulted in the rise in dissolved Cu concentrations in overlying water.

In phase II, under wave action of 5 cm wave height, the concentrations of suspended sediment increased slightly (Figure 3 (b)) and the re-suspension of surface sediments was observed. Dissolved Cu concentrations in water first increased and then decreased; concentrations during the late period of wave action were lower than those during the static diffusion phase (Figure 4). The increase in dissolved Cu concentrations in overlying water in this phase could be explained by two aspects: First, under wave action, the difference between pressure peaks and troughs caused the Cu in sediments to be diffused into overlying water with pore water. Second, after the entry of sediments into overlying water through re-suspension, a portion of the Cu adsorbed on sediment particles experienced desorption, which also increased dissolved Cu concentrations in overlying water. After 30 min under wave action, the suspended sediment concentrations in water slowly declined, accompanied by the decline in dissolved Cu concentrations in a similar trend. Wave action also led to an increase in dissolved oxygen concentrations in overlying water and sediments [14, 15], and the oxidization of Fe and Mn ions in suspended particles. As a result, a Fe-Mn oxide layer formed on the surface of suspended particles and adsorbed a large amount of dissolved Cu, which later returned into sediments through precipitation [16, 17]. In addition, under wave action, suspended particles in water became finer [18, 19]. Given that fine particles had a larger specific surface area and could more effectively absorb dissolved Cu, dissolved Cu concentrations declined. In this phase, dissolved Cu concentrations in overlying water increased only slightly and the release of the Cu in sediments to overlying water was dominated by the desorption of re-suspended sediment and the diffusion of dissolved Cu in pore water.

In phase III, under wave action of 10 cm wave height, the pore water pressure accumulated and increased abruptly, resulting in both the liquefaction of sediments and a rapid rise in suspended sediment concentrations in overlying water (Figure 3 (b)). Dissolved Cu concentrations increased, as well (Figure 4 (c)) and had the same change trend as suspended sediment concentrations. Concentrations of dissolved Cu in water in the liquefaction phase increased by 11 times compared to the non-liquefaction phase. After sediment liquefaction, an intense mixing occurred between sediments and overlying water [20], which facilitated the release of Cu in seabed sediments. After 80 min under wave action, the suspended sediment concentrations in overlying water remained relatively stable; however, with the increase of liquefaction depth, the sediment structure below the liquefied layer was constantly reinforced and featured a more compact structure and smaller gaps between sediment particles. This process caused sediment pore water to seep upwards into overlying water [21]; thus, dissolved Cu concentrations in water still slowly increased. In addition, wave action had been sustained for a relatively long period by the start of phase III and dissolved oxygen concentrations in water had reached relatively high levels. Due to sediment re-suspension, reduced sediments were exposed to an aerobic environment and the organic-bound-state heavy metals and sulfide-bound-state heavy metals in sediments engaged in an oxidizing reaction and were released [17], causing dissolved Cu concentrations to increase.
4.2. Migration and diffusion trends for heavy metal Cu in sediments
The distribution of Cu in sediments was uniform in the horizontal direction, and wave action caused Cu in the polluted layer to diffuse uniformly downward. The peak zone of Cu concentrations emerged within a depth range of 2-3 cm below the polluted layer initially paved in the experiment (Figure 5), and it gradually approached the initial concentration at the depth of 12 cm. According to analysis, the diffusion of pollutants into deeper levels was the combined result of multiple factors. First, sediments within the liquefaction range changed into fluids oscillating from side to side with waves, which intensified the mixing of sediment particles and pore water and caused the vertical diffusion of heavy metal Cu. The maximum liquefaction depth of sediments was about 20 cm. To be specific, heavy metal Cu concentrations in sediments below a depth of 12 cm were close to the initial concentration; therefore, the diffusion depth was about half the liquefaction depth. In addition, due to the difference in pore water Cu concentrations between the polluted sediments paved on the surface and the unpolluted sediments below the surface, Cu diffused towards the low-concentration area below the surface.

5. Conclusion
Based on a wave flume experiment, this paper investigated the migration and release of the heavy metal Cu in sediments under different wave actions, and analyzed those characteristics under different phases. The conclusions drawn in this paper are as follows:

(1) In the static diffusion phase, the primary pathway by which the heavy metal Cu in sediments migrated toward overlying water was the static diffusion of dissolved Cu in pore water. The consolidated drainage of seabed also promoted the release of dissolved Cu to some extent.

(2) In the non-liquefaction and re-suspension phase, the maximum concentration of dissolved Cu in overlying water was about 1.6 times the initial concentration and the effect of 5 cm wave height on Cu release in sediments was not obvious. During the late period of wave action, due to the adsorption of suspended particles, mean concentrations of dissolved Cu in overlying water were lower than in the static diffusion phase.

(3) In the liquefaction & re-suspension phase, seabed liquefaction greatly promoted the release of heavy metal Cu into sediments. Dissolved Cu concentrations in the overlying water during this phase were 18 times those in the static diffusion phase, and 11 times those in the non-liquefaction and re-suspension phase.

(4) Seabed liquefaction intensified the diffusion of the heavy metal Cu in sediments toward deeper levels, and the downward diffusion depth was about half that of liquefaction depth.

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