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Article

The ex-situ immobilization experiment of heavy metals in dredged marine sediments from Bohai Bay, China

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Abstract: The remediation of dredged marine sediments contaminated by heavy metals has drawn increasing attention worldly. The immobilization was regarded as a promising method to reduce adverse impacts on marine ecosystem. In this study, kaolinite and limestone were used as amendments to immobilize heavy metals (e.g. Zn, Pb and Cu) respectively in dredged marine sediments collected from the coastal zone adjacent to Tianjin Port in Bohai Bay. The sequential extraction procedure was applied to identify the mobility of heavy metals and further to evaluate the immobilization effect of amendments. The physical-chemical properties of sediments, such as pH, electrical conductivity (EC), salinity, and total organic carbon (TOC), were also measured to better understand their influence on heavy metals' mobility. In addition, the compositions of clay minerals were also analyzed to identify the transformation process of minerals in the sediments. The results of sequential extraction procedure indicated that mobile fractions of heavy metals were converted into relatively stable fractions because of the two amendments. In addition, EC, salinity and TOC decreased moderately while no obvious variations of pH in the sediments were observed with the addition of the the kaolinite and the limestone. The percentage of montmorillonite decreased to minimum value while that of chlorite increased gradually during the experimental periods for 40 days probably due to complexation reaction. It was confirmed that both kaolinite and limestone can effectively reduce the mobility and bioavailability of heavy metals, particularly for Zn, generally, limestone has a better immobilization effect compared with kaolinite.

Keywords: Dredged marine sediment; heavy metal; immobilization; kaolinite; limestone

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1. Introduction

A large number of dredged marine sediments were generated worldwide due to the management of channel navigation and harbor construction [1, 2]. One of the main concerns raised for dredged marine sediments was their potential risk to marine environment and organisms [3]. As a critical part of geochemical cycle in marine ecosystem, marine sediment plays a role as the largest sink of both organic and inorganic pollutants [4, 5]. Heavy metals represent a crucial category of these pollutants owing to their potential toxicity, durability and bioaccumulation [6, 7]. Once the sedimentary environment (e.g. pH, redox potential and dissolved oxygen) change, heavy metals in sediments can be released into the overlying water again, and even enter the food chain, causing secondary pollution to surrounding areas [8, 9]. Therefore, it is imperative to remediate dredged marine sediments contaminated by heavy metals prior to final disposal [10].

A variety of technologies including physical/mechanical [11], chemical [12, 13], and biological technologies (phytoremediation and microbial remediation) [14, 15] have been applied in remediation of dredged marine sediments contaminated by heavy metals. Of various chemical remediation technologies, immobilization is considered as a promising and alternative option as its high effect, low expenditure and environmental friendliness [16]. The method involves the addition of chemicals to convert mobile and bioavailable fractions of metals into stable fractions [17].

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Successive chemical extraction techniques, such as the four-step BCR proposed by the Community Bureau of Reference and the five-step extraction procedures proposed by Tessier [18], have been widely used to assess mobility and bioavailibility of metals in marine sediments [19, 20].

Immobilizing amendments decrease trace metals' mobility by several processes, which include adsorption, coprecipitation, ionexchange and complexation reactions [21-23]. The most extensively applied amendments in marine sediments include iron-bearing materials, aluminosilicates, phosphates and clay minerals [17, 24]. For example, cement [25], lime [26], red mud and apatite composite [27] were used for the remediation of polluted coastal sediments in Romania, Norway and Republic of Korea, respectively. Despite various kinds of amendments being used, clay minerals have been extensively utilized for immobilization of heavy metals due to simplicity of use, high effect and universal applicability [28]. As one of clay minerals, kaolinite was used as amendment because of the distinctive advantage of specific surface adsorption, large cation exchange capacity and resistance to hydrolysis [29]. In addition, limestone was also one of the oldest and broadest immobilizing agents [30], and the addition of lime played an important role in increasing sediment pH and triggering precipitation of metal oxides, carbonates or hydroxides [31]. However, both kaolinite and limestone were rarely applied in dredged marine sediment.

Located in the northeast of China, Bohai Bay is a typical semi-enclosed bay with shallow water and poor water exchange [32, 33]. Adjacent to Beijing-Tianjin city band and Bohai Rim economic circle, the coastal zones of Bohai Bay are one of the most densely urbanized and industrialized areas in China [34]. Recent research showed that quantities of heavy metals were discharged directly into Bohai Sea in 2018, especially 8237.88 kg for Pb [35]. Tianjin Port, located in Bohai Bay, is the largest comprehensive port in Northern China, where large-scale dredging activities are carried out along the coastal areas annually [34, 36]. It was reported that a total of $466\times104m^3$ of dredged materials were dumped into sites adjacent to the Tianjin Port between 2012 and 2013, resulting in a negative influence on the marine ecosystem in Bohai Bay, and therefore, great importance should be attached to this issue [34, 37, 38].

In recent years, researches about the immobilization of heavy metals in marine sediments have been carried out [39, 40]. However, kaolinite and limestone were seldom used as immobilization agents to remediate heavy metal pollution in marine sediment, and researches reflecting the influence on heavy metals' mobility and transformation behaviors in the immobilization procedures were still rarely carried out, especially in the dredged marine sediment of Bohai Bay. Therefore, the primary objectives of this research is (1) to evaluate the influence of pH, EC, salinity, TOC in marine sediment on immobilization effect, (2) to determine the compositions of clay minerals in marine sediment for a better understanding of the transformation process of minerals in the sediments before and after addition of the amendments, and (3) to assess the effect of limestone and kaolinite as amendments on immobilization of heavy metals on the basis of sequential extraction procedure. This study would be expected to provide technical reference for the remediation of heavy metal pollution in dredged marine sediment.

2. Materials and Methods

2.1. Marine sediment samples collection and pretreatment

In June 2017, the marine surface sediment samples were collected using PVC (polyvinyl chloride) tubes from coastal areas in Tianjin of Bohai bay (39 ° 13 ′ N, 117 ° 58 ′ E). The samples were taken back to the laboratory and reserved at 4℃ in the freezer immediately. After the large particles being removed, the sediment samples were air-dried naturally, crushed fully and passed through 2 mm sieve. A single homogeneous sediment sample was prepared by mixing individual samples.

2.2. Analytical methods

The physicochemical properties of sediment samples are shown in Table 1. Sediment pH was determined by pH meter (Orion Star A211, Thermo Scientific, Indonesia) in ultrapure water using mass ratios of 1:2.5 (sediment to water) , EC was measured in ultrapure water using mass ratios of

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1:5 (sediment to water) by portable multiparameter device (Orion Star A329, Thermo Scientific, Indonesia), the TOC was measured with a TOC analyzer (Vario TOC Cube, Elementar, Germany), grain size of sediment was determined by a laser size analyzer (MalvernMastersizer 2000, Malvern Panalytical Ltd., UK), and clay minerals were measured by X-ray diffraction device (XRD)(D2 PHASER, Bruker AXS, Germany). CEC was measured by standard method (NY/T 295-1995). All chemical reagents were of superior purity and purchased from Beijing culture and commerce center. The ultrapure water was used for all experiments to avoid contamination. The standard working solution comprising three single-element standard solutions were provided by National Chemical Reagent Quality Inspection Center. Basic physical-chemical properties of the sediments are presented in Table 4. The sediment background values in Bohai Bay of Zn, Pb and Cu are 57, 11.5 and 19 mg/kg respectively [41, 42], the concentration of three heavy metals are distinctly above environment background values, particularly for Zn, indicating the current severe pollution status of marine sediment in Bohai Bay.

Table 1. The physicochemical properties of the marine sediments

Property		Sediment
pH		7.91
EC(ms/cm)		8.075
Salinity(‰)		4.496
CEC(cmol/kg)		37.610
TOC(%)		0.778
Zn(mg/kg)		132.500
Pb(mg/kg)		30.850
Cu(mg/kg)		34.150
Grain size	Sand	4.47%
	Silt	57.46%
	Clay	38.07%

2.3. Incubation experiment

The homogeneous sediment sample was randomized into 3 groups (2 immobilizing amendments plus 1 control). Three pots containing 40 g of sediment sample respectively were used to conduct incubation experiment. To study the immobilization effect of heavy metals, in this study, the sediment sample was added with contaminated solution with a concentration of heavy metals of 1 g/L artificially, as suggested by Huang et al. [43]. The synthetic solution containing heavy metals was prepared by dissolving the solids ($Zn(NO_3)_2 \cdot 6H_2O$, $Pb(NO_3)_2$ and $Cu(NO_3)_2$) into the designed concentration. And all groups were artificially added by the 8 mL of the synthetic solution prepared above. Then, the first one was used as control group and the left two pots were added with the 2 g of kaolinite and limestone respectively. The properties of immobilization amendments are listed in Table 2. All the compounds in the experimental pots were mechanically mixed for enough time with stirred equipment until homogeneous blending [44]. Next, the mixture of sediment with additional solution and amendments was kept in dark with room temperature (25℃) for incubation to ensure a better immobilization effect with different periods. In previous studies on immobilization of heavy metals, the different incubation periods from a week to three months [45-47] were applied. In this study, three time periods including 1, 25 and 40 days were set, and the sequential extraction experiment was conducted in each period to determine each fraction of Zn, Pb and Cu.

Table 2. The properties of immobilization amendments

Immobilization agents	Molecular formula	pH	EC (ms/cm)	Salinity (‰)
kaolinite	$Al_2Si_2O_5(OH)_4$	6.70	0.072	0.090
limestone	$CaCO_3$	9.20	0.144	0.122

2.4. BCR sequential extraction procedure

A modified BCR sequential extraction procedure of heavy metals was applied. Each step of the modified BCR was briefly described in Table 3. The method divided the heavy metals into four fractions: acid exchangeable fraction fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4). Trace metals of Zn, Pb and Cu in each fraction were analyzed by volt-ampere spectrometer (797 VA Computrace, Metrohm, Switzerland).

Table 3. The procedure of modified BCR sequential extraction

Step	Fraction	Reagent	Procedure
1	acid exchangeable fraction	40 mL of 0.11 mol/L CH_3COOH	22±5°C for 16h, 3000 rpm for 20 min
2	reducible fraction	40 mL of 0.5 mol/L $NH_2OH{\cdot}HCl$	22±5°C for 16h, 3000 rpm for 20 min
3	oxidizable fraction	10 mL of 8.8 mol/L H_2O_2, 50 mL of 1.0 mol/L CH_3COONH_4	1 h at 25°C, 3 h at 85±2°C, twice; 22±5°C for 16h, 3000 rpm for 20 min
4	residual fraction	0.1000 g remainings, 3 mL HCl ,2 mL HNO_3,1 mL $HClO_4$ and 3 mLHF	2 h at 110°C, overnight, 2 h at 130 °C, increase to 150°C until smoke gone, diluted to 10 mL

2.5. The method used to evaluate immobilization effect

Mobility factor (MF%) has been defined as the percentage of metals in acid exchangeable fraction in the cumulative total extracted amount of the metal, which was used to express the immobilization effect of different immobilizing agents [48, 49]. Among four fractions extracted in sequential extraction, the first fraction (acid exchangeable fraction) contains the metals with the highest mobility and readily available to organisms, thus having the most severe toxicity and ecological risk [50]. The small MF% value means the low mobility and bioavailability of heavy metals, and thus the slight toxicity to marine ecosystem, suggesting the satisfactory immobilization effect. Mobility factor (MF%) could be calculated according to the following equation (1),

$$\mathrm{MF\%} = \frac{F1}{F1+F2+F3+F4} \times 100\% \qquad (1)$$

2.6. Quality control

The standard lake sediment BCR 701 (European Commission, Joint Research Centre) was used to check the accuracy in fraction analysis. Comparison of the concentration values of the first three fractions of BCR 701 determined in our laboratory and that of certified values are shown in Table 4. The results demonstrated a good accordance with reference values. In addition, the recovery of sequential extraction procedure was calculated as follows (2),

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$$\text{Recovery}(\%) = [(C_{F1} + C_{F2} + C_{F3} + C_{F4}) / C_{\text{total concentration}}] \times 100\% \tag{2}$$

where C represented the concentration of heavy metals in sediments [51]. The recovery rate ranged from 93 % to 108 %, suggesting the high reliability of metals' fraction data obtained in this study. On the other hand, all extraction procedures and determination of concentration of heavy metals included two replicates to guarantee the precision of final results.

Table 4. Comparison of results of our laboratory and certified values on BCR 701

Fraction		**Zn (mg/kg)**	**Pb (mg/kg)**	**Cu (mg/kg)**
F1	certified	205	3.18	49.3
	measured	208.81	3.08	53.13
F2	certified	114	126	124
	measured	113.45	118.63	122.36
F3	certified	46	9.3	55
	measured	51.55	8.70	50.23

3. Results

3.1. The properties of in the marine sediments

The mobility and bioavailability of heavy metals depend largely on pH, Eh, organic adsorption and ionic coprecipitation process, and therefore, these crucial parameters have the potential to change the dominant metal fractions in the sediment [52]. The variation of these properties (pH, EC, salinity and TOC) of sediment samples with different amendments over incubation experiment time is shown in Figure 1.

The pH value of sediments in control group decreases slightly from 8.22, 8.13 to 8.06 after 1, 25 and 40 days, respectively, from the beginning of incubation experiment. After the addition of kaolinite and limestone, sediment pH varies from 8.21, 8.09 to 8.29 and from 8.25, 8.20 to 8.24 respectively at the same three periods above. It is worth noting that the addition of high pH limestone (9.20) into sediment sample raises sediment pH slightly compared with control in each experimental period.

The EC value in control sediment sample shows a downward trend from 8.238 ms/cm, 7.080 ms/cm to 6.459 ms/cm after incubation experiment periods for 1, 25 and 40 days, respectively. The similar variation trend has also been observed in sediment with limestone amendment, which EC values are 7.170 ms/cm, 5.919 ms/cm and 3.284 ms/cm, respectively. Especially, EC values of sediment sample with limestone are consistently lower than those of control in each experimental incubation period. By contrast, EC values of sediments with the kaolinite amendment decreases from 7.246 ms/cm at first day to 2.815 ms/cm at the last day during the incubation experiment, with a sudden peak of 10.280 ms/cm at the 25th day.

The salinity values in control sediments drop slightly from 4.609‰, 3.947‰ to 3.570‰ after 1, 25 and 40 days, respectively, from the beginning of incubation experiment. The salinity in sediment with limestone group decreases from 3.980‰, 3.261‰ to 1.766‰ respectively at the same time period above, which are moderately lower than those of the control group in each period. After kaolinite being added, salinity is 4.024‰ at first day of incubation experiment reaches at 5.845‰ at second period and falls to its minimum at 1.508‰ at the end of incubation experiment.

The TOC values of sediment sample are 0.798% , 0.711% and 0.712% in control group after incubation experiment periods for 1, 25 and 40 days, respectively. After kaolinite and limestone are added respectively, the TOC values of both groups show a analogous decline. The kaolinite group decreases from 0.802%, 0.863% to 0.683%, and the limestone group decreases from 0.998%, 0.903% to 0.789% after 1, 25 and 40 days, respectively, from the beginning of incubation experiment.

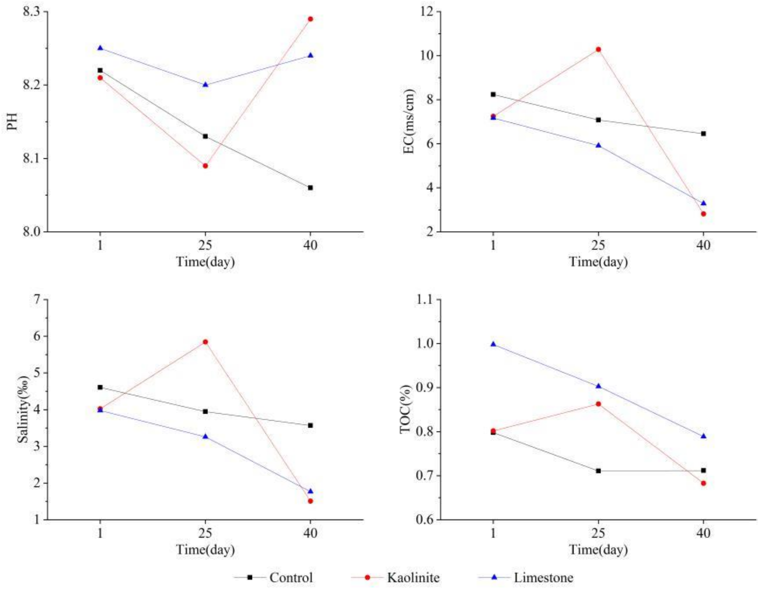

Figure 1. The properties of sediment samples

The properties of sediment samples (pH, EC, salinity and TOC) in sediment samples with different immobilization amendments including control, kaolinite and limestone over thee incubation period times.

3.2. The compositions of clay minerals in the marine sediments

The distribution of four clay minerals is shown in Figure 2. In control group, the concentration of illite is dominant in sediment sample, followed by chlorite, kaolinite and montmorillonite, with average percentage of around 75%, 20%, 3% and 2%, respectively. After the addition of kaolinite, the mean percentage of four clay minerals in sediment sample core are as follows: illite 80%, chlorite 12%, kaolinite 5% and montmorillonite 3%. The percentage of kaolinite in sediment sample decreased to minimum value 2.47%, while that of chlorite increased to maximum 13.82% with increasing incubation time. The similar distribution of proportion of four clay minerals can be observed with limestone. The variation of percentage of chlorite in sediment sample shows an increasing trend, with values from 10.37%, 12.15% to 21.15%. While the percentage of illite in marine sediment drops slightly from 82.39%, 75.37% to 78.55% over incubation experiment period.

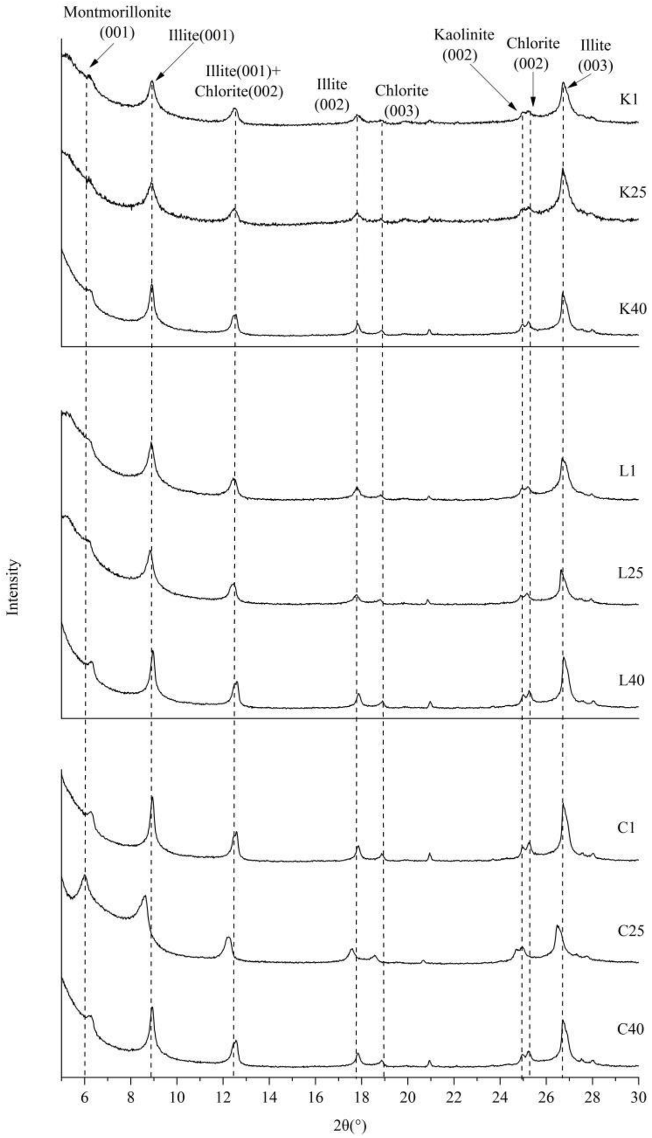

Figure 2. XRD image of clay minerals in marine sediments

C-control, K-kaolinite, L-limestone, 1, 25 and 40-thee incubation period times.

3.3. The chemical fractions of heavy metals in the marine sediments

The sequential extraction procedure was performed to characterize contribution of each fraction in three heavy metals before and after the addition of amendments. The percentage of each fraction of the sum of four fractions is presented in Figure 3. Among all three groups, residual fraction is dominant in Zn with the proportion of nearly 60%, while F1, F2 and F3 accounts for only about 15%, 15% and 10% respectively. The results are in accordance with previous study [53], revealing that the main proportion of Zn was bounded in crystals of mineral and its ecological risk was relatively low. The same main residual fraction is found for Pb, the average proportion of F1, F2, F3 and F4 were about 10%, 35%, 5% and 50% respectively. The percentage of each fraction of Cu is ranked as follows F4 > F2 > F1 > F3, with the proportion of each around 50%, 30%, 15% and 5% respectively.

After the immobilizing agents being added, each fraction accordingly varies to different extents. It can be noticed that F1 of Zn Pb and Cu all significantly reduced while F4 of three metals moderately increased with both amendments compared with control, indicating that the direct mobility and toxicity of metals are alleviated. This is in line with other findings that metal bioavailability was inhibited with the addition of amendments [9][31]. In kaolinite group, the F3 proportion of Zn, Pb and Cu falls by 9.10%, 0.47% and 0.21%, respectively, after 40 days of incubation experiment while that of F4 rises by 24.55%, 2.14% and 2.28%, respectively. The F2 percentage of Zn decreases from 16.85%, 11.90% to 12.82% over three incubation time while no obvious variation observed in that of Pb and Cu. In case of limestone group, both F2 and F3 percentage of Zn, Pb and Cu show a decreasing trend after 1, 25 and 40 days from the beginning of incubation experiment, and the former drops by 5.07%, 3.83% and 1.37% respectively and the latter drops by 9.75%, 1.05% and 0.57% respectively.

Meanwhile, metals can be divided into three different types based on their mobility and bioavailability, including bioavailable fraction (F1), potentially bioavailable fraction (F2 and F3), and nonbioavailable fraction (F4) [54]. After the overall comparison of variation of chemical fractions of three heavy metals, it is observed that bioavailable fraction in group of kaolinite and limestone is lower than that of control of all three heavy metals, while potentially bioavailable and nonbioavailable fractions are obviously higher than that of control. It can be concluded that the mobile and bioavailable fractions of heavy metals are transformed into comparatively stable fraction after the addition of immobilization agents.

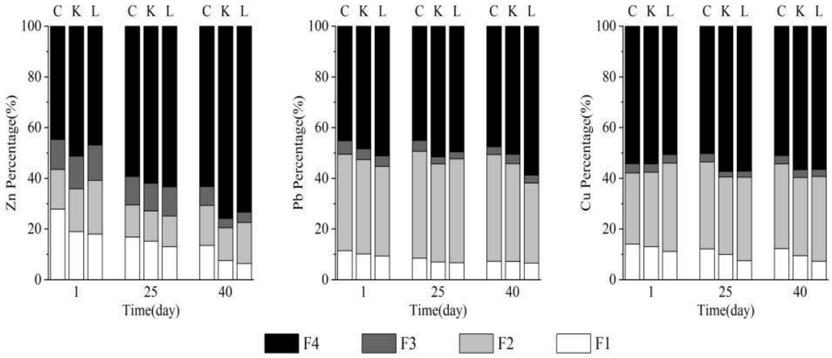

Figure 3. The distribution of chemical fraction of metals in the sediments

C-control, K-kaolinite , L-limestone, 1,25 and 40-thee incubation period times.

3. Discussion

4.1. The properties influencing immobilization effect

Previous researches suggested that increasing sediment pH causes a weak competition of H^+ with metal ions for ligands (e.g. OH^-, CO_3^{2-}, SO_4^{2-}, Cl- and S^{2-}), and makes it easier for metal ions and ligands combines into a relatively more stable form [50]. Cu has a great affinity for oxyhydroxides, and immobilization of Cu in sediment is strongly pH dependent [24][55]. In addition, the affinity of carbonates to Cu is a common reaction causing Cu deficiency of sediments in presence of free $CaCO_3$ [56], and thus the presence of limestone favors the combination of Cu and carbonates [57]. The same behaviors are also found in Zn and Pb, which can reduce the mobility of both metals in sediments [58]. In case of kaolinite, the hydroxyl groups (≡SOH) adsorbed in the surface or edge of kaolinite are amphoteric, and the surface charges are greatly sensitive to pH. At high pH, H^+ is easily to release into solution from surface hydroxyl groups ($\equiv SOH \rightarrow \equiv SO^- + H^+$), therefore, leading to combination of negatively charged ≡SO- sites and metal species, forming metallic surface complexes such as ≡SOMe+ or ≡SOMeOH [59].

The EC can act as a measure of nutrients for both cations and anions [60]. The EC value in each experimental period is moderately lower than that in the control group, suggesting the lower soluble salt concentration [61]. The similar behavior was obtained for previous researchers containing other amendments, probably because adding kaolinite and limestone into the sediment effectively slowed down accumulation of salts [62, 63]. The similar variation trend in salinity as EC of sediments could be confirmed by a strong correlation between two values [64]. As previous study has pointed out, presence of salts in the sediment is strongly associated with complex ionic exchange and osmotic effects, which may contribute to reduce the mobility of heavy metals in marine sediments [65].

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The decline of TOC value means that organic carbon of sediment could be decomposable because of addition of immobilization agents, coinciding with the previous findings [66]. The immobilizing amendments decrease heavy metals leaching by adsorption processes, which favors the formation of stable complexes with organic ligands [24]. It was reported that Cu easily forms complexes with organic matter owing to high stability of Cu compounds [67, 68]. However, organic matter cannot be the dominant control over heavy metal behavior when the concentration of it is relatively low [69]. Cation exchange and complexation with organic ligands were reported to be the primary Zn mobility controlling mechanisms, while Al, Mn and Fe oxides were less important [58]. The organic matter makes it easy for the formation of stable organometallic complexes, which could diminish the mobility of the metal ions in the sediment [70].

4.2. The transformation process of clay minerals in the marine sediments

Various explanations of heavy metal ions adsorption at the mineral have been proposed, including outer-sphere complexation, inner-sphere complexation, lattice diffusion, and isomorphic substitution within the mineral lattice [71]. For example, the immobilization of heavy metals with montmorillonite is primarily by ion exchange, and metals could be readily exchanged for other cations including calcium and magnesium [72]. The percentage of montmorillonite drops to minimum in all groups and illite increases except for limestone group at last may be explained by following reaction (3) [73],

$$\mathrm{Montmorillonite} + \mathrm{Al}^{3+} + \mathrm{K}^{+} = \mathrm{Illite} + \mathrm{Si}^{4+} \quad (3)$$

Researchers also found that the large surface area and cation exchange capability of montmorillonite facilitated its abundant absorption of Pb^{2+} by forming pyromorphite mineral [$Pb_5(PO_4)_3(F,Cl,OH)$] with Pb on its surface [74]. On the other hand, montmorillonite enhances the Pb^{2+} absorption into the inter layer or edge of the mineral crystals due to high CEC value [72]. Studies have also been reported that an increased amount of clay minerals decreased Cu mobility considerably [75]. While some aspects of mechanisms have been clarified, still much studies remains to be carried out to further elucidate the role of clay minerals in immobilization.

4.3. Immobilization effect of heavy metals in the marine sediments

For sediment sample without immobilizing agents, MF% value was 27.85%, 16.88% and 13.56% for Zn, 11.52%, 8.54% and 7.33% for Pb, 14.14%, 12.19% and 12.30% for Cu after incubation experiment periods for 1, 25 and 40 days, respectively. All of values show a decreasing trend, indicating a process of self-purification to some degree within sediments [76]. In case of kaolinite group, the MF% value of Zn, Pb and Cu is 19.10%, 10.18% and 13.11% respectively at first day of incubation experiment, declining to 7.68%, 7.25% and 9.56% respectively at 40th day after experiencing a downward trend. After limestone was added, there was also a decline in MF% value of Zn, Pb and Cu from 18.10%, 9.41% and 11.17% respectively to 6.48%, 6.67% and 7.32% respectively over incubation experiment time. The best immobilization effect is found in Zn, for which F1 drops by 11.42% and 11.61% respectively in kaolinite and limestone group, and F4 is significantly increased by 24.55% and 26.43% respectively. The MF% of kaolinite and limestone is obviously smaller than that of control at each incubation time period, suggesting the satisfactory immobilization effect. Consequently the addition of kaolinite and limestone can effectively reduce the bioavailability and toxicity of heavy metals. It can be further observed that MF% of Zn in limestone group are moderately lower than that of kaolinite group and that for Pb and Cu slightly lower than that of kaolinite group, indicating that limestone has a better immobilization effect than kaolinite generally.

Table 5. The MF% value of three heavy metals with different amendments

	Incubation	Control	Kaolinite	Limestone

	Days			
Zn	1	27.85%	19.10%	18.10%
	25	16.88%	15.32%	13.05%
	40	13.56%	7.68%	6.48%
Pb	1	11.52%	10.18%	9.41%
	25	8.54%	7.09%	6.71%
	40	7.33%	7.25%	6.67%
Cu	1	14.14%	13.11%	11.17%
	25	12.19%	10.07%	7.54%
	40	12.30%	9.56%	7.32%

4. Conclusions

The determination of properties of the sediments (pH, EC, salinity and TOC) revealed that no obvious variations of pH were observed while EC, salinity and TOC dropped moderately over the incubation experiment time because of addition of the two amendments.

The percentage of montmorillonite decreased to minimum value while that of chlorite increased gradually during 40 days of experimental periods probably due to complexation reaction. However, the molecular mechanisms of immobilization need to be further studied and demonstrated to obtain a better immobilization effect.

Results of sequential extraction procedures showed that mobile and bioavailable fractions of heavy metals were transformed into relatively stable fractions with the addition of kaolinite and limestone. The calculation of MF% indicated that the value of Zn, Pb and Cu decreased by 11.42%, 2.93% and 3.55% respectively with kaolinite at the end of incubation experiment, and that was 11.61%, 2.73% and 3.85% in limestone group respectively, both limestone and kaolinite can be useful in immobilizing heavy metals. The smaller MF% and larger reduction in metal mobility was found in limestone, suggesting the better effect in immobilizing heavy metals compared with kaolinite.

Author Contributions: Methodology, software, formal analysis, investigation, data curation, writing—original draft preparation W.Z.; writing—review and editing, X.W.and B.L.

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