Vietnam Academy of Science and Technology

Vietnam Journal of Marine Science and Technology

journal homepage: vjs.ac.vn/index.php/jmst

Fraction distribution of cadmium in surface sediment collected from bivalve species harvesting areas in Binh Thuan province (Tuy Phong, Phan Thiet, Lagi)

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Received: 25 August 2022; Accepted: 21 October 2022

ABSTRACT

This paper aims to provide information about the fractions of cadmium (Cd) and its distribution in surface sediment collected from bivalves harvesting areas in Binh Thuan province (Tuy Phong, Phan Thiet, Lagi). For this purpose, the sediment samples were collected monthly along with these areas in 2015–2016. To analyze the fractions of Cd, a five-step Tessier (1979) sequential extraction process was used, including Fraction 1 (Exchangeable), Fraction 2 (Bound to carbonate), Fraction 3 (Bound to iron-manganese oxide), Fraction 4 (Bound to organic compounds), and Fraction 5 (Residual). The research showed that Cd concentrations contributed mainly to a strong association residual fraction (Fraction 5). However, the percentage of Cd in total Fraction 1 and Fraction 2 (high mobility and bioavailability fractions) in all areas was also relatively high. In the Tuy Phong and Lagi harvesting areas, the sediment distribution follows the trend of F5 > F2 > F3 > F4 > F1, while the trend in sediment in the Phan Thiet harvesting area follows F2 > F5 > F3 > F1 > F4. The Fractions F1, F4, and F5 indicated a weak positive correlation with the total concentration of Cd, while F3 and F2 indicated medium and strong correlations, respectively. According to the Risk Assessment Code (RAC), the results reveal that Cd poses a high environmental risk in this area.

Keywords: Cadmium, fraction distribution, sediment, Binh Thuan.

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https://doi.org/10.15625/1859-3097/17076
ISSN 1859-3097; e-ISSN 2815-5904/

INTRODUCTION

Estuary and coastal sediments are considered reservoirs in place of metals and nonmetals [1, 2]. Metals are distributed throughout the sediments and are existed in various ways, including ion exchange, absorption, precipitation, and complexation. However, they are not permanently fixed in the sediment. Environmental changes, such as acidification, redox processes, and binding to organic compounds, can be responsible for the migration of metals from the solid phase to the liquid phase and the pollution of the surrounding water. It is also presented that the total metal content cannot predict the bioavailability or toxicity of the metal.

The distribution and formation of metals in sediments indicate the current sediment quality and provide helpful information on the metabolism of metals in polluted areas. On the other hand, estuaries and coastal areas have favorable potential for the farming and exploitation of bivalve mollusks outside natural areas. Therefore, studying the distribution fraction of metals in coastal and estuary sediment has become more critical in environmental research and food safety problems.

Cadmium is a highly toxic metal, that presents in most natural places in nature and has no nutritional value [3–5]. In areas where bivalve mollusks (clams, oysters, scallops) are harvested, cadmium can be contaminated in the sediment and water infiltrates the food chain leading to various harmful effects on animals and humans because they are pollutants with long-term accumulation [6]. To better understand the composition, distribution, and metabolism of cadmium present in the sediment samples collected from the bivalve mollusk harvesting area and to determine the level and risk of toxicity due to the accumulation of this metal in the mollusks, we analyzed total metals in the sediments. We used the sequential extraction method of Tessier (1979) [7], which provided information on the distribution of metal-binding forms and different types of phases in the sediments.

The coastline of Binh Thuan was the longest in the south-central coastal region of Vietnam, where many seafood species with high economic values are present [8]. For years, serious pollution problems, including heavy metals in Binh Thuan, have resulted from rapid industrial (mining, thermal power, titanium) and agricultural activities and municipal development. Moreover, the Binh Thuan coastline was the final destination of many large rivers, such as the Dinh, Phan, Ca Ty, and Luy rivers, that could affect coastal ecosystems and fishery. Thus, the investigation, survey, and assessment activity need continuous research to level assessment risk of sediment quality in these areas.

The article was completed based on databases from several surveys on the topic "Research on the causes of Cd and Hg infection in hairy cockles (Anadarasubcrenata), fan scallops (*Mimachlamys nobilis*) and silk clams (*Paphiaundulata*), key and preventive measures" during the survey and sample collection in the bivalves' harvesting areas in Binh Thuan Province in 2015–2016.

MATERIAL AND METHODS

Location survey, sample collection method, and sample pretreatment processing

In 2015–2016, we carried out several sediment samplings in the clams and scallops-specific harvesting areas in Binh Thuan province, such as Tuy Phong, Phan Thiet, and Lagi from March to December once a month in two stations in each survey area. Sediment samples were taken with specialized collecting equipment hoe in surface sediment (0–5 cm) and refrigerated before being returned to the laboratory. These samples were left to dry naturally in a cool place, without sunlight and dust, or taken to an oven to dry at 70^{o}C. Details of the sampling locations are shown in Figure 1 and Table 1.

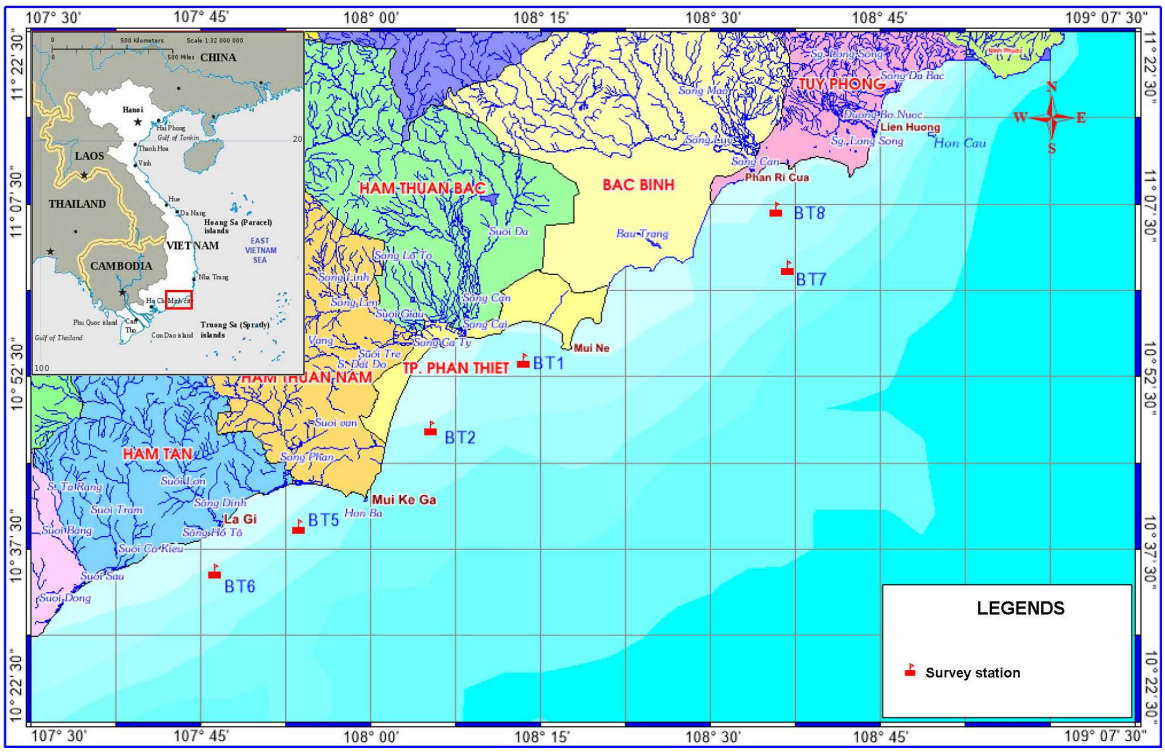

Figure 1. Location of the sediment sampling sites in Binh Thuan province, Vietnam

Table 1. The detailed coordinates of sampling sites for sediment samples from bivalve species harvesting in Binh Thuan province

Sampling sites	Locations	Geographic position	
		Longitude	Latitude
BT7	Tuy Phong	108°36'103"E	11°01'566"N
BT8	Tuy Phong	108°35'371"E	11°06'548"N
BT1	Phan Thiet	108°13'359"E	10°53'403"N
BT2	Phan Thiet	108°05'199"E	10°47'571"N
BT5	LaGi	107°53'066"E	10°39'186"N
BT6	LaGi	107°46'561"E	10°35'314"N

Analytical methods

A treatment method to analyze the Cd-total component in sediment

Sediment samples were treated with high temperature and high pressure in resistance Teflon flasks. A composite sample was prepared at each sampling station by homogenizing by a formula. A 0.5 g dry sediment was weighed after fine breaking and put into a Teflon flask. The digestion solution was a mixture of HNO_3 acid and H_2O_2 solution at a ratio of 8:1. Samples were digested at a temperature range of 100°C in a microwave oven for 2 hours. The samples were then cooled, filtered, and analyzed on a 797 VA Computrace spectrometer. The sample was analyzed in triplicate, and the results used are the average of the measurements.

Method for sequential extraction of Cd fraction

The sediment mass used for the analysis of the presence of Cd was 2 g, which was dried

and homogenized. The extracted sample was based on the method of Tessier (1979) consisting of five fractions, including metal in exchange form - fraction 1 (F1), metal bonded to carbonate (F2), metal bonded to Fe-Mn oxide (F3), metal bound to organic compound (F4), and residue (F5). The process of this method is described in Table 2.

Table 2. The sequential extraction method of Cd in sediment according to Tessier's method [7]

Fraction	Reaction	Condition
F1: Exchange form	20 mL CH_3COONH_4 1 M	Stirring for about 1 h at room temperature
F2: Bounding to carbonate form	40 mLCH_3COONH_4 1 M (Adjusting to pH 5 throughout CH_3COOH solution)	Stirring for about 5 h at room temperature
F3: Bounding to Fe-Mn oxide	40 mL $NH_2OH.HCl$ 0.02 M contains CH_3COOH 25%	Treatment in microwave oven for about 5 h at 95–100^oC.
F4: Bounding to the organic compound	20 mL CH_3COONH_4 3.2M in HNO_3 20%	Stirring about 0.5 h at room temperature
F5: Residual	HNO_3 10M and H_2O_2 with a ratio of 5:1	Treatment in microwave oven for about 1 h at 100^oC

After each extraction, the samples were centrifuged to separate the extraction solution. The extracted solution was filtered through filter paper before analyzing for metal Cd content using Computrace-VA 797 equipment at room temperature (20-25^oC). The residues were washed with distilled water to remove the suspensions and residual chemicals from the previous fraction. The sample was analyzed in triplicate, and the results used are the average of the measurements.

Cd analysis method on anodic-dissolved differential pulse spectrometer (according to SMEWW 3130; 3–39÷3–42, 19th ed., 1995) [9]

All solutions were prepared with deionized (DI) water. Merck (USA) commercial Cd standard solutions (1,000 mg.L^{-1}) were used for analysis. The standard solutions were prepared by diluting an appropriate aliquot of the standard stock solutions. All glassware was treated with a mixture (H_2SO_4 and $K_2Cr_2O_7$) and was immersed in 15% (v/v) HNO_3 for 24 h. Samples were then rinsed three times with deionized water before use. Cd was determined with Computrace-VA 797 equipment at room temperature (20–25^oC). The detection limit of Cd was 0.09 ppb. The analytical solutions contained acetate buffer with CH_3COOH (2 mol/L) and NH_3 (1 mol/L), pH = 4.6. The process was performed in a three-electrode stand bath. The auxiliary, reference, and working electrodes were a platinum rod, Ag/AgCl/KCl (3 mol/L), and a hanging mercury drop electrode (HMDE), respectively.

Firstly, each sample solution was placed in a voltammetric cell, and a fresh nitrogen flow (99.9995%) was used for purging the solution to remove dissolved oxygen at a pressure from 1.2 atm to 1.5 atm within 300 seconds. Next, the solution was stirred at 2,000 rpm; and a fixed potential of -1.2 V was applied to the WE for a period of 90 s (deposition step). Then, the stirrer was switched off, and after 5 s, an anodic potential scan was initiated from -0.8 V to -0.4 V in the differential-pulse mode. Peak potential Cd was -0.58 ± 0.05 mV. The following values were taken for the rest of the instrumental settings: Stirrer speed, 2,000 rpm; mercury size, 0.40 mm^2; pulse amplitude, 50 mV; pulse time, 0.04 s; v sweep rate, 30 $mV.s^{-1}$. After each new addition, the solution was stirred and deoxygenated again for the 30s.

Risk assessment code

The risk assessment code (RAC) was determined based on the percentage of the total metal content found in the exchangeable and acid-soluble fraction (F1 + F2). Percentages of 1 < RAC < 10% may reflect low risk, 11 < RAC < 30% medium risk, and 31 < RAC < 50% high risk (Table 3) [13]. When the percentage mobility is less than 1%, the sediment has no risk to the aquatic environment.

Table 3. The RAC (Risk assessment code) of metal in sediment

Risk assessment code (RAC)	Criteria (%)
No risk	< 1
Low risk	1–10
Medium risk	11–30
High risk	31–50
Very high risk	> 50

Data analysis

Statistical analysis: All data were presented as the mean and standard deviation. Statistical analysis of data was carried out using SPSS 16.0 version. A one-way analysis of variance (ANOVA) was performed, followed by LSD post-comparisons for the source of statistically significant differences. Differences in mean values were accepted as being statistically significant if $p < 0.05$. Correlation is significant at the 0.05 level (two-tailed).

RESULTS AND DISCUSSION

Identifying and quantifying a metal present in sediment play an essential role in an accurate understanding of the potential effects of a metal contained in sediment and assessing its transport, deposition, and dispersion processes [10]. The division of metals in the mineral and organic phase components contained in the sediments and the physicochemical mechanisms of the metal enrichment process are essential issues in the research process. In sediments, trace metals can be present in several chemical forms and are generally indicators due to their chemical interactions, mobility, bioavailability, and potential toxicity. The mechanism of trace metal accumulation is shown in five forms, including the exchange form, the form bound to carbonate, the form associated with the reducing phase (iron and manganese), and the form associated with organic compounds [11]. These patterns involve mobility in changing environmental conditions.

Analysis results of the total content and fraction distributions of Cd in sediments

The total Cd concentrations in all sediment samples are described in Figure 2. Generally, spatial distribution results indicated that a high concentration of Cd was found in the bivalve samples, ranging from 1.32 mg/kg to 2.34 mg/kg, dry weight. The highest Cd concentration in sediment was recorded in Tuy Phong (1.95 ± 0.56 mg/kg dry weight), while the lowest Cd was presented in Phan Thiet (1.43 ± 0.67 mg/kg dry weight). According to seasonal variations, the Cd in all sediment samples in the rainy season (June to September) (1.96 ± 1.25 mg/kg dry weight) was higher than in the dry season (March, April, October to December) (1.62 ± 0.82 mg/kg dry weight). The fundamental cause could be that coastal sediments with various pollutants were brought into the river by rainfall in summer, which may also contribute to the rapid enrichment of heavy metals in sediments in the wet season than the dry season. Besides, all results analyzed also exhibited that the mean concentration of Cd in all samples was lower than the maximum permissible levels (MPLs), the acceptable limits set by the Ministry of Environment, Vietnam applied to coastal sediment quality (QCVN 43-MT:2017) (set up 4.2 mg/kg) [12].

The variation of Cd in a fraction in sediment was presented in Figure 3. The exchangeable Cd (F1) ranged from 0.04 mg/kg to 0.37 mg/kg, averaging 0.16 mg/L; the Cd carbonate bond component ranged from 0.18 mg/kg to 0.68 mg/kg, an average of 0.35 mg/kg; the Cd component of Fe-Mn oxide bond ranged from 0.06 mg/kg to 1.11 mg/kg, with an average of 0.24 mg/kg; The Cd in the form of bound organic compounds ranges from 0.05 mg/kg to 0.26 mg/kg, with an average of 0.12 mg/kg; The Cd in stable form (residual) ranged from 0.38 to 0.94 mg/kg, with an average of 0.66 mg/kg. Generally, the Cd residual content was the highest percentage, except for some samples with changes in the

composition of other forms higher than the residue. The form associated with organic compounds accounts for a lower proportion than the other forms. The reason is due to the sediment characteristics and the grain-grade composition of the sediment samples in the bivalve mollusk harvesting area. F1and F2 fractions are exchange and soluble forms susceptible to fluctuations when there is a change in the environment. It can be seen that these two forms have variations in the collected sediment samples. Comparing the analysis results of the Cd existence form in other studies, it can be seen that the Cd content in the forms present in the sediments of the harvest area is similar to the study on the existing form in the sediments of the Bay Laizhou area (China) [14] (F5 ranges from 0.658 mg/kg to 0.893 mg/kg; F4 ranges from 0.124 mg/kg to 0.397 mg/kg); northwest of the Red Sea, Egypt (The concentration of Cd varied 0.549 mg/kg, 0.18 mg/kg, 0.17 mg/kg, 0.31 mg.kg for F2, F3, F4, F5, respectively) [15].

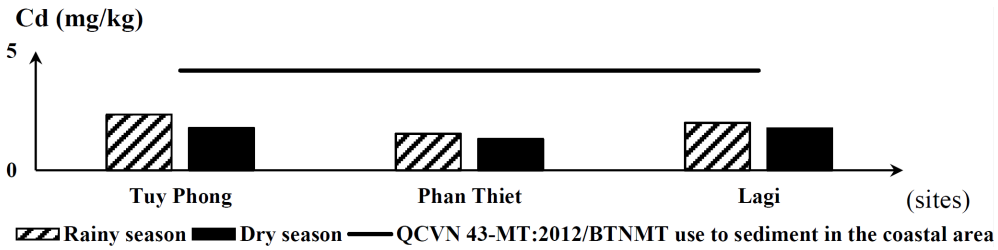

Figure 2. The spatial distribution and season variation of Cd in sediments in the Binh Thuan coastal areas in 2015–2016

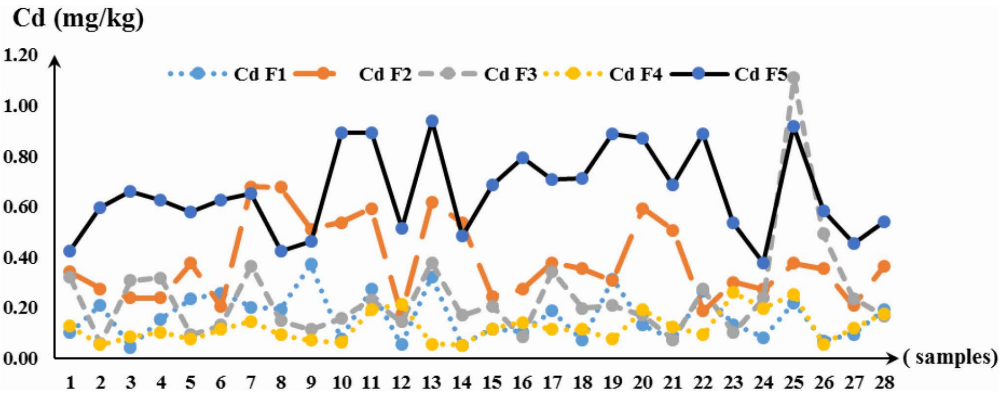

Figure 3. Cd speciation (mg/kg) in sediment samples collected from bivalve species harvesting in the Binh Thuan coastal areas

In the sediment samples collected in the Tuy Phong (S-BT7 and S-BT8), the proportion of F1 and F4 forms account for the minor proportion, fluctuating between 4–19% and 4.5–9.6%, respectively. Next, The F2 forms range from 15–27%, the F3 forms range from 5–30%, and the F5 forms range from 28–49%, accounting for the highest percentage. The distribution of the proportions of Cd forms present in the sediments in this area is as follows: F5 > F3 > F2 > F1 > F4 (Figure 4).

In Phan Thiet (S-BT2 and S-BT3), the rate of the F1 form ranges from 4–24%, the F2 form ranges from 22–50%, the F3 form ranges from 7-27%, the F4 form ranges from 2.3–19.4%, and the F5 form ranges from 16–52% (Figure 5). In general, in this area, the form of exchange was still at a low level. However, Cd in sediment-bound to carbonate (F2) has a considerable difference in Cd content in the sampling periods, showing that this area has a significant fluctuation, which

strongly occurs in redox reactions affecting the distribution of Cd in this region. The F2 form accounts for a high percentage in the rainy season months (20–38%). In this area, the sediment distribution follows the trend of F2 > F5 > F3 > F4 > F1. With this trend, the amount of Cd in F2 and F3 is high, and the risk of Cd released from the sediment entering the aquatic environment is enormous.

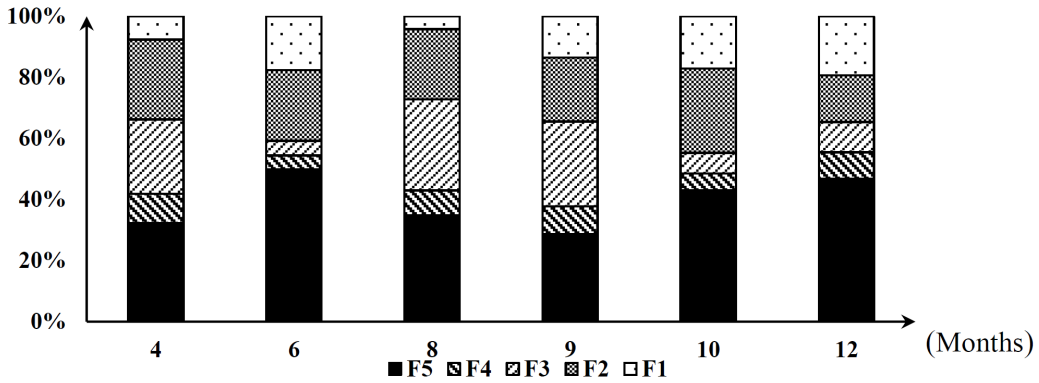

Figure 4. Fraction distribution of Cd in sediments at Tuy Phong sites in 2015–2016

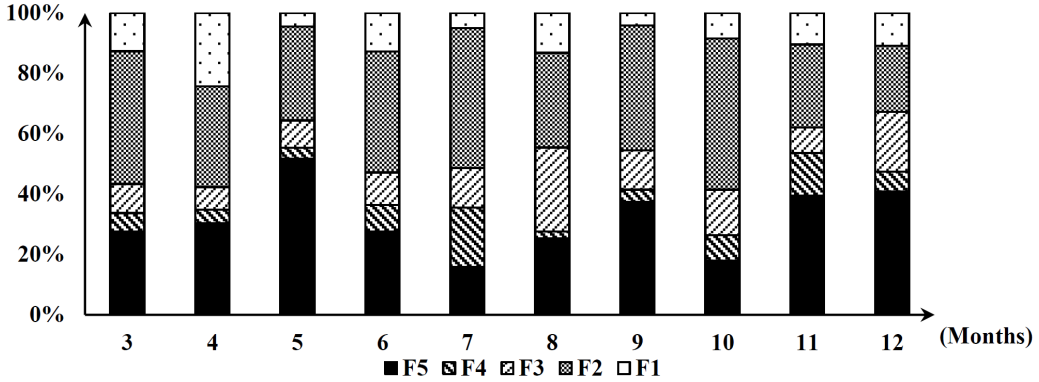

Figure 5. Fraction distributions of Cd in sediments at Phan Thiet sites in 2015–2016

In Lagi (S-BT5 and S-BT6), the rate of the F1 form ranges from 4.5–21.9%, the F2 form ranges from 12-34%, the F3 form ranges from 4.9–39%, the F4 form ranges from 3.5–21.2%, and the F5 form ranges from 23–46% (Figure 6). In this area, there is an apparent fluctuation of Cd content in the studied forms during the sampling periods, especially the concentration of Cd in F2, which increases sharply in the rainy season. In general, Cd metal distribution in this area follows the F5 > F2 > F3 > F4 > F1 trend. With this trend, metal-bound in the form of F2- a weakly bound form has a high risk of releasing Cd from the sediment into the water, which can enter bivalve mollusks through the food chain, and affect the quality of the water, food hygiene, and safety, especially in the rainy season months.

Based on the experimental results and speciation findings, Cd can pose a severe problem to the ecosystem in all sites surveyed with medium risk to high risk, especially Phan Thiet sites, have very high risk. RAC (Risk Assessment Code) [13] of Cd in three sites is shown in Table 4. Thus, in the three study areas, Phan Thiet has a higher percentage of Cd metal in F1, and F2 (more bioavailable form than F3, F4, and F5) than in the study area Tuy Phong and Lagi. Therefore, sediments in the Phan Thiet sites have a higher risk of Cd contamination in the water environment,

accumulation in organisms in general, and bivalve mollusks in particular, higher than in other areas. Therefore, there is a possibility that cadmium may enter the food chain in this area.

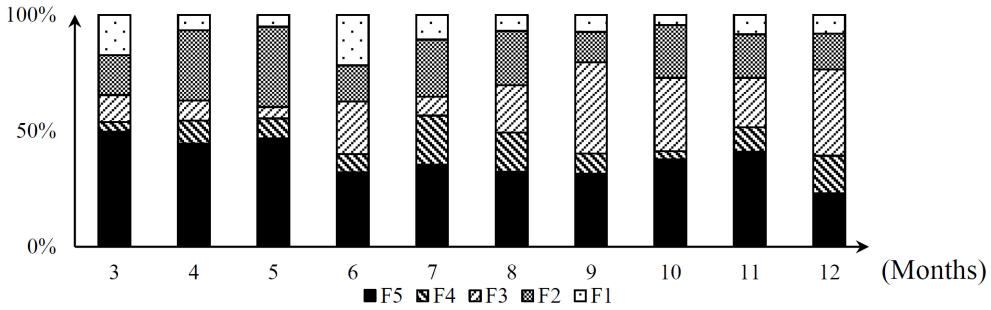

Figure 6. Fraction distributions of Cd in the sediment of Lagi sites in 2015–2016

Table 4. The RAC (Risk Assessment Code) of Cd in the sediment sample in Binh Thuan

Sites	Total (F1 + F2)%	RAC
Tuy Phong	27.1–44.6	Medium risk - High risk
Phan Thiet	32.6–58.4	High risk - Very high risk
Lagi	20.5–39.7	Medium risk - High risk

Correlation between distribution patterns of Cd and total Cd in sediment samples

The correlation between the existing forms of Cd and the total Cd content in the studied sediments is shown in Figure 7. All correlation coefficients (r) have positive values, showing a positive correlation between the number of existing forms and the total content. In other words, when the total Cd content increases, the content of all forms also tends to increase. However, the five forms of Cd show that forms F1, F5, and F4 were weakly correlated with the total Cd content, where the correlation coefficients were R^2 = 0.011, R^2 = 0.028, and R^2 = 0.052, respectively. The F3 form correlates with the total content more closely, on average, with a higher correlation coefficient (R^2 = 0.23) than the three previously mentioned forms. The F2 form shows a strong relationship with the total content with a correlation coefficient of R^2 = 0.52. Thus, when the total Cd content increases, the Cd content exists in the form of F2 - the form associated with carbonate, also a weak link, with the highest ability to separate from the sediment and enter the aquatic environment.

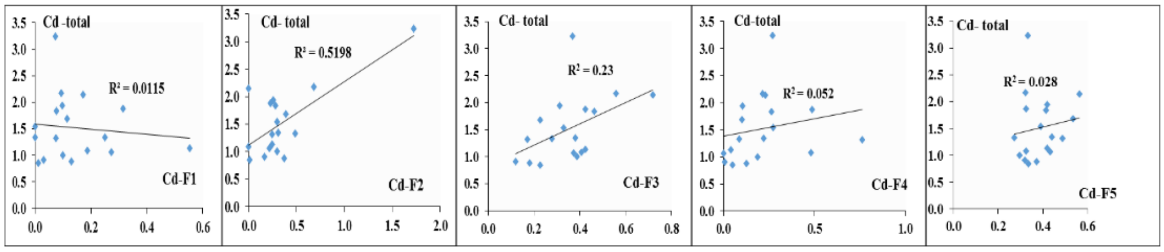

Figure 7. The correlation between Cd-total in sediments and other fractions

CONCLUSION

The total Cd concentration in the sediments of the Tuy Phong area is the highest, followed by Phan Thiet, and the lowest is Lagi. All sediment samples show the most increasing trend in the rainy season months.

The Cd fraction distribution in Tuy Phong sites was F5 > F3 > F2 > F1 > F4. In Phan Thiet sites were in the order F2 > F5 > F3 > F4 > F1, and in Lagi were in the order F5 > F2 > F3 > F4 > F1. The percentage of Cd in the total fraction of F1 and F2 was very high. Cd can pose a serious problem to the ecosystem in all sites survey has a medium to high risk.

All forms of Cd in the sediments were positively correlated with the total Cd content. Forms F1, F4, and F5 show weak correlation, while F3 is moderately correlated and F2 is strongly correlated. As the total Cd content increased, the concentration in the F2 form consistently increased, which was the highest of the five studied forms.

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