Title

Research to use analytical equipment serve assessment trace metal and harmful toxins in marine aquaculture environment

Members' names and affiliations

Name	Institute and deparment	Employment position
Ngoc Thien Luu	Research Institute for Marine Fisheries, RIMF	Researcher
Nguyen Van Nguyen	Research Institute for Marine Fisheries, RIMF	Doctor of Philosophy
Cong Thanh Nguyen	Research Institute for Marine Fisheries, RIMF	Doctor of Philosophy
Akihiko Morimoto	Faculty member of Lamer	Professor
Xinyu Guo	Faculty member of Lamer	Professor

Aim

The study was aimed at collaborative research with Prof. Guo Xinyu and Prof. Morimoto Akihiko of Ehime University on the changes of Cd, Pb and Hg in the seawater aquaculture area in Quang Ninh (Gulf of Tonkin), Kien Giang (Gulf of Thailand) in Vietnam from 2022 to 2024. In addition, this study also discussed the responsible accumulation and distribution of Cd speciation in sediments in this area from historical data from 2014 to 2016 (Figure 1).

Procedure

Principal Investigator (PI) showed an oral presentation on the transformation of Cd, Pb, and Hg in seawater aquaculture through their analysis by ICP-MS (Inductively Coupled Plasma Mass Spectrometer, PerkinElmer NEXION 2000B) from seawater samples collected in Quang Ninh, Kien Giang in Vietnam.

High temperature and high-pressure treatment of sediment samples in Teflon resistive flasks were used to determine total metal concentrations. Sequential extraction of Cd from sediments, according to Tessier's (1979) method, was used before the analysis of ICP-MS.

A pollution risk index (RAC) was determined to assess the risk level in sediments. RAC was determined based on the percentage of total metal content found in the exchangeable fraction and the acid-soluble fraction (F1 + F2). A ratio of $1 < RAC < 10\%$ may reflect low risk, $11 < RAC < 30\%$ medium risk, and $31 < RAC < 50\%$ high risk.

We will carry out futher research with Prof. Guo on the information related to Ha Long Bay (The World Heritage in Quang Ninh, Vietnam) to set up a international joint research project base on the observation data obtained.

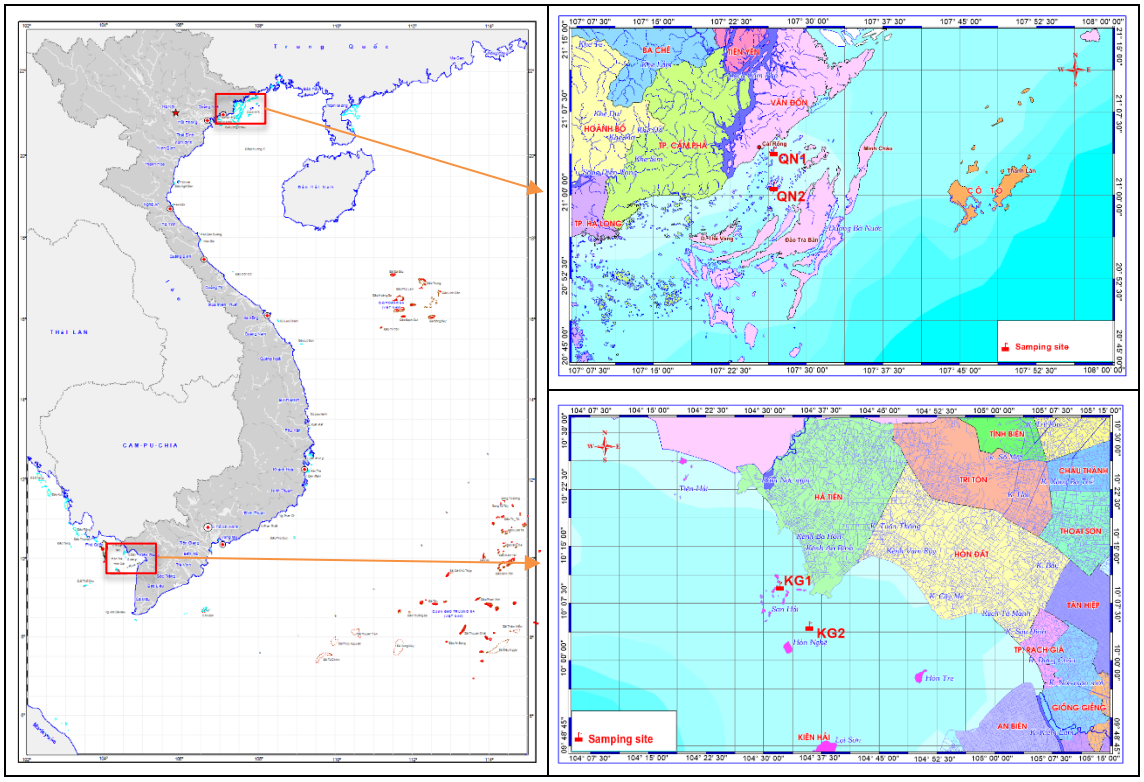

Figure 1. Map of study area with all samplings

Results

The results of Hg, Cd, and Pb concentration measurements in seawater samples collected from surface and bottom sampling points in Quang Ninh from 2022 to 2024 are presented in Figure 2. Regarding Hg concentration, the method detection limit (MDL) was lower than that of ICP-MS when analyzed directly. The average concentration values of CD, and Pb ranged from 0.05 to 0.14 µg/l; ranged from 1.37 to 1.41 µg/l. The highest Cd concentration was observed in November 2022 with a value of 0.22 µg/l while the highest Pb concentration was in October 2022. According to the seawater column, the concentration of heavy metals in the surface layer was higher than that in the bottom layer.

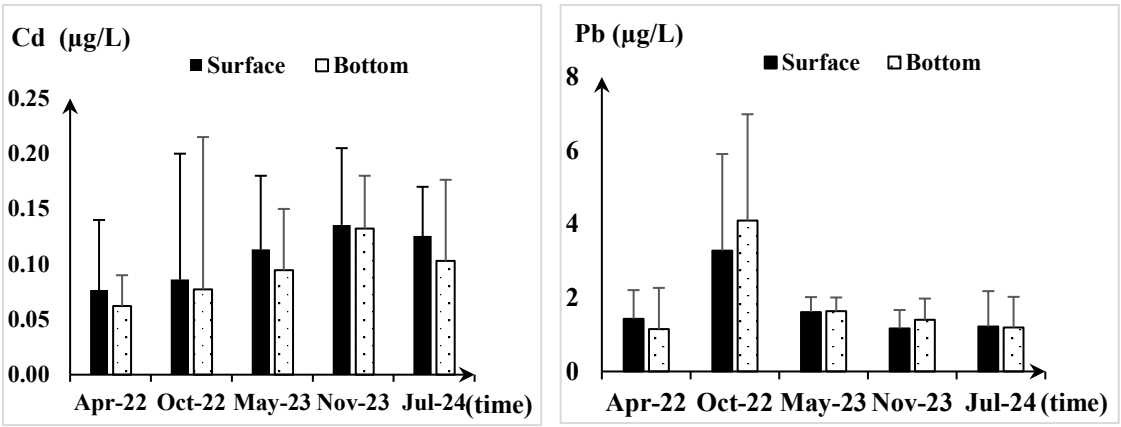

Figure 2. Variation of Cd, Pb in aquaculture seawater according to April 2022 to July 2024 in Quang Ninh, Vietnam.

The results of Cd and Pb concentration measurements in seawater samples collected

from surface and bottom sampling points in Kien Giang from 2022 to 2024 are presented in Figure 3. The average values of Cd and Pb concentrations ranged from 0.04 to 0.14 µg/l; from 1.21 to 3.01 µg/l. The highest Cd concentration was recorded in November 2023 with a value of 0.21 µg/l while the highest Pb concentration was recorded in July 2024 with a value of 4.5 µg/l.

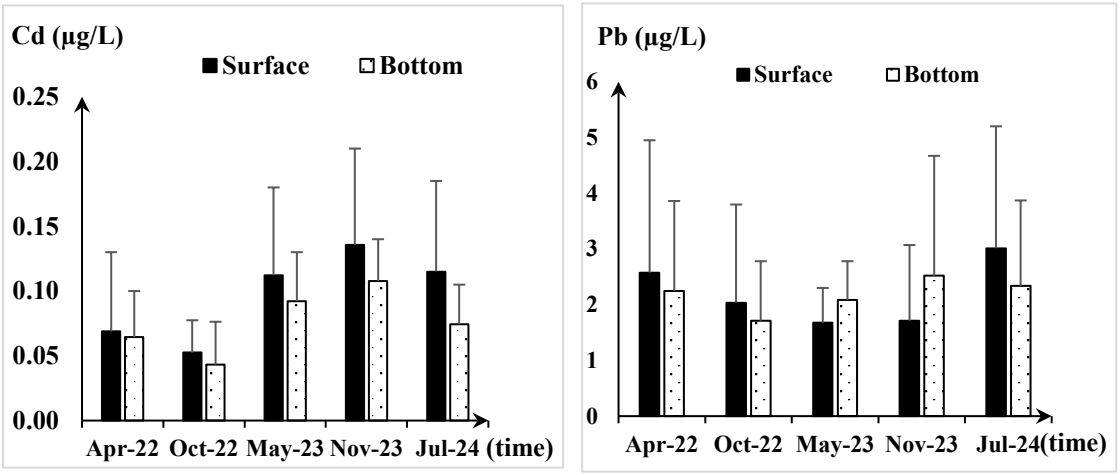

Figure 3. Variation of Cd, Pb in aquaculture seawater according to April 2022 to July 2024 in Kien Giang, Vietnam.

The results of the analysis of Cd-tot metal content in sediments in Quang Ninh and Kien Giang are shown in Figure 4. The results show that the total Cd concentration in sediment samples in Kien Giang tended to be higher than that in Quang Ninh. The Cd concentration in sediments in Quang Ninh was 1.41 ± 0.37 mg/kg dry weight, while that in Kien Giang was 1.75 ± 0.31 mg/kg dry weight. In addition, all the analysis results also show that the average Cd concentration in all samples was lower than the maximum allowable level (MPL), the allowable level issued by the Ministry of Natural Resources and Environment in Vietnam for coastal sediment quality (QCVN 43-MT:2017) (regulated at 4.2 mg/kg).

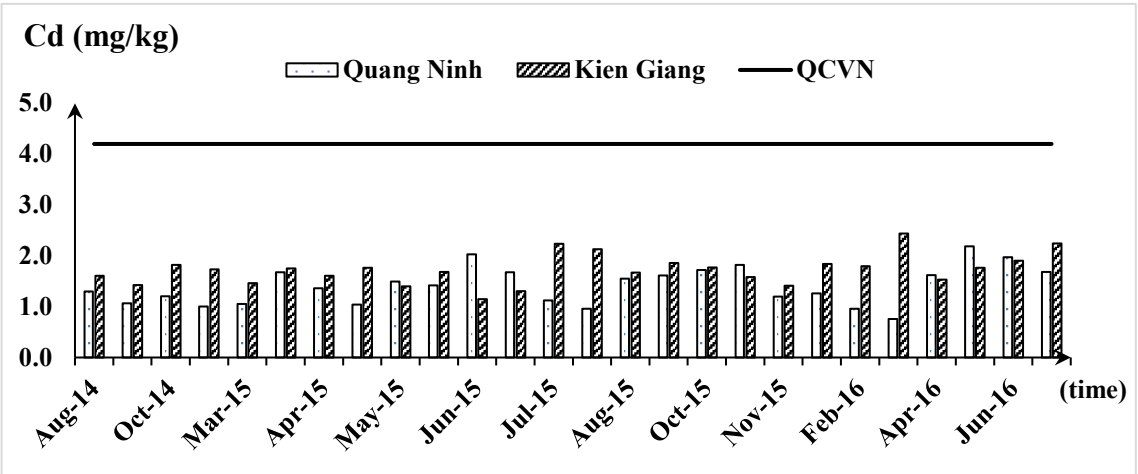

Figure 4. Variation of total-Cd in sediments in mariculture areas in the Quang Ninh, Kien Giang, Vietnam, 2014–2016.

The recovery of the sequential extraction was calculated based on the ratio of total (F1-F5) to total-Cd. The analysis showed that the sum of the five fractions ranged from

76.6 -118.5%

Exchangeable Cd (F1) ranged from 0.016 mg/kg to 0.404 mg/kg, with an average of 0.092 mg/kg; the carbonate bound Cd ranged from 0.021 mg/kg to 0.724 mg/kg, with an average of 0.204 mg/kg; the Fe-Mn oxide bound Cd ranged from 0.025 mg/kg to 0.885 mg/kg, with an average of 0.209 mg/kg; Cd in the form of bound organic compounds ranged from 0.021 mg/kg to 0.367 mg/kg, with an average of 0.157 mg/kg; Cd in stable (residual) form ranged from 0.296 to 1.769 mg/kg, with an average of 0.838 mg/kg. In general, the residual Cd content was the highest in weight. In the sediment samples collected in Quang Ninh, the proportions of F1 and F4 forms accounted for a small proportion, ranging from 1.05–18.6% and 1.16–24.02%, respectively. Next, F2 form ranged from 1.43–26.86%, F3 form ranged from 5.74–48.19%, and F5 form ranged from 25.1–81.1%, accounting for the highest proportion. The distribution of Cd forms in sediments in this area was as follows: F5 > F3 > F4 > F2 > F1 (Figure 5).

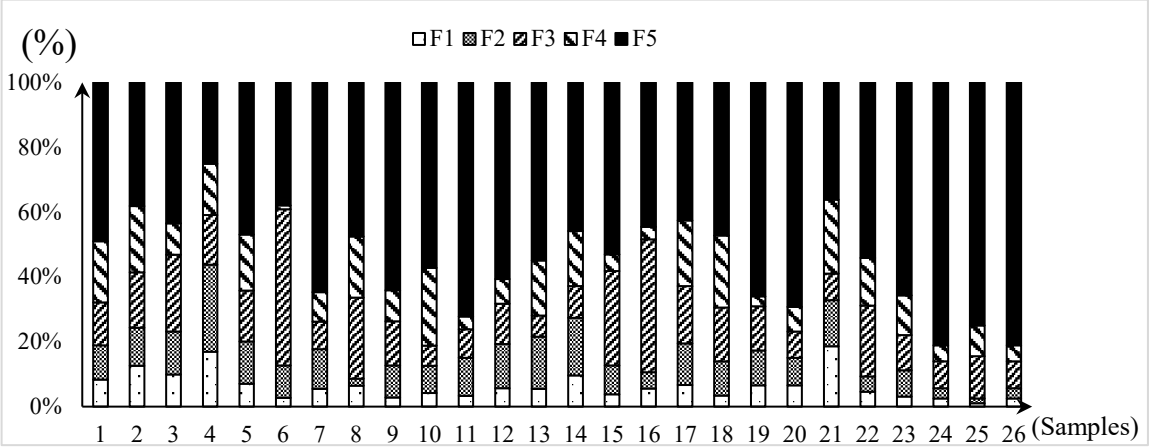

Figure 5. Fraction distribution of Cd in sediments at Quang Ninh sites, 2014–2016

In the sediment samples collected in Kien Giang, F1 and F4 forms accounted for a small proportion, ranging from 1.09 to 21.37% and 2.08 to 19.86%, respectively. Next, F2 forms ranged from 1.73 to 33.86%, F3 forms ranged from 4.69 to 30.59%, and F5 forms ranged from 28 to 49%, accounting for the highest proportion. The distribution of Cd forms in the sediments in this area is as follows: F5 > F2 > F3 > F4 > F1 (Figure 6).

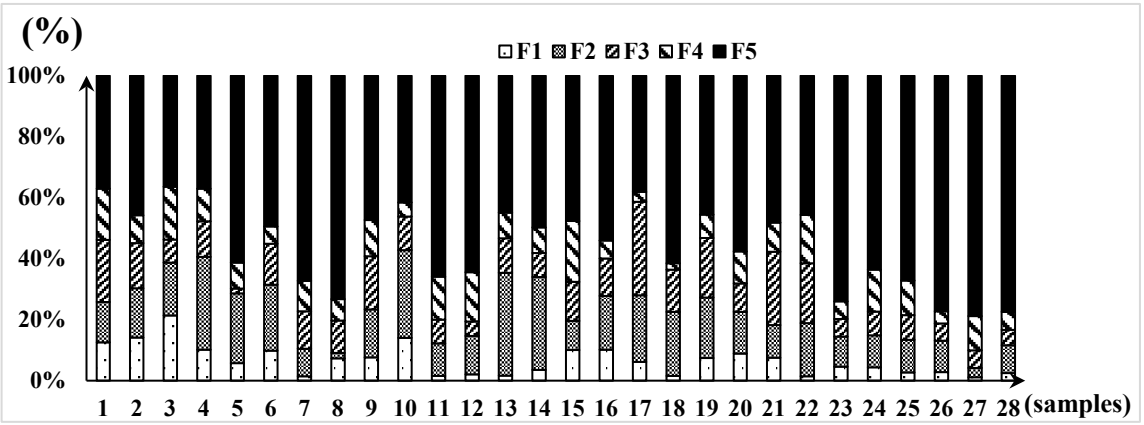

Figure 6. Fraction distribution of Cd in sediments at Kien Giang sites,Vietnam in 2014–2016

Based on the experimental results and speciation findings, Cd can pose a severe problem to the ecosystem in all sites surveyed with low risk to high medium except some samples presented medium risk to high risk according to RAC index.

All forms of Cd in the sediments were positively correlated with the total Cd content. Forms F1, F4, and F1 showed weak correlation (R^2 = 0.062 and R^2 =0.024), while F3, F2 was moderately correlated (R^2=0.287 and R^2=0.231) and F5 was strongly correlated (R^2=0.633). As the total Cd content increased, the concentration in the F5 form consistently increased, which was the highest of the five studied forms.

The correlation between Cd-total in sediments and other fractions (Pearson)

Correlations						
	F1	F2	F3	F4	F5	Total
F1	1	.348**	-0.065	0.124	-0.377**	0.062
F2		1	0.084	-0.022	-0.246	0.287*
F3			1	-.289*	-0.199	0.231
F4				1	-0.041	0.024
F5					1	0.633**
Total						1
**. Correlation is significant at the 0.01 level (2-tailed).						
*. Correlation is significant at the 0.05 level (2-tailed).						

Perspectives in future

This study clarified variation of Cd and Pb in seawater, distribution of Cd species in sediment of aquaculture area of Vietnam. We will study transfỏmation mechaism of them from seawater and sediment to suspended material and species of creatures; the correlation between heavy metal fractions and their presence in organisms body. Simulation and modelling of Cd and Pb in marine aquaculture areas will setup in the future in study others.