

Distribution and Potential Impact of Metal Pollutants in the Coastal Environment: A Case Study with Special Reference to Coastal Aquaculture in Red River Delta of Viet Nam

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Abstract

Study was conducted to investigate the distribution pattern and impact of metal pollutants in the fast growing coastal aquaculture industry of Viet Nam. Mud and water samples were collected from randomly selected eleven stations of two aquaculture prone coastal zones of Northern Viet Nam and fourteen metals were analysed using ICP-MS. Production data (shrimp and fish) of the respected stations were also collected from local farmers and fisher man. Results revealed that excepting few locations the distribution of As (mud, 180 - 383 µg/kg and water, 14.26 – 31 µg/l), Pb (mud, 4.9 – 207.3 µg/kg and water, 0 – 0.15 µg/l), Cd (mud, 0.62 – 44.1 µg/kg and water, 0 – 0.06 µg/l), Cr (mud, 117 – 192.5 µg/kg and water, 1.42 – 4.58 µg/l), Ni (mud, 49.9 – 100 µg/kg and water, 0 – 0.111 µg/l), Be (mud, 4.06 – 10.5 µg/kg and water, 0.02 – 0.051 µg/l), Ba (mud, 194.3 – 5153 µg/kg and water, 18.52 - 50 µg/l), Fe (mud, 42642 – 72397 µg/kg and water, 192 – 669 µg/l), Se (mud, 0 – 21 µg/kg and water, 18 – 82.23 µg/l) and Sb (mud, 348.36 - 1463 µg/kg and water, 0 µg/l) showed a higher values than the WHO permissible limit of drinking water concentration, whereas remaining four metal elements (Cu, Hg, Al and Ag) pronounced normal level in their concentration. A remarkable decreasing (20 - 40%) trend was observed in the production (shrimp and fish) within last five years in all investigated places. From the present study, therefore, it may be concluded that various metal containing industrial wastes contaminating the food chain of coastal ecosystem via water and sediment which ultimately affect severely to the cultured and wild species of coastal domains. Consequently, cultured and wild species as well as production in cultured farm is surprisingly decreasing which leading to the total devastation of fishery industry along the coastal zone due to coastal water pollution and loss of ecosystem stability by biodiversity loss.

Keywords: Metal pollutants; aquaculture; coastal ecosystem; Red River Delta; Viet Nam.

1. Introduction

All trace metals are naturally occurring elements that become potential contaminants in the arena of environmental pollution when concentrations are greatly increased due to indiscriminate anthropogenic activities. Though many of them are significantly essential in the physiological process of biota on earth, nonetheless excess concentration causes a negative impact on the body. It is generally occurred in high concentration in the mining (extractive sites) as well as industrial zones which is greatly responsible for the contamination of the surrounding local ecosystems. Olade have showed that around the few lead-zinc and tin-zinc mines in Nigeria, acidic drainage from disused mine shafts and open pits and dumps have contributed to localized metal pollution [1]. As mining, industrial waste and effluent discharges and contaminates the local surface water bodies and soils that are finally carried by runoff and river water to the coastal area [2, 3]. Studies of heavy metal contents of surface waters at Ibadan showed that levels of Pb may reach 50µg/l [4] and in waters of the Lagos lagoon, Pb levels exceeding 120µg/l have been obtained by Olade [1].

Recently, metal pollution in coastal area is one of the crucial environmental problems worldwide. Developed and developing countries are suffering from various metal pollutions differently. As developed countries, which have water pollution problem due to industrial proliferation and modernised agricultural technologies, are now on the way of combating the problems through improving wastewater treatment technique in one hand, whereas developing countries with lack of technical know how, weak implementation of environmental policies and with limited financial resources are still facing problems on the other hand. Enormous increase in pollution due to discharge of untreated effluents from industrial fields to lakes, rivers and coastal area is a matter of great concern in developing countries. In developing India, different lakes receive a heavy influx of sewage,

industrial effluents, domestic and agricultural waste which consists of varying hazardous chemical and causing deleterious effects on fish and other aquatic organism [5]. Apart from that, coastal lagoons receive a variety of pollutants from different sources. The primary sources of heavy metals pollution in coastal lagoons are input from rivers, sediments and atmosphere as mentioned earlier. Coming from such point-sources, there are normally localized hot-spots of heavy metal concentrations in the coastal zone, often near particular river-mouths. Despite the functions as water for irrigation in agriculture, drinking water for animals and for human use, a major part of this water source was used in coastal aquaculture industry. The aquatic environment is more susceptible to the harmful effects of heavy metal pollution because aquatic organisms are in close and prolonged contact with the soluble metals. Various substances in shrimp farm ponds can contaminate waters, including nutrients (nitrogen and phosphorus), metabolic wastes, antibiotics, or other medicines to protect shrimp, and suspended soil particles from erosion [6].

Viet Nam is one of the South East developing country rapidly developed industries leading to immense problem in their coastal environment. In last decades, aquaculture industry recognized as an important livelihood and developed rapidly because of heavy demand and attractive returns in the coastal region especially in the Red River Delta, Northern Viet Nam and in the large alluvial deltas of the Mekong River, Southern Viet Nam. Recently, the water and soil in this area has been deteriorated due to contamination by some heavy metal elements as a result of industrial activities and application of a large quantity of agricultural chemicals. National Groundwater Monitoring Network of Vietnam reported the high arsenic concentrations in the groundwater of the Red River delta, in the Mekong River Delta and on the Thai Nguyen Plateau. It also evaluates the situation in Red River delta where groundwater arsenic concentrations vary from 1-3050 $\mu\text{g/l}$ (average 159 $\mu\text{g/l}$) [7-9]. Present investigation is associated with the aquaculture prone deltaic region of Red river in the North Viet Nam. Thus, from the above points of view, this study is of great importance because metal pollution can affect all ecosystems and human health directly or indirectly through the food chain. The present study has been aimed to investigate the distribution, contamination status and potential impact of metal pollutants in the coastal environment of Red River delta.

2. Materials and Methods

2.1 Geographical and geological setting of study sites

The main part of Red river (between $106^{\circ}00'$ and $107^{\circ}00'$ east longitude and $19^{\circ}45'$ and $21^{\circ}00'$ north

latitude) is $169,020 \text{ km}^2$, in which $86,660 \text{ km}^2$ (51.35%) is in northern Vietnam's territory. The Red River flows for over 500 km through Vietnamese territory before entering the sea in the Gulf of Tonkin (Figure 1A). The triangular delta ($16,666 \text{ km}^2$) has its apex in the region of Hanoi (about 120 km from the coast) where the river divides into its two main distributaries, the southern Song Hong (Red River) and the northern Song Duong. The mean annual discharge of the Red River at Sontay is 114 cubic kms, equivalent to an average flow of 3,640 cubic metres per second. Red River Delta is considered as potential area for aquaculture development comprising 126500 ha area for freshwater culture and 55800 ha area for tidal farming. This area consists of 9 whole provinces (Hanoi, Hatay, Haiduong, Hungyen, Haiphong, Namdinh, Hanam, Ninhbinh, and Thai Binh) and 23 districts of five other provinces (Bacninh, Quangninh, Vinhphuc, and Phutho) (Figure 1B). The major soils found in the delta are Fluviol and Acrisol according to the classification of FAO. The soil in this area is fertile and more than about 50% of the area is being used for aquaculture and approximately 47% of the delta ($820,800 \text{ ha}$) is agricultural land.

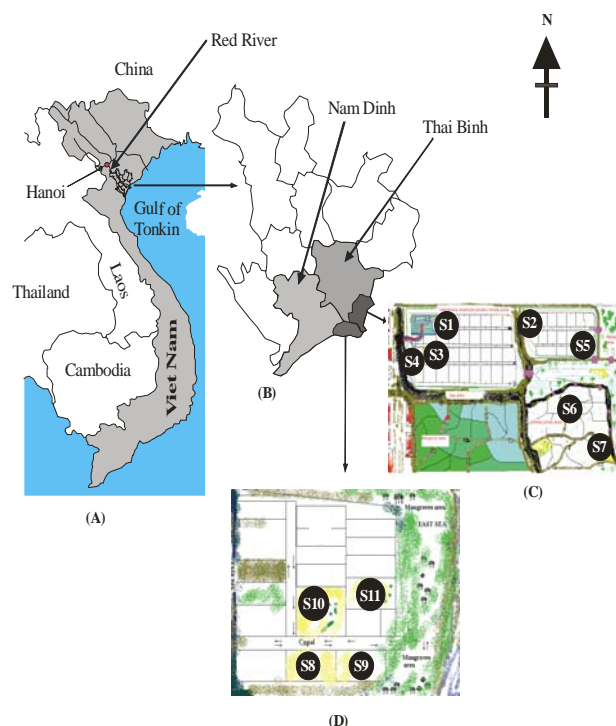


Figure 1. Figure representing - (A) Whole map of Viet Nam with Red River Deltaic zone (B) Sampling sites in Thai Binh and Nam Dinh provinces in the Red River Delta (C) Location of sampling stations (S1 - S7) in Giao Thuy districts and (D) Locations of sampling stations (S8 - S11) in Tien Hai Districts.

2.2 Study sites

Present investigated sites Tien Hai, Thai Binh ($20^{\circ}26'59''\text{N}$ and $106^{\circ}20'24''\text{E}$) Giao Thuy, Nam Dinh ($20^{\circ}25'47''\text{N}$ and $106^{\circ}10'12''\text{E}$) is located in the

Red river deltaic region (Figure 1B). Among randomly selected eleven study stations, seven (S1 - S7) were situated in the Tien Hai, Thai Binh province and remaining four stations (S8 - S11) were located in the Giao Thuy, Nam Dinh province shown in Figure 1C and Figure 1D.

2.3 Mud and water sampling

Mud samples were collected (> 5mm) from randomly selected eleven stations of two sites using hand Grab sampler. Mud from four different places of each station were mixed very well, pooled into one and preserved with 0.5 N HCl in clean glass bottle (500 ml). In the laboratory, the samples were evenly shaken and processed with 1% HCl in a bottle (100 ml) and preserved at - 18°C. Surface water sample also collected by a special hand made sampler from each station and immediately preserved in refrigerator at same temperature for analysis.

2.4 Metal analysis

All mud and water samples were used for analysis of fourteen metal elements (As, Pb, Al, Be, Ba, Fe, Se, Sb, Cd, Cr, Cu, Ni, Hg, and Ag) using ICP-MS (detection limit is 10^{-11} - 10^{-12} µg/l) in the Laboratory of ICP-MS of Faculty of Chemistry, Vietnam National University, Hanoi. Mud and water samples are prepared according to the protocol of the Inductively Coupled Plasma Mass Spectrometer (ICP-MS) equipments using simplest acid digestion procedures involves the digestion of 50-100 mg of fine, homogenous sample powder in a mixture of HNO₃ and HF in heated, closed teflon beakers, followed by evaporation to complete dryness and two further stages of digestion in HNO₃ and evaporation. The final stage of sample preparation involves dissolution in ~ 2 % HNO₃ internal standard stock solution containing 10 ppb of all the internal standards required for analysis. Solution of ICP-MS analysis requires the introduction of dilute solutions with total dissolved solids (TDS) less than 0.1%. All solutions were filtered to free the particulates and diluted with 2-3% nitric acid for analysis.

2.5 Production data

Production (fish and shrimp) data were collected separately from local fishery farmers and fisherman of respective sampling stations using short questionnaire prepared during the period of investigations.

2.6 Statistical analysis

All data obtained were statistically interpreted. To compare the concentration of metals content in the mud and water samples of different stations, a one-way ANOVA was followed. If the main effect was found to be significant, the ANOVA was followed by a LSD (least significance difference) test. All

statistical tests were performed at 5% probability level using statistical package EASE and MSTAT.

3. Results

3.1 Metal distribution

Arsenic (As) – The concentration of As varied between 180 to 383 µg/kg in mud and 14.26 to 31 µg/l in water of all investigated stations of two sites (Table 1). The values were 7.8 – 23 times higher in mud than that of the water in all locations (Figure 2). In case of mud, the value was maximum (383 µg/kg) in the S2 and exhibiting the following order of variations: S2>S5>S6>S10>S7>S3>S4>S9>S8>S1>S11, whereas in water, order of variation was 7>11>10>6>9>2>1>8>3>5>4 showing the highest value 31 µg/l in S7 (ANOVA, $p > 0.05$).

Lead (Pb) – The Pb content of mud ranged from 4.9 to 207.3 µg/kg and from 0 to 0.15 µg/l in mud and water sample, respectively in all stations (Table 1). Though there was no detectable concentration limit of Pb concentration in water of all stations excepting S11 (0.15 µg/l) but a significantly high concentration were observed in mud of all stations investigated. The maximum (207.3 µg/kg) and minimum (4.9 µg/kg) values were pronounced in the mud of S11 and S5, respectively (Figure 2).

Cadmium (Cd) – Though there was very low concentration of Cd was found in water (0 – 0.06 µg/l), but mud exhibited a significantly higher value ranging from 0.62 – 44.1 µg/kg (Table 1). The highest value was observed in the mud of S1 (44.1 µg/kg) followed by S4 (9.82 µg/kg), S7 (9.2 µg/kg), S8 (8.1 µg/kg), S2 (4.3 µg/kg), S5 (3.7 µg/kg), S11 (3.58 µg/kg), S10 (3.53 µg/kg), S6 (2.7 µg/kg), S3 (0.78 µg/kg), and S9 (0.62 µg/kg), respectively.

Chromium (Cr) – Likewise Cd, lower concentration of Cr was also revealed in water (1.42 – 4.58 µg/l) and significantly higher concentration in the mud (117 – 192.5 µg/kg) (Table 1). The highest and lowest values were in S6 and S9 of mud, respectively (Figure 2).

Nickel (Ni) – Excepting S1 (0.033 µg/l) and S2 (0.111 µg/l), there was no detectable limit of Ni in water, whereas, Ni occurred in high concentration level in mud (49.9 – 100 µg/kg) (Table 1). The mud of S6 appeared with highest content of Ni (100 µg/kg) among the eleven stations (Figure 2).

Beryllium (Be) – The value of Be concentration varied from 4.06 to 10.5 µg/kg in mud and from 0.02 to 0.051 µg/l in water of all stations investigated of two provinces (Table 1). Be showed 88 to 318 times higher concentration in mud than that of the water in all locations. The S2 and S9 exhibited highest (10.5 µg/kg) and lowest (4.06 µg/kg) concentration in mud whereas S8 (0.051 µg/l) and S3 (0.02 µg/l) in water showed the highest and lowest value (Figure 2).

Table 1. Range of concentration in different stations investigated and permissible limit of WHO drinking water guidelines of fourteen metals.

Metal	Range of concentration		RPL of WHO drinking water guidelines ($\mu\text{g/l}$)
	Mud ($\mu\text{g/kg}$)	Water ($\mu\text{g/l}$)	
As	180 - 383	14.26 - 31	10
Pb	4.9 - 207.3	0 - 0.15	10
Cd	0.62 - 44.1	0 - 0.06	3
Cr	117 - 192.5	1.42 - 4.58	50
Ni	49.9 - 100	0 - 0.111	70
Be	4.06 - 10.5	0.02 - 0.051	10
Ba	194.3 - 515	18.52 - 50	700
Fe	42642-72397	192 - 669	300
Se	0 - 21	18 - 82.23	10
Sb	348.36-1463	0	20
Cu	52.1 - 138	7.68-136.27	2×10^3
Hg	0.049 - 0.2	0 - 0.336	6
Al	52488-77512	0 - 198.29	100×10^3
Ag	1.75 - 12.9	0 - 0.198	100

Note: RPL=Recommended Permissible Limit.

Barium (Ba) – In all stations, the Ba content ranged from 194.3 to 515 $\mu\text{g/kg}$ and 18.52 to 50 $\mu\text{g/l}$ in mud and water sample, respectively (Table 1). A markedly higher concentration was observed in S11 (5153 $\mu\text{g/kg}$) than that of the remaining ten stations (194.3 – 816.4 $\mu\text{g/kg}$) in mud but the maximum value 50 $\mu\text{g/l}$ (S3) and minimum value 18.52 $\mu\text{g/l}$ (S10) were registered in water (Figure 2).

Iron (Fe) – There was a significantly higher concentration of Fe was pronounced in mud (42642 – 72397 $\mu\text{g/kg}$) than that of the water (192 – 669 $\mu\text{g/l}$) in eleven stations (Table 1). The maximum and minimum content of Fe was found in S6 and S9 for mud, respectively whereas S1 and S7 for water, respectively (Figure 2).

Selenium (Se) – Though, the concentration of Se in mud (0 – 21 $\mu\text{g/kg}$) was noticeably low but a significantly greater value (18 – 82.23 $\mu\text{g/l}$) was observed in water (Table 1). Excepting S2, S4, S6 and S11, there was no detectable concentration of Se in mud (Figure 2).

Antimony (Sb) – There was no detectable limit of Sb concentration in water, whereas mud exhibited a significantly higher value ranging from 348.36 - 1463 $\mu\text{g/kg}$ (Table 1). The highest and lowest values 1463 and 348.36 $\mu\text{g/kg}$ was found in S11 and S4 among all stations investigated (Figure 2).

Other metals – In spite of above ten elements remaining four metals was observed within permissible and negligible concentrations in all surveyed stations (Figure 2). In eleven stations, the range of concentrations of these metals in both mud and water were as follows: Copper (Cu), 52.1 – 138 $\mu\text{g/kg}$ in mud and 7.68 – 136.27 $\mu\text{g/l}$ in water; Mercury (Hg), 0.049 – 0.2 $\mu\text{g/kg}$ in mud and 0 – 0.336 $\mu\text{g/l}$ in water; Aluminium (Al), 52488 – 77512 $\mu\text{g/kg}$ in mud and 0 – 198.29 $\mu\text{g/l}$ in water; and Silver (Ag), 1.75 – 12.9 $\mu\text{g/kg}$ in mud and 0 – 0.198 $\mu\text{g/l}$ in water (Table 1).

3.2 Production data

According to fish farmers and fisherman, the production (fish and shrimp) decreased surprisingly compared to the previous five years. The per cent decrease of production varied 20 to 40% within five years in all stations. Some fishery and shrimp farms completely devastated and suspended the production.

4 Discussion

Distribution data of above fourteen metal elements clearly demonstrated that except four metals (Cu, Hg, Al and Ag) remaining all metal elements (As, Pb, Cd, Cr, Ni, Be, Ba, Fe, Se and Sb) revealed the higher concentrations over the permissible limit recommended by WHO drinking water guidelines in almost all stations without few exceptions in some cases (Table 1). From this point of view, it is obvious the Red River Deltaic coastal region, Viet Nam is contaminated with a number of metal pollutants (Figure 2). It has been reported that As pollution is widely distributed in the Red River Delta, Viet Nam [10], in Hanoi, Viet Nam [11, 12, 9], Mekong River Delta, Viet Nam [8].

In spite of that, all metal elements appeared as higher concentration in the mud than that of the respective water excepting Se, this also implied that deposition and adsorption of these metals occurred for long periods onto the mud from overlaying water column introduced from the main Red river or his tributaries which is being carried by the upper stream of river passing through the rural and industrial zones. A frequent change of water is the main reason for low metal concentration in the water of few stations. The Cd contamination of soils is more serious in peri-urban area of Red river delta that has been affected by discharge from traditional rural handicraft production villages [13]. Huy and Wada also proposed that a massive amount of untreated wastewater and solid wastes is discharged into the river water and a variety of fertilizers and chemicals are applied by the farmers to enhance the production which causes the heavy metal accumulation in the soil of Red River Delta [13].

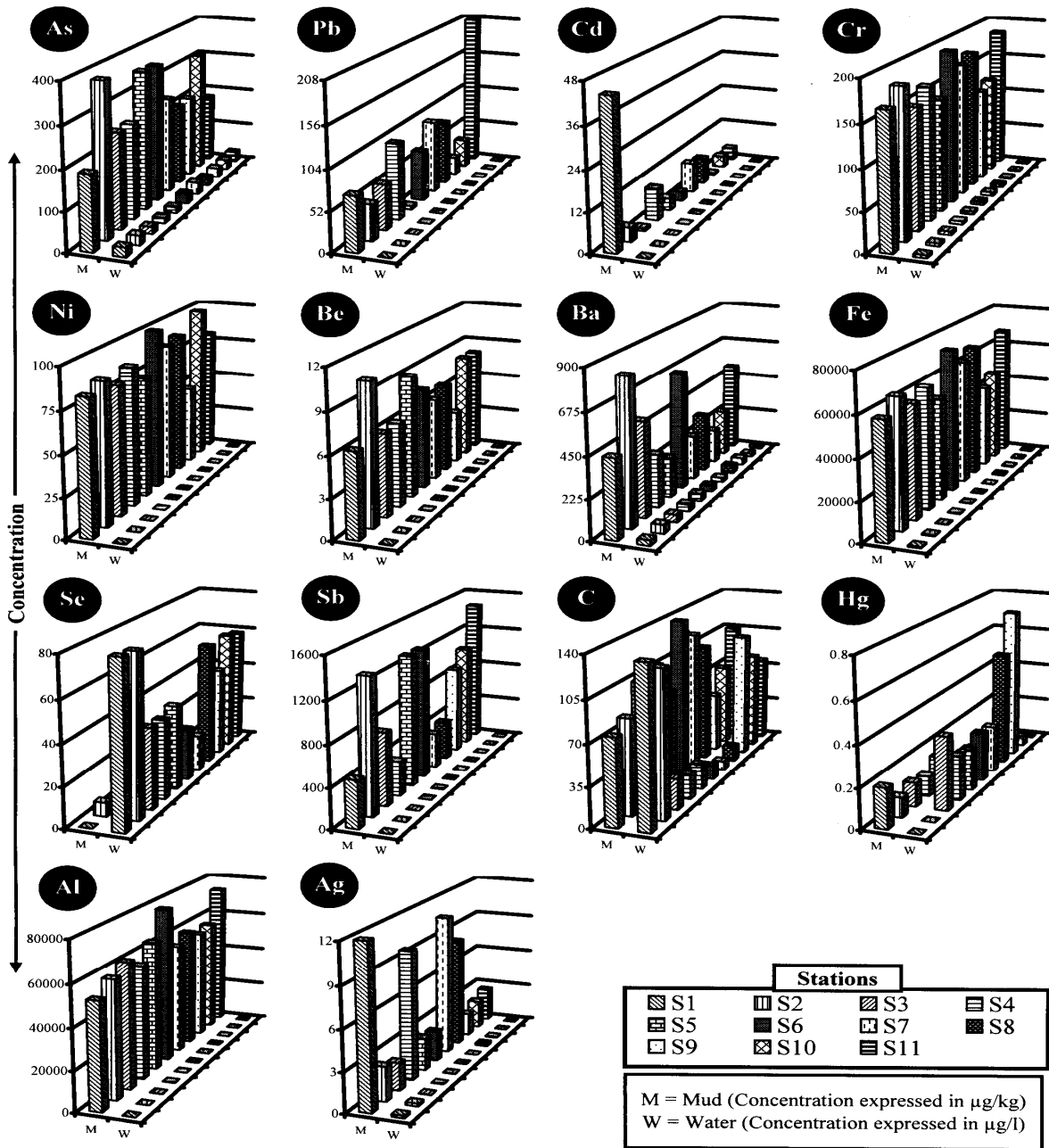


Figure 2. Distribution pattern of fourteen metals in the eleven stations investigated in Tien Hai of Thai Binh provinces and Giao Thuy of Nam Dinh provinces of Northern Viet Nam.

Though water showed a negligible concentration of metals but their higher concentration in mud poses an adverse impacts on the benthic as well as aquatic organisms. Because any substrate of mud and water compartment always has a tendency to reach an equilibrium state within an ecosystem by means of absorption, adsorption and desorption process from higher concentration to lower concentration. The soil involve inputs and losses of substances, movement of substances within pond water and soil, transfer of substances across the soil-water interface, and uptake or release of substances by the soil through ion exchange, dissolution and decomposition [14, 15]. On the

basis of these facts, it is justified that mud-water interfaces interaction is an important governing factor in the productivity of an aquatic ecosystem. From this point of view, it therefore also be indicated that a permissible limit of metals concentration in overlaying water is not save for the aquatic organism inhabited or cultured where having a measurably higher concentration of metal content in their bottom mud. This condition equally effects the growth and health condition of aquatic organism as directly is manifested by the high metal content water. Therefore, it may be concluded that metal concentration in the water as well as mud is an important concern to the aquaculture system in this

coastal zone of Thai Binh and Nam Dinh provinces of Viet Nam.

As fish production percentage decreased year after year in all stations of Tien Hai districts of Thai Binh provinces and Giao Thuy districts of Nam Dinh provinces of Northern Viet Nam, it may clearly be inferred that the higher metal concentration may causes a negative impact in the productivity system of this coastal ecosystem which badly influencing the shrimp and fish production.

5 Conclusions

Above study clearly stated that the Thai Binh and Nam Dinh provinces in Red River Delta of Viet Nam contaminated with different metal pollutants that severely affecting the food chains of this ecosystem. Waste water pollution can affect all ecosystems and human health directly or indirectly as in food chain [16]. As a consequence of heavy load of metals, not only growth and production of cultured and wild species of shrimp and fish is hampering remarkably but also it has a potential impact to decrease the abundance of the species i.e., biodiversity loss in the coastal zone that ultimately resulting in the loss of ecosystem stability. Studies often explain that lowering species diversity is a response to pollution [17]. Coastal sediments and oyster farming is severely affected by the industrial effluents in the coastal region near LuGong, Taiwan [18].

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