



Assessment of Heavy Metals Impact in the Ecosystem in Bandon Bay at  
Surat Thani Province and Using the Oyster as a Biological Index

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A Thesis Submitted in Partial Fulfillment of the Requirements for the  
Doctor of Philosophy in Environmental Management

Prince of Songkla University

2015

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**Thesis Title**      Assessment of Heavy Metals Impact in the Ecosystem in Bandon Bay at Surat Thani Province and Using the Oyster as a Biological Index

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### **ABSTRACT**

This study was conducted using secondary data, a field survey and laboratory analysis to investigate the problem of heavy metal contamination in Bandon Bay, Surat Thani, Thailand. It was estimated that the amounts of Cd, Cr, Pb, Cu, Mn and Zn discharged from inland into Bandon Bay were 10.4, 26.2, 47.1, 66, 156 and 423 ton per year, respectively. A survey of heavy metal concentrations in seawater and sediments in Bandon Bay during 2011-2012 at 7 points along the bay revealed to have risks of Pb and Cd contamination of sediments. The study implied that cockle harvesting in the bay had a significant impact on seawater quality. In laboratory experiments, it was found that the association of heavy metals in terms of Cd and Pb with seawater and sediments was caused by adsorption and desorption reactions during mixing of resuspended sediment particles in seawater which caused changes to the heavy metal concentrations in seawater.

Oysters were examined as potential bioindicator and found to be better suited for Cd than for Pb contamination. For this purpose their growth was observed at three locations over 9 months. It was found that the highest growth of oysters were at Kradae. The Cd accumulation rates in oysters were 0.103-0.280 mg/kg per month (wet weight), those for Pb were 0.03-0.065 mg/kg per month (wet weight). Based on these results, 1.15 kg of Cd and 0.29kg of Pb were removed from Bandon Bay by harvesting the oysters accumulating Cd and Pb. The results of the ecological risk study indicated the risk that Cd and Pb accumulated in sediments and contaminated oyster, particularly in Chaiya, Kradae and Tatong. Furthermore, the study examined the economic impact of oyster contamination by heavy metals and, finally, measures to control the heavy metal pollution problem, included of continue heavy metal monitoring, in particular use of oyster as biomonitoring for Cd and Pb, zoning of aquatic culture, use of good practice protocol for oyster cultivation, control generation sources and further research were recommended.

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# CHAPTER 1

## INTRODUCTION

### 1. Background and Rationale

Bandon Bay is not only beneficial for Surat Thani residents but also as a wetland of international importance (Makpun, *et al.*, 2007). It contains wide and flat mud which intrudes into the sea around 1-2 kilometers long. The depth of water is around 1-5 meters. The bay is a shallow coastal line with mangrove forest around the bay. The area covers 8 districts, including Tha Chana, Chaiya, Tha Chang, Phunphin, Muang Surat Thani, Kanchanadit, Don Sak, and Ko Samui (Ariyadet, *et al.*, 2008). The coastal ecosystem of Bandon Bay enriches with biodiversity dealing with economic important species. Moreover, mangrove forest, sea grass, and coral reef ecosystem in the area are essential for future development of fishery economics (Office of Strategic Management, Southern Provinces Group on the Gulf of Thailand, 2009). It is also a nourishment area resulting from sediment deposits at the estuary.

The pollutants discharging from the main rivers in the upper South of Thailand, it is also an area that receives and accumulates pollutants such as heavy metals draining from the Tapi River. There were some reports illustrated heavy metals in the Tapi River. For example, in 2001 Pukitipan, reported that contaminations of heavy metals such as lead, chromium and cadmium in the Tapi River were higher than Thai Surface Water Quality Standard (1992) which could be harmful to human consumptions. The five years data from 2004 to 2009 of the Tapi River indicated that heavy metals in the river (Cu, Ni, Mn, Zn, Cd, Cr, Pb, Fe, As) were lower than the Thai Surface Water Quality Standard of type 3-4. However, the Office of Environmental Region 14 (2010) monitored and reported that heavy metals were still determined in the Tapi River. These could be transported to Bandon Bay and accumulated there.

The report on lead in sediment of Kradae canal which flows into Bandon Bay illustrated to be high level, exceeding the standard level of lead in sediment of the Sediment Quality Standard – the threshold effect level of Florida

Department of Environmental Protection in USA (Aquatic Resources Research Institute, Chulalongkorn University, 2006). This might result in the accumulation of heavy metals in aquatic animals, water, and sediment through food chains. In turn, this may exert impact on human beings who consumed aquatic animals from the bay. In addition, Wibunpan (2006) also studied heavy metals contamination in oyster from Bandon Bay, Surat Thani. The results of average 4 years from 1998-2002, illustrated that average cadmium contamination was at 1.412 mg/kg with the range of 0.173-3.640 mg/kg. The high level contamination of cadmium exceeded the standard level of cadmium in oysters. In 2008, Roekdee investigated surrounding environments of the watercourses around the oyster aquaculture areas at Kanchanadit, Surat Thani province and determined heavy metals concentrations (cadmium, lead, and mercury) contaminated in oyster samples collected from the aquaculture areas. The high level contamination of cadmium exceeded the standard level of cadmium in oysters (the maximum level is 1.0 mg/kg) set by The Commission of the European Communities (EC) No. 1881/2006 (Fish Inspection and Quality Control Division, 2004). In the past, there were some reports from 2001 to 2009 of the Tapi River and Bandon Bay illustrated tendency of heavy metals problem, particularly Cd and Pb.

The information reflected the heavy metals contamination problem in Bandon Bay area. The high quantity of cadmium in oyster causes difficulties on its export activity because the countries importing aquatic animals have rules and regulations to control quality of aquatic animals. The acceptable levels of heavy metals in oysters were regulated differently in various countries. (Kumsuk and Songkong, 2004; Priyanka, *et al.*, 2008). Bandon Bay area is also an area for important economic aquaculture such as oysters and ark shells. Oyster is essential economic for Surat Thani province. Oyster farming gave high income employment and made Surat Thani well known for oyster (Gannarong and Sopakul, 2004). There are many oysters that were adopted as a tool for bio-monitoring to study the effect of heavy metals in water ecosystem. There were reports the use of oysters as bio-monitoring index for heavy metals contamination (Zauke, 2008). Oysters have been used widely as a biological index for coastal pollution with its reasonable qualities as follows; aggregate in the area such as estuaries and coastal areas; filter-feeding organism



could receive pollutants that related to the environment; long life cycle for the effect of long contamination period and various ages in the specific area and environment; abundant and widely distribute geographically which can study pollution in broad area; very important in the food chain; contain different age classes in a given area and environment; and could be beneficial for research purpose from commercial activities.

Although, there were many studies and reports of the situation of heavy metals contamination in Bandon Bay area, however most of them focused only separated parts, study not showing the relationships of the situation of heavy metals contamination of all components in Bandon Bay ecosystem. Hence, the level of problem, mechanism and effect were not comprehensible. It is necessary to do further research for heavy metals contamination in Bandon Bay ecosystem included of physical and biological components, as well as generated sources in order to reflects all related data of heavy metals contamination in Bandon Bay. For example, pollution sources of heavy metals, the accumulation of heavy metals in seawater and sediment, heavy metals leaching between seawater and sediment and heavy metals in aquatic animals should be conducted in the same time.

In addition, the study of the level of heavy metals contamination in oyster farming at Bandon Bay, as well as the data of risk assessment of heavy metals contamination in Bandon Bay ecosystem should be determined in parallel. These data are essential for the Bandon Bay ecosystem management. Therefore, the study of “Assessment of heavy metals impact in the ecosystem in Bandon Bay at Surat Thani province and the use of oyster as a biological index” would aim to provide the technical information which could clarify the heavy metals problem in Bandon Bay area. The results of this study could be used for management and planning, or provide specific and appropriate guidelines to mitigate heavy metals problem and bring to a sustainable management of the area.

## 2. Objectives

1. To determine point sources/non - point sources/activities of heavy metals generation and it's amount draining into Bandon Bay via the Tapi and Pumduang Rivers.

2. To assess the contamination levels of heavy metals in seawater and sediments of Bandon Bay and to study the heavy metals leaching phenomenon from sediments to seawater in Bandon Bay.

3. To investigate the use of oyster as bio-indicator for Cd and Pb pollution in Bandon Bay.

4. To assess the impact and risk of heavy metals contamination in Bandon Bay ecosystem by using system analysis approach and to provide the control and management measures for the heavy metals contamination problem in Bandon Bay.

## 3. Literature Review

### 3.1 The study area: Bandon Bay in Surat Thani Province

The Tapi River is geographically located at the center of Surat Thani Province. In the west there are limestone mountains mostly covered with forests. The Khao Sok National Park is located in these mountains. It is the largest province of the South located 685 km far from Bangkok. The province covers an area of approximately 12,892 km<sup>2</sup>. The north and the east of Surat Thani Province borders with the Gulf of Thailand. Border area connects with Chumphon Province to the north, Nakhon Si Thammarat and Krabi Provinces to the south, Phangnga and Ranong Provinces to the west and Nakhon Si Thammarat Province next to the east. (Surat Thani Provincial Administrative Organization, 2012 A). Surat Thani consists of the Tapi River and coastal plain area which make the area plenty of wetlands such as Bandon Bay. It is the wetland of both international importance and for Surat Thani residents. Bandon Bay is a marine ecosystem which has high biodiversity containing mangroves, sea grass, coral reefs which are the habitat, egg laying, nursery ground and food

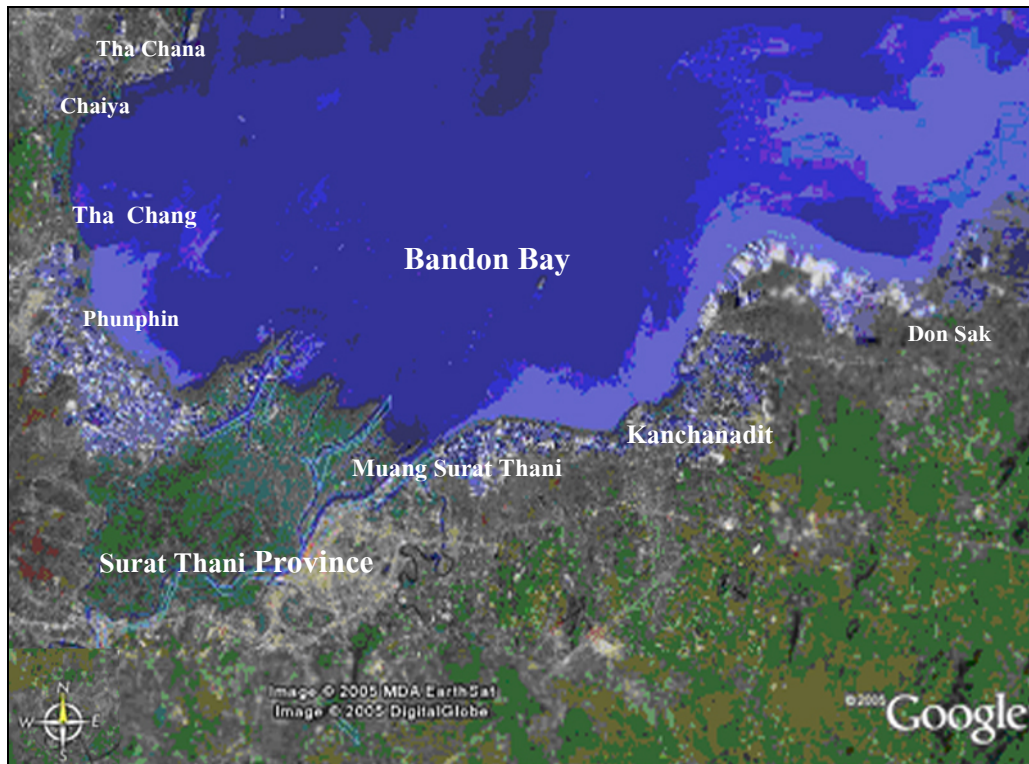
sources for all aquatic organisms including rare animal such as dolphin (Surat Thani Provincial Administrative Organization, 2008). The characteristics of Bandon Bay are as follows;

### **3.1.1 The background of Bandon Bay**

Bandon Bay is located to the east of Surat Thani Province and covers an approximate area of 1,070 km<sup>2</sup>. The inner bay covers an area of 480 km<sup>2</sup> with 80 km of coastline. The coastal area has a gradual slope and the water is shallow. Bandon Bay is a wetland of international importance (Wattayakorn, *et al.*, 2001; Makpun, *et al.*, 2007). It has a broad mud flat intruding in the sea 1-2 km from the shore. The area along the coastline is shallow seawater with mangroves alongside the bay. (Ariyadet, *et al.*, 2008). The bay area contains high sediment and broad mud flat along the coastline around 2 kilometers from the shore (Wattayakorn, *et al.*, 2001). Bandon Bay map is shown in Figure 1.

### **3.1.2 Climate patterns**

Bandon Bay at Surat Thani has a tropical monsoon climate. The area is under the influence of the Northeast monsoon traveling through Thai Gulf and the Southwest monsoon traveling from Indian Ocean. The average rainfall is 129.92 millimeters per day. The highest rainfall is 286 millimeters per day. The temperature range is between 21.11 and 34.51 degree Celsius (Thai Meteorological Department, 2009; Surat Thani Provincial Administrative Organization, 2012 B). There are two seasons in Surat Thani which are dry season starting from February to June. During the season, the influence of the Northeast monsoon is reduced and replaced by the Southwest monsoon, leads to hot weather and higher temperature with less rain. Rainy season starts from July to January. The Southeast monsoon and the Northeast monsoon cause the rain during the season.



**Figure 1:** Aerial map of Bandon Bay, Surat Thani

Source: Google earth

### 3.1.3 Oceanography

1) **Tidal current.** Tidal current in Bandon Bay has amplitudes range from around 0.70 m at neap tides to 1.90 m at spring tides. The average tidal range is 1.0 m. The coastal plain is gradually slope with average shallow water around 2.9 meters with the different from 1 to 5 meters near the bay-mouth. The system is a mixed tidal type with principally semidiurnal tide. (Hydrology and Water Management Center for Southern Region, 2010).

2) **Sea current.** Sea current in the coastal area of Surat Thani resulting from the tidal current and wind, the direction of current at spring tide is the Northeast and changes to the South and Southeast at neap tide. The current of water in Surat Thani is at 2.04 kilometers per hour (Hydrology and Water Management Center for Southern Region, 2010).

**3) Wind and waves.** The coastal plain of Surat Thani is under the influence of the Northeast monsoon during November to April with the speed of 4.3-6.2 kilometers per hour (the lowest speed of wind is in October and the highest speed is in June). From the calculation of wind speed it should be speculated that during the Northeast monsoon the wave is around 0.32 meters high in the coastal area of Surat Thani (Hydrology and Water Management Center for Southern Region, 2010).

**4) Sedimentation.** Sediments at the coastline consists of 2 types which are the sedimentation at the river mouth taken by rivers and canals to accumulate at the river mouth, for example at the Tapi River mouth. The sediment could shallow the coastal area and cause mud flat along the coastline. The second type of the sedimentation is the sedimentation by seawater current. The first type of sediment is carried away by sea current further and settled with the sand which becomes a peninsular. At Bandon Bay, the mud flat should be seen and it is also the place for cockle and oyster growth (Deacharat, 2002).

## 3.2 Oysters

### 3.2.1 Basic information of oyster

Oyster is a marine animal which is farmed for consumption for a long time. It contains high nutrition and is popular for consumers in the South of Thailand such as Surat Thani, especially the big oyster or cup-oyster (Department of Fishery, 2007). The National Heart, Lung, and Blood Institute Health Information Center indicated in 2009 that oyster contains high nutrition. It is a source of vitamin A, B1, B2, B3, C and D. Consuming 4-5 medium sized oysters would provide ferrous, copper, iodine, magnesium, calcium, zinc, manganese and phosphorus to the body. Oyster could be classified based on taxonomy as follows; Phylum Mollusca, Class Lamellibranchiata and Bivalvia, Order Ostreoida, Family Ostreidae, Genus *Crassostrea* / *Saccostrea*, Species *belcheri* / *irdelei* / *cucullata* (Gannarong and Sopakul, 2004).

Basic characteristics of large type of oyster or white cup- oyster are bivalves with asymmetric shells. Left side of the shell is bigger and has the shape similar to a cup which is the side for attachment. The right side of the

shell is flat as shown in Figure 2. Most of the oyster shell consists of calcium carbonate. Both shells connected with a hinge. The shape characteristic of large type oyster is influenced by the environment condition.



**Figure 2:** White cup - oyster (*Crassostrea belcheri*)

Source: Roekdee (2008)

The inside of oyster has oyster meat contains mantle which is a sheet of tissue wrapping internal organ. The mantle spreads to the mouth hole and both sides of oyster's shell as shown in Figure 3. Mantle consists of three parts which are outer part, middle part and inner part. The mantle tissue of both sides do not blend together that makes the mantle cavity contains water. Mantle cavity is responsible for water and food transportation to oyster's body. There are two gills for food filtering, respiration and excretion. The middle part of oyster's body contains one large muscle to fix the shell and to open or shut the valve. All organs such as digestive system, nervous system, excretion system, circulation system and reproductive system are located inside the shell.



**Figure 3:** Inner part of white cup-oyster (*Crassostrea belcheri*)

Source: Wangsuk (2005)

Oysters have important role on economic of Thailand and could be classified into three types, the smaller one which is rock oyster or hooded oyster (*Saccostrea cucullata*) and the bigger size which is pacific oyster or cup-oyster including black cup-oyster (*Crassostrea irdelei*) and white cup - oyster (*Crassostrea belcheri*). These types of oyster are extensively farmed in the South of Thailand especially white cup - oyster (*Crassostrea belcheri*) which is widely farmed in Kanchanadit district, Surat Thani province (Gannarong and Sopakul, 2004).

### **3.2.2 Site selection for oyster farming**

Site selection is a basic foundation for oyster farming which should be considered and chosen according reasonably and appropriately methods. Several factors that should be considered are; 1) brackish water area or seawater inundation area for at least 7-8 months per year which no influence of fresh water during rainy season that results in low salinity which might cause high mortality rate; 2) should have natural oyster which makes it convenient to find oyster spat for farming and could reduce the cost; 3) safe from wave and strong wind that might damage farming materials, shallow water, mud soil or mud with sand; 4) convenient transportation and close to the market; 5) have a certain

distances from mining industries which might harm oyster including consumer; 6) water could flow through the area and contain high natural nutrients and water flow rate should be around one meter per second (Brohmanonda, 1986).

Consideration of the Bandon Bay seawater characteristics, it was reported that the average pH of water in Bandon Bay is 7.9, average dissolved oxygen (DO) is 6.1 mg/l, biochemical oxygen demand (BOD) is 1.5 mg/l, average alkalinity is 11.2 mg/l, average ammonia is 0.06 mg/l, average nitrate is 0.03 mg/l, average phosphate is 0.05 mg/l, plankton quantity is 100-13,350 cell/ml. These are in the appropriate guideline for aquatic animal farming. A sudden change in salinity results in the death of oyster spat. Moreover, when salinity increases at the higher level, the growth rate, development of reproductive organ and reproductive cell generation will be inhibited. Salinity causes the contraction of oyster's mantle including filter feeding system. The reduction of salinity might cause the reduction of filter feeding system (Wongpanit and Sukswan, 2007).

### **3.2.3 Methods of oyster farming**

The study of Siripan (2006) stated that those are various methods of oyster farming based on geography and climate in each area. These of them are as follows;

**1) Oyster farming on rock.** This method used rock as a media for young oyster to attach till reach the size. This is an easy and conventional way of oyster farming and still widely use at present especially in the area where natural rock could be easily found. Rocks were put in pile and each pile contains 5-10 rocks. The rocks were arranged to gain highest area for young oyster to be attached. The distance between piles is around 50 cm and arranged in a row. This method is used at the border area of the highest water level to the lowest level along the coastline, open bay, hard mud, sand with hard mud or rock. To prevent the rock to sink or to cover up, bamboo is used as a base of the box. Strips of split bamboo were made as a place for putting on the rock in the farming area until the oyster attached on the rock and then continue to be farmed during the mud cover up. This method could



be seen at open bay and river mouth. It is widely used for small oyster in Chon Buri and Sawee Bay, Chumphon Province (Siripan, 2006).

**2) Oyster farming in wooden box.** This method is appropriate for the open space of bay area along river mouth or along the riverbank that brackish water or seawater covers regularly. The wooden box is rectangular at any size but the mostly used is 80 cm X 200 cm X 25 cm, made of iron wood or other hard wood at the four edges and the bed of the box made of bamboo for water to flow easily. The wooden box is fixed firmly on a carrying pole above the ground around 30 cm. Smaller type of oyster should be at the age of 6-7 months or the size of 3.5-4.5 cm which removes from the rock. In the case of young oyster attaches with other shell, the oyster could be placed in the wooden box directly. It should take around one and a half year for the oyster to be in the market. Pacific oyster should be collected into the wooden box at the age of 3-4 months or at the size of 3-4 cm. It should take around 7-8 months to obtain the size for the market. This method could be found in Prachuap Khiri Khan Province (Siripan, 2006).

**3) Oyster farming on cement rod.** This appropriated for the same area as farming on rocks or could be farmed with both methods. Cement rods were placed between the rocks row and leave the area for pathway. This method is used in mud area. The cement rod should be made especially for oyster farming. To resist the wind and wave, wood is used as the core of cement rod. Mangrove or other hard wood are being used and put in the soil to support cement rod. The size of cement rod is depends on water level but for a good result the size of 50-70 cm with the square front top area of 12 X 12 cm and the wood 1 meter long embedded in cement rod of 50 cm and leave the wood to stick into the soil for 50 cm (Siripan, 2006).

**4) Oyster farming on wooden pole.** This most appropriates for open bay, soft mud or mud with sand, no wind and wave protection. Moreover, this method could be used to farm along the bank of the river with strong current. The wood should be hard wood such as black mangrove for young oyster to attach and grow to the appropriate size. The wooden pole for oyster is similar to the wooden stick for mussel. Pacific oyster's shell or mussel's shell could be made as a cluster to collect oyster spat from nature. Oyster spat will be attached on the shell till 1-2 months then

the shell will be moved to fix with the wire to the wooden pole. The pole then will be put in a row at the depth of 30-40 cm for a hard mud area but in a soft mud area it should be deeper (Siripan, 2006).

**5) Oyster farming using hanging method.** This method is widely used in Japan, USA and European country because of the high growing rate and productivity. This method could be made into two types, hanging under the raft and hanging from ropes. Most important, the place for farming should be closed area which could prevent wind and waves. The raft could be any size and anchors all four sides. Water should be 5-10 meters deep. Oyster spat collection uses the same method as described in wooden pole oyster farming method. When oyster spat attaches to the shell, those shells are made as a cluster through no.10 wire and they are separated by about 15 cm. Small bamboo is used to separate each shell. The cluster is then moved to hang at the raft till the size is right for the market. Hanging method in Thailand is widely practiced in river or brackish canal such as Phangnga Province. Pacific oyster farming which uses shell cluster and hang on the rope is practiced at Bang Nangrom canal, Prachuap Khiri Khan. In Ang Sila, Muang, Chon Buri Province, small type of oyster is farmed by hanging method under the bamboo rack. Oyster farmer buys cluster of ropes 1.5-2.6 cm with oyster spat attaches on cement material. The cluster of ropes is hanged under the bamboo rack of 8X6 meter which could hang 4,500 ropes with 360,000 oyster spats for each rack. The problem of small type or hooded oyster farming is the slow growth rate of the oyster at the middle of the rack. This might results of insufficient plankton as the oyster on the inner side of the rack filter. The plankton could not reach the inside part or middle part of the rack (Siripan, 2006).

**6) Oyster farming on tube or cement cylinder.** Cement is comprised of calcium oxide (CaO), silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and ferrous oxide (Fe<sub>2</sub>O<sub>3</sub>). These chemicals react to form a compound which contains very fine crystal (Department of Mineral Resources, 2007). This method is used for inundated area such as shallow water along the coastline, river and canal mouth and lake. The soil should be mud or soft mud with sand. Wood poles, mangrove or bamboo, should be placed in a row with 1 meter wide between each row. Then cement cylinder

with the size of 15 X 40 cm attached with 20 oyster spats is put on wood rod or PVC cylinder with size of 3.2 X 120 cm. The rods are placed in mud, rows are spaced 30 cm and each rod is 20 cm. The wood is put as a basement to prevent the rod to remove under the mud. One sized open cement cylinder could be put on the wood rod which could be put around 1,600 cylinders per Rai. Recently, oyster farmer increased the size of the cylinder for more attachment area and uses cement as a basement instead of the wood for longer life cycle and more convenient. This method is widely practices in Surat Thani Province (Siripan, 2006).

The increase of oyster farming has a direct impact on water environment. Because, excretion from oyster increases as the number of oyster farming. Changes in water and sediment quality will affect growth rate and oyster production. The spreading of sediment caused by cockle dredging and the problem of sediment accumulation in the area of oyster farming also affected to oyster production. The area characteristics and sediment nourishment are essential for the growth of oyster. Moreover, thief and fluctuation of the price are also the problems of oyster farming. Oyster farmer has less technical knowledge. The water quality, oyster's disease and chemical contamination such as heavy metals should be provided by related organizations to gain some guidelines to solve oyster farming problem situation (Meksumpan, and Srisomwong, 2002)

### **3.3 Basic information of heavy metals**

Basic information of heavy metals is a foundation of heavy metals study. The study of heavy metals contamination in Bandon Bay ecosystem related to this information. The heavy metals term refers to any elements that has specific gravity more than 5 and located in group 4-7 of Periodic Table which includes mercury, cadmium, lead, zinc, copper, nickel, chromium, iron, manganese, etc. Heavy metals are considered as trace metals which mostly in transition elements. Moreover, there are some other elements which are representative elements group such as arsenic, antimony and selenium (Sithikrom, 2001).

### 3.3.1 Sources of heavy metals

Heavy metals disperse into the environment from two main sources which are natural and anthropogenic.

**1) Natural sources.** Heavy metals can be found naturally with little amount in soil, rock in the mining area such as zinc, lead and copper (Rudnick, 2004). Heavy metals distribute though out the earth crust, therefore the contamination in the environment occurs easily from geological process such as weathering, erosion and transportation into water resources (Richardson, *et al.*, 2001).

**2) Anthropogenic sources.** Wastes from human activities are disposed and end up in the sea, which result in adverse impacts on living organism and human health themselves. In addition, it will have an impact on other activities such as fishery. Seawater quality especially coastal area which intensively inhabited by human or industries, agriculture and mining might contains heavy metals that being washed and transported from land into water resources (Water Quality Management Bureau, 2003). Sources of water pollution can be classified into two main types which are non-point source, for example agriculture, and point source such as community, industry (Water Quality Management Bureau, 2010).

- **Non-point source.** Non-point source refers to pollution that does not have one specific source, for example in agricultural area, agricultural activities such as paddy field, orchard, farming and animal farming are sources of pollution which have an impact on the environment. Nutrients from fertilizer or animal wastes discharge contaminated with pesticide (Pollution Control Department, 1999). In addition, livestock and fishery are also included in non-point source of pollution. Most popular livestock are cow, buffalo, swine, chicken and goat. In the area of fishery, there are salt water fishery, brackish water fishery, aquatic farming at the coastline and inland fishery. In watershed area it was found that water pollution caused by agricultural activities. The study of pig farm wastewater illustrated that most wastewater which contained urine, manure and feed leftover. The average biochemical oxygen demand (BOD) was 3,000 mg/l which was 750 times of BOD in natural water. The average mercury contamination was 0.0023 mg/l caused by the use of antibiotics and chemicals (Teekakul and Klinsukon, 2004).

- **Point source.** Point source refers to single identifiable source of pollution from which pollutants are discharged such as communities, factories and mining. For examples, communities are important point sources which produce domestic wastewater from bathing, and washing. Its wastewater will be discharged into natural water. The study of Panutrakul and Mekkongpai (2000) at Bangkok River mouth stated that most of the cadmium might be from anthropogenic and the cadmium was prone to attach with organic matter when released in water resources. In addition, factories related to heavy metals discharge contaminated wastewater into natural water. This might be possible to contaminate into the sea. (Academic Resources Center Surat Thani, 2010).

Mining processes include soil removal and dumping. The process of mineral excavation, washing and mineral processing also cause heavy metals contamination into the environment which also impact water quality (Office of Natural Resources, Environmental Policy and Planning, 2005). Characteristics of lead related chemically to organic matter in the sediment which could mostly found in fine sediment. Land opening for mining leads to arsenic and lead washing into natural water resources. Noticeably, high concentration of lead could be found in the southern part of Thailand (Mineral Resources Department, 1998).

Cadmium is the mineral that could be found together with other minerals such as zinc, lead and copper but mostly found with zinc at 0.1- 5 part per hundred. The amount of cadmium related to the amount of zinc in mineral ore. The distribution of cadmium into the environment could be from lead and zinc industries, burning waste containing cadmium such as plastic, color pellet and iron and phosphate fertilizer. Phosphate rock contains cadmium and when applies together with ammonium fertilizer, cadmium could be more soluble in water (Hazardous Waste and Solid Waste Management Department, 1998).

The study of the Pollution Control Department in 1999 demonstrated the amount of cadmium in sediment at 0.005 – 0.23 mg/kg dry weight. The sources might be from fertilizer industries especially at the Mabtapud port. Oil spill was another cause of heavy metals contamination which has an adverse impact on the environment while loading. The use of ship/boat for transportation including oil

consumption activities affects water and aquatic animals (Water Quality Management Bureau, 2003).

### 3.3.2 Chemical reactions of heavy metals

A chemical reaction is a process of the transformation of chemical to other substances which contains different properties. The chemical reaction needs reactants which are the starting materials for a reaction to get new substances which called products (Panichsiti, 2003).

**1) Complexion reaction.** This is chemical reaction that combines one or more negative ion or molecule (ligand) to another positive metal ion. In complexion reaction, some metal ions are soluble in water and combine with ion and other molecules to form complex ion which could be dissolved in seawater. Metal ion is free ion which combines with stable complex ion. The concentration of free ions is reduced and the solid could be more soluble to keep the balance.

**2) Precipitation.** Precipitation occurs in aqueous solutions that forms solid compound called precipitate. The shallow water along the coastline and estuary, where freshwater from the river and seawater mixing, are the areas that contain high quantity of suspension. The chemical reactions between suspended solids and soluble minerals occur in these areas. For example, adsorption on the surface of suspension or adsorption on the surface of hydroxide and oxide of ferrous and manganese such as  $\text{Fe}(\text{OH})_3$  which is less soluble in water and forms colloid which would suspend in seawater for a long time without precipitate unless there is other process involve. When colloids formed and become bigger in size, ferrous hydroxide precipitation might occur. Estuary area is high in suspended solids, therefore it is an appropriate area for ferrous hydroxide and manganese oxide could be coated on suspension and precipitate into sediment at the bottom of the estuary. In the precipitation process, the absorption of other heavy metals (cadmium, copper, lead, nickel) on the surface of suspended solids that coated with hydroxide and oxide of ferrous and manganese are also happened and precipitated together. This is an essential heavy metals removal process from seawater and accumulates in sediment at the bottom of water body along the coastline (Sawangwong, 2003).

**3) Adsorption.** This is the process of molecules or particles binding to a surface of other substance. The substance is called adsorbate while adsorbent is the molecules or particles that bind to the adsorbate (Panichsiti, 2003). The chemical geology controlling process of various heavy metals in seawater by adsorption on the inorganic sediments includes many chemical reactions such as oxidation and reduction. The reaction between heavy metals and inorganic sediment is controlled by redox potential and pH of water. In general, pH of seawater changes insignificantly. Adsorption process of trace metals depend on oxidizing and reducing environment of water condition.

Oxidizing environment is the condition that is mostly found in seawater. It is found that manganese and ferrous are withdrawn from seawater as a result of ferrous hydroxide and manganese oxide precipitation and form manganese nodule which could be found at deep sea floor. The accumulation rate of manganese nodule formation is very slow. At the same time, this manganese nodule also accumulates other heavy metals such as copper, lead, zinc and cadmium while being formulate. The adsorption process of heavy metals on the surface of manganese nodule also causes heavy metals to remove from seawater.

Reducing environment is the condition of lacking oxygen in water body. Mostly found in closed water body or deep seawater. In both cases, there are organic materials accumulated in water result in chemical reaction to digest organic material through oxidized reaction by oxygen. The reaction causes the lack of oxygen condition which makes bacteria to reduce free sulfate ion in seawater and reacts with heavy metal ions to form metal sulfide in reducing environment. Under the condition, ferrous and manganese in water are high in concentration. Moreover, ferrous sulfide and manganese sulfide have high solubility product constants ( $K_{sp}$ ). MnS and FeS dissolve very well at pH 6-7. Some metals such as copper and lead which have low solubility product constants are found in small amount in reducing condition. This condition is suitable for precipitation and accumulation of heavy metals under the sea floor (Hungsapruet, *et al.*, 2003).

### 3.3.3 Chemical speciation of heavy metals.

Chemical speciation describes the distribution of element or compound at any chemical states such as aqueous solution, organic compound or inorganic compound. The species concentration of element or compound is equal to bulk concentration (Salomonsel, 1988). Chemical speciation of heavy metals could be categorized into 5 forms as follows;

**1) Exchangeable forms of heavy metals adsorbed with soil.** The ion exchanged through chemical process while negative ion in soil binds positive ion of metal. Negative charge in soil is depended on the concentration of  $H^+$  in soil. Generally, in acid soil there is low negative charge while alkaline soil has high negative charge. The soil would be neutral when there is positive ion in the solution. One positive metal ion will be replaced by higher ionic potential of other metals. The change of ionic potential and water pH affects the adsorption on the soil (Deacharat, 2002).

**2) Carbonate forms.** It is the form of metal adsorbed with carbonate. Metals in this group are in carbonate precipitate such as  $PbCO_3$  and  $ZnCO_3$ . The pH in the soil decreased results increase of the solubility of metal.

**3) Iron and manganese oxide forms.** They are the form that metals adsorbed with ferrous and manganese oxides. Fe-Mn oxides influence the change in chemical speciation of metals in water. The surface areas of Fe and Mn have high capacity of adsorption which also affects the concentration of heavy metals (Deacharat, 2002).

**4) Organic forms of heavy metals.** There are many forms of organic heavy metals. Organic matters contain negative charge like soil. Negative charge varies base on pH value. Increase in acidity resulted in high attachment of  $H^+$  and organic matters (Deacharat, 2002).

**5) Mineral crystals form of heavy metals.** It is the form that heavy metals bound to mineral lattices which are primary minerals and inactive. For example, lead and zinc in the form of  $PbS$  and  $ZnS$ . Cadmium could be in solid form in mineral lattices ( $CdS$ ) (Deacharat, 2002).



### 3.3.4 Mechanism of heavy metals accumulation in aquatic organisms.

As a good solvent, water solves elements easily. Many elements could be found in seawater and highly active for the reaction especially adsorbed with suspended solids in water and participated together with the suspension. They are manganese, lead, cadmium, copper, ferrous and zinc. Some heavy metals play an important role on biochemical process of living organisms in seawater. High concentration of heavy metals is toxic to organisms in seawater while some elements are essential for their growth. It was found that to add trace amount of ferrous in seawater could increase the growth rate of phytoplankton which also means that the primary production in the sea is increased. Most elements have low concentration in seawater therefore only trace amount could influence a significant change. Living organisms in the sea could accumulate elements in their body. Some might accumulate one element more than other elements. Heavy metals in seawater are consumed by living organism which could be measured in their tissue (Sawangwong, 2003).

Elements with multiple oxidation numbers could be changed into many forms depending on different environments. They might be reduced or oxidized form such as some metallic compounds when decomposed would release reduced form to seawater then being oxidized later. Environmental condition related to redox state controls the solubility equilibriums. For example, ferrous in seawater is low in concentration, mostly found in suspended solids, for more reduced condition ferrous could be more soluble in water as well as cobalt and manganese which are more soluble in reduced condition. In oxidation condition metal would precipitate in oxide form which is part of suspended solids in the sea. Many elements could be found in suspended solids which further accumulate in living organism's tissue or skeleton which could be recycled (Sawangwong, 2003; Hungsapruerk, *et al.*, 2003).

Matter on earth that eroded by water till become small particles, combine with organic matter and leaching elements in water including small particles in water itself such as plankton and other living organisms and sediment at the bottom of water body. These are significant for both ecosystem and

environment as it provides habitat and food sources for benthos. Sediments could be as accumulation or pollution source which could be nutrients for plants and animals or source of heavy metals in water body as well. When heavy metals contaminate in water resources, the accumulation in sediments and aquatic animals occur. Heavy metals are stable pollutants which hardly degradable but could change chemical form. Chemical speciation of heavy metal is different as explained in the previous topic (Kim *et al.*, 2003).

Most heavy metals in water body could accumulate with mediums such as soil, plant, aquatic animal or suspension at different quantity. Heavy metals that contaminated or accumulated in these medium could change their form or transfer through food chain. Metal accumulated in water could be in dissolved and suspended solids forms. The concentration of heavy metals changes all the time due to different abilities to form with suspended solids or to dissolve in water. Residence time for the suspended solids to form heavy metals is longer than in dissolved form. Water body always moving which causes re-suspension including adsorption and desorption process between heavy metals and sediment (Sithikrom, 2001). Sediments might be a sinking place and source of pollutants which might be as nutrients for plants and aquatic animals, or where heavy metals in water might be accumulated and transferred to aquatic animals (Kim, *et al.*, 2003). For a better understanding of the relationship between heavy metals and food chain, an example of mercury transfer through food chain is explained as follows.

Mercury transfer through food chain cycle. The main two sources of mercury spreading into the environment are natural source and anthropogenic source. Natural forms of mercury are metallic mercury and mercuric sulfide. Natural caused of mercury contamination in the environment are erosion and leaching by rainfall as a geological processes and then flows into the river (Chaikumkao, 2002) as shown in Figure 4.

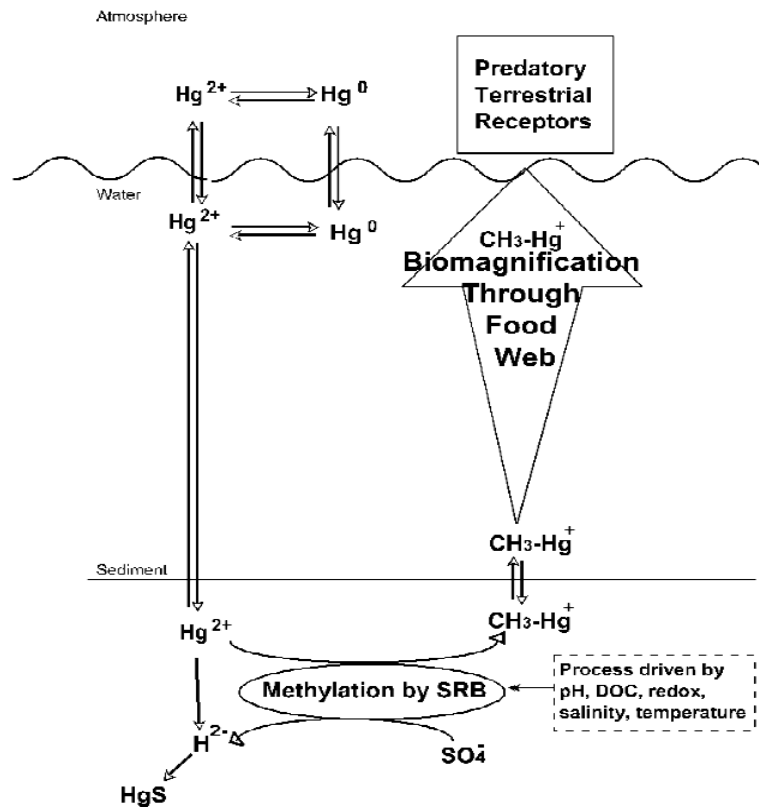


Figure 4: Mercury transfer through food chain cycle.

Source: Harmon (2008)

In the area of anthropogenic causes both direct and indirect human activities could release mercury into the environment such as from air to soil, from soils to water and from water to living organisms. The transferring and accumulating increase through each tropic level (Hudson, *et al.*, 1992). There are many ways that methyl - mercury in seawater could be changed, it could be increased or decreased by biological process and could be accumulated in aquatic animals including sedimentation which leads to demethylated process and methyl mercury decomposition. The accumulation of mercury in aquatic animals is depended on the concentration of mercury in water as aquatic animals exchange oxygen by letting water flow through their gills. Other important factor is the consumption of mercury contaminated food. Most of the increase in concentration of methylmercury in fish caused by food consumption (Kulachol, *et al*, 1998). Factors that affect the quantity of mercury in aquatic animals are type of aquatic animals, type of food, growth rate

and temperature. However, the main source of mercury in aquatic animals is from their food and the concentration is increased through each trophic level in the food chain (Harmon, 2008)

### 3.3.5 The effects of heavy metals to human health

Presently, health risk that related to seafood contaminated with heavy metals consumption is considered. Cadmium, lead and mercury are more harmful heavy metals than chromium, selenium, copper, ferrous and zinc (Perera, 2004). Toxicity of some heavy metals is explained as follows;

**1) Cadmium poisoning.** It causes vertigo and nausea which had occurred in Japan. The disease of cadmium poisoning in Japan called itai-itai disease. The patients complained about high blood pressure, anemia, joint pain, bone damage and osteoporosis, difficulties of arms and legs movement. The lack of the ability of bone formation will result in bone loss. There are more than 100 people died because of cadmium contamination in rice from zinc mining factory (Panichsakpatana, 2002).

**2) Chromium toxicity.** When breathing in, chromium could produce lung tumor which could lead to lung cancer. Chromium also irritates digestive system when consumed. This metal is rarely accumulated in urban area except the area for waste disposal from some industries such as leather tannery. The study of corn farm for livestock through wastewater containing chromium 320 mg/kg did not show any sign of toxicity (Panichsakpatana, 2002). However, sodium dichromate has high toxicity (James and Bartlett, 1983). Chromium hexavalent has a very high toxicity for skin expose, inhale or swallow. Health impacts that could be as skin disease, hormonal system disorder, liver and kidney function disorder. It is also considered as a carcinogen (Water pollution study and monitoring unit, Greenpeace Southeast Asia, 2010).

**3) Selenium toxicity.** It is a trace mineral that is essential for body even found in small amount. Selenium interacts with vitamin E activities. Food that contain high selenium are Brewer's yeast, entrails, animal muscle, fish, shell, brown rice, cereal and dairy products, garlic, mushroom, broccoli, shallot, tomato, poultry,

egg and seafood. Selenium is a component in glutathione peroxides which accelerates hydrogen peroxide elimination and organic peroxide from lipid acid. Selenium works closely with vitamin E to protect tissues from peroxide of lipid. Vitamin E prevents peroxide production while selenium eliminates peroxide. Selenium and vitamin E boost the activity to preserve tissues and delay natural cell die off. Selenium deficiency leads to aging because selenium helps muscle flexibility. However, high dose of selenium is toxic, only 5 mg of selenium could cause vomit, diarrhea, loss of hair and nail. Some people believe that selenium consumption might prevent cancer but it was only in animal testing and no evident about the use of it in human (Thai Health and Nutrition Center, 2009).

**4) Copper poisoning.** It is a very essential element for human health because it helps the formation of hemoglobin and the work of enzyme. Human body need only trace amount of copper (2.0 mg per day). Copper salt also helps in the growth process and catalyzes manganese oxidization process. The lack of copper might be harmful to liver. However, too much of it could result in anemia. In drinking water, copper should not be exceeded 1.0 mg/l. In food and grass for livestock the copper should not be exceeded 20 mg/kg. Copper toxicity in animal feed could be reduced by adding high zinc, ferrous or molybdenum feed. Copper contamination in water could harm aquatic animals because they are very sensitive to copper toxicity (Panichsakpatana, 2002). Overdose of copper affects human health especially in children and pregnant woman, for example reduce growth rate and increase fetal and neonatal mortality rate (Water pollution study and monitoring unit, Greenpeace Southeast Asia, 2008).

**5) Lead poisoning.** It was reported that lead had has less toxicity than mercury and cadmium to aquatic animal. However lead is very toxic for human, it prohibits enzymes related to the formation of hems, a fundamental component of hemoglobin in red blood cells, resulting in anemia. The guideline for wastewater regulated by industrial environment section, Ministry of Industry indicates that lead should not exceed 0.2 mg/l (Sangchindawong, 2002). Blood poisoning of lead would occur at the level of 500 mg/dl. Adult who has lead level higher than 35 mg/dl might show no significant symptoms but most of them have high blood pressure.

Level of lead at 25 mg/dl in children for 10 year will show anemia symptom causes by small and decrease red blood cell. Moreover, brain cell might be damaged and weaken remembrance. Some children might be retarded and some might have problem with speech such as babbler. Irregular behavior such as angry and aggressive might be experienced. If lead level in the body is higher than 80 microgram/dl, it would affect nervous system and digestive system and cause stroke or epilepsy. Moreover, lead that accumulated in the bone will inhibit cartilage processes. Lead will replace calcium in the bone and destroy vitamin D in the body. It also causes tumor and cancer. In case of acute toxicity, severe abdominal pain, colic, diarrhea and muscle, bone, liver and kidney failure might occur following by coma and lead to death of the person (Sangchindawong, 2002).

**6) Mercury poisoning.** Mercury is one of toxic metals which have been considered by the world about its toxicity in Minamata cases in Japan. Mercury could destroy tissues in many organs such as liver tissue, muscle fiber, heart, kidney tubule, stomach and duodenum. It could reduce red blood cell formation from bone marrow. When mercury enter the body it will react with enzyme containing sulfhydryl group which results in enzyme prohibition such as reduce hemoglobin to carry oxygen or inhibit mitochondria function (Pollution Control Department, 1999).

Organic mercury which has the highest toxicity is methyl mercury. It could be absorbed in digestive system about 95-98 percent but rarely excrete out of the body. Methyl mercury is a stable compound and hardly decomposed to become inorganic. This form of mercury can attach with red blood cell and transfer to every part of the body, around 15 percent will accumulate in the brain. Metal mercury can be easily absorbed through skin and breath. The most toxic form of mercury is in vapor form which can cause acute toxicity if inhale at 1,200 - 8,500 microgram/cubic meter. Inorganic mercury has the least toxicity because it can be absorbed in digestive system at only 2 percent and easily to excrete by the body. Mercury that accumulated in the body destroys nervous system. It could transfer through central nervous system and most of mercury accumulated in cerebellum and cerebral cortex. Brain tissues that control visual and sense might be damaged and cause central and peripheral nervous system disorder (Noranattrakul, 2003).

**7) Iron toxicity.** Iron is a trace element which is essential to human. Iron is a component of hemoglobin in red blood cells. Hemoglobin carries oxygen from the lung to the rest of the body's cell and collects carbon dioxide back to the lung. Iron deficiency causing from low iron food consumption or decrease of iron in body might induce fatigue, headache, lack of concentration, pale complexion following by anemia. Iron can be found as oxide form in 4 minerals; hematite, magnetite, siderite and limonite. There are some minerals mixing in those minerals such as silicon, carbon, phosphorus, sulfur and manganese (Cheangkun and Yuchun, 1999).

**8) Zinc toxicity.** Zinc might affect human health if the body consumes overdose of zinc. Some examples of zinc poisonous are skin disease, nausea and vomit. High concentration of zinc might affect pancreas and protein adsorption system (Water pollution study and monitoring unit, Greenpeace Southeast Asia, 2008).

### **3.3.6 Effect of heavy metals on aquatic animals**

The study of heavy metals contamination in aquatic animals is essential for the prevention of human health from heavy metals toxicity. Moreover, it is also a mean to monitor contamination and distribution of heavy metals from the sources. Aquatic animals could accumulate heavy metals in their tissue that contaminated in water resource and sediments. The transferring of heavy metals through the food chain will impact human health as top consumers. Heavy metals contamination in each aquatic animal differs in concentration depending on many factors such as age, size, sex, season and habitat (Amundsen, *et al.*, 1997). Seafood consumption might increase the chance of contamination into the consumer (Lobet *et al.*, 2003; Usero, *et al.*, 2003). Many researchers interested in the issue of heavy metals contamination in marine animals from many parts of the world including Thai Gulf area as shown in Table 1.

**Table 1:** Concentration of some heavy metals in marine animal from different areas.

Area	Type of marine animals	Age of marine animals	Cadmium (mg/kg) (wet weight)	Lead (mg/kg) (wet weight)	References
Bang Pakong River	Cockle	-	0.427	0.222	Muangdej (2000)
Ang Sila	Oyster	12 months	0.894	5.296	Tongraar, <i>et al.</i> (1989)
Nakorn Si Thammarat Bay	Undulated surf clam	-	0.160	0.690	Wibunpan (2006)
Pattani Bay	Oyster	-	0.964	0.420	Wibunpan (2006)
	Cockle		0.984	0.512	
	Mussel		0.410	0.592	
Bandon Bay	Oyster	-	1.412	0.400	Wibunpan (2006)
	Cockle		1.742	0.460	
	Mussel		0.542	0.690	
	Oyster	18 months	1.128	0.210	Roekdee (2008)
	Oyster	-	0.454	0.250	Kumsuk and Songkong, (2004)
Bengal Bay	Fish	-	0.066	-	Kaewbuppa (2008)
Andaman Sea	Squid	-	0.002-0.036	-	Jeenmun (2008)
West Indian Ocean	Oyster	-	1.04	1.38	Kojadinovic, <i>et al.</i> (2007)
Australia	Oyster	22 months	15.3*	-	Hayesa, <i>et al.</i> (1998)
Canada	Oyster	36 months	13.5*	-	Christie and Bendell (2009)

Note : \*dry weight

Perera (2004) found that some heavy metals such as Ag, Cu, Zn, Fe and Mn are essential for living organism. However, the accumulation of heavy metals in living organism is not limited for merely essential element which is crucial for biochemistry processes but including some other metals. Cadmium, lead and mercury are not found to have any role in living organism processes. In contrast, high quantity of these metals might be harmful for life especially sea animals that accumulate these elements at the concentration exceed the



limitation guideline. For examples, tissue inflammation, gene mutation and growth retardation which depend on type of heavy metals as following examples.

- *Crassostrea gigas* from Tasmania was consumed and found 173 mg/kg of Cd, 57,600 mg/kg of Zn. Consumer experienced vertigo and vomit. Cadmium contaminated in seawater around 2,000 ton/year which half of that caused by human activities and the rest by nature. Cadmium does not accumulate in digestive system, therefore fish and sea mammals contain lower concentration of cadmium. Although it can accumulate slightly in kidney, fish can neutralize cadmium toxicity by changing it into methallothionein. *Crassostrea gigas* could accumulate more cadmium, for example scallop in Family Pectinidae. In some *Crassostrea gigas*, cadmium in the liver could be as high as 2,000 mg/kg. *Symplectotenthis oralaniensis* and oyster show the result 1,900 mg/kg of Cd (Sangchindawong, 2002).

- Mussel can neutralize lead toxicity and can accumulate it in digestive gland. Therefore, in England mussels are analyzed for lead and the concentration is allowed not to exceed 10 mg/kg. Practically, it is found that the concentration is lower than the guideline. Fish accumulate lead at very low concentration between 0.05-0.15 mg/kg. The concentration of lead in sea bass from California coastline was as high as 22 mg/kg (wet weight) (Sangchindawong, 2002).

- Mercury is one of the most toxic heavy metals for living organism and human. The phenomenon that made the world concern about mercury toxicity was Minamata case in Japan in 1950. Many people who consumed aquatic animals contaminated with mercury show the result of dead, had brain or body damage. This proved that it is very toxic to living organism and human (Pollution Control Department, 1999). It also found that mercury affected oyster blood cell which was the main cause of dead in oyster. It might also affect immune system function of oyster (Gagnairea, *et al.*, 2004).

### 3.4 Heavy metals contamination in Bandon Bay ecosystem and the Gulf of Thailand.

In Bandon Bay area, heavy metals used in agriculture, industry and other contaminating activities. Therefore, heavy metals might be contaminated Bandon Bay ecosystem. Researchers studied heavy metals contamination in Bandon Bay ecosystem through water quality, sediment quality, aquatic animal including oyster which is an economical aquatic animal of Bandon Bay. However, there is less information on heavy metals contamination in sediments. The previous study of heavy metals contamination in Bandon Bay ecosystem illustrated differently contamination level as follows.

The Pollution Control Department (2008) analyzed the quality of coastal water covering all areas in the country including 23 coastal provinces. The results showed that heavy metals as irons and manganese in the lower Thai Gulf was exceeded the guideline, especially at Kradae canal mouth of Surat Thani Province. Water qualities in 2007 continue deteriorated. Moreover, it was found that heavy metals as iron in the lower Thai Gulf at Ta Chang district, Surat Thani Province found to be 1,312.7 ug/l which were exceeded the standard guideline for coastal water.

The study of metals concentration in sediment of activities along the coast and in the sea such as agriculture, aquatic animals farming, petroleum and natural gas extraction in the sea showed impact on marine environment. Moreover, the pollutants also accumulated in the sediment especially heavy metals. The detection of heavy metals such as arsenic and lead or arsenic and mercury are related. Arsenic could be found in different forms of mineral such as lead, silver and copper. The erosion processes from physical, chemical or biological lead to arsenic transferring to accumulate in the environment especially in the southern part of Thailand which had been widely clearing the land for mining. (Pollution Control Department, 1998 A).

The Pollution Control Department (1999) analyzed lead concentration in cockles and mussels at the coastline of the Tapi - Pumduang River mouth and found that the average was 0.09-0.20 mg/kg. Noranattrakul (2003) analyzed water quality and heavy metals concentration in water and at undulated surf clam fishery

site, Bandon Bay, Surat Thani Province in July 2002 – June 2003. It was found that heavy metals concentration in water was within the guideline except cadmium and lead which were higher than the guideline. Heavy metals contamination in undulated surf clam was at low level (below aquatic animal contamination concentration guideline) and safe for consumption.

Kumsuk and Songkong (2004) studied heavy metals contamination in aquatic animals, seawater and sediments in Bandon Bay, Surat Thani Province. It was found from 2003 to 2004 that oyster from Bandon Bay, Surat Thani Province contained cadmium at the range of 0.3352 - 0.5730 mg/kg, lead at the range of 0.1519-0.3480 mg/kg and mercury at the range of 0.0122 - 0.0274 mg/kg. Wibunpan (2006) also studied heavy metals contamination in oyster from Bandon Bay, Surat Thani. The result of average 4 years from 1998-2002, illustrated that average cadmium contamination was at 1.412 mg/kg with the range of 0.173-3.640 mg/kg. Lead contamination was analyzed which found that the average concentration was at 0.400 mg/kg with the range of 0.059-0.902 mg/kg. Average mercury contamination was 0.045 mg/kg with the range of 0.007-0.110 mg/kg.

Roekdee (2008) studied heavy metals contamination in oyster, sediments and seawater from oyster farming at Karnchanadit District, Surat Thani Province. It was found that average cadmium, lead and mercury in oyster were 1.128, 0.210 and 0.069 mg/kg (wet weight), respectively. The high level contamination of cadmium was found to be approximately 45 % of samples in dry season which exceeded the standard level of cadmium in oysters with the maximum level (1.0 mg/kg) set by The Commission of the European Communities (EC) No. 1881/2006 (Fish Inspection and Quality Control Division, 2004).

In addition, seasonal change affects the quantity of cadmium, lead and mercury contamination in sediments and seawater. From the study, it was found that heavy metals contamination affects oyster as an economic aquatic animal of Bandon Bay. The impacts of heavy metals to ecosystem in Bandon Bay, income of fishermen and aquatic animal consumer's health should be concerned. Consequently, ecosystem risk assessment would useful to cover all information about heavy metals contamination.

### 3.5 The use of oyster as a biological index for heavy metals contamination.

It could be seen that chemical analysis of the environment in various dimensions such as water and sediment is a direct investigation to illustrate the status of heavy metals contamination in the environment. However, it could not use as an evidence for integrate impact and toxicity for living organism and ecosystem. The use of living organism to indicate environmental quality is a biological investigation which is one of scientific techniques for environmental assessment including human activities that harm the environment. Basically, this technique includes sampling and analyzing tissue and liquid of each living organism to indicate the residue of the chemicals. The indicator might be the chemical itself or by product after the reaction or biological change within living organisms from the reaction with the chemical. The result from the analysis will give information about the number of natural chemicals and chemicals from human activities which are in the organism and the effect from those chemicals. There is relationship between living organism and habitat. Consequently, biological analysis will give future trend information and the impact from toxicity of each pollutant. This also reflects the level of environmental destruction related to real situation. There are many advantages of biological analysis such as detects chronic effect from low level of pollutant, high sensitivity and high integration (Qunfanq, *et al.*, 2008).

The use of biological index might be an evidence for water quality guideline such as industrial wastewater discharge and could be used for risk analysis of pollutant level in water and the estimation of wastewater treatment efficiency. The investigation of chronic toxicity of low level toxin could be practiced by molecular reaction, gene mutation, toxicity to embryo, change in tissue and abnormal behavior. Biological analysis is used for testing chronic toxicity or to analyze toxin residues. The accumulation data as many of chemicals are interpreted the increase toxicity in living organism (Boening, 1999; Zauke, 2008).

Chemicals analysis is used for testing the distribution and the change of pollutant characteristic in target organism. When comparing biological analysis and chemical analysis in the environment such as water or sediments, the advantage of biological analysis illustrates biological change of contaminated organism, holistic

impact of complex pollutant and high sensitivity. The response of living organisms to pollutants could help with the prevention as it can be detected at very low level. Moreover, chronic toxicity in the environment from exposing long period of low level pollutants could be detected from this method (Goldberg and Bertine, 2000).

Biological monitoring is an interesting tool for pollutant status assessment in the environment especially when analyzing heavy metals in water ecosystem. It is found that the accumulation of heavy metals in aquatic animal can be used as environmental indicator especially bivalves. Bivalve mollusks are the most effective as a bio-indicator for toxicity caused by heavy metals in seawater and brackish water (Phillips and Rainbow, 1992). Bivalve mollusks are used for water quality analysis and ecosystem status assessment because they rarely move and could not swim unlike fish. They also have long life cycle which could accumulate pollutant to high level. As they are filter feeder, it is possible to expose and accumulate heavy metals (Qunfanq *et al.*, 2008).

Bivalves are known worldwide as an organism that can accumulate heavy metals and use for monitoring and assessing the trend both in area and time of heavy metals contamination in brackish water and along the coastline. Bivalves such as oysters, mussels and freshwater mussels are used as bio-index for trend of heavy metals contamination in seawater. The advantages of the use of these bivalves are; widely distribute geographically, more abundant in nature, rarely move, can tolerate changing in environment, can tolerate high contamination. There are factors that contribute to high accumulation concentration such as low level of enzyme in metabolism activities of organic contaminant, stable population, widely distribution, long life cycle, appropriate size and can tolerate laboratory environment and field study in cage (Boening, 1999).

There are many bivalves that were adopted as a tool for bio-monitoring to study the effect of heavy metals in water ecosystem. There were reports of the use as bio-monitoring index for heavy metals contamination. Moreover, many studies were focus on bioaccumulation and distribution of heavy metals in bivalve mollusks and their tolerance against heavy metals. For example,

study of biological responses (such as respiration), biochemical responses (such as enzymatic activities) to heavy metals such as cadmium and copper of bivalve mollusks. The relationship between pollutants in bivalve mollusks and habitat could be used for water pollution indicator (Zauke, 2008).

Oyster is used widely as a biological index for coastal pollution with its reasonable qualities as follows; aggregate in the area such as estuaries and coastal areas; filter-feeding organism could receive pollutants that related to the environment; motionless organism which could be demonstrated pollution level at specific area; long life cycle for the effect of long contamination period and various ages in the specific area and environment; abundant and widely distribute geographically which can study pollution in broad area; very important in the food chain; contain different age classes in a given area and environment; and could be beneficial for research purpose from commercial activities.

Oysters are effective filter feeders and can caused large effects to the water columns in which oysters occur. As filter feeders, oysters eliminate plankton and organic particles from the water. Oysters consume nitrogen which has compounds, phosphates, plankton, waste, bacteria, and dissolved organic matter, transferring them from the water. Things which not used for animal growth were then expelled as solid waste compressed mass of a substance, which finally decompose into the atmosphere as nitrogen. (Songkaew, 2001).

In addition, the study also found that the major source of contamination should be carried out. Oyster digestive system and tissue were analyzed. It could be concluded that at least 40% of oyster's food contaminated with cadmium. The concentration of cadmium in the digestive system and in the tissue depends on the area. Found cadmium in digestive system and tissue were 30.4 ug/g and 6.0 ug/g. The comparison of oyster samples from the coastline in the North of Pacific contained cadmium 43.0 ug/g and in the tissue at 10.2 ug/g. (Christie and Bendell, 2009). It was found that high concentration of cadmium in oyster's gut tissue causing by an uptake of cadmium by phytoplankton and passes through food chain (Priyanka, *et al*, 2008).

Oyster was used as a biological index for heavy metals contamination along the coastline and at the bay. It was found that the dispersion of sediments caused by pier construction causing higher concentration of heavy metals accumulation in oyster (Hedge *et al.*, 2009). In Canada, when cadmium concentration in oyster is higher than the guideline of European Commission it would impact on the import market. Therefore, the study of ocean location and sediments analysis for cadmium accumulation have conducted and it was found that there was cadmium in the sediment which then was transferred to phytoplankton. When oyster consumes phytoplankton, heavy metals accumulate in oyster tissue. However, there are more factors involve such as physical appearance, consumption pattern and geological factor (Priyanka *et al.*, 2008).

In New Zealand, it was found that the concentration of cadmium in oyster exceeded the guideline of European Commission. The study of oyster at many river mouths in Oakland reported the agricultural contamination of fertilizer which contained cadmium. The oyster near agricultural area found cadmium accumulation in the tissue and impact on the consumer through the tropic level of the food chain (Carmen *et al.*, 1994; Perera, 2004). The research of the Pollution Control Department (1998 B) confirmed that phosphate fertilizer contains cadmium around 2-170 mg/kg. Therefore, the use of phosphate fertilizer would increase the concentration of cadmium in soil. Cadmium phosphate has low solubility in water and plants could not absorb this part of cadmium. Hence it is accumulated in the soil. However, the use of ammonium fertilizer assists cadmium to be dissolved more in water which could increase the possibility of the contamination in the environment (Hazardous Waste and Solid Waste Management Department, 1998).

All aquatic animals have high possibility to accumulate cadmium. Cadmium has chemical characteristic similar to zinc therefore it could replace zinc in some enzymes which made the metabolic function change from normal. Cadmium could be accumulated in aquatic animal's tissue at the concentration of 100 to 1,000 times more than in water (Hazardous Waste and Solid Waste Management Department, 1998; Rebelo *et al.*, 2003). Age and tissue weight on cadmium levels in Pacific oyster have grouped into 4 groups at the age of 1, 2, 3 and 4 years. The

weight and age are correlated within 1-2 years but at 3-4 years showed weak correlation (Rasmussen and Morrissey, 2002).

The use of oyster biological index would provide direct evidences of changes in the ecosystem due to pollutants in the environment. Moreover, bio-monitoring practice could reflect a holistic environmental quality from heavy metals contamination in the environment including the possible impact that might occur. Recent research on bio-monitoring analysis for environmental pollution especially heavy metals had made more advanced in this area. There are several proposed bio-indicators for their special response behaviors after exposing to heavy metals such as the ability to accumulate. Bio-indicator at molecular level has been improved as it is very sensitive which could be useful as a warning sign from recent pollutants. In addition, it could explain potential toxicity processes. There are many models that have been invented to predict heavy metals toxicity.

However, the study for more information about the use of living organism as bio-indicator to indicate heavy metals toxicity in the ecosystem is needed to develop a standard guideline for the area to assess ecological risk. Consequently, efficient natural resources utilization should be promoted for planning, solving and controlling activities related to heavy metals contamination which could lead to ecosystem protection and guidelines formation in the future (Boening, 1999; Goldberg and Bertine, 2000).

### **3.6 Risk assessment**

Risk assessment is a systematic process of study to explain and measure risk that correlated to threats. Risk assessment is a quantitative study because factors measured in number (Wiwadtanadej, 2004).

Generally, risk assessment could be categorized into two field classes which are environment or ecological risk assessment and health risk assessment. Moreover, economic dimension should be considered in the process of risk assessment.



### 3.6.1 Environmental or ecological risk assessment

Environmental or ecological risk assessment is a process to assess the possibility and impact level of ecosystem from environmental pressure. Ecological risk assessment is an essential tool for environmental decision making as it can determine environmental problems and priority level of problems including scientific principle for taking action. There are many situations that ecological risk assessment could be practiced such as assess ecologically risk status, predict ecological risk from development plan, compare the risk of alternative development activities, assess the effective of all alternatives impact remedies and set priority from different pressures. Consequently, measures for impact mitigation should be focused including development of standards for affected area. The ecological risk assessment processes are as follows; (Mekong mission, 2004);

**1) Problem identification.** This is the first step and the most significant step to assess the risk. In this process, boundary and important point of interested of the assessment were set. Problem identification is the foundation of the whole processes of ecosystem risk assessment, therefore reliable problem identification lead to the advantage of risk assessment.

**2) Information compilation.** This is to find how to get appropriate information about pressure, specific characteristic and type of exposure in risk ecological area. The compilation information at the early stage is to produce conceptual framework or identify assessing purpose. For example, the more we know about type and quantity of wastewater discharge and biological status of living organism that expose to wastewater, the more we could find the route of exposure and relationship between them (Mekong mission, 2004).

**3) The explanation of studied area.** This is one crucial component for problem identification and help risk assessor to learn about the studied area. In this step, the compilation of various former studied should be assisted with the boundary of ecological risk assessment. For example, the assessment of studied area which has been investigated before to find contamination history, the description of surrounding area to find any other areas which might put more pressure to the ecosystem (Mekong mission, 2004).

**4) Pressure identification.** This is the next step of problem identification. Pressures could be physical (natural disaster or loss of habitat), chemical (organic or inorganic) or biological conditions which could affect ecological components. However, most risk assessments focus on natural chemical pressure. Therefore, to mitigate the impact, chemical pressure has to be considered. Pressure identification and environmental characteristic information should be recorded to select ecological components that are at risk, possible ecological impact including medium such as air, soil, surface water, ground water or animal tissues (Mekong mission, 2004).

**5) Impact receiver identification and description.** After identify pressure, the next process is to describe possible impact receiver. Impact receiver is ecosystem components such as population, community or ecosystem which could be affected from pressures. Generally, impact receivers are human or animal population in the area. Selected impacted receiver should be based on area components and ecosystem that related to pressures, sensitivity to pressure, and status of nearly extinct or threatened species, ecosystem importance, aesthetics/local culture value, recreation/commercial importance and valuable/sensitive habitat.

After impact receiver selected, it might be possible to choose assessment measurement purpose. Assessment purpose is one specific ecosystem component or impact receiver that should be protected. For example, the purpose of the assessment might be to conserve fish species in Mekong River which is crucial for the economy. The purpose might be identified into different levels such as species, population, community and ecosystem. However, if the ecosystem impacted to receivers were not in the list of protected species or nearly extinct, the alternatives might be at population or higher level which gain more interested. For example, the change in community pattern, benthos is a bio-indicator for pollutants in the water ecosystem.

The purpose of measurement is an essential tool to correlate study area characteristic and management purpose that is formulated at the step of assessment purpose. The purpose of measurement should measure the assessment purpose in number and use to find ecological response from the pressure and could reflect back to the value of environmental component or description of the assessment purpose. The purpose of measurement should be obtained by field study or in laboratory. It should

include the measurement of impact (such as death status, reproduction abnormality) or exposure (such as pollutants contamination concentration in tissues). For example, economic importance of fish species could be used as purpose of the assessment. The purpose of measurement might be the successful of economic importance of fish species reproduction (Mekong mission, 2004).

**6) General conceptual framework refers.** This is the descriptive writing to show image for the prediction of the relationship among ecological components and related pressures. Diagram is used to propose the theory how pressure effects impact receiver. The diagram will include the explanation of the status of risk ecosystem and the correlation between assessment and measurement purpose.

**7) Exposure assessment.** This is the second process of the ecological risk assessment. It is an essential process because if there is no exposure, there will be no risk. The exposure is integrated situation between pressure exposure and impact receiver. The exposure estimation related to the description of pressure including other factors such as sources, magnitude, frequency, duration and route of exposure. The main component of exposure estimation includes source of pollution, disposing characteristic of pollution source, pollutant transfer and mechanism, route of exposure and concentration of exposure. The purpose of exposure estimation is to estimate the concentration or the distribution of the concentration of each pollutant in each medium related to impact receiver (Mekong mission, 2004).

**8) Risk characteristic description.** This is the last process of ecological risk assessment that assist risk assessor to describe the correlation among pressure, impact and ecological component. The conclusion from the process provides situation of exposure and damage from predicted impact. Risk characteristic description is the sum of exposure assessment and impact assessment to find possible negative impact that would happen from pressure including the magnitude of the impact. Risk characteristic description has three steps which are; calculating for risk estimation, uncertainty analysis and the interpretation of the importance of ecosystem (Mekong mission, 2004).

**9) Risk estimation.** This could be calculated using many methods and techniques. Generally, quotient method is used which is for one contaminant and one route of exposure to effected area. This method could determine risk but not for

magnitude or probability of risk. A risk quotient calculates by dividing expected environment concentration (EEC) or chemical exposure concentration with benchmark effects concentration (BC). The result is hazard quotient (HQ) or risk quotient (RQ) as shown below;

EEC could be measured directly or predicted from environmental fate models. Benchmark is the concentration of contaminants in the environmental medium such as surface water or fish tissue that is considered “safe” on the other hand, the concentration is very low and will not have any negative impact. The benchmark level of each studied area could be obtained from impact assessment or general governmental guideline for environmental protection. The benchmark could be used for every projects or activities that have similar impacts. During the problem identification process, the acceptance level of impact should be consulted with environmental management officer. Commonly, if HQ number is less than 1, the studied area has less risk and do not need any other process. If HQ number is more than 1, the area has risk that should be analyzed further (Maria *et al.*, 2005; Mekong mission, 2004).

**10) Uncertainty analysis.** This is the second step to explain risk characteristic. Uncertainty analysis is used to identify uncertainty and magnitude of uncertainty for problems, exposure and impact estimation and risk characteristic explanation. Moreover, environmental management officer can determine strength and weakness of ecological risk assessment. However, if accepted standard guideline is too low might due to important knowledge gap which lead to less protection of ecosystem components. On the other hand, more information might cause a very strict protection guideline such as high cost of wastewater treatment system management. The result of uncertainty analysis is to assess the impact of uncertainty in the ecosystem risk assessment and explain the process to reduce the uncertainty (Maria *et al.*, 2005; Mekong mission, 2004).

**11) The interpretation.** The importation of ecosystem in the risk assessment leads to high reliability and essential correlation between risk estimation and the communication of assessing result. The interpretation of the importance of

ecosystem should explain nature and magnitude of the impact, area and ecosystem model of the impact and rehabilitation potential after removing the pressure. These questions should be answered; which species is at high risk, what time in a year that the risk occurs, the risk occur for all the area or only at high risk point, how pollutants transfer from the source to the impact receiver for example, from runoff, underground water, food web or soil (Maria *et al.*, 2005; Mekong mission, 2004).

**12) Impact assessment.** This is the process to find the correlation between the pressure and impact receiver to relate with the pollutant impact on ecosystem. To describe impact characteristics such as the impact from the pressure to relate the impact with the purpose of the assessment is essential. Then assesses how the impact change according to the magnitude of the pressure. The correlation could be obtained from literature review about toxicity information or analyze toxicity in laboratory. However, other areas of information should be included such as ecology, biology, behavior of risk species, at what state in life cycle that living organisms are at higher risk, are there any other concerns about these species which could be a factor to build habitat or food source for them, what is the gap between knowledge and information that is an obstacle to create an appropriate risk estimation (Maria *et al.*, 2005; Mekong mission, 2004).

**13) Risk management.** After the ecological risk assessment processes, environmental manager and government organization should make a decision based on ecosystem risk components, ecosystem value and the cost of natural resources protection and non-protection. Environmental manager not only considers the result of risk assessment but also social, economic and political dimension. Ecological risk assessment could be an essential tool to integrate environmental management and environmental impact assessment. When using appropriately, standard method will be obtained including conceptual framework of ecosystem analysis and uncertainty identification. The result from ecological risk assessment is useful for decision maker as it will assist to solve difficult problem. For example, how much natural resources abundance could be exchanged with possible social and economic benefit from the project or activities (Maria *et al.*, 2005; Mekong mission, 2004).

The estimation of ecosystem or environmental risk status could have more than one indicator to indicate the quality of the environment. The use of bioindicator will indicate biological impact in the ecosystem or environment which might lead to risk of human health especially coastal area contamination (Edwards, *et al.*, 2001).

### 3.6.2 Health risk assessments

Risk assessment is a process that Codex Committee on Food Additive and Contaminants (CCFAC) under the supervision of World Health Organization (WHO)/Food and Agriculture Organization of United Nations (FAO), responsible for food guideline and international food additives, chose as a guideline to reduce 3 risks which are physical, chemical and biological risk in food. It is also a method to obtain scientific information to assist decision-making process in case of disputed over business, goods, foods that related to food safety at international level. Health risk assessment could be defined as risk assessments that investigate the impact of the environment which effect human health. The investigation could be divided into two groups (Wiwatthanadej, 2004) included of:

**1) Quantitative risk assessment** Quantitative risk assessment focuses on the investigation based on scientific principle that can measure each factor in number using scientific instruments or laboratory analysis that can explain cause and effect principle and can be re-analysis. The goal of quantitative risk assessment is to obtain input information for a quantitative risk assessment.

**2) Qualitative risk assessment.** Qualitative risk assessment focuses on the description of social science and anthropology. Methods of data collection are in-depth interview, focus group interview including other techniques such as participatory action research. Qualitative method emphasized on diversity and cover all aspects of information to present the result at different angles. In many cases, both method of risk assessments are practiced together as input and output information for each other. The result from these two methods will reduce weaknesses of each method. Therefore, the research becomes more reliable and can be useful to solve problem at the root cause (Wiwatthanadej, 2004).

Risk assessment component as formulated by FAO/WHO or Codex (CAC, 2005), consists of four processes, which are;

- **Hazard identification.** This refers to the process of determining hazard of physical, chemical or biological agent in food or food status or some foods status that might be harmful to human health. Two types of information needed are the information about symptoms occurred from threaten agent and the receiving of threaten agent into body and cause symptoms. To identify which threaten agent has adverse impact on human health, information from animal testing study and epidemiology are needed (National Bureau of Agricultural Commodity and Food Standards, 2005).

- **Hazard characterization.** This description refers to the assessment of health adverse impact qualitatively or quantitatively. Type of chemical hazards that might be found in food should have a dose-response assessment. The hazards from physical and biological agent should be assessed for dose-response when obtain more information (National Bureau of Agricultural Commodity and Food Standards, 2005).

- **Exposure assessment.** This refers to qualitative or quantitative assessment of hazard that entered human body through food, water, air or soil. Exposure assessment is a method to estimate or measure the quantity of threats for each person, population or ecosystem. Therefore, the purpose of the exposure assessment is to investigate element or threat that each living organism received including quantity, route and duration of exposing under any circumstances.

Risk characterization refers to the estimation of possibility and magnitude of impact that might affect health in any population group both qualitatively and quantitatively. In addition, possible uncertainties which could be obtained by hazard identification, hazard characterization and exposure assessment (National Bureau of Agricultural Commodity and Food Standards, 2005).

### **3.7 Mathematical model and analysis used for environmental system approach.**

Mathematical model is the use of mathematics to explain the system. Mathematical model has been used in the area of science, sociology, humanities and economics. The definition of mathematical model is a process of generating important parts in the system or under construction system to demonstrate system

knowledge in the form that can be utilized (Samandeeep, 2011). Information analysis to assess pollution loads by using mass balance.

The principle of analysis or mass balance is based on mass conservation which means mass will constant overtime without any loss or damage. Considering the system which contain input and output of mass, common equation of mass balance in each unit and system is as below (Baccini and Bader, 1996; Brunner and Rechberger, 2003).

$$\text{system mass accumulation} = \text{mass input} - \text{mass output}$$

The basic process of mass flow mechanism analysis can be divided into 2 parts which are system analysis and data collection. Each part can be separated into sub-process (Brunner and Rechberger, 2003) System analysis consists of system boundary identification; element and duration of study and data collection; identify production, production processes, transportation, and processed related to interested element. This can be done by drawing diagram to show the relation between sub - process and element transfer. The following is data collection such as quantity of production (production, transportation, and consumption), quantity of expired products which become waste to dispose or recycle, concentrations of chemicals in the product including concentrations of pollutants in the environment.



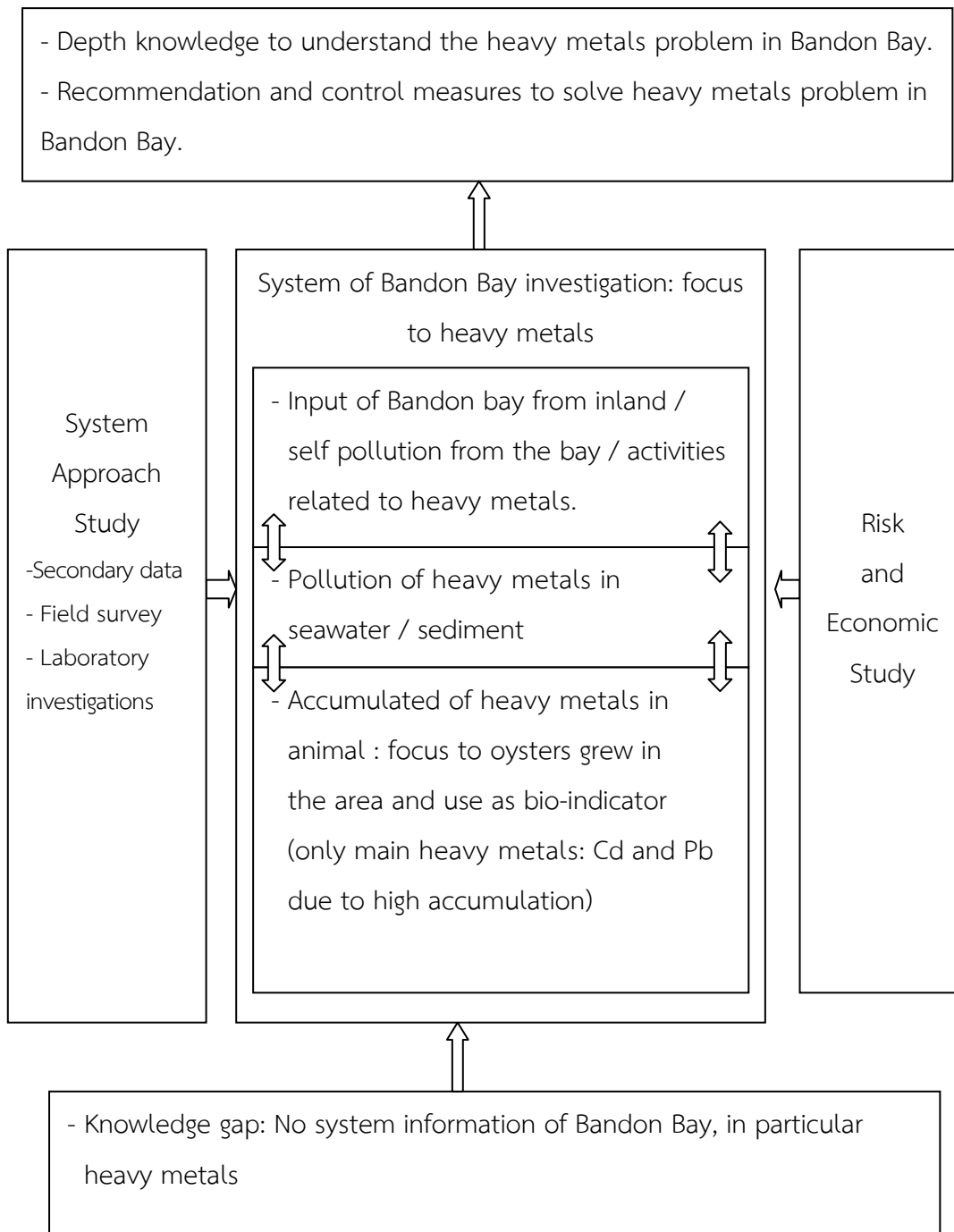
## CHAPTER 2

### RESEARCH METHODOLOGY

#### 1. Scope of the Study

This research focused on the assessment of heavy metals contamination in Bandon Bay ecosystem, including freshwater system, saltwater system, and sediments. Oyster was used as a biological index for this study, specifically the white cup-oyster (*Crassostrea belcheri*) with 6 months age which was taken from oyster farms in Bandon Bay.

This research analyzed and assessed heavy metal point sources of surrounding activities from inland, and the rate of heavy metals discharging from the Tapi River into Bandon Bay. Assessment of heavy metals contained in sediments and seawater in Bandon Bay was conducted as well as analysis of heavy metals leaching from sediments at Bandon Bay. Experiment for assessment of heavy metals contamination in oyster samples, which was used as biological indicator in this study was also conducted. In addition, assessment of impact and risk from heavy metal problem in Bandon Bay ecosystem was conducted to develop recommendation and guideline to solve and control the problem. The conceptual framework of this study showed in Figure 5.



**Figure 5:** Conceptual framework in this study

## 2. Instruments, Materials and Chemicals

### 2.1 Instruments

Instruments were used in this study are as follows:

- (1) Inductively coupled plasma optical emission spectrometry (ICP-OES)
- (2) Mercury Analyzer
- (3) Microwave digestion
- (4) UV-VIS spectrophotometer
- (5) Centrifuge
- (6) Hot air oven
- (7) Desiccators
- (8) Water bath
- (9) Shaker
- (10) pH meter
- (11) Salinometer
- (12) Homogenizer
- (13) Thermometer
- (14) Grab sampler and water sampler

### 2.2 Equipment and accessories

Equipment and accessories used in this study are as follows:

- (1) Pipette
- (2) Beaker
- (3) Cylinder
- (4) Stirring rod
- (5) Funnel 250 ml
- (6) Volumetric flask
- (7) Micropipette
- (8) Dropper
- (9) Sieve
- (9) Test tube rack
- (10) Plastic bottle for water sample keeping

- (11) Plastic bag for sediment samples keeping
- (12) Sharp knife to separate oyster from shell
- (13) Plastic tube with screw cap size 50 ml.

### 2.3 Chemicals

Chemicals used in experiments and samples analysis are:

- (1) Heavy metals standard solution (Fe, Mn, Cu, Ni, Zn, Cd, Cr, Pb, As, and Hg)
- (2) Certified Reference Materials (CRM 2702) produced by the National Institute of Standard and Technology Certificate of Analysis, Department of Commerce, United States of America was used for marine sediments.
- (3) Certified Reference Materials (CRM 1566b) produced by the National Institute of Standard and Technology Certificate of Analysis, Department of Commerce, United States of America was used for oyster tissue.
- (4) Hydrochloric acid (HCl)
- (5) Nitric acid (HNO<sub>3</sub>)
- (6) Potassium permanganate (KMnO<sub>4</sub>)
- (7) Sodium hydroxide (NaOH)
- (8) Sodium acetate (C<sub>2</sub>H<sub>3</sub>NaO<sub>2</sub>)
- (9) Ammonium acetate (NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)
- (10) Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

### 3. Methodology

The sampling and experimental sites of this research are the area at the Tapi River mouth and 6 points in the coast of Bandon Bay. However, the experiments and sample analysis were carried out in the laboratory of the Faculty of Environmental Management, Prince of Songkla University. Details of research activities are described as follows:

### 3.1 Reviews of secondary data

#### 3.1.1 Water quality of the Tapi River and Bandon Bay

Secondary data was obtained from four governmental agencies, including the Pollution Control Department (PCD), the Office of Environmental Region 14 (OER14), the Southern Industrial Environmental Research and Development Center (SIERDC) and the Surat Thani Coastal Fisheries Research and Development Center (SCFRDC). The PCD and SCFRDC have monitored estuary and coastal water quality of Bandon Bay, while the OER14 and the SIERDC have monitored water quality of the Tapi River. The 10 year water quality data (during 2000-2010) by means of seasonal or monthly water monitoring obtained from 4 agencies were collected and used in the study. Data were edited and cross-checked by time and place before further used for analysis.

#### 3.1.2 Generation sources of heavy metals from inland to Bandon Bay

The study of generation sources of heavy metal generation sources of related studies, which have been recorded by the Department of Pollution Control, Surat Thani Provincial Office, the Surat Thani Provincial Industrial Office, Agriculture Office of Surat Thani Province, Surat Thani Coastal Fisheries Research and Development Center, Department of Primary Industries and Mines were reviewed. The information presented and calculated in this study was taken from the provincial statistics provided by the individual organizations as mentioned above.

The non - point sources of heavy metals in wastewater caused by agriculture, mining and disposal site of solid waste, and point sources caused by domestic, industries, and animal farming were reviewed and used for analysis. These data were used to estimate heavy metals load discharging from the inland of Surat Thani province in compartment of the Tapi - Phum Duang River watershed to Bandon Bay.

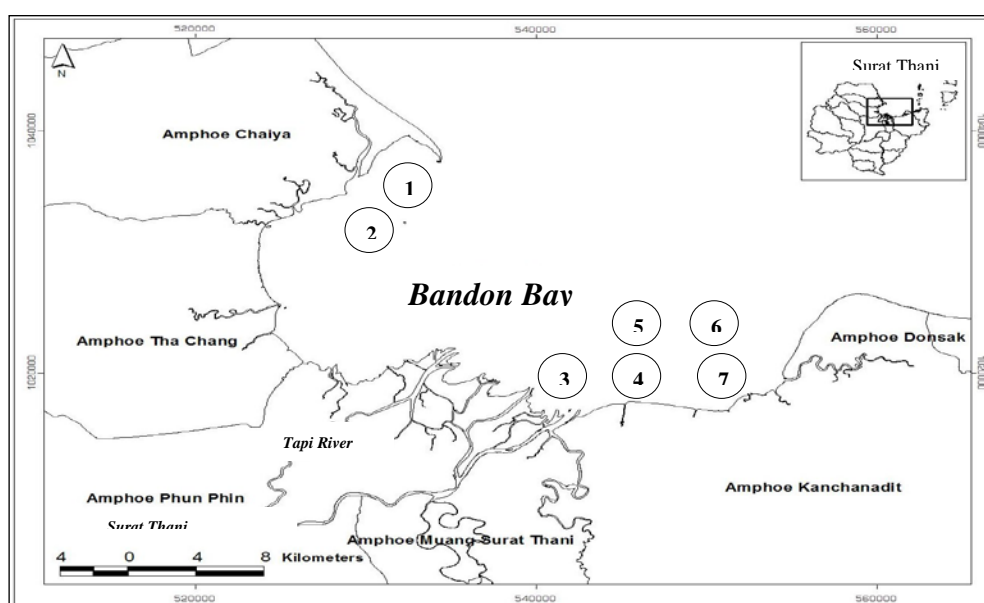
## 3.2 Field survey and experimental study

### 3.2.1 Study sites

Bandon Bay is located on the eastern coast of Surat Thani province. It covers the areas from Chaiya district to Don Sak district of Surat Thani province. The study sites of this research were at the Tapi River mouth and other 6 points in the coast of Bandon Bay. The seven investigation points are shown in Figure 6

### 3.2.2 Sampling points for seawater and sediments

The samples of seawater and sediment were taken from seven sampling points in Bandon Bay (see Figure 6). All samples were taken within every two months from February 2011 to January 2012, covering raining and summer seasons. Four sampling points located at the mouths of rivers and canals are Pumreang sub-district, Chaiya District (point 2), the Tapi River mouth (point 3), Kradae sub-district (point 4), and Tatong sub-district, (point 7), Kanchanadit District. The other three points were in the oyster culture areas located near Pumreang canal mouth, Chaiya District (point 1), near Kradae canal mouth, (point 5) and Tatong River (point 6), Kanchanadit District, as presented in Figure 6 and Table 2.



**Figure 6:** Investigation points for seawater, sediments sampling and oysters experimental points in Bandon Bay

**Table 2:** Details of study points in this study

Study points	Details	Geographic coordinate		Type of samples
		Latitude	Longitude	
1	At oyster farm near the Pumreang canal mouth, Chaiya District.	09°11'731''N	99°22'930''E	seawater, sediments, and oysters
2	At the Pumreang canal mouth, Chaiya District.	09°12'983''N	99°28'436'' E	seawater, and sediments
3	At the Tapi river mouth, Muang District	09°13'043''N	99°28'291'' E	seawater, and sediments
4	At the Kradae canal mouth, Kanchanadit District.	09°13'042''N	99°28'291'' E	seawater, and sediments
5	At oyster farm near the Kradae canal mouth, Kanchanadit District.	09°13'408''N	99°29'603'' E	seawater, sediments, and oysters
6	At oyster farm near the Tatong canal mouth, Kanchanadit District.	09°23'313''N	99°17'559'' E	seawater sediments, and oysters
7	At the Tatong canal mouth, Kanchanadi District.	09°22'335''N	99°16'248'' E	seawater, and sediments

### 3.2.3 Study points of oysters and preparation before experiment

There were three study points for oysters: the oyster farms located near Pumreang Canal, Chaiya District, near Kradae Canal, and Tatong River, Kanchanadit District. The samples of oysters used in the study were 6-month-old oysters bred from farms at Bandon Bay. In each study point, 100 oysters were put in the oyster farm. The technique used for oysters that exposed in the sea was done by following the technique used in each farming location (see Figure 7). After 3, 6, and 9 months of

exposure in the sea, 20 of oysters in each sampling point were analyzed. The investigation was conducted during April 2011 to January 2012.



**Figure 7:** Pictures showed the techniques used for oyster exposure in 3 study areas.

(A, B: Oyster farms at Chaiya used of attached oysters with cement rod; C,D : Oyster farms at Kradae used of attached oysters with cement cylinder; E,F: Oyster farms at Tatong used of attached oysters with hanging method.



### 3.2.4 The laboratory quality control for heavy metal analysis

In this research, heavy metals were analyzed based on the principles of Good Laboratory Practice (GLP). The laboratory quality control was conducted for heavy metals determination in seawater, sediments and oysters. The laboratory quality control was described below.

A blank sample was used for each heavy metal analysis. The Certified Reference Materials for marine sediments (CRM 2702) and Certified Reference Materials for oysters (CRM 1566b) were applied in order to check the accuracy of the results. The recovery test was also carried out during the heavy metal analysis. Precision was assessed by replicating analysis. The accuracy was also examined by duplicable analysis of the CRM. Each sample of seawater, sediments and oysters was analyzed 3 times in order to achieve precise and accurate results of heavy metal determination.

### 3.2.5 Preparation of seawater, sediments and oyster samples for heavy metals analysis.

**1) The seawater samples:** Heavy metals of seawater samples were determined for total and dissolved forms. Seawater samples were filtered with 45 micron glass fiber filters type GF/C before being used for dissolved heavy metals determination. The heavy metals in seawater samples were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), following by the method described by APHA, AWWA and WPCF (2005).

**2) The sediments samples:** After the sediments samples were taken, they were dried in oven at temperature of 60 - 75°C for 5 - 7 days. Samples of 0.25 g sediments were digested with concentrated HNO<sub>3</sub> by microwave digester. All the digested samples were analyzed for heavy metals concentration according to EPA 3051A method of the United States Environmental Protection Agency (US.EPA, 2007). After digestion, the sample was filtered and adjusted with its volume with 2M HNO<sub>3</sub>. Then, they were determined to find out heavy metals concentration using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

**3) The oyster samples:** The oyster samples taken at every 3 months exposure were cleaned, meat separated and put in a container (as shown in Figure 8). Each piece of meat sample was cut into small pieces of about 300 g and homogeneously mixed as a composite sample. Then, it was freeze-dried. Approximately  $0.50 \pm 0.02$  g of freeze - dried sample was placed in a Teflon tube, added with 2 ml perchloric acid and 5 ml nitric acid, then, they were digested in a microwave oven. After the samples were cold, their volume were adjusted to 25 ml with distilled water, and transferred into a glass flask before the analysis of heavy metals concentration. Cd and Pb in digested oyster samples were determined by using ICP- OES. The method for heavy metals analysis in oyster samples followed the method of US.EPA (2007).



**Figure 8:** Samples of oysters

### 3.2.6 Characterization of seawater, sediments and oyster samples

The characteristics of sediments samples were determined for soil texture, organic matter, TN, TP, TS, VS, pH, and heavy metals in terms of Fe, Mn, Cu, Ni, Zn, Cd, Cr, Pb, As and Hg. Seawater samples were determined for pH, temperature, salinity, DO, TDS, TDVS, SS, Chlorophyll a, and heavy metals (Fe, Mn, Cu, Ni, Zn, Cd, Cr, Pb, As and Hg). At last, oyster samples were determined for MC, Cd and Pb. The analysis methods used in this study were the method described in APHA, AWWA and WPCF (2005), AOAC (2000), and US.EPA (2007), as shown in Table 3.

**Table 3:** Parameters and method used to analyze of seawater, sediments, and oyster samples

Parameters	Seawater	Sediments	Oysters	Method of analysis
Chlorophyll a	√			Spectrophotometric determination*
Temperature	√			Thermometer *
pH	√	√		Electrometric method *
Salinity	√			Salinity meter*
DO	√			DO meter*
SS	√			Dried at 103–105 ° C*
TDS	√			Filtrated and evaporated at 103-105° C*
TDVS	√			Dried at 550 ± 50 ° C*
MC/TS		√	√	Dried at 103–105 ° C**
VS		√		Dried at 550 ± 50 ° C**
Soil texture		√		Hydrometer method*
Organic matter		√		Walkley-black*
TN		√		Kjeldahl method*
TP		√		Ascorbic acid method *
Heavy metals (dissolved) : Fe, Mn, Cu, Ni, Zn, Cd, Cr, Pb, As and Hg	√			ICP-OES*, Mercury analyzer for Hg*
Heavy metals (total) : Fe, Mn, Cu, Ni, Zn, Cd, Cr, Pb, As and Hg	√	√	√*** (Cd, Pb only)	ICP-OES*, Mercury analyzer for Hg*

Note: \* Followed by APHA, AWWA and WPCF (2005), \*\* Followed by AOAC (2000), and \*\*\* Followed by US.EPA (2007)

### 3.2.7 Study of oyster growth rate

In this study, growth rate of oysters was determined in order to use as an index for further evaluation. Total wet weight and oyster shell weight of oyster samples were determined. Cultured oyster samples from start and 3, 6, as well as 9 months were determined for total wet weight and their shell weight. To investigate the oyster samples, 20-30 oysters from each point were randomly selected for analysis. The obtained data was calculated for monthly growth rate (K) based on equation (1) as follows (Shpigel *et al.* 1993; Songkeaw *et al.*, 2008):

$$K (\% \text{ growth rate, per month}) = \left[ \frac{(W_f - W_i) \times 100}{W_i} \right] / T \quad (1)$$

$W_f$  : average wet weight of the oysters at 3, 6 and 9 month (g.)

$W_i$  : average wet weight of the oysters at the beginning

T : time duration for oyster exposure and culture in the investigation points

### 3.2.8 Field work investigation: A case of cockle harvesting

The research did not only investigate the contamination levels of heavy metals in seawater and sediments in Bandon Bay but also studied the heavy metal contamination in seawater from sediments generated from cockle harvesting. This investigation aimed to indicate the amount of heavy metals in the forms of Cd and Pb transferred to seawater column and seawater quality change due to cockle harvesting. Seawater sample collection was carried out three times at before harrowing, during harrowing, and after the harrowing for 30 minutes. Figure 9 illustrates seawater sampling during cockle harvesting. After the seawater sampling, it was then analyzed to determine heavy metal concentration, both total and dissolved Cd and Pb. It also determined temperature, pH, turbidity, salinity, SS, TDS and TDVS of the seawater samples. The analysis method followed the method as presented in Table 3.



**Figure 9:** Seawater sampling during cockle harvesting

### 3.2.9 The study of heavy metals (Cd and Pb) Leaching from sediments: A case of investigation in laboratory.

To assess the accumulation level of heavy metal contamination in sediments of Bandon Bay, not only the information of heavy metals contamination from inland discharging into Bandon Bay were determined but also the leaching study of heavy metal contamination from sediments to seawater with laboratory experiment were also carried out.

Since the highest and lowest levels of heavy metals (Cd and Pb) were found in oyster farms at Chaiya and at Kradae, respectively, in this study, the samples of sediments and seawater were taken from such 2 points and were used for study leaching test. The study was divided into 2 parts as follows:

**1) Leaching test with in short period:** The experiment was done by using the batch test. Sediment samples in (150 g wet weight) each point were put in 500 ml flask and added with 250 ml filtered seawater taken from the same area of collected sediments. There were 2 sets of experiments; each set of experiment was conducted with duplication. Total of 10 flasks of each set were used to study as shown in Figure 10. All flasks were kept at 25 °C and continually shaken for 0, 2, 4, 12 and 24 hours. After that, each flask was taken to determine characteristics of soluble part of seawater inside. Filtered seawater samples from 0, 2, 4, 12 and 24 hours were analyzed to examine the heavy metals (Cd and Pb).

The concentration of Cd and Pb were observed at 5 periods of time and used further to determine leaching rate of heavy metals in seawater. In addition pH, SS, TDS and TDVS of seawater from each flask were determined.



**Figure 10:** Batch test for study of heavy metals leaching from sediments

**2) Leaching test with longer period:** The evaluation of accumulation level and heavy metal contamination in sediment problems at Bandon Bay was not only done by investigating the heavy metals contamination releasing from inland to Bandon Bay, but also the heavy metal contamination in seawater caused by sediments as shown in Figure 11. This experiment was performed to explain the phenomena of heavy metals transferred to seawater due to resuspension of sediments from the activity of cockle harvesting. In this study, 300-liter-volume polyethylene plastic tanks were used as a reactor for investigation. There were 2 tanks used for examination of each 20-liter sediment taken from sampling points of Kradae and Chiya oyster farms. The sediment samples were put in each tank and added with 150 liter of seawater taken from the same sampling points. It was stirred on the surface of sediments by sweeper with the velocity of 0.06 m/s (done similarly to sweeping sediments when cockle harvesting) for two hours a day and continue to examine for 30 days. Sampling of seawater during sweeping in 1, 5, 10, 15, 30 days was carried out. The seawater sample at the mid depth of seawater in the tank was taken. The seawater samples were analyzed to determine quantity of heavy metals in total and dissolved forms of Cd and Pb. The samples were also determined to find

out the values of SS, pH, TDS, TDVS, temperature and settleable solids (using imhoff cone). Settlement of sediments was investigated by collected 1 liter of seawater sample during sweeping and put in a cylinder and left for 24 hours. The amount of settleable part and turbidity of seawater were observed at the beginning, 30 minutes, and 1, 2, 4, 8, 16 and 24 hours.

In addition, sediment samples at the beginning and after experiment were analyzed for pH, MC, TS, Cd and Pb. Moreover, the samples of seawater used at the beginning and after experiment were analyzed to determine heavy metals in the forms of Cd and Pb, and also analyzed for SS, pH, TDS, TDVS. The analysis methods used for seawater and sediment samples were done as described in Table 3. The data obtained were used further for performance determination of settleable sediments and heavy metals transferred to seawater caused by the resuspension of sediments.



**Figure 11:** The study of heavy metals leaching from sediments

### 3.2.10 Data analysis for seawater, sediments and oyster samples

In this study, data analysis was carried out by using SPSS Version 19 in 2010. The data analysis of this study was described as follows:

- Range, mean and standard deviation were used for investigating heavy metals concentration of oysters, seawater and sediments samples.

- T-test and F-test were used to determine the difference of heavy metal concentration in seawater and sediments when investigating the effect of

seasonal variation. The parametric statistic of T-test and F-test were determined at the significance level of 0.05 when investigating the influence of seasonal variation on the heavy metal concentrations in seawater and sediments samples during the rain and dry seasons.

- Linear correlation analysis was used to determine the correlation between chlorophyll a and SS, as well as the heavy metal concentration leaching from sediments with time observation.

In addition, concentration of heavy metals determined in seawater were used to compare with Thai coastal water quality standards issued in 2006, but the sediments, were compared with the Probable Effect Levels (PEL) of the coastal sediments quality guidelines given according to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002). Moreover, the heavy metals in cultured oysters' meat were compared with the standard criteria of European Union (EU) appeared in Commission of the European Communities (EC) No. 1881/2006 (Fish Inspection and Quality Control Division, 2004).

### **3.3 Determination of heavy metal contamination profile in Bandon Bay and assessment of economic impact and risk of heavy metal contamination in Bandon Bay ecosystem**

#### **3.3.1 Heavy metal contamination profile in Bandon Bay**

All data obtained from the investigation were analyzed to determine heavy metal pollution loads from inland and accumulation in Bandon Bay, as well as phenomenon of heavy metals leaching / transferring from sediments to seawater column. Heavy metal contaminations in oysters with the exposure time and concerned with difference area of cultivation were determined. Mass balance analysis of the system was used in this study. Picture diagram was used to present a profile of heavy metal contamination in Bandon Bay.



### 3.3.2 Ecological and health risk assessment

**1) Ecological risk:** From the obtained data, in particularly heavy metals in the forms of Cd and Pb, in seawater, sediments and biological indicator (oysters) in Bandon Bay were used to determine ecological risk. Risk assessment of ecological system of Bandon Bay was conducted by using quotient method (qualitative risk analysis). The risk study was conducted covering three areas of Pb and Cd contaminations in seawater, sediments and the accumulation in oysters. The analysis was based on Thai coastal seawater quality standard used for coastal aquaculture purpose, the criteria of the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002). In addition, for risk assessment of Pb and Cd in oysters, the standards of food and duct of the USA and the European Union were studied (The USA Food and Drug Administration (FDA) guideline, and The European Communities (EC) No. 1881/2006 standards). Risk values of each component investigated in the system were expressed as Hazard Quotients (HQ). In general, if HQ value is less than 1, it indicates less risk in that area, and it is not necessary to do anything more. However, if the HQ value is more than 1, it indicates the risk and necessity to do something (Maria et al., 2005).

**2) Health risk:** Health risk assessment in this study was determined by comparison with the relevant standard values based on the limitation consumption of Cd and Pb given by the Joint FAO / WHO Food Standard Programme Codex Committee on Contaminants in foods (2011). The calculation of health risk was also based on the average Thai body weight values of 68.32 kg for men and 57.4 kg for women as given by the National Science and Technology Development Agency (2014).

### 3.3.3 Economic impact evaluation

High contamination of heavy metals in oysters will lead to income loss of the oyster farmers in Bandon Bay due to inability to sell the oysters to market. In this study, the economic impact from heavy metal contamination in oyster problem was determined with consideration of the opportunity loss as mentioned above. This

determination made clear severity level of heavy metal contamination problem at Bandon Bay.

### **3.4 Recommendation for environmental management**

Recommendation for environmental management of heavy metal contamination at Bandon Bay was given based on the study results. It included control measurement of heavy metals pollution in Bandon Bay for further implementation in order to achieve an efficiency conservation of Bandon Bay with integrated approach and public participation of local people in the area.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### 1. Facts and Profile of Heavy Metals in Water and Sediments in the Tapi River and Bandon Bay: Data from Reviews

The first part of the study was conducted by using secondary data in order to get an overview and determine the facts and the profile of heavy metals discharged into Bandon Bay via the Tapi – Phum Duang Rivers as well as to determine the point sources and non – point sources of heavy metals and their amounts discharged from inland into Bandon Bay. The details of the study results are as follows.

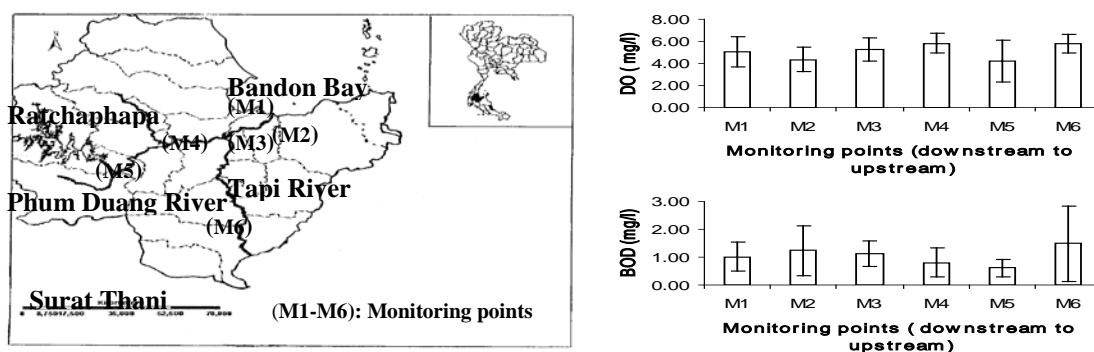
##### 1.1 Water quality in the Tapi River and Bandon Bay

This study was carried out using secondary data of water quality over a period of 10 years (2000-2010) from four governmental agencies, including PCD; OER14; SIERDC and SCFRDC. Before analyzing the data, location and time data for each water quality obtained from the four agencies was edited and cross-checked.

The Tapi River and Bandon Bay have received pollutants from land-based activities associated with urbanization, industrialization and agricultural activities. Figure 12 presents the average and median values of water quality in terms of pH, turbidity, DO, BOD, TP, SS, coliform bacteria, fecal coliform bacteria, NO<sub>3</sub>-N, NH<sub>3</sub>-N Cd, Cr, Pb, Zn, Cu, and Mn in the Tapi and Phum Duang Rivers during 2000-2010. The main pollutants impacting water quality were organic matter, bacteria, nutrients and heavy metals. It was observed that DO concentrations in the rivers decreased towards the estuary, and 13 % of water samples monitored data had a DO of less than 4 mg/l and 3.8 % of them were also found to have less than 2 mg/l of DO. In Muang and Phunphin Districts, DO was found to be sometimes lower than 2-4 mg/l.

The BOD concentration in the river mouth of the Tapi River showed an increasing trend. It was determined that 13 %, 11 % and 2 % of the monitored water data revealed a BOD higher than 1.5 mg/l, 2.0 mg/l and 4 mg/l, respectively. In addition,

coliform bacteria and fecal coliform bacteria with concentrations higher than 5,000 MPN/100 ml and higher than 1,000 MNP/100 ml were detected in 25 % and 35 % of water samples data, respectively. Heavy metals in the Tapi River including Cd, Cr, Pb, Zn, Cu, and Mn were determined as the average values of 0.001, 0.001, 0.003, 0.014, 0.017, and 0.113 mg/l respectively. The most significant heavy metals detected in the Tapi River were Zn, Cu and Mn.



<b>pH</b>	: average : median : CV (%)	6.98-7.42 7.10-7.50 5-7	(M6) (M1,M6)	<b>TP (mg/l)</b>	: average : median : CV (%)	0.03-0.09 0.02-0.07 59-101	(M6) (M6)
<b>Turbidity (NTU)</b>	: average : median : CV (%)	10.36-53.14 5.0-14.0 89-275	(M4) (M6)	<b>SS (mg/l)</b>	: average : median : CV (%)	7.71-50.16 4-36 59-175	(M1) (M6)
<b>DO (mg/l)</b>	: average : median : CV (%)	4.24-5.82 4.5-6.2 14-44	(M5)* (M2)*	<b>Cd (mg/l)</b>	: average : median : CV (%)	ND-0.001 ND-0.001 0-85	(M2, M3, M5) (M2, M3, M5)
<b>BOD (mg/l)</b>	: average : median : CV (%)	0.61-1.49 0.6-1.1 50-90	(M6) (M6)	<b>Cr (mg/l)</b>	: average : median : CV (%)	ND-0.002 ND-0.002 0-147	(M2,M3,M5) (M2,M3,M5)
<b>Coliform Bacteria (MPN/100ml)</b>	: average : median : CV (%)	1,797-7,986 130-5000 86-229	(M1) (M1,M2)	<b>Pb (mg/l)</b>	: average : median : CV (%)	ND- 0.003 ND- 0.003 0-167	( M2, M3, M5) (M2, M3, M5)
<b>Fecal Coliform Bacteria (MPN/100ml)</b>	: average : median : CV (%)	369-5,620 20-2,400 79-212	(M2) (M2)	<b>Zn (mg/l)</b>	: average : median : CV (%)	0.01-0.24 0.01-0.24 11-124	(M4, M6) (M4,M6)
<b>NO<sub>3</sub>-N (mg/l)</b>	: average : median : CV (%)	0.09-0.22 0.10-0.17 42-172	(M4) (M6)	<b>Cu (mg/l)</b>	: average : median : CV (%)	0.01-0.04 0.01-0.04 0-95	(M4) (M4)
<b>NH<sub>3</sub>-N (mg/l)</b>	: average : median : CV (%)	0.09-0.19 0.02-0.14 113-247	(M5) (M5)	<b>Mn (mg/l)</b>	: average : median : CV (%)	0.04-0.18 0.03-0.11 12-129	(M3) (M5)

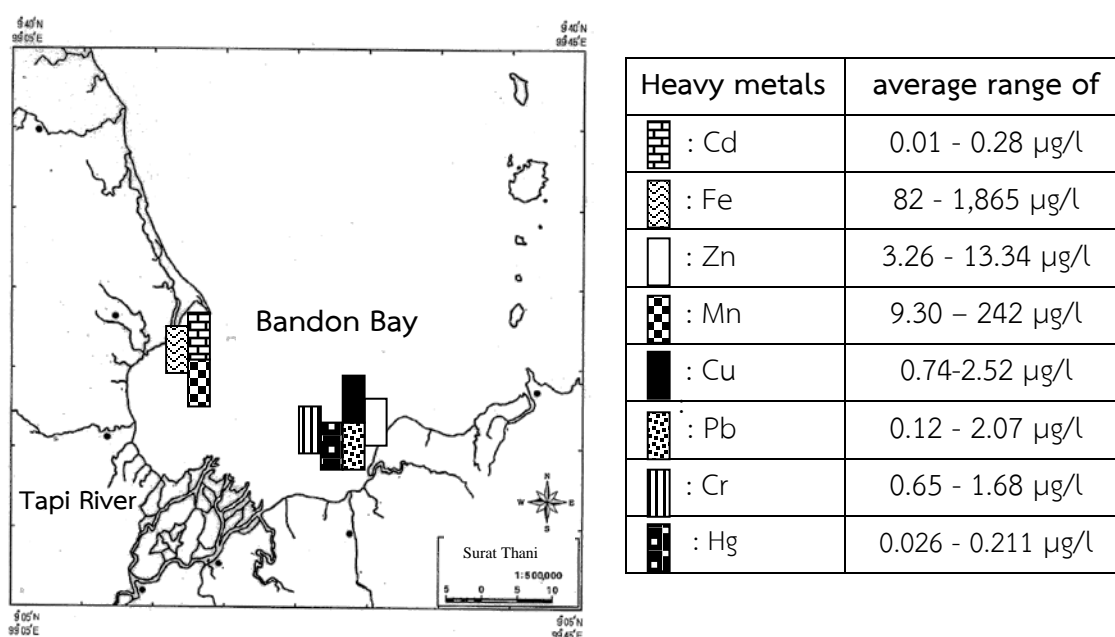
Note: Monitoring point code in parenthesis illustrating the points given highest average of water quality, except \*, expressing the lowest average.

Data Sources: Office of Environmental Region 14 and Southern Industrial Environmental Research and Development Center.

Figure 12: Water quality profile of the Tapi - Phum Duang Rivers during 2000 – 2010.

An assessment of the water quality status of the Tapi - Phum Duang Rivers in accordance with the surface water standard issued by the National Environmental Board in 1994 revealed that river water quality still largely complied with the water quality standards of level 2–4. Figure 13 shows the range values of average heavy metal concentrations at the Tapi River mouth and the coastal area of Bandon Bay during 2000-2010. The highest concentration of heavy metals was observed at the coastal line, in particular at the river mouth in Pumreang and Kanchanadit Districts.

Since these areas are used for oyster farming, it is necessary to carefully monitor the heavy metal pollution in Bandon Bay. Although the concentrations of heavy metals were lower than the coastal water standard values of Thailand announced in 2006 (Pollution Control Department, 2012 A) heavy metals could accumulate throughout the food chain and affect the health of people consuming oysters from Bandon Bay.



**Figure 13:** Average heavy metal concentrations in Bandon Bay during 2000 – 2010.

Data Sources: Pollution Control Department and Surat Thani Coastal Fisheries Research and Development Center.

Besides reviews on monitored data of heavy metals from 4 agencies, several studies on heavy metals in Bandon Bay were found. For example, Noranattrakul, (2003) determined heavy metal concentration in the seawater of Bandon Bay in July 2002 – June 2003. He reported that the averages of Cd, Cr, Cu, Fe, Mn, Pb and Zn in seawater were 23, 34, 47, 272, 67, 51, and 55 µg/l, respectively. Kumsuk and Songkong (2004) studied the heavy metal contamination in seawater of Bandon Bay from 2003 to 2004, and reported that seawater contained Cd, Pb and Hg at the average values of 15.3 µg/l, 16.4 µg/l, and 0.03 µg/l respectively. In addition, Roekdee (2008) examined the heavy metal contamination of seawater at oyster farms in Karnchanadit District. The study results illustrated that the average values of Cd and Pb in seawater were 2.1 and 8.9 µg/l respectively, but Hg was not detected.

## **1.2 Sediment quality in the Tapi River and Bandon Bay**

Various studies were conducted on sediment quality, particularly heavy metal contamination in the sediments of Bandon Bay and several studies on sediments in the Tapi River, released from inland into Bandon Bay.

Deacharat (2002) studied the quantity of metals in the sediment mud of a water filter plant using untreated water from the Tapi-Phum Duang Basin. It was reported that cadmium in the sediment mud was at 0.06 - 0.21 mg/kg, with an average of 12.32- 20.82 mg/kg, and Roekdee (2008) studied heavy metal contamination in sediments from oyster farms at Bandon Bay. Averages of Cd, Pb and Hg contaminations in sediments were reported at 0.176, 17.212, and 0.207 µg/g (wet weight), respectively. Moreover, in 2008 the Pollution Control Department analyzed Cd, Hg, Cr, Pb, Cu, Zn and As in sediments in the areas of Pumriang canal mouth, Tapi River mouth, Kradae canal mouth and Donsak canal mouth. It was reported that Hg, Cd, Cr, Pb, Cu, Zn and As averaged at values of 0.0034-0.04, <0.01-0.06 , 0.34-43.26, 7.63-34.79, 0.55-14.18 , 2.61-69.65 and 0.42-19.28 mg/kg (dry weight), respectively.

### 1.3 Sources of heavy metals and their drain to the Tapi River and Bandon Bay

Due to literature review from secondary data sources, it was possible to evaluate the sources/activities in the area of the Tapi – Phum Duang Basin and estimate the amount of heavy metals released from the Tapi River to Bandon Bay in Surat Thani province.

#### 1.3.1 Non-point sources

The Tapi and Phum Duang Rivers join together at Phunphin District before mounding into Bandon Bay. The non-point sources of heavy metals generated in the Tapi – Phum Duang basin in Surat Thani are as follows:

**1) Mining.** The mining data of Surat Thani province in 2012 showed that there were 46 mines in 6 districts, namely Don Sak, Ban Na San, Kanchanadit, Wiang Sa, Khiri Rat Nikhom and Ban Na Doem. The total operating area of mining was 5,367 rai (8,588,000 m<sup>2</sup>) (Table 4). The mines produced mainly gypsum, dolomite, anhydrite and limestone. The ratios of gypsum mines, dolomite mines and limestone mines numbers were 52.44%, 25.64% and 21.92%, respectively. A report presented the leaching of sulfate acid and heavy metals from soil above mine stratum of gypsum mines in Surat Thani province using the standard leaching, SPLP (synthetic precipitation leaching procedure) and WET (waste extraction test). The report showed that the main metals involved in the leaching process detected in soil samples were Fe and Al. The test was extended to check the heavy metals Pb, Mn and Cu in some samples. The results illustrated that mining, involving the process of digging ground soil and excavating minerals, causes the contamination of the environment with heavy metals which also affects water quality (Kunlawong and Kijjanapanich, 2012).

**Table 4:** Mining data of Surat Thani province in 2012

Districts	Amount of mining operations	Mining area (rai)	Type of mining
Don Sak	5	524	limestone and dolomite
Ban Na San	14	1,422	gypsum and anhydrite
Kanchanadit	13	1,877	gypsum, anhydrite, dolomite, and limestone
Wiang Sa	10	854.75	gypsum and anhydrite
Khiri Rat Nikhom	5	524.75	limestone and dolomite
Ban Na Doem	2	165	limestone
<b>Total</b>	<b>49</b>	<b>5,367.5</b>	

Data Sources: Department of Primary Industries and Mines (2012)

**2) Agriculture involving oil palm and rubber plantations.** The area used for oil palm and rubber plantations in Surat Thani province in 2010 was reported at 866,006 rai and 2,921,114 rai respectively (Agriculture Office of Surat Thani Province, 2010). Table 5 shows the oil palm plantation area and Table 6 shows the area of rubber plantations in Surat Thani province in 2010. However, in this study it was estimated that there were about 788,664 rai of oil palm and 2,705,269 rai of rubber plantations contributing to runoff into the Tapi – Phum Duang basin. The use of chemical fertilizers in the oil palm and rubber plantations in Surat Thani province was reported to be in the range of 60-100 kg/rai/year (Office of Environmental Region 14, 2001).

Therefore, agricultural fertilizers used in these areas were considered to be a potential source of heavy metals. Table 7 illustrates the estimated annual input of heavy metals in rubber and oil palm plantations in Surat Thani province. This information was calculated based on the following information: Chemical fertilizers are always contaminated with heavy metals, especially phosphate fertilizer, which is contaminated with Cd due to the mainly used phosphate rock which contains Cd at approximately 2-170 mg/kg. Utilization of phosphate fertilizers could increase quantity of Cd in the soil as the prevailing cadmium phosphate had a very low



solubility and was taken up by plants poorly. As a result, the Cd then reportedly accumulates in the soil. However, a potential increase in ammonia fertilizer utilization might cause an increased Cd dissolution. Cd can be changed into a soluble form by ammonia and thus mixed with it (Pollution Control Department, 1998 B). Hence, heavy metals from fertilizers could contaminate the runoff and flow into the Bandon Bay.

**Table 5:** Oil palm plantations in Surat Thani province in 2010

Districts	Plantation (rai)	Harvesting (rai)	Before harvesting (rai)
Muang Surat Thani	24,491	17,401	7,090
Phunphin	131,527	111,037	20,490
Ban Na San	9,895	6,236	3,659
Khian Sa	52,542	40,100	12,442
Wiang Sa	13,534	8,718	4,816
Ko Samui	224	-	224
Ko Pha-ngan	-	-	-
Chaiya	50,472	38,187	12,285
Kanchanadit	76,809	62,414	14,395
Khiri Rat Nikhom	26,671	22,175	4,496
Don Sak	25,501	18,253	7,248
Tha Chang	58,616	50,111	8,505
Tha Chana	75,605	46,754	28,851
Ban Ta Khun	9,678	8,970	708
Ban Na Doem	9,201	4,733	4,468
Phanom	61,704	49,705	11,999
Phrasaeng	162,418	145,103	17,315
Chai Buri	61,671	57,121	4,550
Vibhavadi	15,447	13,250	2,197
<b>Total</b>	<b>866,006</b>	<b>700,268</b>	<b>165,738</b>

Data Sources: Agriculture Office of Surat Thani province (2010)

**Table 6:** Rubber plantations in Surat Thani province in 2010

Districts	Plantation (rai)	Harvesting (rai)	Before Harvesting (rai)
Muang Surat Thani	54,150	45,489	8,661
Phunphin	328,524	297,817	30,707
Ban Na San	83,149	70,951	12,198
Khian Sa	276,971	260,177	16,794
Wiang Sa	126,899	92,091	34,808
Ko Samui	1,355	1,179	176
Ko Pha-ngan	493	488	5
Chaiya	340,499	263,159	77,340
Kanchanadit	178,453	123,687	54,766
Khiri Rat Nikhom	108,257	83,500	24,757
Don Sak	135,063	105,562	29,501
Tha Chang	274,642	254,459	20,183
Tha Chana	194,486	194,486	0
Ban Ta Khun	48,346	40,008	8,338
Ban Na Doem	83,149	70,951	12,198
Phanom	134,416	113,320	21,096
Phrasaeng	338,266	287,017	51,249
Chai Buri	109,665	89,323	20,342
Vibhavadi	104,332	64,175	40,157
<b>Totals</b>	<b>2,921,114</b>	<b>2,457,839</b>	<b>463,275</b>

Data Sources: Agriculture Office of Surat Thani province (2010)

Table 7 shows oil palm and rubber plantation areas in Surat Thani province in 2010 that are suspected of generating runoff into the Tapi – Phum Duang basin. The relevant areas covered about 788,664 rai of oil palm and 2,705,269 rai of rubber plantations. Based on the report, chemical fertilizers in oil palm and rubber plantations in Surat Thani were used in the range of 60-100 kg/rai/year, and the heavy metals contained in fertilizers were estimated at an average value of 0.18 mg/kg of Cd, 19.03 mg/kg of Pb and 60.33 mg/kg of Cu (Sanethaog, 2008). Therefore, the amount of fertilizers used in the basin of Surat Thani was considered a potential

source of heavy metals with an input amount of Cd, Pb, and Zn in rubber and oil palm plantations of 4.21 and 16.215, kg/year of Cd 445.42 and 1,714 kg/year of Pb and 1,412 and 5,435 kg/year of Zn respectively.

**Table 7:** Potential sources of heavy metal pollution from rubber and oil palm plantations

Items	Oil palm plantations	Rubber plantations
Area (rai)	788,664	2,705,269
Chemical fertilizers used (ton/year)	23,406.25	90,085.44
Cd input (kg/year)	4.21	16.215
Pb input (kg/year)	445.42	1,714
Zn input (kg/year)	1,412	5,435

Data Sources: Office of Environmental Region 14 (2001) and Sanethaog (2008)

3) **Landfill.** In Surat Thani province, the environmental pollution problem of solid waste has seriously increased of waste, especially in Muang District. The average daily solid waste generated in Surat Thani province was 362 tons/day in municipal areas and 234 tons/day in non-municipal areas (Pollution Control Department, 2012 B). However, the disposal sites for municipal solid waste in Surat Thani were mostly open dumping sites which has caused leachate problems and thus affected the environment. It was highlighted that the disposal site is located near a river (at Tha Rong Chang). It is about 5.22 kilometers from the Tapi River and 3.76 km from the Phum Duang River (Office of Environmental Region 14, 2012). Anuluxtipun *et al*, (2002) reported that the leachate from the solid waste disposal site was contaminated with Pb and Cd ranging from 0.004-0.076 mg/l, and 0.0004-0.01 mg/l respectively. Moreover, the directions of the lead and cadmium dispersion near the landfill site were detected. Due to their practices, disposal sites might well be contributing to the contamination of Bandon Bay with heavy metals via runoff.

### 1.3.2 Point sources

Concerning the point sources, the quantity of wastewater generation and heavy metals discharged from each point source from inland to Bandon Bay could be estimated from available data as follows:

**1) Domestic wastewater.** Domestic wastewater is a main pollution source generating wastewater by bathing, cleaning, or cooking and small scale commercial activities as it is directly released into watercourses. The quantity of domestic wastewater generated by both municipal and rural areas in the Tapi – Phum Duang River basin in Surat Thani province was approximately 166,013 m<sup>3</sup>/day or 60.595 million m<sup>3</sup>/year (calculated from the population count of 2011 totalling 1,020,639 inhabitants, Surat Thani Provincial Administrative Organization, 2012A). The wastewater generation rates are shown in Table 8.

**Table 8:** Wastewater generation rates used in this study to calculate wastewater generation by point sources.

Pollution sources	Criteria /Data used for calculation
1. Domestic	- 210 liter/capita/day (for small community/city) - 300 liter/capita/day (for large community/city) (Department of Pollution Control, 1997)
2. Hospital	- 800 liter/bed/day (Department of Pollution Control, publishing year not found)
3. Industry	- follows the data reported by the Provincial Industrial Office, Surat Thani ( Provincial Industrial Office, Surat Thani , 2011)
4. Pig farm	- 24 liter/animal/day (Department of Pollution Control, 2010)
5. Shrimp farm	- 2,274 m <sup>3</sup> /rai, with 70% discharged when harvesting and 2 harvests per year. (Department of Pollution Control, 2011)

Data Source: Roekdee, *et al.*, (2013)

**2) Hospital wastewater.** Hospitals are another major source of water pollution generating heavy metal pollutants from medicines and chemicals used in medical treatments. In Surat Thani province, there were both public and private hospitals categorized in this study into health centers, general hospitals and

community hospitals with sizes of 600-1,000 beds, 100-200 beds, and 30 beds respectively. The amount of wastewater generated by the 23 hospitals in Surat Thani was calculated as 1,361 m<sup>3</sup>/day or 0.497 million m<sup>3</sup>/year (calculated using the wastewater generation rates as shown in Table 8).

**3) Industrial wastewater.** In 2011, there were 1,129 industrial factories in Surat Thani province that potentially generated wastewater. 39 of them generated wastewater and discharged it into the Tapi - Phum Duang Rivers at approximately 24,457 m<sup>3</sup>/day. The wastewater volume data were obtained from the Provincial Industrial Office, Surat Thani (2011). Although there were many types of industries in Surat Thani province, there were not many factories involving heavy metals. The calculation of industrial wastewater containing heavy metals was based on those factories directly discharging their effluent into the Tapi River and only those with heavy metal contents in their effluent.

**4) Pig farms.** The data of 2010 (Agriculture Office of Surat Thani Province, 2013) identified that there were 80 pig farms in Surat Thani province; in the areas of Kanchanadit, Muang Surat Thani, Ban Na Derm, Chaiya, Don Sak and Wiang Sa Districts. Each farm had between 500-4,800 pigs. The total number of pigs was 45,971. The wastewater generated by the farms was 1,103.3 m<sup>3</sup>/day. This was calculated based on the wastewater generation rate as shown in Table 8.

**5) Shrimp farms.** In the coastal area of Bandon Bay, 70% of people were fishermen who also ran farms of aquatic animals for a living (Jarenpornnipat, et al., 2004). Vannamai shrimp was found to be the main species cultured in Surat Thani province as presented in Table 9. SCFRDC (2013) reported that small farms and large farms of shrimp cultivation in Surat Thani covered 14,079 rai and 4,556 rai respectively. Shrimp farming was found to concentrate in Muang, Phunphin, Kanchanadit, Chaiya, Tha Chang, Tha Chana, and Don Sak Districts adjacent to Bandon Bay. According to the report of Pollution Control Department (2011), shrimp farms typically discharged 70% of the water contained in the ponds for shrimp harvest. The water used per rai averaged at 2,274 m<sup>3</sup>. Based on this wastewater generation rate, the wastewater discharged by shrimp farms into Bandon Bay was estimated to be  $59.3 \times 10^6 \text{ m}^3/\text{year}$ .

**Table 9:** Amount of shrimp farms in 2010 - 2011 at Bandon Bay, Surat Thani province.

Districts	Shrimp farms (small farm)			Shrimp farms (large scale)		
	Number (farms)	Pond area (rai)	Farm area (rai)	Number (farms)	Pond area (rai)	Farm area (rai)
Muang Surat Thani	43	612.00	848.50	1	91.77	242.49
Kanchanadit	197	5,241.50	8,039.00	22	3,604.48	10,386.85
Don Sak	32	1,052.26	2,118.00	3	416.30	968.00
Phunphin	221	3,838.30	5,862.00	-	-	-
Tha Chang	55	1,229.50	1,798.00	1	116.00	256.00
Chaiya	60	1,375.00	2,479.00	-	-	-
Tha Chana	21	730	1,579.00	3	327.32	790.43
<b>Total</b>	<b>629</b>	<b>14,078.56</b>	<b>22,687.50</b>	<b>30</b>	<b>4,555.87</b>	<b>12,643.77</b>

Data Source: Surat Thani Coastal Fisheries Research and Development Center (2013)

## 1.4 Assessment of heavy metal loads discharged from inland into Bandon Bay

### 1.4.1 Quantity of heavy metals in wastewater generated from point sources

Estimates based on previous information indicated that the largest amount of wastewater discharged into Bandon Bay stemmed from communities totalling 60.595 million m<sup>3</sup>/ year. Wastewater from shrimp farms accounted for 59.325 million m<sup>3</sup>/ year while industrial wastewater contributed only 8.805 million m<sup>3</sup>/ year. Some relevant information based on the literature review regarding the amount of heavy metal contamination generated by these 5 point sources, is given in Table 10. Figures calculating heavy metal contents in wastewater discharged into the Tapi river and Bandon Bay from this information are shown in Table 11. The obtained data illustrated that domestic wastewater contained the highest amount of heavy metals discharged into the environment. These data were calculated based on raw wastewater generated by all municipalities in Surat Thani except for Ban na Sarn municipality, the only municipality having a central domestic wastewater treatment plant.

**Table 10:** Wastewater characteristics concerning heavy metals

Pollution sources	Heavy metal characteristics used for calculation
1. Domestic (raw wastewater)	-Fe : 2.63 mg/l, Ni: 0.008 mg/l, Cr : 0.002 mg/l, Cd : 0.004 mg/l, Pb : 0.004 mg/l (Hat Yai Municipality, 1996)
2. Hospital (treated wastewater)	- Cr : 0.014 mg/l, Cd : 0.002 mg/l, Pb: 0.012 mg/l (Danchaivijitr <i>et al.</i> , 2005)
3. Industry : concentrated latex factory (treated wastewater)	- Ni : 0.013 mg/l, Cd: 0.001 mg/l, Pb : 0.05 mg/l, Zn:0.23 mg/l (Hat Yai Municipality, 1996 and Kritsamphan, <i>et al.</i> , 2012)
4. Pig farm (treated wastewater)	- Ni : 0.05mg/l, Hg: 0.0003mg/l, As :0.037mg/l, Cd: 0.074mg/l, Pb : 0.05mg/l, Zn : 0.878mg/l (Kanto, 2011)
5. Shrimp farm (treated wastewater)	- Cd: 0.001mg/l (Bunsirichai, 2004)

Data Source: Table adapted from Roekdee, *et al.*, (2013)

**Table 11:** Estimated heavy metal amounts discharged from point sources into Bandon Bay

Discharged into Bandon Bay	Shrimp farms	Domestic	Hospitals	Pig farms	Industry
Wastewater volume discharged ( $10^6$ m <sup>3</sup> /year)	59.3	60.6	0.50	0.40	8.81
Zn (ton/year)				0.35	0.26
Cd (ton/year)	0.06	0.24	0.001	0.03	0.001
Pb (ton/year)		0.24	0.006	0.02	0.06
Fe (ton/year)		159			
Ni (ton/year)		0.48		0.02	0.01
Cr (ton/year)		0.12	0.007		
Cu (ton/year)					0.02
Hg (kg/year)				0.12	
As (ton/year)				0.014	

Data Source: Roekdee, *et al.*, (2013)

#### 1.4.2 Estimation of heavy metals discharged into Bandon Bay via Tapi - Phum Duang Rivers

Based on water quality data of the Tapi River monitored by the Office of Environmental Region 14 and the Southern Industrial Environmental Research and Development Center during 2000-2010, (data in Figure 12) and the water flow rate of the Tapi River ( $119-186\text{m}^3/\text{sec}$  or an average value of  $141.45\text{m}^3/\text{sec}$ ) and the Phum Duang River ( $77-177\text{m}^3/\text{sec}$  or an average value of  $118\text{m}^3/\text{sec}$ ) (Wattayakorn, *et al.*, 2001; Hydrology and Water Management Center for the Southern Region, 2010), heavy metal quantities discharged into Bandon Bay in the form of Cd, Cr, Pb, Cu, Mn and Zn were calculated as 10.4, 26.2, 47.1, 66, 156 and 423 ton per year, respectively. Comparing these values with those previously reported, the present values were found to have decreased. Mahaphol, (1989) reported that about 566.3 ton of Pb and 90 ton of Cd were discharged into the Gulf of Thailand via the Tapi - Phum Duang Basin per year.

In addition, heavy metals such as Zn, Pb and Cu could be found in soil and rock, especially in mining areas (Rudnick, 2004). Heavy metals are distributed throughout the earth crust. Therefore, environmental contamination may occur easily due to geological processes such as weathering, erosion and transportation into watercourses (Richardson *et al.*, 2001). Based on the study of heavy metals pollution sources reviewed, the load generation from point sources and the concentrations found in the Tapi - Phum Duang Rivers, it was apparent that heavy metals discharged from inland into Bandon Bay originated mainly from non-point sources.

This result was consistent with the report of Deacharat (2002) who studied the contamination of the sediment mud in the Tapi River by Pb and Cd by investigating sediment mud samples from a water filtering plant using untreated water from the Tapi River for tap water production. Fractionation was applied to determine the quantities of heavy metals. The results revealed high concentrations of Pb and Cd in upstream sediment samples and low concentrations in sediment samples from the river mouth. The chemical properties of the Pb detected indicated that it was included in an internal structure of a mineral crystal, while the chemical properties of Cd mostly related to absorption by iron and manganese oxide. The study illustrated that the Pb



contamination of the watercourse was mainly linked to mining areas located upstream and was not in a bioavailable form, while most of the Cd was generated by uncertain sources but could be in a bioavailable form.

Nevertheless, the generating point sources must be emphasized, especially domestic wastewater, since it contributes the largest share of wastewater discharged directly into the basin without previous treatment. The wastewater contained several heavy metals although in low concentrations, however this could cause an accumulation of heavy metals in Bandon Bay.

## 2. Heavy Metal Concentration Levels in Seawater and Sediments in Bandon Bay, Investigated during 2011-2012

This is the second part of this study that investigated the heavy metal contamination levels in sediments and seawater in Bandon Bay. The details of the study results are as follows:

### 2.1 Quality control of heavy metals in seawater and sediment analysis

The recovery test was used to control quality analysis of heavy metals in the seawater samples. Table 12 presents the recovery test and detection limits of the heavy metals Fe, Mn, Cu, Ni, Zn, Cd, Cr, Pb, As, and Hg in seawater.

**Table12:** Recovery test and detection limits of heavy metals in seawater samples.

Heavy metal	Detection limit	Recovery test (%) (mean $\pm$ SD)
Fe	7.73 $\mu$ g/l	96.0 $\pm$ 8.3
Mn	0.79 $\mu$ g/l	103.9 $\pm$ 8.2
Cu	1.24 $\mu$ g/l	109.3 $\pm$ 8.8
Ni	0.25 $\mu$ g/l	105.5 $\pm$ 10.9
Zn	2.83 $\mu$ g/l	90.4 $\pm$ 9.6
Cd	0.13 $\mu$ g/l	102.5 $\pm$ 9.5
Cr	0.15 $\mu$ g/l	101.6 $\pm$ 6.4
Pb	0.22 $\mu$ g/l	101.3 $\pm$ 9.7
As	0.12 $\mu$ g/l	108.0 $\pm$ 7.9
Hg	1.95 ng/l	96.1 $\pm$ 12.1

The quality control of the heavy metal analysis of the sediments applied the recovery test and Certified Reference Material (CRM) to the sediments. The results of the recovery test and the CRM analysis are presented in Table 13. The results of the latter showed differences from CRM concentrations but not exceeding  $\pm 5\%$ . Detection limits are also shown for each heavy metal in Table 13.

**Table 13:** Recovery test, CRM determination and detection limit values of each heavy metal in sediment

Heavy metal	Detection limit (mg/kg)	Recovery test result (%) (mean $\pm$ SD)	CRM value (mg/kg)	Tested average value of CRM (mg/kg)
Fe*	0.37	100.4 $\pm$ 12.7	7.91 $\pm$ 0.24*	7.86 $\pm$ 0.08*
Mn	1.48	102.9 $\pm$ 11.3	1,757 $\pm$ 58	1,589 $\pm$ 450
Cu	0.78	106.1 $\pm$ 14.3	177.7 $\pm$ 5.6	167.9 $\pm$ 8.48
Ni	2.30	102.8 $\pm$ 10.9	75.4 $\pm$ 1.5	75.5 $\pm$ 1.52
Zn	2.25	96.8 $\pm$ 9.9	485.3 $\pm$ 4.2	474.9 $\pm$ 16.1
Cd	0.27	105.4 $\pm$ 7.5	0.82 $\pm$ 0.01	0.84 $\pm$ 0.04
Cr	2.74	98.8 $\pm$ 7.7	352 $\pm$ 22	337 $\pm$ 11
Pb	0.29	91.2 $\pm$ 7.6	132.7 $\pm$ 1.1	132.7 $\pm$ 2.09
As	0.50	100.4 $\pm$ 12.7	45.3 $\pm$ 1.8	44.24 $\pm$ 2.19
Hg	1.444	103.69 $\pm$ 6.37	0.438 $\pm$ 0.02	0.429 $\pm$ 0.01

Note: Detection limit units are mg/kg (dry weight), except Hg with ng/g, and Fe with the unit of %.

## 2.2 Water quality and heavy metals in seawater in Bandon Bay

### 2.2.1 General water quality

The results of the water quality analysis from 7 points in the area of Bandon Bay within 1 year from 2011-2012 are presented in Table 14 recording depth, temperature, pH, salinity, DO, SS, TDS, TDVS, and chlorophyll. At Chaiya oyster farm (point 1), the average depth was 2.68 meters. The seawater temperatures ranged from 27.88 - 29.63°C, pH from 7.39 - 8.01. At Kradae canal mouth (point 4) the highest average pH was found. Salinity was in the range of

7.0-21.33 ppt among the 7 points, with the highest detected at Chaiya oyster farm, while at Kradae and Tatong oyster farms, the observed salinity was lower with 7-14ppt. In the bay at the mouth of canals, salinity was found lower at 5.17-21.00ppt. The Tapi River mouth showed the lowest level of salinity.

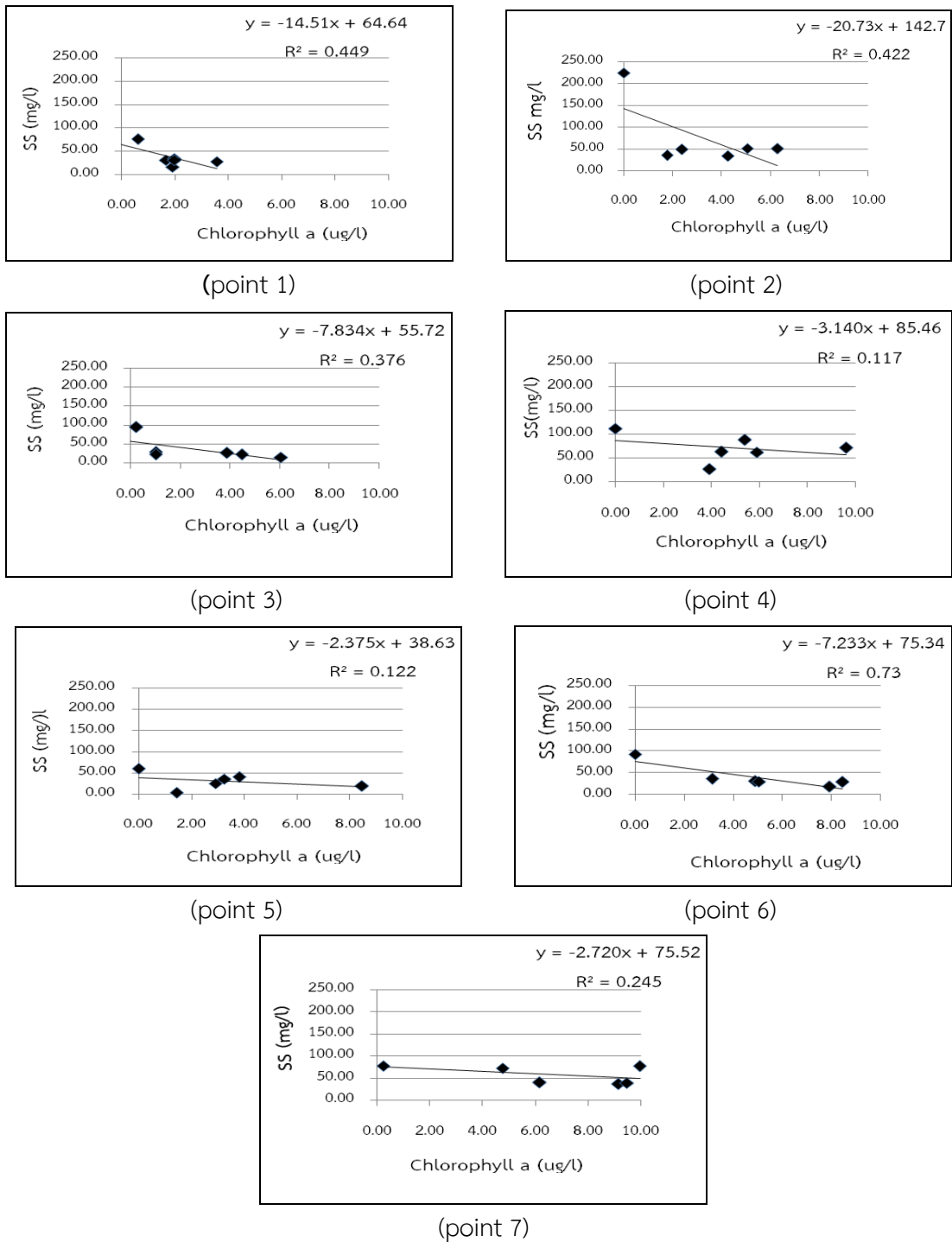
At the three oyster farms, DO levels of 4.84-6.80 mg/l were detected with Chaiya oyster farm presenting the highest average DO at 6.80 mg/l while at the four canal mouths average DO values of 4.58-5.88mg/l were lower than those determined at the three farms. Furthermore, the average SS values at the three farms ranged from 27.56 - 52.96mg/l while at the mouths of the four canals from 23.04 - 56.00mg/l. At Kradae canal mouth, the highest average SS was found. The concentrations of TDS and TDVS at the 7 study points varied between 3.14 and 11.37mg/l and from 0.90 to 2.17mg/l respectively, whereby the lowest average values of SS were found at the Tapi River mouth which was due to the influence of freshwater dilution in seawater. The ratios of TDVS and TDS at all 7 points ranged from 15.39 to 34.74 %. At the Tapi River mouth, the highest ratio of TDVS and TDS was found at 34.73 % while those at the Tatong canal mouth and Chaiya oyster farm were 25.64% and 23.75 % respectively. The Kradae canal mouth showed the lowest average ratio of 15.39%. This indicates that seawater quality at the Tapi River mouth was the most compromised by soluble organic substance.

Regarding chlorophyll a, the values found at the 3 oyster farms investigated were 2.24-7.91 µg/l, at the four canal mouths 3.28-6.46µg/l. At Kradae oyster farm, the highest average value of chlorophyll a was observed. Moreover, the analysis of seawater samples revealed that there was little or no correlation between chlorophyll a and SS at each studied point as shown in Figure 14 ( $R^2 \leq 0.73$ ).

Table 14: Results of seawater quality at Bandon Bay determined in 2011-2012.

Parameters	Seasons	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7
Depth (m)	Dry season Mean $\pm$ SD	2.57 $\pm$ 1.21	1.27 $\pm$ 1.08	1.67 $\pm$ 1.26	1.37 $\pm$ 0.98	1.40 $\pm$ 0.17	1.27 $\pm$ 1.08	1.60 $\pm$ 0.69
	Rainy season Mean $\pm$ SD	2.60 $\pm$ 0.69	0.73 $\pm$ 0.12	1.30 $\pm$ 0.17	1.37 $\pm$ 0.32	0.70 $\pm$ 0.17	0.73 $\pm$ 0.12	1.67 $\pm$ 0.76
temperature ( $^{\circ}$ C)	Dry season Mean $\pm$ SD	29.07 $\pm$ 2.12	28.87 $\pm$ 1.53	28.07 $\pm$ 1.07	28.07 $\pm$ 1.07	27.10 $\pm$ 0.46	28.23 $\pm$ 0.32	27.57 $\pm$ 0.51
	Rainy season Mean $\pm$ SD	28.13 $\pm$ 1.50	27.80 $\pm$ 1.22	29.00 $\pm$ 2.52	28.50 $\pm$ 2.34	28.27 $\pm$ 1.99	28.57 $\pm$ 0.45	27.90 $\pm$ 0.17
pH	Dry season Mean $\pm$ SD	7.89 $\pm$ 0.30	7.89 $\pm$ 0.01	7.37 $\pm$ 0.04	7.86 $\pm$ 0.42	7.82 $\pm$ 0.42	7.35 $\pm$ 0.00	7.55 $\pm$ 0.26
	Rainy season Mean $\pm$ SD	7.71 $\pm$ 0.05	7.92 $\pm$ 0.08	7.31 $\pm$ 0.04	7.76 $\pm$ 0.49	7.79 $\pm$ 0.50	7.76 $\pm$ 0.34	7.75 $\pm$ 0.14
DO (mg/l)	Dry season Mean $\pm$ SD	6.11 $\pm$ 0.12	5.11 $\pm$ 0.12	5.00 $\pm$ 0.70	5.00 $\pm$ 0.69	5.00 $\pm$ 0.68	5.10 $\pm$ 0.71	4.86 $\pm$ 0.90
	Rainy season Mean $\pm$ SD	6.23 $\pm$ 0.46	5.90 $\pm$ 0.69	4.60 $\pm$ 0.10	4.77 $\pm$ 0.64	5.03 $\pm$ 0.58	5.57 $\pm$ 0.83	4.83 $\pm$ 0.58
Salinity (ppt)	Dry season Mean $\pm$ SD	22.5 $\pm$ 3.54	21.5 $\pm$ 2.12	7.0 $\pm$ 1.73	13 $\pm$ 7.6	11.0 $\pm$ 1.41	15.0 $\pm$ 0.00	12.0 $\pm$ 0.00
	Rainy season Mean $\pm$ SD	21.0 $\pm$ 1.73	20.0 $\pm$ 0.00	3.3 $\pm$ 11.2	11 $\pm$ 7.9	10.0 $\pm$ 2.00	13.0 $\pm$ 1.73	10.0 $\pm$ 2.00
SS(mg/l)	Dry season Mean $\pm$ SD	21.00 $\pm$ 9.6	20.40 $\pm$ 1.1	35.30 $\pm$ 0.4	33.80 $\pm$ 11.0	37.10 $\pm$ 0.4	26.80 $\pm$ 10.7	24.10 $\pm$ 7.7
	Rainy season Mean $\pm$ SD	38.80 $\pm$ 6.4	24.80 $\pm$ 3.10	44.80 $\pm$ 9.50	70.80 $\pm$ 8.76	63.53 $\pm$ 5.30	32.0 $\pm$ 3.80	29.87 $\pm$ 6.80
Chlorophyll a ( $\mu$ g/l)	Dry season Mean $\pm$ SD	2.75 $\pm$ 1.16	5.26 $\pm$ 1.11	3.40 $\pm$ 1.32	7.98 $\pm$ 1.33	9.32 $\pm$ 0.24	6.13 $\pm$ 1.29	8.21 $\pm$ 0.38
	Rainy season Mean $\pm$ SD	6.23 $\pm$ 0.46	5.90 $\pm$ 0.69	4.60 $\pm$ 0.10	4.77 $\pm$ 0.64	5.03 $\pm$ 0.58	5.57 $\pm$ 0.83	4.83 $\pm$ 0.58
TDS (mg/l)	Dry season Mean $\pm$ SD	1,3686 $\pm$ 746	12,304 $\pm$ 298	3,753 $\pm$ 137	11,525 $\pm$ 531	13,908 $\pm$ 684	11,089 $\pm$ 202	13,412 $\pm$ 583
	Rainy season Mean $\pm$ SD	9,092 $\pm$ 116	10,747 $\pm$ 634	2,735 $\pm$ 322	7,450 $\pm$ 214	8,381 $\pm$ 979	6,663 $\pm$ 488	10,004 $\pm$ 565
TDVS (mg/l)	Dry season Mean $\pm$ SD	3,120 $\pm$ 342	1,898 $\pm$ 746	3,442 $\pm$ 199	2,492 $\pm$ 207	3,165 $\pm$ 317	3,227 $\pm$ 367	2,314 $\pm$ 104
	Rainy season Mean $\pm$ SD	2,040 $\pm$ 80	2,207 $\pm$ 257	1,090 $\pm$ 302	1,482 $\pm$ 75	1,434 $\pm$ 46	1,846 $\pm$ 317	1,809 $\pm$ 364

Note: (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)



**Figure 14:** Correlation of SS and Chlorophyll a in seawater at each investigated point

**Note:** (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)

## 2.2.2 Quantity of heavy metals in seawater of Bandon Bay

**1) Total of heavy metals.** The results of average heavy metal (Cd, Pb, Ni, Fe, Zn, Mn, Cr, Cu, Hg and As ) concentrations in the seawater of Bandon Bay determined during 2011-2012 are presented in Figure 15 -24. The average amounts of Cd found were 0.68 - 2.01  $\mu\text{g/l}$ . The highest level of Cd was detected at the Chiya farm, the lowest at the Tapi River mouth.

Among all study points, the average concentrations of Pb ranged from 0.52 to 4.10  $\mu\text{g/l}$ . At the Kradae oyster farm, the highest Pb concentration was found, at the Chaiya oyster farm the lowest. The results showed average Ni concentrations at the 7 points of 0.50-0.93  $\mu\text{g/l}$ . The highest Ni concentration was found at the Tatong oyster farm, the lowest at the Chaiya oyster farm. The average concentrations of Fe in seawater at Bandon Bay were in the range of 662-1,435  $\mu\text{g/l}$ . Samples from the Kradae canal mouth had the highest concentrations of Fe, those from the Pumreang canal mouth at Chaiya the lowest.

The average concentrations of Zn in seawater at the 7 points were 30.53-70.95  $\mu\text{g/l}$  with the highest found at the Tapi River mouth. The average concentrations of Mn detected at the 7 study points were 4.07-6.98  $\mu\text{g/l}$ , whereby the values recorded at the Kradae oyster farm were the highest. Cr concentrations found at the 7 points varied between 0.15 and 058  $\mu\text{g/l}$ . The highest Cr value was found at the Tapi River mouth.

For Cu, the average concentrations of 3 study points at 3 oyster farms were 19.14-20.06  $\mu\text{g/l}$ . The highest level was found at the Kradae oyster farm. The average concentrations of Cu at the four canal mouths varied from 12.63 to 16.98  $\mu\text{g/l}$ . The average concentrations of Hg detected among the seven study points were lower than those of the other heavy metals examined, ranging from 0.008 to 0.187  $\mu\text{g/l}$ , with the highest level found at the Tapi River mouth. The concentrations of As were mostly found below the detection limit, (0.12  $\mu\text{g/l}$ ). The highest level of As was found at the Tapi River mouth.

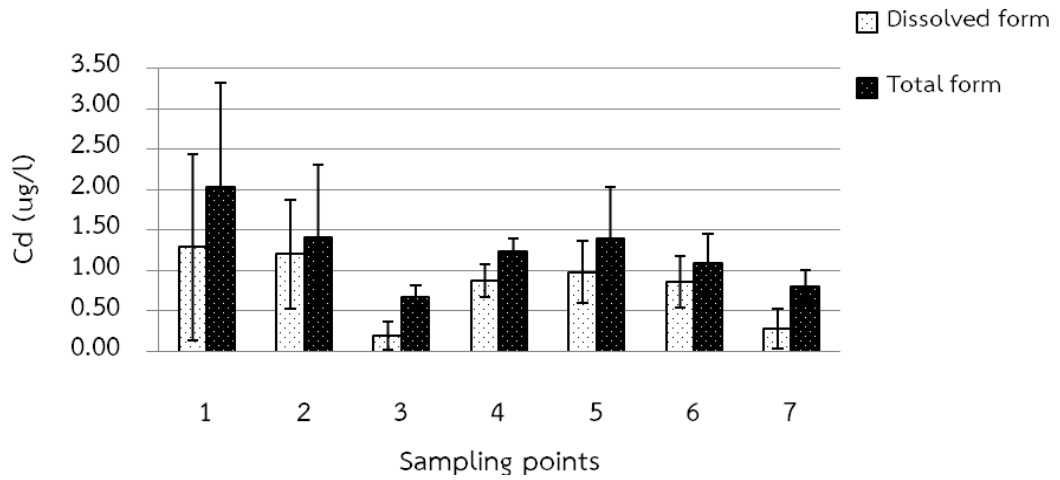


Figure 15: Average values of cadmium in seawater

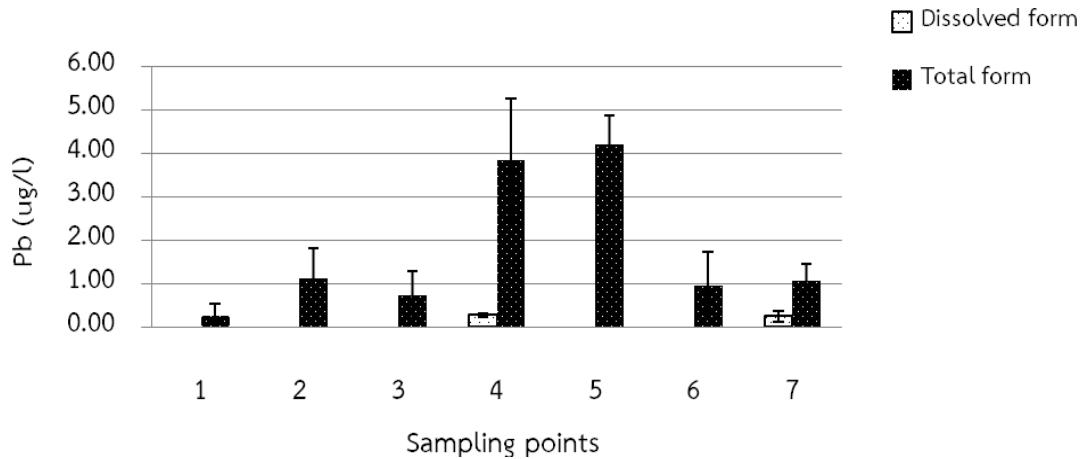


Figure 16: Average values of lead in seawater

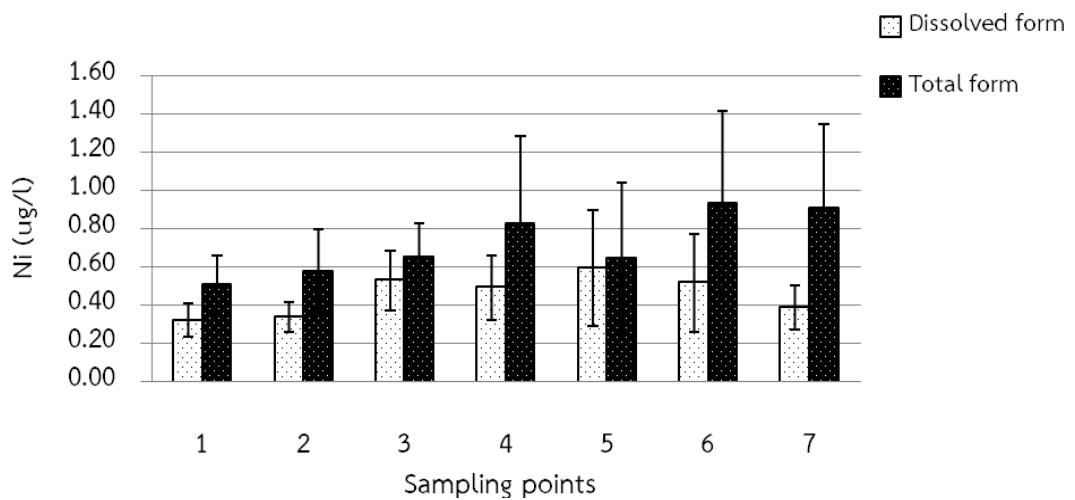


Figure 17: Average values of nickel in seawater

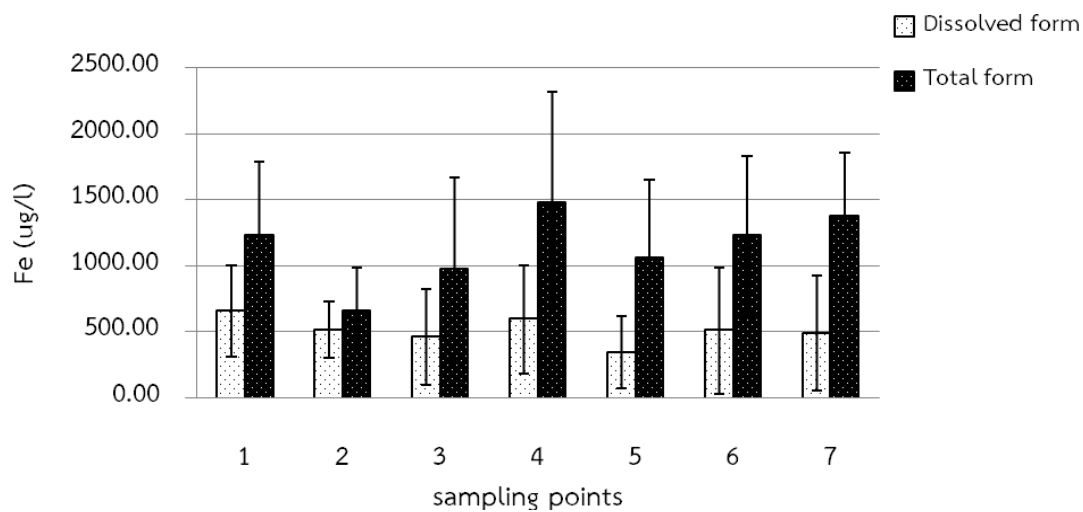


Figure 18: Average values of iron in seawater

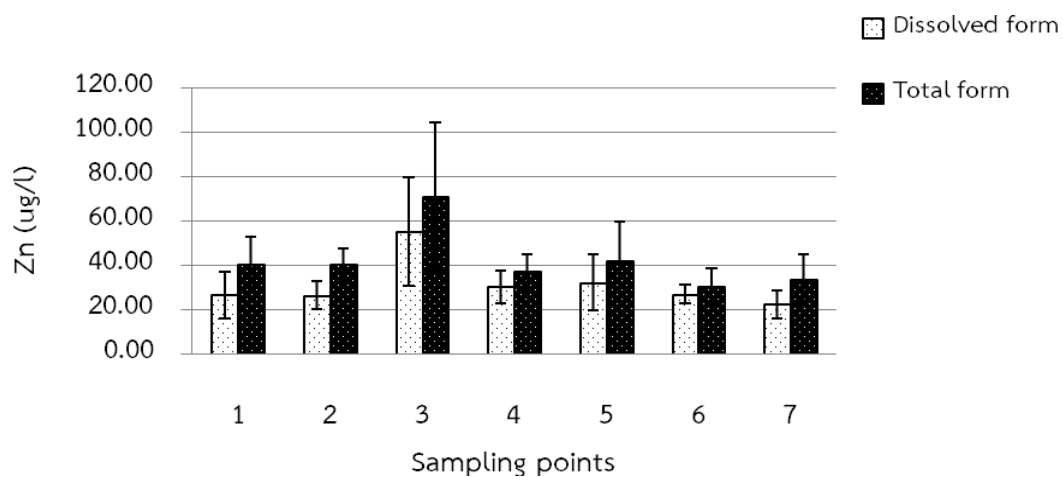


Figure 19: Average values of zinc in seawater

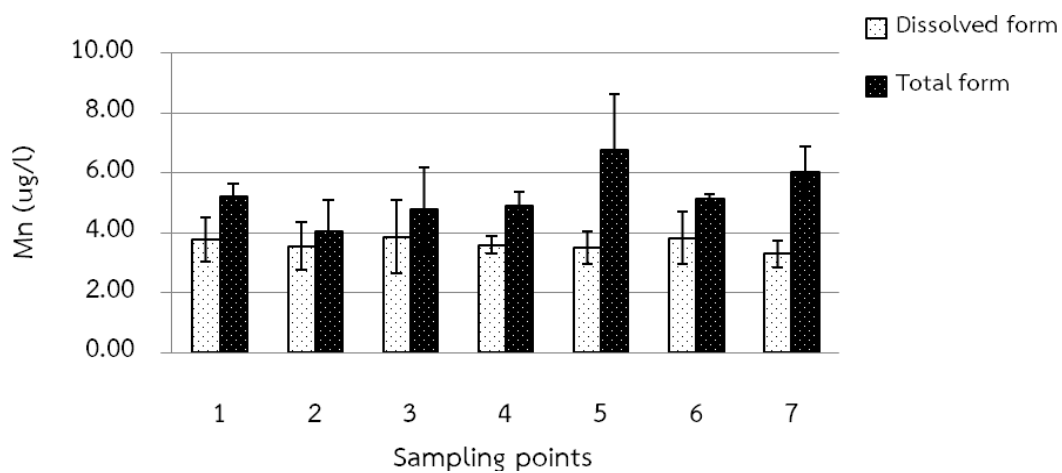


Figure 20: Average values of manganese in seawater



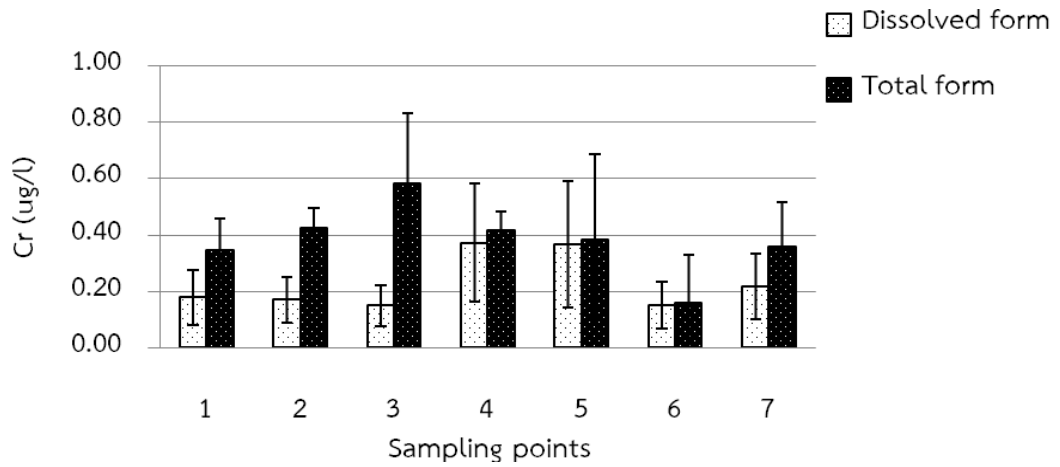


Figure 21: Average values of chromium in seawater

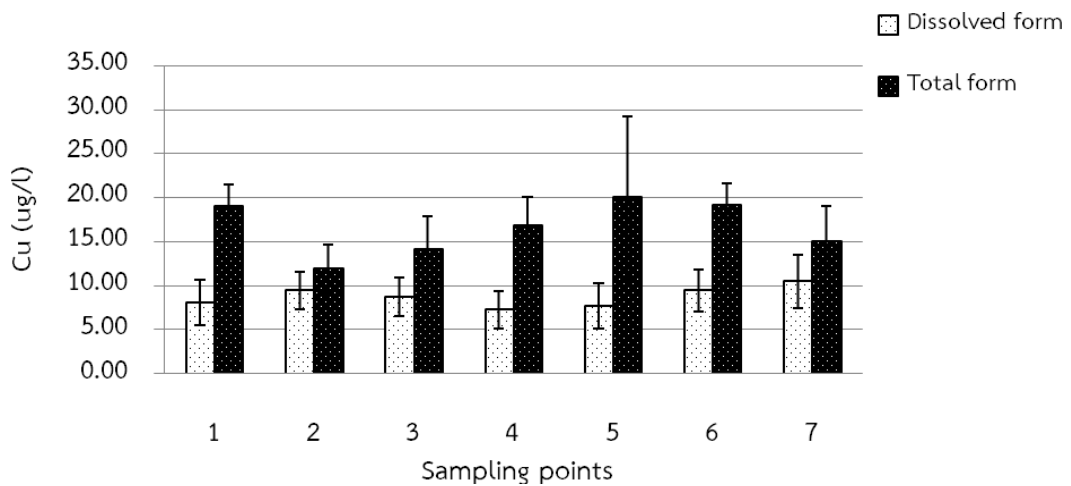


Figure 22: Average values of copper in seawater

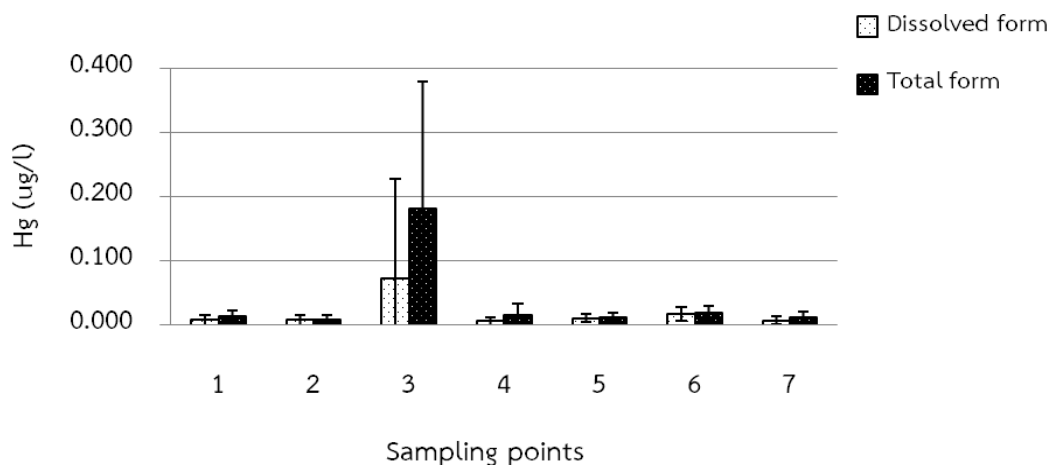
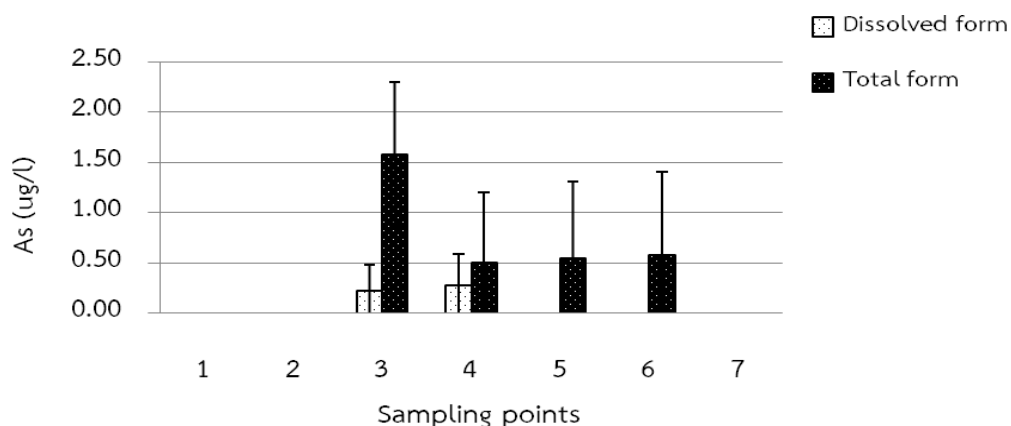


Figure 23: Average values of mercury in seawater



**Figure 24:** Average values of arsenic in seawater

**2) Quantities of dissolved heavy metals.** Figure 15-24 presents the quantities of heavy metals in seawater in both dissolved and total forms. The study results revealed that the ratios of dissolved heavy metals to total forms regarding Cd, Pb, Ni, Fe, Zn, Mn, Cr, Cu, Hg and As were in the in the ranges of 65-97, 5.3-6.2, 31-71, 58-79, 55-90, 43-88, 74-96, 43-58, 41-48 and 8-83%, respectively. Dissolved Cd was 0.20-1.28 µg/l. The highest amount of dissolved Cd was found at the Chaiya oyster farm, the lowest at the Tapi River mouth. Notably, Pb was the only metal that could be found mainly in non-dissolved form while all other heavy metals were mostly found in both forms, dissolved and non-dissolved.

### 2.2.3 Statistical study of heavy metals in seawater

The study covered the period of the extreme event of summer floods in March 2011. The results reflect that heavy metal concentrations in seawater after this summer flood (in April, 2011) were not too different from the other months monitored. Seasonal changes of heavy metal concentrations in seawater during dry season (February, April and June) and rainy season (August, December and January) were analyzed by t-test. The results are given in Table 15 and show that seasonal variation had a significant influence on the levels of heavy metals in seawater regarding Mn, Cr, Hg, and Ni ( $p \leq 0.05$ ) with lower average heavy metal concentrations during rainy season than during summer season.

**Table15:** Heavy metal concentrations in seawater at Bandon Bay as determined in this study.

	Heavy metal (dissolved) (mean± SD)*		Heavy metal (total) (mean± SD)*		Reported by PCD** (2003 - 2009) (ug/l)	Coastal Water Standard (ug/l)***
	Dry season (ug/l)	Rainy season (ug/l)	Dry season (ug/l)	Rainy season (ug/l)		
Fe	389 ±176	843±710	1,251± 654	1,041±608	276 - 1,543	300
Mn	4.83 ± 1.88	3.53 ± 1.1 <sup>a</sup>	5.69 ± 0.72	5.12 ± 1.19	36.34 -148.3	100
Cu	7.51 ± 2.3	10.2 ± 2.4	15.5 ± 4.01	18.05 ± 2.86	0.93 - 1.49	8
Ni	0.59 ± 0.1	0.29 ± 0.08	0.88 ± 0.21	0.40 ± 0.17 <sup>a</sup>		
Zn	35.9 ± 15.1	27.2 ± 3.0	49.0 ± 15.6	41.75 ± 7.01	2.50 - 7.83	50
Cd	1.16 ± 0.48	0.66 ± 0.10	1.35 ± 0.61	0.91 ± 0.61	0.05 - 0.29	5.0
Cr	0.18 ± 0.12	0.42 ± 0.09 <sup>a</sup>	0.36 ± 0.29	0.24 ± 0.14	0.03- 0.15	100
Pb	0.35 ± 0.00	0.24 ± 0.03	1.64 ± 0.78	1.64 ± 0.40	1.12 - 3.48	8.5
As	LD	0.46 ± 0.13	LD	1.05 ± 0.16		10
Hg	0.03 ± 0.01	0.003 ± 0.04 <sup>a</sup>	0.04 ± 0.05	0.004 ± 0.01	0.006 - 0.007	0.1

**Note:** LD: Below detection limit

\* 7 study points 1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth in 2011-2012. Heavy metal concentrations were expressed as mean± SD.

\*\* 5 study points: Phumreang canal mouth, Takei canal mouth, Tapi River mouth, Kradae canal mouth, Don Sak canal mouth in 2003-2009.

\*\*\* Seawater standard, Type 3 (seawater quality for aquatic culture).

a: illustrates the statistical difference at  $p < 0.05$ .

#### 2.2.4 Comparison of heavy metals in seawater in this study and previous studies

The heavy metal concentrations (Cd, Hg, Cr, Pb, Cu, Mn, Zn and Fe) in seawater of Bandon Bay from Phumreang canal mouth, Takei canal mouth, Tapi River mouth, Kradae canal mouth and Don Sak canal mouth found by the Pollution Control Department from 2003 – 2009 are given in Table 15. The comparison of these data and

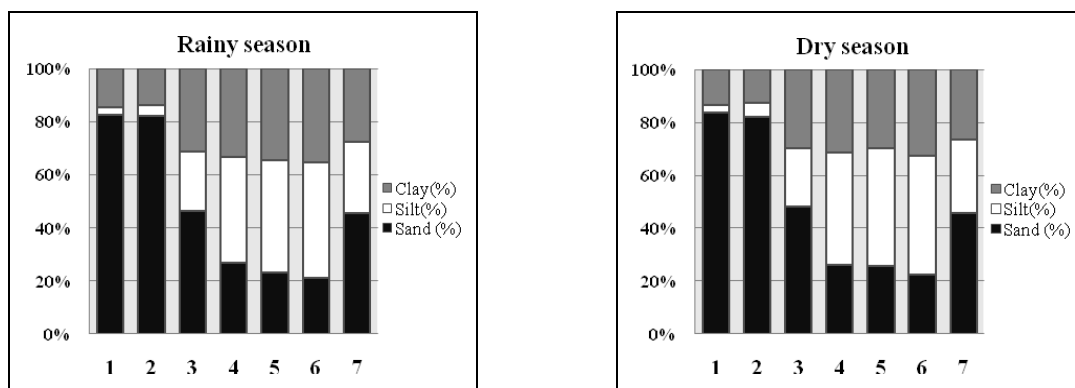
those obtained by this study revealed that the results of this study were consistent with the previous reports. Moreover, the results obtained were found to be close to comply with the Thai coastal water quality standard issued in 2006. These standard values were determined considering also aquaculture purposes. However it is to be noted that the average concentrations of Fe and Cu were found to be higher than the standard values while the rest of heavy metal concentrations (in terms of average values) observed were within the standard.

### **2.3 Sediment characteristics and heavy metal contamination at Bandon Bay**

The studies of coastal sediment characteristics at the seven study points in Bandon Bay were conducted during February 2011 – January 2012 covering both dry season (February, April and June) and rainy season (August, December and January). The results are as follows.

#### **2.3.1 General characteristics of sediments**

The sediment samples from the Chaiya oyster farm and the Phumreang canal mouth were sandy loam. The percentages of sand, silt, and clay in the sediment at the Chaiya oyster farm were in the ranges of 82.5-83.52 %, 2.79-2.81 % and 13.7-14.7 %, respectively, those of the sediment at Phumreang canal mouth at 81.98-82.15 %, 4.37-4.99 % and 12.87-13.65 %, respectively. By contrast, the sediment samples from the Tapi River mouth and Tatong canal mouth were sandy clay loam. The sediment samples from the Tapi River mouth consisted of sand, silt, and clay percentages of 46.36-47.88 %, 22.09-22.21 % and 30.03-31.47 %, respectively, while the sediment at Tatong canal mouth contained 45.49 %, 26.74-27.98 % and 26.53-27.77 %, respectively. The sediments at the Kradae canal mouth, Kradae and Tatong oyster farms were clay loam consisting of sand, silt, and clay in the ranges of 21.03-26.95 %, 39.72-45.25 % and 30.05-35.46%, respectively, as shown in Figure 25.



**Figure 25:** Soil texture of sediments in Bandon Bay during dry and rainy seasons

**Note:** (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)

The results of pH, TS, VS, organic matter, N, P and moisture content measurements of sediment samples collected from seven points in Bandon Bay are shown in Table 16-17. The average pH values of dry and rainy seasons were  $7.22 \pm 0.45$  and  $7.43 \pm 0.21$  respectively. The sediments at the area of the Kradae canal mouth had the lowest average pH values. The average values of TS of dry and rainy season were  $51.86 \pm 2.04$  and  $53.32 \pm 3.79\%$  respectively. The average VS values of the sediments in dry and rainy seasons were  $2.81 \pm 0.79$  and  $3.30 \pm 1.19\%$  respectively. The lowest average VS values among sediment samples were found at the Chaiya oyster farm while the highest average VS values were observed at the Tatong oyster farm. Average organic matter (OM) values of the rainy season were  $3.86 \pm 0.85\%$ , those of the dry season averaged at  $1.94 \pm 0.24\%$ . Thus, the average OM of the rainy season was clearly higher than that of the dry season. Moreover, the average concentrations of N and P were determined at  $0.10 \pm 0.06$  and  $0.10 \pm 0.03\%$  (dry weight) for the dry season and  $0.04 \pm 0.03$  and  $0.06 \pm 0.05\%$  (dry weight) for the rainy season, respectively, showing a considerable difference between seasons as shown in Table 17.

**Table 16:** pH, TS, VS, organic matter, N, P and moisture content in sediment samples at Bandon Bay.

Parameters	Sediment samples						
	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7
pH	7.29±0.32	7.29±0.36	7.07±0.19	6.99±0.71	7.17±0.36	7.16±0.42	7.28±0.36
TS (%)	41.2±1.11	47.0±4.93	45.4±4.08	52.0±5.76	46.5±2.13	51.8±2.78	47.9±4.06
MC (%)	58.8±1.11	53.0± 4.93	54.6±4.08	48.0±5.76	53.5±2.13	48.2±2.78	52.1±4.06
VS (%)	1.25±0.38	3.14±1.54	3.36±1.60	8.00±2.11	5.54±2.13	9.66±2.42	7.18±1.49
Organic matter (OM) (% dry weight)	1.32-3.19	1.62-1.91	1.94-1.98	1.62-2.63	1.60-3.86	1.28-1.32	1.30-2.57
N (%) (dry weight)	0.053-0.166	0.028-0.079	0.075-0.086	0.052-0.097	0.066-0.166	0.009-0.009	0.017-0.108
P (%) (dry weight)	0.046-0.053	0.046-0.063	0.034-0.053	0.037-0.041	0.051-0.060	0.015-0.017	0.011-0.050

**Note:** (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)

**Table 17:** Characteristics of sediments at Bandon Bay during dry and rainy seasons

Parameters	Dry season (mean± SD)	Rainy season (mean± SD)
pH	7.22 ± 0.45	7.43 ± 0.21
TS (%)	51.86 ± 2.04	53.32 ± 3.79
VS (%)	2.81 ± 0.79	3.30 ± 1.19
OM (%) (dry weight)	1.94 ± 0.24	3.86 ± 0.85
TN (%) (dry weight)	0.10 ± 0.06	0.04 ± 0.03
P (%) (dry weight)	0.10 ± 0.03	0.06 ± 0.05

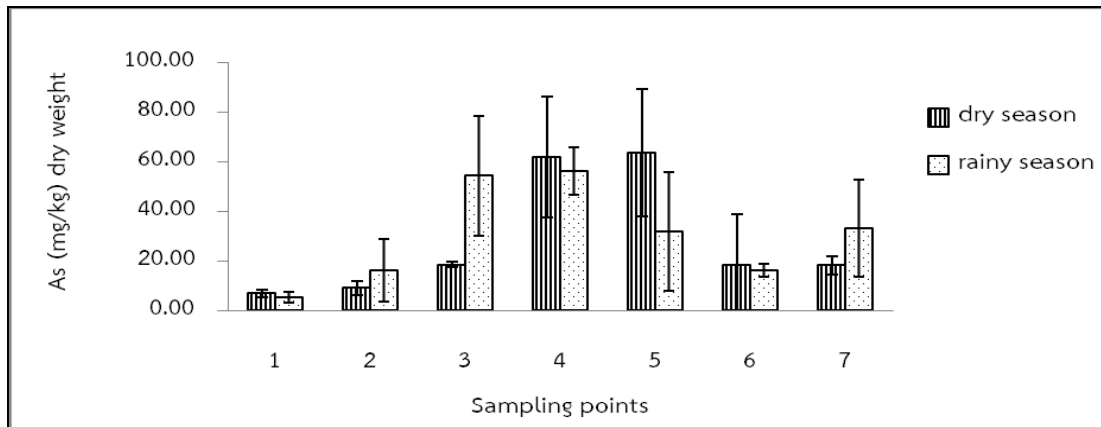
### 2.3.2 Heavy metals in sediments at Bandon Bay

Figure 26-29 presents the average concentrations of heavy metals in sediments from the seven study points in Bandon Bay, expressed in both dry season and rainy season. The average concentrations of As were 5.83 - 60.87 mg/kg (dry weight). The highest average value of As was found in the sediment sample from the Kradae oyster farm, the second highest at the Kradae canal mouth. The average concentrations of Cd were in the range of 0.92-2.49 mg/kg (dry weight). The sediment sample from the Kradae canal mouth had the highest average concentration values of Cd, the second highest was observed at the Kradae oyster farm while the lowest were found at the Chaiya and Pumreang

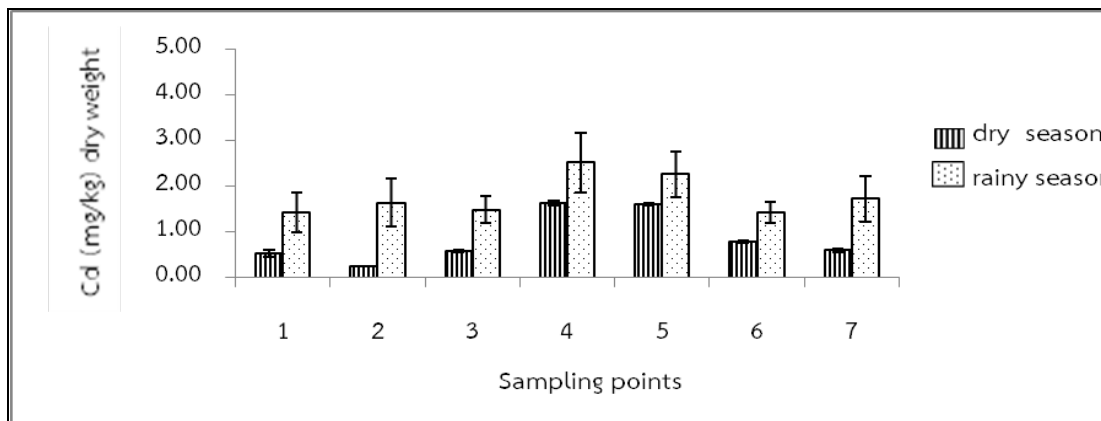
canal mouths. The concentrations of Cu in the sediment was determined at 4.23-19.41 mg/kg (dry weight). The sediment at the Kradae oyster farm had the highest average values of Cu, followed by Tatong canal mouth and Kradae canal mouth. At the Chaiya oyster farm, the sediments had the lowest average concentration of Cu.

The concentrations of Cr, Fe and Hg in the sediments retrieved from Bandon Bay are shown in Figure 27. The average concentrations of Cr were in the range of 31.85-77.32 mg/kg (dry weight), with the highest found in the sediment from the Chaiya oyster farm, followed by the samples from Kradae canal mouth. At the Tapi River mouth, 48.47 mg/kg (dry weight) were observed. The average concentrations of Fe in the sediments were 0.73-2.73 % (dry weight). These levels were found to be higher than those of the other heavy metals investigated. The Kradae canal mouth had the highest concentration of Fe in sediments, followed by the Tatong and Kradae oyster farms. Hg in sediments was found to have the lowest concentration level with average values of 0.03-0.189 mg/kg (dry weight). The Tatong oyster farm showed the highest average value of Hg, followed by the Tapi River mouth, while the lowest level was found at Chaiya canal mouth.

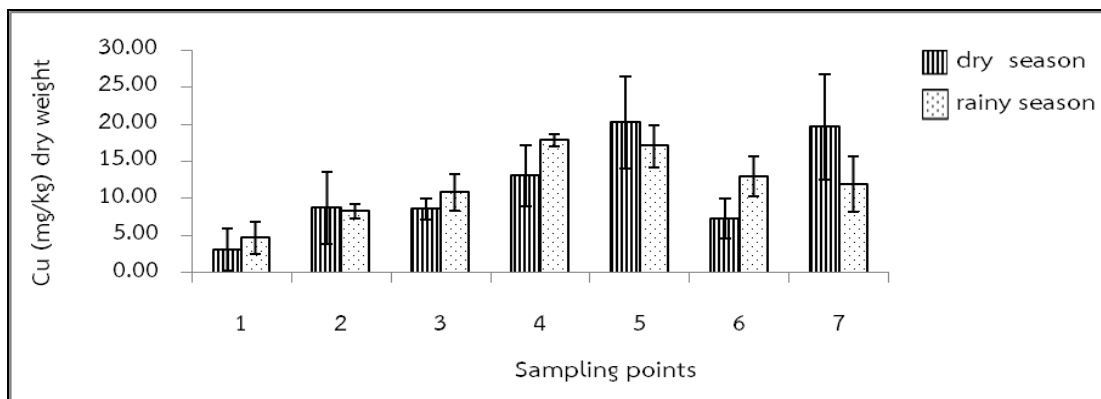
The average concentrations of Mn in the sediments were found in the range of 192-676 mg/kg (dry weight). The highest value was found at the Tatong oyster farm, followed by the Kradae oyster farm. The lowest value was determined at the Chaiya oyster farm. Furthermore, the average concentrations of Ni in sediment were in the range of 8.13 -61.49 mg/kg (dry weight). The Tapi River mouth had the highest value, followed by the Kradae canal mouth, while the lowest value was found at the Chaiya oyster farm. Finally, the average concentrations of Pb in the sediment were in the range of 18.08-33.95 mg/kg (dry weight). The Kradae oyster farm had the highest value, the Chaiya oyster farm the lowest as shown in Figure 28.



Concentrations of As



Concentrations of Cd

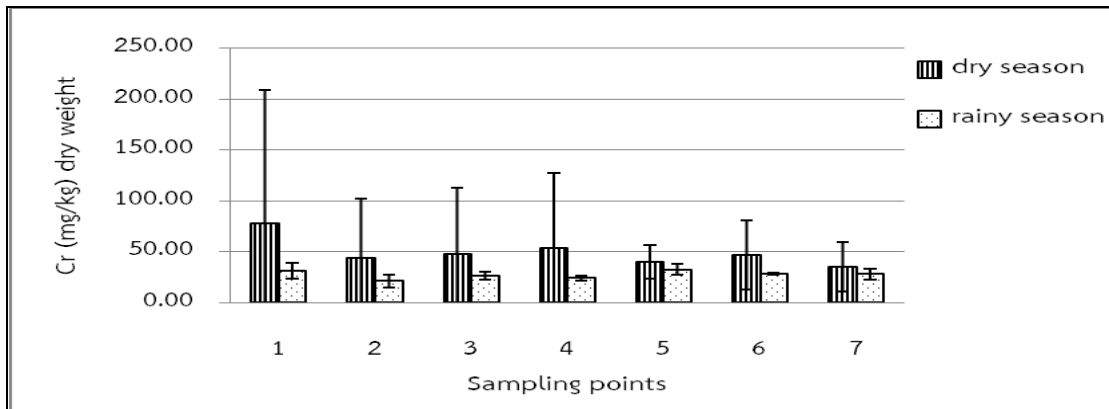


Concentrations of Cu

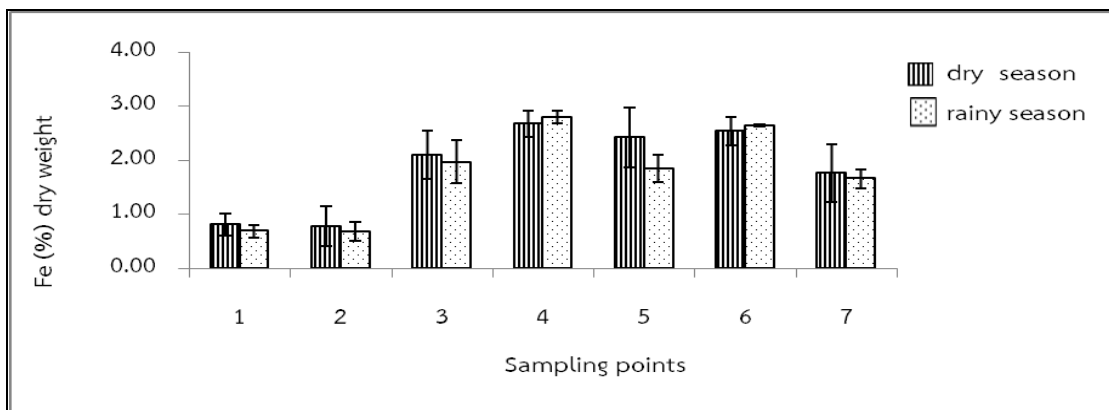
**Figure 26:** Concentrations of AS, Cd, and Cu in the sediments of Bandon Bay in dry season and rainy season

**Note:** (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)

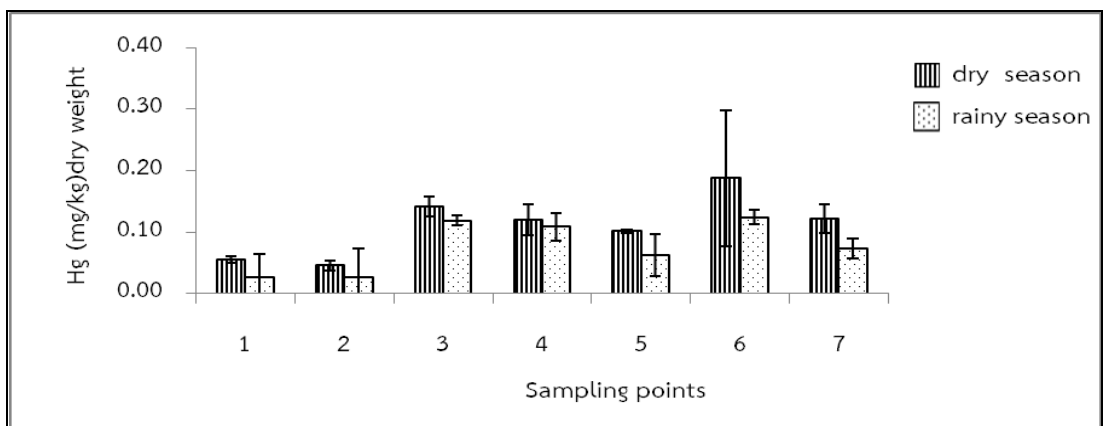




Concentrations of Cr



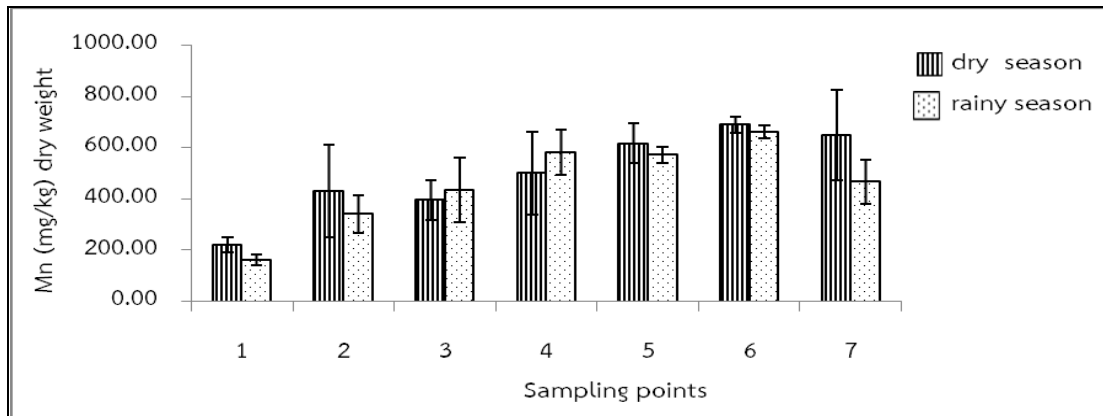
Concentrations of Fe



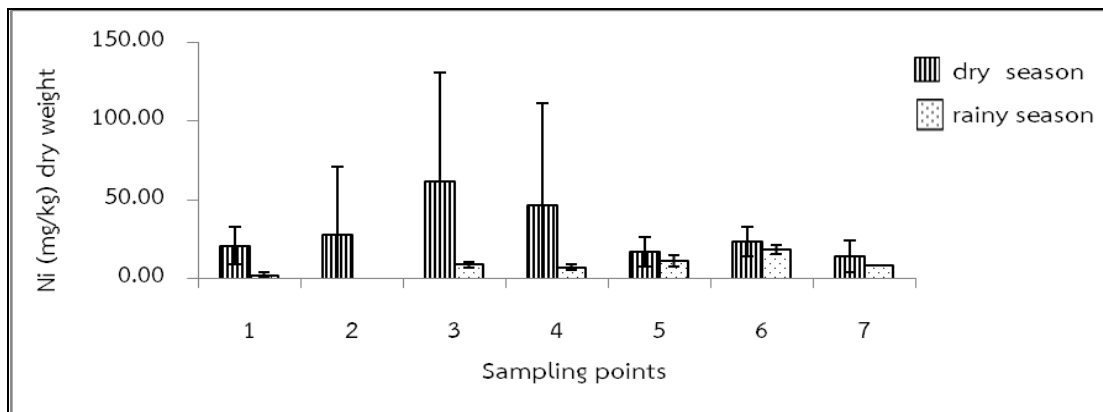
Concentrations of Hg

**Figure 27:** Concentrations of Cr, Fe, and Hg in the sediments of Bandon Bay in dry season and rainy season

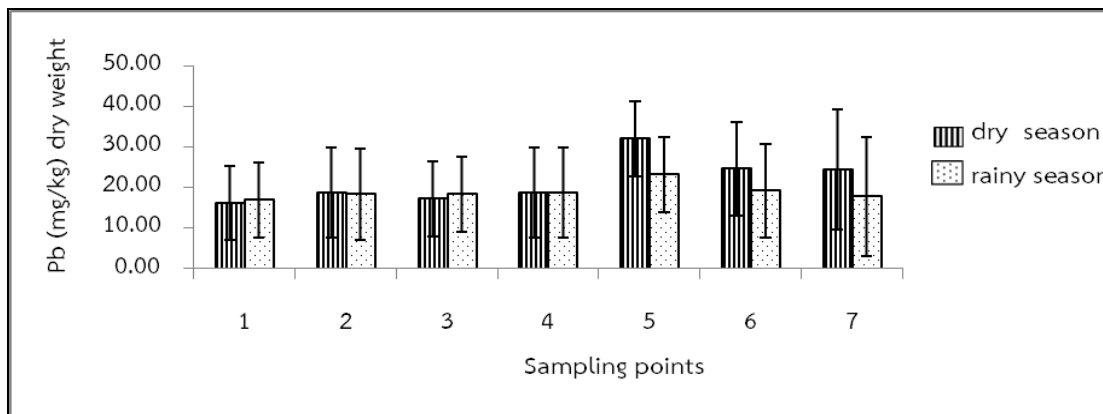
Note: (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)



Concentrations of Mn



Concentrations of Ni

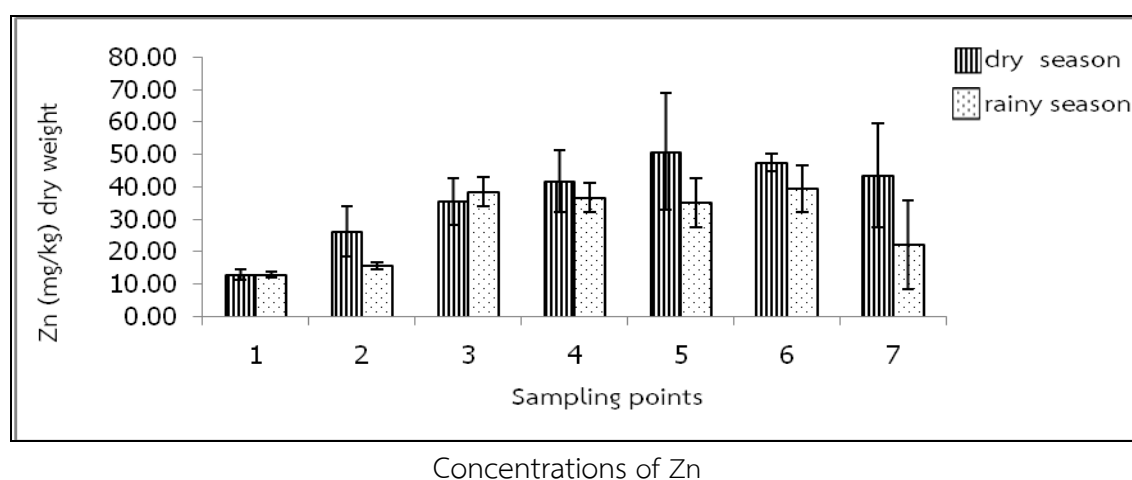


Concentrations of Pb

**Figure 28:** Concentrations of Mn, Ni, and Pb in the sediments of Bandon Bay in dry season and rainy season

Note (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)

Zn average concentrations in the sediments ranged from 12.87-43.63 mg/kg (dry weight). The highest value was found at the Kradae oyster farm, followed by the Tatong oyster farm. The lowest was found at the Chaiya oyster farm as presented in Figure 29.



**Figure 29:** Concentrations of Zn in the sediments of Bandon Bay in dry season and rainy season

**Note:** (1: Oyster farm at Chaiya, 2: Pumreang canal mouth, 3: Tapi River mouth, 4: Kradae canal mouth, 5: Oyster farm at Kradae, 6: Oyster farm at Tatong, 7: Tatong canal mouth)

The results of the investigation of heavy metal concentrations in the sediments retrieved from the sample points in Bandon Bay revealed that at the Kradae canal mouth and the oyster farms at Kradae and Tatong carried the highest values, while concentrations at the oyster farm at Chaiya and the Pumreang canal mouth were found to be lower.

### 2.3.3 Statistical analysis of the results of the investigation in heavy metal concentrations in sediments

Table 18 illustrates the statistical analysis of the obtained results. The t-test was used to investigate the differences between average heavy metal concentrations influenced by seasonal variation. The statistical analysis of the data

obtained during dry and rainy seasons revealed that the seasonal variation had a significantly effect on the concentration levels of all types of heavy metals investigated, except Cd. The results showed that the average heavy metal concentrations in dry season were significantly higher than during rainy season (at  $p \leq 0.05$ ). However, the average Cd concentrations contrasted to the other heavy metals investigated. They were lower in dry season than in rainy season.

**Table 18:** Statistical test results of heavy metal concentrations in sediments of Bandon Bay.

Heavy metal	Dry season (mg/kg) (dry weight)	Rainy season (mg/kg) (dry weight)
Fe*	*1.88 ± 0.37 <sup>a</sup>	*1.75 ± 0.18
Mn	517.9 ± 105.3 <sup>a</sup>	442.7 ± 65.0
Cu	13.15 ± 4.17 <sup>a</sup>	10.35 ± 2.19
Ni	33.61 ± 38.22 <sup>a</sup>	8.13 ± 1.62
Zn	38.12 ± 8.98 <sup>a</sup>	27.52 ± 5.64
Cd	1.36 ± 0.84	1.49 ± 0.45
Cr	65.74 ± 72.90 <sup>a</sup>	25.89 ± 4.59
Pb	14.94 ± 5.51 <sup>a</sup>	12.73 ± 3.20
As	32.51 ± 10.06 <sup>a</sup>	24.34 ± 4.62
Hg	0.12 ± 0.02 <sup>a</sup>	0.07 ± 0.02

Note: The concentrations of heavy metals were expressed as mean ± SD, and units were mg/kg, (dry weight), except Fe\* with the unit of % (dry weight)

<sup>a</sup> illustrates the statistical difference at  $P < 0.05$  of data obtained due to seasonal variations (dry season is higher than rainy season)

#### 2.3.4 Discussion of the study results and previous reports

Several studies have been conducted on heavy metal concentrations in sediments of the Tapi River basin, for example, Deacharat, (2002) investigated the traces of Pb in sediment mud from a water supply filtering plant using untreated water from the Tapi - Phum Duang Rivers. The results showed

that the average concentrations of Pb in sediment mud were 12.32 - 20.82 mg/kg which was higher than the average value of normal soil (15 mg/kg). The averages of Cd were reported at 0.06-0.21 mg/kg. These concentration levels were considerably higher than the standard level of Cd in normal soil (0.14 mg/kg). The literature review found an analysis of sediments from Bandon Bay by the Pollution Control Department in 2006, which examined Cu, Zn, Cd, Cr, Pb, As and Hg concentrations at Phumreang canal mouth, Tapi River mouth and Kradae canal mouth and reported average values of 0.6 - 14.2, 2.6 - 69.7, 0.01-0.07, 0.3-43.3, 7.6-34.8, 0.5-19.3 and 0.004-0.05 mg/kg (dry weight), respectively. Comparing these values with the results obtained in this study, Cu, Cr, Cd, As, and Hg values in this study were higher than those of the PCD's report as shown in Table 19. Roekdee (2008) investigated heavy metal contaminations in sediments of oyster farms in Bandon Bay and reported average values of Cd, Pb and Hg concentrations of 0.176, 17.212 and 0.207 mg/kg (wet weight), respectively.

By contrast, the average contaminations of Pb and Cd found in the present study were  $27.25 \pm 10.09$  and  $1.42 \pm 0.64$  mg/kg (dry weight) respectively which shows that the average concentrations of Pb and Cd in sediments of Bandon Bay were higher than those found in sediment mud in the Tapi - Phumduang Rivers basin as reported by Deacharat, (2002). However, the results of this study revealed that the average values of heavy metals investigated were still lower than the standards of heavy metal concentrations in sediments of the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life from Heavy Metal, Canadian Council of Ministers of the Environment, (2002), (see Table 19).

The heavy metal concentrations in sediments of Bandon Bay ranked, increasing order, as follows:  $Hg < Cd < Cu < Ni < Pb < Zn < As < Cr < Mn < Fe$ . Notably, the maximum values of relevant heavy metal concentrations were found at the oyster farms in Chaiya, Kradae and Tatong. This indicates a potential impact on oyster cultures and a likely heavy metal contamination of oysters.

**Table 19:** Comparison of the heavy metal concentrations in sediments obtained in this study with the report of the PCD in 2006 and the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002)

Heavy metal	Report by PCD (2006)	Present study (during 2011-2012)		Sediment Quality Guidelines of Aquatic Life <sup>A</sup>
	Range	Range	Mean $\pm$ SD	
Fe		0.38 - 3.0	1.81 $\pm$ 0.81	
Mn		117.8-811.5	480.3 $\pm$ 179.7	
Cu	0.6 - 14.2	LD - 24.8	11.68 $\pm$ 6.19	108
Ni		LD - 164.2	19.05 $\pm$ 31.95	
Zn	2.6 - 69.7	9.6 - 68.5	32.83 $\pm$ 14.59	271
Cd	0.01 - 0.07	0.30 - 2.49	1.42 $\pm$ 0.64	4.2
Cr	0.3 - 43.3	11.2 - 341.0*	45.82 $\pm$ 61.27	160
Pb	3.4 - 34.8	18.03 - 33.9	27.25 $\pm$ 10.09	112
As	0.5 - 19.3	1.6 - 97.8*	28.42 $\pm$ 25.67	41.6
Hg	0.004 - 0.05	0.01 - 0.3	0.10 $\pm$ 0.06	0.7

Note: The unit of heavy metal concentrations is mg/kg, (dry weight), except Fe, whose unit is %.

\* shows the higher values as compared to the Probable Effect Levels (PELs), (dry weight) according to the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002).

A: represents the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002).

LD: Below detection limit

The results of heavy metals in sediments found as mentioned before might associate with the sediment texture. As Usero, et al., (2003) reported that sediment deposition was accelerated by clay mineral due to salinity change and promote the accumulation of heavy metals adsorbed on clay particles. The sediments of the Kradae canal mouth, oyster farms at Kradae and Tatong sample points were determined to be clay loam. On the other hand, the sediments at the oyster farms and the Pumreang canal mouth at Chaiya were sandy. This explain why heavy metals found in sediments as mentioned before.

### **3. Association of Heavy Metals in Sediments and Seawater: A Case Study by Observations in Laboratory Experiments and Field Observation**

Heavy metals in seawater can occur in dissolved and undissolved form attached to particulates in the water column. This part of the study aimed to investigate heavy metals associated in sediments and water column. When the sediment is disturbed, it can be suspended in the water phase. One activity in Bandon Bay causing significant disturbances of the sediment is the harrowing of cockles. Therefore, the investigation of the impact of cockle harrowing on water quality was carried out as detailed below.

#### **3.1 Water quality effects of cockle harrowing activities in Bandon Bay: A case study using field work observation**

In order to determine effects of surface sediment disturbance on seawater quality, in particular, that caused by cockle harvesting in Bandon Bay, samples were taken during such activities and analyzed the seawater quality. An increased turbidity of the seawater in areas of cockle harrowing was observed as shown in Figure 30. Table 20 presents the results of the analysis of seawater quality before, during and after cockle harrowing. A considerable change in seawater quality was found, especially concerning turbidity caused by cockle harvesting which was increased 3 times after cockle harvesting, and 9 times increased SS concentration was observed.

TDS and TDVS in seawater were also found increased during and after cockle harvesting, and pH slightly decreased. Seawater samples collected before, during and after cockle harvesting were also analyzed for Cd and Pb, in both total and dissolved forms. Figure 31 illustrates the results which show that cockle harvesting/harrowing activities affected heavy metal concentrations in seawater, especially those of Cd and Pb. It was found that cockle harvesting caused an increase in total Cd but a decrease in total Pb in seawater. Cd and Pb appearing in total forms were similar the dissolved forms.

The ratios of dissolved Cd to total forms in seawater before, during and after cockle harvesting were determined at 50.0, 44.9 and 58.7 %, respectively.

respectively, while the ratios for Pb were 11.9, 8.4 and 2.8 %, respectively. The results showed that desorption of Pb and adsorption of Cd in particles suspended in seawater happened during cockle harvesting. This finding was reconfirmed by the investigation in the laboratory.

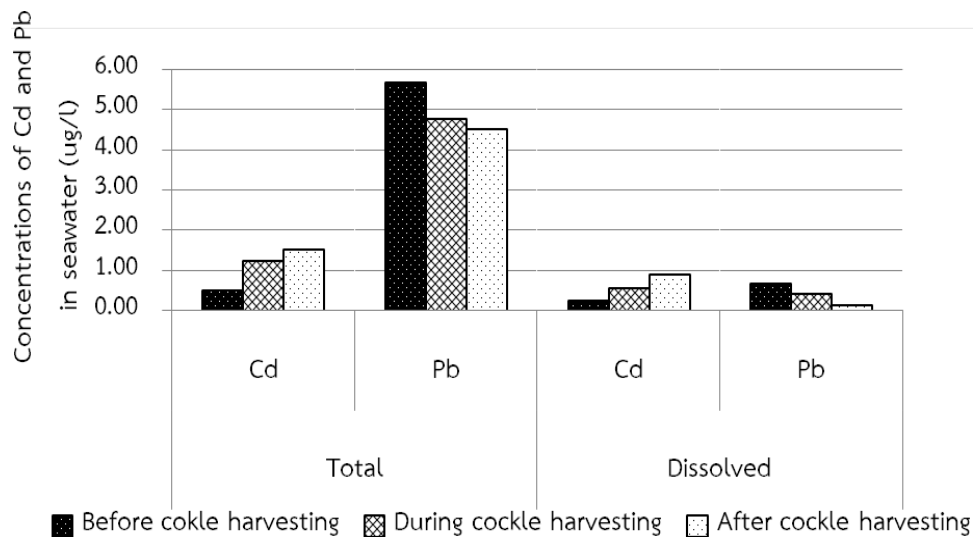


**Figure 30:** Seawater quality before and after cockle harvesting

**Table 20:** Seawater quality characteristics before, during and after cockle harvesting

Harrowing activity	Time	Temp (°c)	pH	Turbidity (NTU)	Salinity (ppt)	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)
Before	09.05 a.m.	29.20	7.64	19.5	10.0	31	8,868	982
During	09.35 a.m.	29.60	7.53	68.0	10.0	295	9,978	1,162
After	10.05 a.m.	30.50	7.48	60.0	10.0	252	9,768	1,194





**Figure 31:** Cd and Pb concentrations in seawater before, during, and after cockle harvesting

### 3.2 Effects of sediment disturbance on water quality: A case study by laboratory investigation

#### 3.2.1 Disturbance of the sediment surface: A case for long time observation.

1) **Seawater quality change.** The experiment simulating surface sediment disturbance by cockle harrowing was carried out in 2 sets of experiments using seawater and sediment from oyster farms in Kradae and Chaiya. Table 21 and Table 22 present the results of the investigation for each location. Results obtained from both samples illustrated that the disturbance of the sediment surface by harrow caused an increase in turbidity in the seawater column (30 cm above the sediment's surface) by 4-5 times. SS, TDS and TDVS concentrations in seawater were also found increased by 46-161, 1.2 and 1.2-1.4 times, respectively while pH was observed to vary during the experiment and salinity remained unchanged.

However, the concentrations of SS, TDS and TDVS in seawater during harrowing the sediment surface differed between the two experimental sets. The case using seawater and sediment from Chaiya showed lower concentrations than the case using samples from Kradae. This might be due to the different sediment

characteristics. The sediment obtained from Kradae was found to contain more clay while the sediment from Chaiya was sandy clay which made the sediment particles of the latter settle more quickly and caused lower concentrations than determined in the case of Kradae samples. The experiment was stopped after harrowing once a day for 30 days and the seawater samples were analyzed. The seawater characteristics had changed considerably compared to the initial ones. The parameters with significant changes found were SS, TDS and TDVS. This indicated that a solution of some substances from sediment phase to water phase had taken place.

**Table 2 1:** Results of the laboratory test on seawater quality after disturbing the sediment once a day over 30 days, case of Kradae samples

Experiment date	Time	Temp (°C)	pH	Turbidity (NTU)	Salinity (ppt)	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)
<b>start*</b>	06.05 a.m.	27.20	8.15	8.10	12.0	43.5	16,708	2,922
<b>1</b>	06.00 a.m.	27.50	6.98	32.0	12.0	6,896	20,282	3,450
<b>5</b>	06.20 a.m.	27.20	7.02	38.80	12.0	6,910	20,318	3,466
<b>10</b>	06.00 a.m.	28.10	7.05	37.90	12.0	6,982	20,324	3,438
<b>15</b>	06.10 a.m.	28.60	7.03	39.0	12.0	6,994	20,334	3,438
<b>20</b>	06.50 a.m.	28.50	6.96	36.0	12.0	6,934	20,336	3,434
<b>25</b>	06.50 a.m.	28.00	7.09	37.0	12.0	6,940	20,346	3,446
<b>30</b>	06.50 a.m.	29.10	7.03	39.0	12.0	6,962	20,418	3,444
<b>stop*</b>	08.50 a.m.	28.30	7.06	40.0	12.0	273	16,988	3,362

Note: \*-start means seawater samples taken before filling into the reactor

-stop means seawater samples taken 2 hrs. after finishing harrowing. Data of days 1-30, whereby the seawater was taken during harrowing

**Table 22:** Results of the laboratory test on seawater quality after disturbing the sediment once a day over 30 days, case of Chaiya samples

Experiment date	Time	Temp (°C)	pH	Turbidity (NTU)	Salinity (ppt)	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)
start*	09.05 a.m.	27.20	8.10	5.0	18.0	39.5	13,572	2,222
1	09.00 a.m.	27.60	7.38	28.8	17.0	1,810	16,434	3,114
5	09.20 a.m.	28.20	7.32	29.2	17.0	1,818	16,454	3,118
10	09.00 a.m.	29.10	7.36	29.2	17.0	1,818	16,486	3,022
15	09.10 a.m.	28.70	7.33	30.2	17.0	1,822	16,502	3,034
20	09.50 a.m.	28.50	7.36	30.2	17.0	1,822	16,506	3,040
25	09.50 a.m.	29.00	7.39	31.5	17.0	1,826	16,510	3,044
30	09.50 a.m.	28.60	7.33	31.8	17.0	1,830	16,516	3,046
stop*	11.50 a.m.	28.70	7.46	32.8	17.0	133	13,738	2,840

Note: \*-start means seawater samples taken before filling into the reactor.

-stop means seawater samples taken 2 hrs. after finishing harrowing. Data of days 1-30, whereby the seawater was taken during harrowing

## 2) Performance of dissolved and total forms of Cd and Pb.

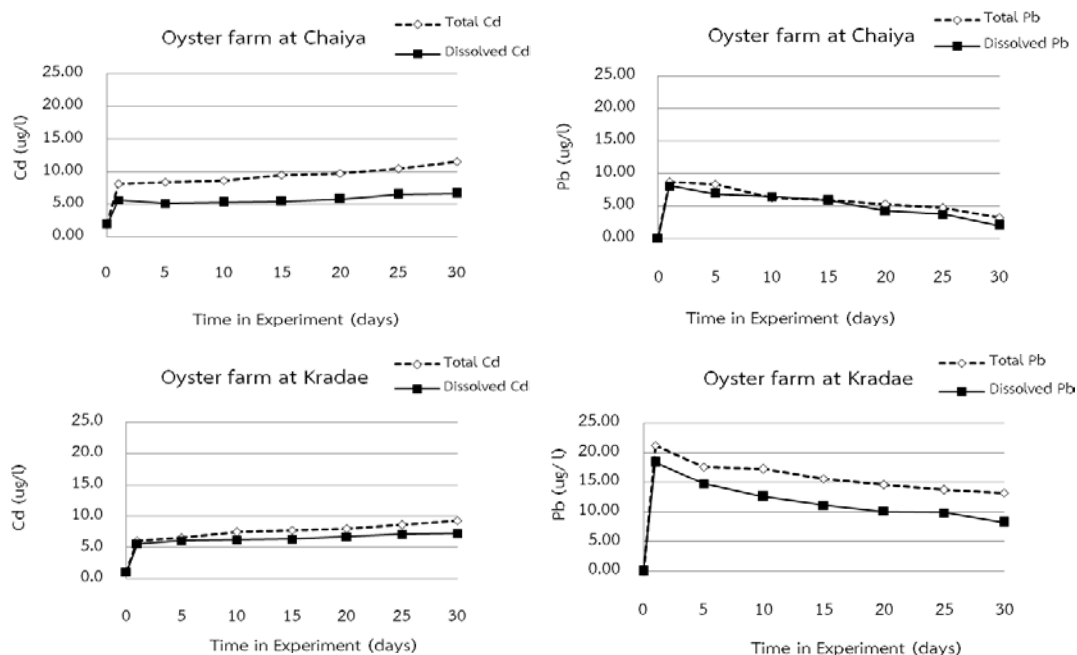
The results of Cd and Pb concentrations in seawater during the experiments are presented in Table 23 and Figure 32. The results of Cd and Pb were similar to those of SS, TDS and TDVS mentioned before. The concentrations of Cd and Pb in seawater were increased due to the suspension of sediment particles in the seawater and their solution occurring due to the sediment being disturbed by harrowing. It was found that an extended disturbance could lead to a decrease of Cd solubility in seawater. But Pb did not display a similar behavior. The longer the disturbance of the sediment, the less Pb was solubility in seawater was observed during harrowing. However, at the beginning of the harrowing, the percentages of the dissolved forms of Cd in seawater was observed to decrease while that of Pb increased. This result reflected the different behaviors of desorption and adsorption of Cd and Pb. This was rechecked again by batch test.

**Table 23:** Results of the laboratory test on seawater quality to determine heavy metals in Kradae and Chaiya samples over 30 days of sediment disturbance

Experiment sets	Experiment date	Time	Total		Dissolved		(% of dissolved form)	
			Cd (ug/l)	Pb (ug/l)	Cd (ug/l)	Pb (ug/l)	Cd	Pb
Oyster farm at Kradae	Start*	06.05 a.m.	1.10	<0.22	1.10	<0.22	100	1.8
	1	06.00 a.m.	6.10	21.20	5.60	18.35	91.8	86.8
	5	06.20 a.m.	6.60	17.60	6.10	14.85	90.1	84.6
	10	06.00 a.m.	7.50	17.30	6.25	12.90	83.9	74.8
	15	06.10 a.m.	7.80	15.60	6.40	12.60	82.1	75.0
	20	06.50 a.m.	8.10	14.60	6.75	11.10	83.9	74.5
	25	06.50 a.m.	8.70	13.70	7.15	10.10	82.7	72.7
	30	06.50 a.m.	9.30	13.20	7.25	9.90	78.0	72.3
	Stop*	08.50 a.m.	9.00	13.10	6.65	8.25	74.3	63.0
Oyster farm at Chaiya	Start*	09.05 a.m.	1.85	<0.22	1.85	<0.22	100	1.08
	1	09.00 a.m.	8.05	8.70	5.60	8.05	69.6	92.5
	5	09.20 a.m.	8.35	8.35	5.10	6.85	61.1	82.0
	10	09.00 a.m.	8.60	7.25	5.25	6.40	61.0	88.3
	15	09.10 a.m.	9.50	6.80	5.40	5.85	56.8	86.0
	20	09.50 a.m.	9.75	5.20	5.75	4.20	59.0	80.8
	25	09.50 a.m.	10.40	4.70	6.50	3.70	62.5	78.7
	30	09.50 a.m.	11.55	3.20	6.60	2.00	57.1	62.5
	Stop*	11.50 a.m.	10.65	1.31	6.55	1.15	61.5	60.2

Note: \*-Start means seawater samples taken before filling to the reactor

-Stop means seawater samples taken 2 hrs. after finishing harrowing. Data of days 1-30, whereby the seawater was taken during harrowing



**Figure 32:** Characteristics of Cd and Pb in seawater after harrowing the sediment samples from oyster farms at Chaiya and Kradae.

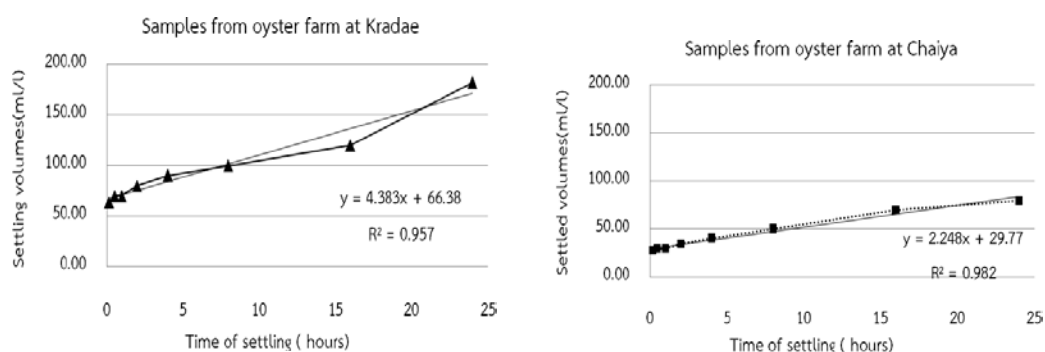
In the study, not only the seawater phase was determined, but the sediments used in the experimental reactors were also analyzed for Cd and Pb. Table 24 shows the concentrations of Cd and Pb in the sediments before and after the harrowing test. At the end of the 30 day experiment, Cd concentration in the sediments of experiment units using samples from Chaiya and Kradae were found to be lower than at the beginning. However, Pb in sediments from only Chaiya was determined to be lower than at the beginning.

**Table 24:** Concentrations of Cd and Pb in sediments before and after the harrowing test

Samples	Chaiya		Kradae	
	Cd(mg/kg) (dry weight)	Pb(mg/kg) (dry weight)	Cd(mg/kg) (dry weight)	Pb(mg/kg) (dry weight)
Start of experiment	0.69	9.20	1.54	17.96
End of experiment	0.61	8.92	1.09	17.98

The reasons for this observation were a resuspension of sediment particles into the seawater column and a transformation change of heavy metals to liquid phase via adsorption and desorption reactions. This is similar to the explanation by Sithikrom, (2001) and Kim *et al.*, (2003). They mentioned that sediments and suspended solids could occur in water in different ways, heavy metals concentrated or accumulated in the medium could reshape or move. Both dissolved and suspended solid forms constituting the heavy metals concentration in seawater probably change all the time, because of the capabilities of substantial integration of suspended solid and dissolved forms are different. As the seawater was mixed by cockle harvesting, a resuspension of sediments occurred causing adsorption and desorption of heavy metals between seawater and sediments.

**3) Settling characteristics in the laboratory test of sediment disturbance.** The settling performance after sediment surface harrowing was determined using an Imhoff cone. The results are given in Figure 33. Settleable parts of Chaiya samples were found to be less than in Kradae samples. This was due to a higher SS concentration in the seawater during harrowing of Kradae samples than in the Chaiya case. However, settling of suspended solids after harrowing increased over time. Calculating the settling over a 24 hour observation period, settling rates of 4.383 ml/l per hour and 2.248 ml/l per hour were determined for the experimental sets of the Kradae and Chaiya cases, respectively.



**Figure 33:** Settling characteristics of samples from Kradae and Chaiya

### 3.2.2 Behaviors of Cd and Pb associated in sediment and seawater: A case study using a batch test

1) **Characteristics of seawater and sediments before experiment start.** Tables 25 and 26 present the characteristics of seawater and sediment samples obtained from the oyster farms at Kradae and Chaiya for investigation. Seawater samples used for this batch test was from Kradae were found to contain higher TDVS, Pb and SS concentrations than the samples from Chaiya, while TDS and Cd levels of seawater from Chaiya were higher than those of the seawater from Kradae. The higher TDS values of seawater from Chaiya reflected its higher salinity compared to Kradae seawater. The sediment samples used in the batch test are given in Table 26. Sediment from Kradae showed higher VS, Cd, and Pb levels than the sediment samples from Chaiya.

**Table 25:** Characteristics of seawater before use in the batch test

Samples		Parameters					
		pH	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)	Cd (ug/l) (total)	Pb (ug/l) (total)
Oyster farm at Kradae	test (1)	7.18	40.80	6,583	1,385	2.3	0.6
	test (2)	7.16	40.20	6,586	1,378	2.8	0.5
Oyster farm at Chaiya	test (3)	7.32	31.20	13,504	991	5.0	<0.02
	test (4)	7.33	31.40	13,506	986	5.5	<0.02

**Table 26:** Characteristics of sediments before use in the batch test

Samples		Parameters				
		pH	TS (%)	VS (% of TS)	Cd (mg/kg) (dry weight)	Pb (mg/kg) (dry weight)
Oyster farm at Kradæ	Test (1)	7.08	53.06	0.74	2.39	24.75
	Test (2)	7.10	53.15	0.60	2.32	24.60
Oyster farm at Chaiya	Test (3)	7.14	43.00	0.21	1.23	17.43
	Test (4)	7.14	43.01	0.20	1.05	18.00

2) **Characteristics of the mixed solution in the batch test.** Table 27 shows the results obtained from batch test at 25°C. Both experimental sets using samples from Chiaya and Kradæ gave the same trend results of SS, TDS, and TDVS. These parameters did not change with mixing time. However, the pH values were found slightly decreased.

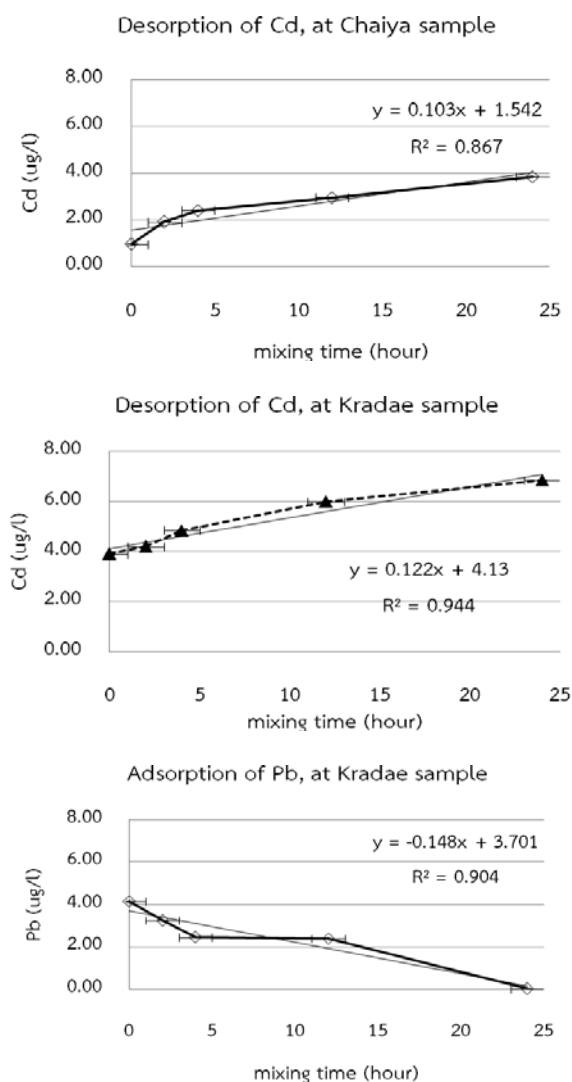
By contrast, the dissolved form of Cd concentrations in the mixed solutions of seawater and sediment were found to increase with mixing time while Pb dissolved form concentrations showed a decrease with mixing time. These trends were observed in both experimental sets. This indicated that when sediment was disturbed and mixed with seawater, Cd was dissolved into the seawater phase and a desorption reaction took place. In contrast, Pb was attached to particles/SS in the mixed solution, and an adsorption reaction occurred.

In order to estimate the reaction rate of Pb adsorption and Cd desorption, the obtained data were subjected to further linear correlation analysis. The results are given in Figure 34. The Cd desorption rates were 0.103 and 0.122ug/l per hour for the cases of Kradæ and Chaiya, respectively, while the Pb adsorption rates (in Kradæ case) was 0.148ug/l per hour. It was remarked that the Cd desorption rate in the Kradæ case was lower than in the Chaiya case.



Table 27: Results of batch test at 25 °C

Experimental set	Observation time (hours)	Test	Characteristics of mixed solution						
			pH	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)	Cd (ug/l) (dissolved form)	Pb (ug/l) (dissolved form)	
Samples from oyster farm at Kradae	0	1	7.58	24,656	6,548	1,382	1.00	4.30	
		2	7.59	24,676	6,528	1,308	0.90	4.00	
	2	1	7.56	24,664	6,568	1,644	1.90	3.40	
		2	7.57	24,676	6,532	1,582	1.90	3.10	
	4	1	7.50	24,660	6,580	1,230	2.40	2.50	
		2	7.52	24,668	6,556	1,266	2.40	2.40	
	12	1	7.56	24,676	6,568	1,320	3.00	2.50	
		2	7.55	24,660	6,584	1,380	2.90	2.30	
	24	1	7.33	24,664	6,580	1,304	3.90	<0.22	
		2	7.36	24,668	6,532	1,240	3.80	<0.22	
	Samples from oyster farm at Chaiya	0	1	7.65	16,796	13,524	1,026	3.90	<0.22
			2	7.66	16,764	13,536	1,048	3.90	<0.22
2		1	7.58	16,700	13,520	944	4.10	<0.22	
		2	7.56	16,668	13,516	992	4.30	<0.22	
4		1	7.60	16,648	13,512	812	4.80	<0.22	
		2	7.62	16,744	13,532	852	4.90	<0.22	
12		1	7.60	16,708	13,508	790	6.10	<0.22	
		2	7.58	16,656	13,540	810	5.90	<0.22	
24		1	7.35	16,692	13,556	800	6.90	<0.22	
		2	7.34	16692	13,520	794	6.80	<0.22	



**Figure 34:** Estimation of Pb adsorption and Cd desorption in the seawater and sediment mixtures from batch test

Exchangeable forms of heavy metals adsorbed with soil could explain with ion exchanged through chemical process while negative ion in soil binds positive ion of metal. Negative charge in soil is depended on the concentration of  $H^+$  in soil. Generally, in acid soil there is low negative charge while alkaline soil has high negative charge. The soil would be neutral when there is positive ion in the solution. Positive metal ion will be replaced by higher ionic potential of other metals. The change of ionic potential and water pH affects the adsorption on the soil (Deacharat, 2002). Desorption and adsorption reactions of heavy metals in seawater is influenced

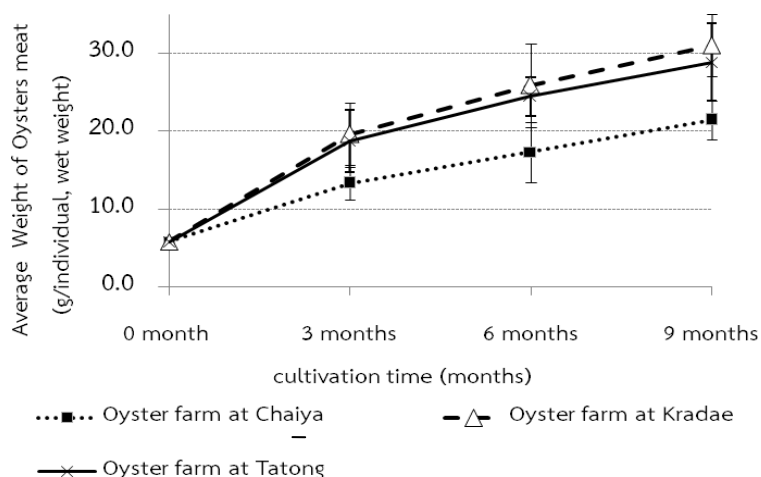
by various factors such as pH, oxidation potential, quality and quantity of SS as well as aerobic or anaerobic conditions. These factors and their actual interaction should be further investigated separately and in combinations.

#### **4. Heavy Metal Accumulation in Oysters Cultured in the Coastal Areas of Bandon Bay**

The analysis of heavy metal concentrations in seawater and sediment did not directly show the impact of heavy metals contamination of the environment. It cannot be used as an evidence for an integrated impact on and toxicity for living organism and the ecosystem. The use of living organism to indicate environmental quality is a biological investigation and as such is one of the scientific techniques for environmental assessment that are harmful to the environment. (Qunfanq, *et al.*, 2008). Bioaccumulation study is a method of biomonitoring water quality using aquatic organisms as detectors and their responses as a measure to check the aquatic ecosystem. In this study oysters, filter feeding organisms, were used for biomonitoring the aquatic ecosystem in Bandon Bay. It was focused to Cd and Pb only due to having previous report on these heavy metals accumulated in oysters with high concentrations.

##### **4.1 Oyster growth rates in the study area**

At 6 months of age, oysters were cultured for 9 months at 3 farms in Chaiya, Tatong, and Kradae coastal areas between April 2011 and January 2012. The results of oyster growth measurements based on weight increase of oyster meat after cultivation periods of 3, 6, and 9 months are shown in Figure 35. The oysters grown at the farm in Kradae showed the highest growth rate, followed by those grown in farms at Tatong. Chaiya oysters showed the lowest growth rate. These results were obviously influenced by seawater characteristics, in particular chlorophyll a levels as explained under the previous subheading (average chlorophyll a concentrations at oyster farms in Kradae, Tatong and Chaiya were 7.91, 5.91, and 2.24  $\mu\text{g/l}$ ). Chlorophyll a is a substance produced by phytoplankton that is consumed by oysters.



**Figure 35:** Growth rates of oysters in the three study areas in Bandon Bay

A high concentration of suspended solids in seawater reduces transparency and thus the less amount of light penetrating the seawater. This obstructs the photosynthesis of phytoplankton causing a decrease in natural food and oxygen in seawater, thus directly affecting oyster growth since the oysters feed by filtering the phytoplankton. The higher the quantity of suspended solids, the higher the danger to the oysters. Since the suspended solids also congest oysters' gills and thus cause a decrease in breathing and oxygen exchange and affect oysters' growth even more (Roekdee, 2013 and Wongpanit et al., 2007). However, the highest concentration of SS were found in Kradae oyster farm and the lowest was at Chaia. Therefore SS is not the factor for growth limit of oysters found in 3 study areas. The oyster farms at Chaia also had the highest average level of salinity which might affect the oysters' growth by stimulating the oysters' adductor muscle to contract (Wongpanit et al., 2007), further contributing to the lowest oyster growth at this location.

## 4.2 Cadmium and lead accumulation in oysters

### 4.2.1 Quality control of heavy metal analysis in oysters

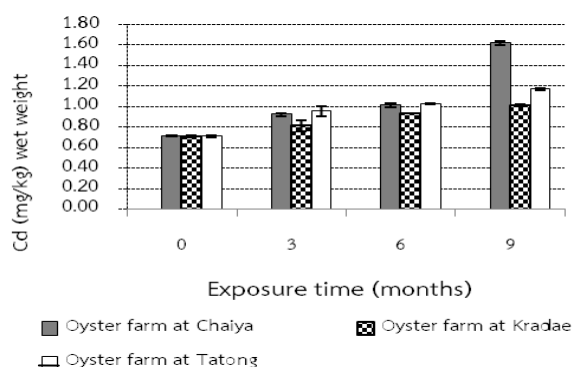
The quality control of the heavy metal analysis of the oyster samples was carried out by examining the recovery rate and applying CRM (Certified

Reference Material) to oyster samples. The results of the recovery test on Cd and Pb were  $94.94 \pm 14.58\%$  and  $89.34 \pm 9.87\%$ , respectively. The CRM of oyster samples regarding concentrations of Cd and Pb are  $2.48 \pm 0.08$ , and  $0.308 \pm 0.009$  (mg/kg dry weight) respectively, the sample analysis returned values of  $2.45 \pm 0.07$  and  $0.310 \pm 0.03$  (mg/kg dry weight) for Cd and Pb, respectively, thus diverging less than  $\pm 5\%$  from the CRM concentrations. In addition, the detection limits of Cd and Pb in oyster were determined at 0.15 and 0.13 mg/kg dry weight, respectively.

#### 4.2.2 Cd and Pb accumulation in oysters

The study results detailing cadmium and lead accumulation in oysters cultured as described above were as follows:

**1) Cd accumulation in oysters.** Before oysters were tested, the average concentrations of Cd detected in oysters were in the range of  $0.71 \pm 0.02$  (mg/kg wet weight). The Cd accumulation rates in oysters after 9 months of growth in the three observed areas are shown in Figure 36 and Table 28. Cd accumulation levels in oysters cultured at the Chaiya farm were the highest, ranging from 0.71-1.62 mg/kg wet weight, the lowest level was found at Kradae, in the range of 0.71-1.02 mg/kg wet weight, while those from Tatong were 0.71-1.17 mg/kg wet weight. These results were consistent with Cd levels in seawater determined at the respective oyster farms as mentioned before. The high Cd levels at the Chaiya oyster farm promoted the potential accumulation of Cd in tissues of aquatic animals growing in the area. Cadmium was reported to replace zinc in some types of enzymes in aquatic animals which caused changes of metabolic functions allowing cadmium to accumulate in tissues in 100–1,000 times higher concentrations than found in seawater (Rebelo *et al.*, 2003).



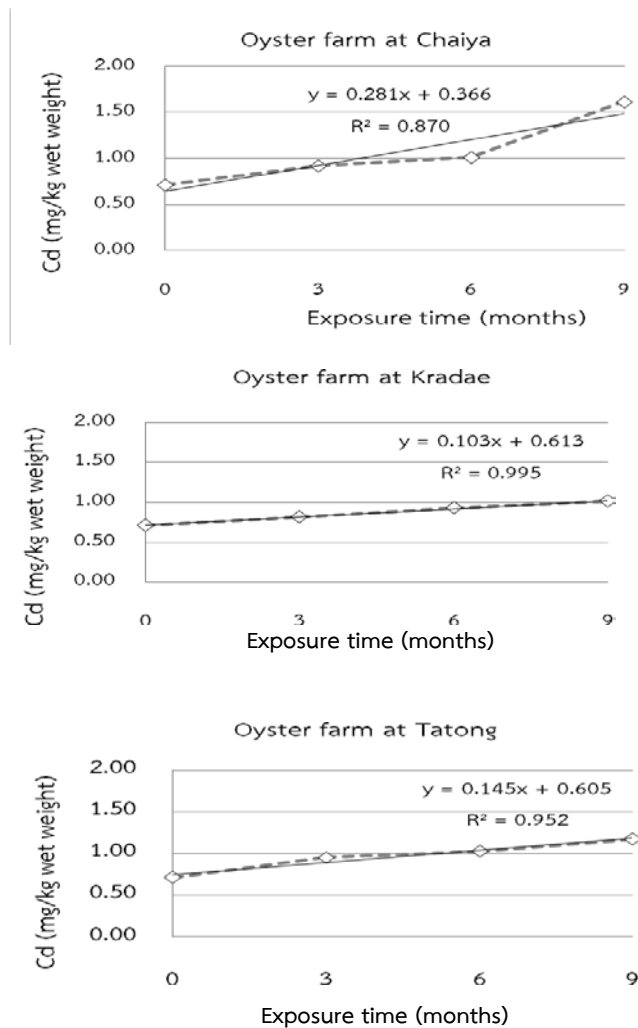
**Figure 36:** Cd accumulation in oysters cultured for 9 months in three farms in Bandon Bay.

**Table 28:** Heavy metal concentrations in oysters exposed to 3 farms in Bandon Bay.

Stations to investigate	Exposure time (months)	Cadmium (mg/kg)		Lead (mg/kg)	
		dry weight	wet weight	dry weight	wet weight
Oyster farm at Chaiya	at start	4.11±0.07	0.71±0.02	LD	LD
	3	6.57±0.16	0.92±0.02	LD	LD
	6	7.63±0.08	1.02±0.02	0.38±0.03	0.05±0.00
	9	7.95±0.07	1.62±0.05	0.42±0.03	0.08±0.01
Oyster farm at Kradae	at start	4.11±0.07	0.71±0.02	LD	LD
	3	5.32±0.04	0.82±0.00	LD	LD
	6	6.30±0.06	0.94±0.02	0.64±0.05	0.09±0.01
	9	6.64±0.04	1.02±0.00	0.66±0.03	0.10±0.00
Oyster farm at Tatong	at start	4.11±0.07	0.71±0.02	LD	LD
	3	5.88±0.01	0.96±0.00	LD	LD
	6	6.60±0.01	1.03±0.01	0.84±0.05	0.13±0.01
	9	6.92±0.06	1.17±0.01	1.03±0.08	0.17±0.01

Noted\* LD: means lower than detection limit

Cd accumulation found in oysters associated with exposure time was determined and is shown in Figure 37. From results obtained the Cd accumulation rates could be calculated. The highest was detected at the Chaiya oyster farm with 0.280 mg/kg/month (wet weight), followed by the Tatong and Kradae oyster farms with 0.145 and 0.103 mg/kg/month (wet weight), respectively. These rates indicate that oysters could be used as a bio-indicator of a hazardous Cd contamination of the ecosystem in Bandon Bay. Moreover, it could illuminate the background of Cd contaminations in the area. The higher the Cd accumulation rate in oysters, the higher the likely Cd contamination of seawater. There were reports of the use as bio-monitoring index for heavy metals contamination.



**Figure 37:** Correlation of exposure time and Cd accumulation in oysters grown at 3 oyster farms in Bandon Bay

**2) Pb accumulation in oysters.** The Pb accumulations found in the oysters are shown in Table 28 and Figure 38. The results showed that the longer time the oysters were grown, the higher the Pb accumulation in their meat. The Pb concentrations in the investigated oysters from the Chaiya, Kradae, and Tatong farms were in the ranges of <0.02-0.08 mg/kg wet weight, <0.02-0.10 mg/kg wet weight and <0.02-0.17 mg/kg wet weight, respectively. These results contrasted to the Cd accumulations in oysters from the three locations mentioned before. The Pb accumulations in oysters from the Tatong oyster farm were the highest, the second were Kradae values while those from the Chaiya oyster farms were the lowest.

The accumulation of Pb in oysters might be indirectly associated with Pb concentrations in seawater and sediment. Pb concentrations in seawater and sediments observed at Kradae oyster farms were the highest, followed by those at Tatong or Chaiya oyster farms respectively. Notably, Pb accumulations in examined oysters were below the detection limit (0.13 mg/kg dry weight) during the first three months of exposure at all 3 oyster farms but after 6-9 months of exposure time, Pb accumulations were found significant. From the obtained data, accumulation rates of Pb in oyster meat was calculated for each study site as shown in Figure 39. The highest rate was found at the Tatong oyster farm with 0.065 mg/kg/month (wet weight), followed by Kradae and Chaiya oyster farms with 0.04 and 0.03 mg/kg/month (wet weight), respectively. However, heavy metal accumulation rates differed in concentration of aquatic animals depending on various factors such as pH, salinity, temperature, oxidation potential, age, size, sex, season, phytoplankton and other environmental conditions (seawater and sediment quantity) (Amundsen, *et al.*, 1997). The results of the examination of Pb accumulation in oysters indicated that the mechanism of Pb accumulation in oysters might be more complex than that of Cd since the Pb accumulation rate in oysters was found not to correlate well with the concentrations of Pb in seawater and sediments. Therefore, it is suggested that utilizing oysters as bioindicator suits Cd better than Pb contamination.



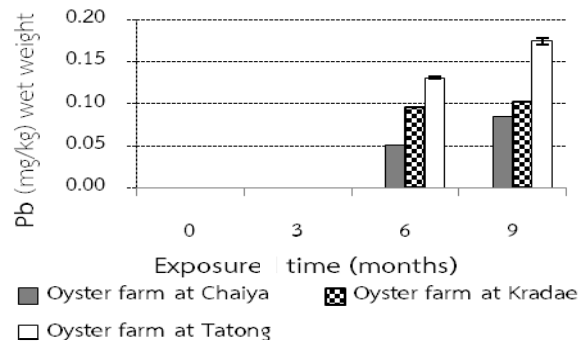


Figure 38: Pb accumulation in oysters cultured for 9 months in three farms in Bandon Bay

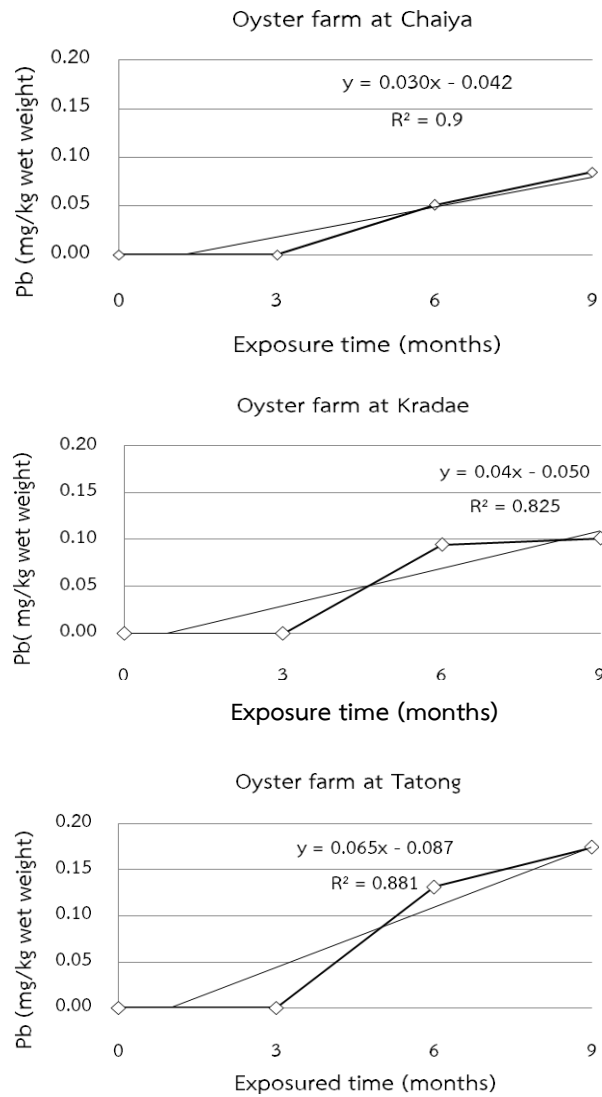


Figure 39: Correlation of exposure time and Pb accumulation in oysters grown in 3 oyster farms in Bandon Bay

## 5. Cd and Pb Contamination and Accumulation Profiles in Bandon Bay

In this section, all available data obtained from the study such as concentrations of heavy metals in seawater and sediments, estimated heavy metal discharge into Bandon Bay as well as accumulations of heavy metals in oysters were analyzed and discussed together in order to identify existing heavy metal contaminations and accumulations, focusing on Cd and Pb profiles in Bandon Bay.

As mentioned before, Cd and Pb sources polluting Bandon Bay from inland can be non-point as well as point sources. It was estimated that Bandon Bay might receive an annual Cd and Pb input of 10.4 ton and 47.1 ton, respectively. These amounts of Cd and Pb could accumulate in seawater and sediment in Bandon Bay. However, not only discharges from inland contribute to the Cd and Pb contamination in Bandon Bay but also self-pollution by heavy metals from sediments, in particular regarding Cd, can occur and affect seawater quality. On the other hand, self-purification of heavy metals influenced by sediments may occur, especially in Pb. Both can be related to human activities disturbing the sediment surface, in particular cockle harvesting. The main mechanisms of self-pollution and purification of Cd and Pb in the seawater ecosystem of Bandon Bay are based on adsorption and desorption reactions. Bandon Bay is used for oyster farming. Uptake of Cd and Pb by the oysters from the physical system and accumulation in their meat occurred at rates ranging from 0.103 to 0.280 mg/kg/month for Cd and from 0.03 to 0.065 mg/kg/month for Pb. The uptake by oysters led to some decrease of Cd and Pb concentrations in seawater and sediment in Bandon Bay as the heavy metals accumulating in oysters could be removed from the Bandon Bay ecosystem by oyster harvesting. The phenomena exhibited by the Bandon Bay ecosystem as addressed above are shown in Figure 40.

The Department of Fisheries (2012) reported a harvest of about 4,804 tons of oysters per year generated in Bandon Bay (statistical data of the Department of Fisheries of 2012). Based on the average weight of sellable oysters of 0.239kg/individual (according to data determined in this study, after 9 months

of further growth of 6 months old oysters) some estimated 20,100,418 oysters were harvested annually in Bandon Bay. Based on the culture time before harvesting was about 9 months the Pb and Cd accumulation in the oysters could be calculated as 0.176 and 0.045 mg/kg/individual (wet weight) respectively. In addition from data obtained for 9 months of oyster cultured gave the average meat weight of 0.027kg/individual). If all oysters were harvested and sold, the transport of Cd and Pb from the bay to the inland can be roughly estimated at about 1.150 and 0.294 kg per year, respectively. Comparing these numbers with estimated Pb and Cd load inputs into the bay, the input was clearly higher than the output load based on the amounts of accumulated heavy metals in oysters from the bay. This implied that the accumulation of heavy metals, especially Pb and Cd, still continued in Bandon Bay.

The behaviors of Cd and Pb concentrations were found to differ from area to area. The investigation results showed significantly higher Cd and Pb contamination levels in sediments from Kradae than in Tatong and Chaiya samples respectively and revealed that the main heavy metal self-pollution in Bandon Bay, in particular by Pb, occurred in the Kradae area, followed by Cd at Chaiya area. However, the accumulations of Pb and Cd in the oysters were found to differ. The highest Cd accumulation in oysters was found at Chaiya, the highest Pb accumulation at Tatong. Therefore, the risk areas of heavy metal contamination and accumulation differed depending on the aspects concerned, either accumulation levels in seawater/sediments or accumulation in aquatic animals grown in the area. The risks posed by heavy metals, in particular ecological and health risks are discussed under the next heading.

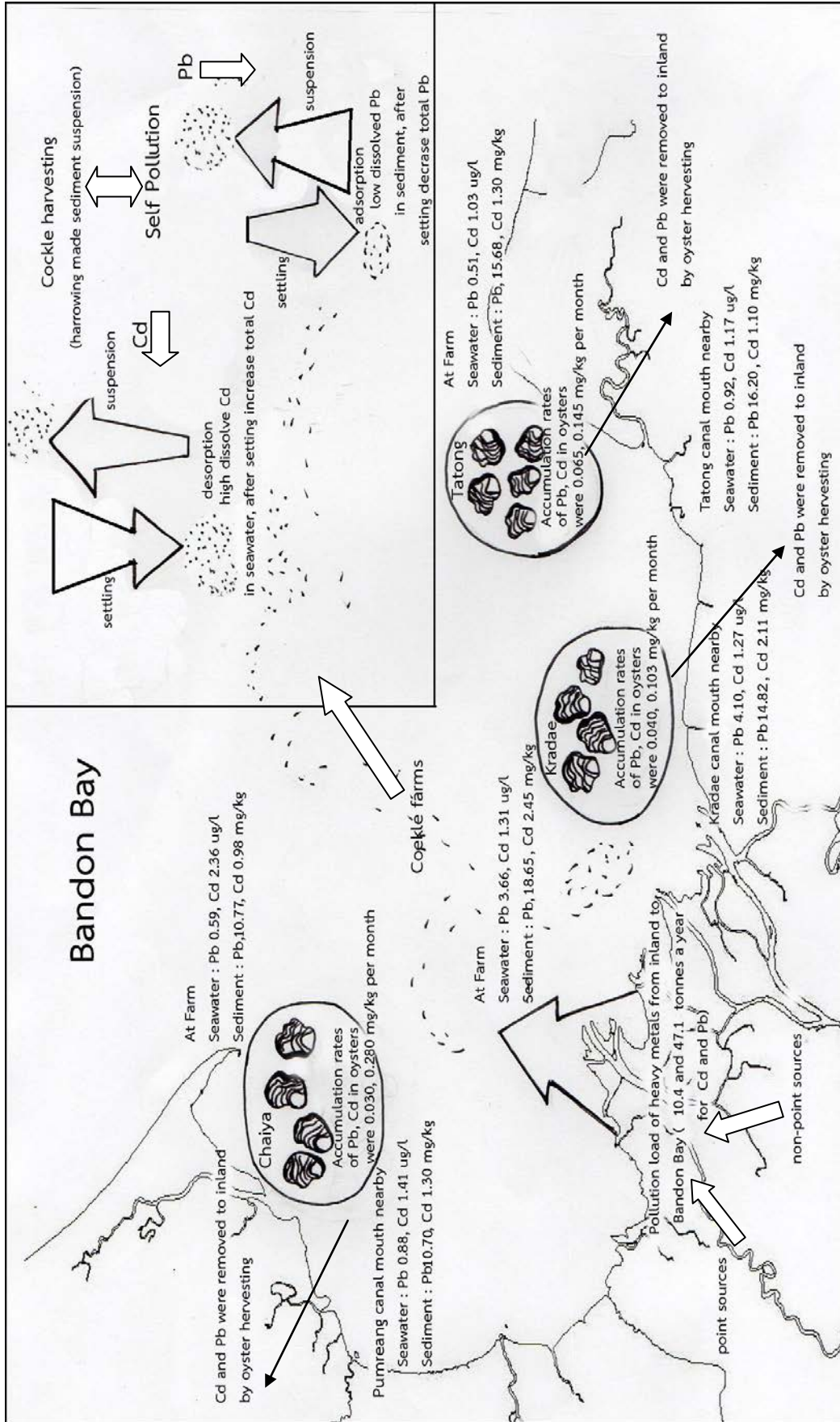


Figure: 40 Cd and Pb contamination and accumulation profile in Bandon Bay.

## 6. Ecological and Health Risk Assessment of Heavy Metal Pollution in Bandon Bay

### 6.1 Ecological risks

From the obtained data mentioned before, ecological risks of heavy metal pollutants were estimated, focusing on Pb and Cd using a quotient method to qualify risks. The risk study was conducted covering three areas to investigate the risks of Pb and Cd contaminations of seawater, sediments and the accumulation in oysters and based on the Thai coastal seawater quality standard used for coastal aquaculture purpose. Hereby, the maximum values for contaminations with Pb and Cd were 8.5 µg/l and 5 µg/l, respectively. For risk assessment of Pb and Cd concentrations in sediments, the study applied the criteria of the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002) for comparison. This guideline limits the effective Pb and Cd threshold levels in sediments for living animals at 0.68 mg/kg (dry weight) and 30.2 mg/kg (dry weight), respectively. In addition, for risk assessment of Pb and Cd in oysters, this study applied the standards of food and duct of the USA and the European Union. The USA Food and Drug Administration (FDA) guideline limited the concentrations of Pb and Cd in oyster at 1.7 and 4.0 mg/kg (wet basis), respectively. Regarding the European Communities (EC) No. 1881/2006 standards, Pb and Cd concentrations in bivalve mollusks were limited to 1.5 and 1.0 mg/kg, (wet basis), respectively.

The maximum average values of Pb and Cd contained in seawater, sediments and oysters investigated in this study were used to calculate the hazard quotients (HQ). Based on the criteria and investigated data, the hazard quotients were determined as shown in Table 29. HQs for Pb and Cd concentrations in seawater turned out lower than 1, but HQs for Pb and Cd concentrations in sediments were higher than 1. However, for Pb and Cd contents of oyster, hazard quotients were less than 1 using the US guideline but greater than 1 for Cd applying EC standards.

**Table 29:** Hazard quotients (HQ) of Pb and Cd concentrations in seawater, sediment and oyster investigated in the study

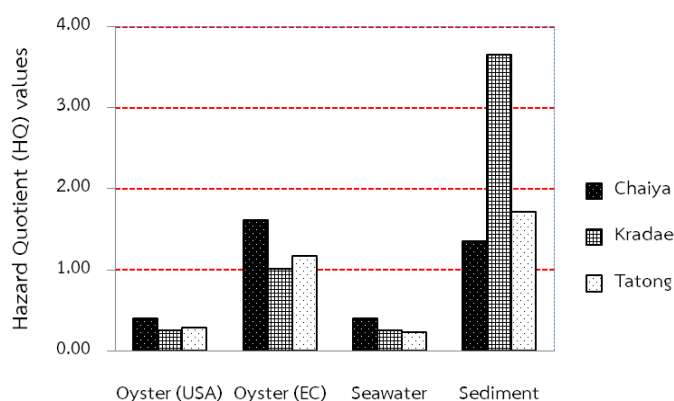
Items	Pb and Cd concentration range	Hazard Quotient (HQ) value
<b>Seawater</b> (ug/l)	Cd : 0.68-2.01	0.402
	Pb : 0.52-4.27	0.502
<b>Sediment</b> (mg/kg, dry basis)	Cd : 0.92-2.49	3.662
	Pb : 18.08-33.95	1.124
<b>Oyster</b> (mg/kg, wet weigh)	Cd : 0.71-1.62	0.405* (1.62)**
	Pb : 0.02-0.77	0.452* (0.513)**

Noted \* : comparing to US Food and Drug Administration standards

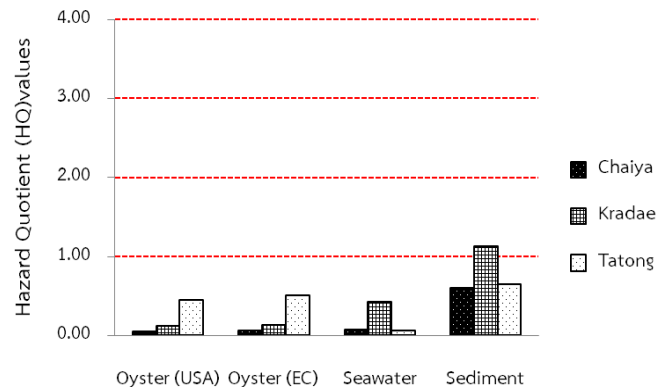
\*\* : comparing to European Communities standards

An HQ below 1 implies low risk and no urge to take action while an HQ greater than 1 implied an imminent risk requiring further action (Maria et al., 2005). Thus, the obtained HQs indicated some risks due to Cd and Pb accumulations in sediments of Bandon Bay as well as the contamination levels of Cd in oysters grown in Bandon Bay.

To determine the risks in each area of Bandon Bay the HQs of seawater, sediment and oysters in 3 areas at Chaiya, Kradae and Tatong were determined by the same method as mentioned before. The HQ results of each area are presented in Figure 41-42.



**Figure 41:** Hazard quotient (HQ) values of Cd in seawater, sediment and oyster investigated in the study.



**Figure 42:** Hazard quotient (HQ) values of Pb in seawater, sediment and oyster investigated in the study.

The area of Chaiya was found to have the highest risk in terms of Cd accumulation in oysters while all 3 areas were at risk of contamination of sediments by Cd. At Kradae, the risk of sediment contamination by Cd was found to be higher than at Tatong and Chaiya. Concerning Pb, the only risk of contamination found pertained to sediment in the Kradae area. Overall, the data indicated that the areas of Chaiya, Kradae, and Tatong were hotspots of heavy metal pollution in Bandon Bay.

## 6.2 Health risks

The results of the study of Pb and Cd accumulation in oysters raised in Bandon Bay were compared to various previous reports and standards as shown in Tables 30 and 31. Kumsuk and Songkong (2004) studied heavy metal contaminations in aquatic animals, seawater and sediments in Bandon Bay from 2003 to 2004 and reported that oysters contained cadmium at the range values of 0.3352 - 0.5730 mg/kg (wet weight) and lead at the range values of 0.1519 - 0.3480 mg/kg (wet weight). Wibunpan (2006) also studied heavy metal contamination of oysters from Bandon Bay. The results covered 4 years from 1998-2002, whereby an average cadmium contamination of 1.412 mg/kg (wet weight) was found within a range of 0.173-3.640 mg/kg (wet weight). Lead

contamination was found at an average concentration of 0.400 mg/kg in a range of 0.059-0.902 mg/kg (wet weight). Roekdee (2008) also studied heavy metal contamination of oysters, sediments and seawater at an oyster farm in Karnchanadit District, Bandon Bay. Average concentration of cadmium and lead in oysters of 1.128 and 0.210 mg/kg (wet weight) were reported respectively, as presented in Table 30.

**Table 30:** Concentrations of some heavy metals in oyster from this study and previous reports.

Area	Age of oysters (months)	Cd (mg/kg) (wet weight)	Pb (mg/kg) (wet weight)	References
Chaiya oyster farm at Bandon Bay	6-15	0.71-1.62	<0.02-0.08	Results of this study in Bandon Bay
Kradae oyster farm at Bandon Bay	6-15	0.71-1.02	<0.02-0.10	
Tatong oyster farm at Bandon Bay	6-15	0.71-1.03	<0.02-0.77	
Ang Sila	12	0.894	5.296	Tongraar, <i>et al.</i> (1989)
Pattani Bay	-	0.964	0.420	Wibunpan (2006)
Bandon Bay	-	0.454	0.250	Kumsuk and Songkong (2004)
	-	1.412	0.400	Wibunpan (2006)
	18	1.128	0.210	Roekdee (2008)
	-	0.325-0.538	0.039-0.084	Vichaidist (2009)
West Indian Ocean	-	1.04	1.38	Kojadinovic, <i>et al.</i> (2007)
Australia	22	15.3*	-	Hayesa, <i>et al.</i> (1998)
Canada	36	13.5*	-	Christie and Bendell (2009)

Note \*: dry weight



**Table 31:** Comparison with standard limits for Cd and Pb.

Country	Products	Cd*	Pb*	References
Thailand	Food	-	1	Ministry of Public Health (1986) <sup>3</sup>
	Fish	0.05	0.2	Codex Thailand <sup>2</sup>
	Shrimps	2.0	0.5	
	Squid	2.0	1.0	
Denmark	Mollusks	0.5	-	FAO <sup>1</sup>
Netherland	Oyster and surf clam	0.7	-	
Australia New and Zealand	Molluscs	2.0	2.0	The Australia and New Zealand Food Standards Code (Standard 1.4.1 Contaminants and Natural Toxicants) <sup>4</sup>
USA	Oyster	4.0	1.7	The US Food and Drug Administration (FDA Guidance Document), <sup>4</sup>
Europe	Bivalve molluscs	1.0	1.5	The Commission of the European Communities (EC) No. 1881/2006 <sup>4</sup>

Note \*: wet weight (mg/kg)

Data Sources: 1. Water Quality Management, Pollution Control Department, Ministry of Natural Resources and Environment (Jungprasid and Suksomjid, 2003)

2. Codex Thailand

3. Standard of Ministry of Public Health (1986)

4. Fish Inspection and Quality Control Division (2004), Department of Fisheries.

The results of this study regarding Pb concentrations in oysters were in the same range as those of previous reports, whereas the range of Cd values in oysters was found to be higher than in previous reports. The comparison with the relevant standards values allowed revealed that Cd values were lower than the limits defined by the FDAs of USA, Australia and New Zealand, but higher than the European Communities standard. Pb levels determined in this study were lower than the Thai food standard, as well as USA, EU, Australia and New Zealand standards.

From the study of HQ in oysters, the ecological risk results were obtained. This depended on the criteria used for comparison. It was found that Cd and Pb clearly accumulated in oysters raised in Bandon Bay. This might result in a health risk from consuming these oysters which was also a function of the amount of oyster uptake. In this section, health risks from oyster consumption were determined based on the consumption limitation values of Cd and Pb as determined by the Joint FAO / WHO Food Standard Programme Codex Committee on Contaminants in foods (2011). The values of Provisional Tolerable Weekly Intake (PTWI) for Cd and Pb were given as 7 and 25 ug/kg body weight respectively. The calculation was based on the average Thai body weight values of 68.32 kg for men and 57.4 kg for women as given by the National Science and Technology Development Agency (2014). As a result, a person should consume not more than 14 (for men) and 12 (for women) oysters/week with regard to Cd. In the case of Pb, the limit calculated was 96 and 80 oysters/week, for men and women respectively. It should be noted that in this calculation no uptake of other food containing Cd and Pb was considered. Table 32 shows the results of the calculation. In case oyster/meal/day is consumed, it can be said that 2 oysters per meal are safe, based on the Joint FAO / WHO Food Standard criteria.

Moreover, considering the specifics of oyster cultivation in the Bandon Bay area, it can be said that consumption of oysters grown at Chaiya oyster farms carry the highest health risk allowing for a consumption of only 2 and 1 oysters/meal/day for men and women, respectively, with regard to Cd while for Pb, a safe maximum of 83 and 70 oysters/meal/day was calculated for men and women, respectively. In contrast, consumption of oysters raised at Kradae oyster farms carried the lowest risk with a safe consumption of 2 and 2 oysters/meal/day for men and women respectively as shown in Table 33.

**Table 32:** Calculation results of safe weekly uptake of oysters (oysters/week)

Oyster culture station	Exposure time (months)	Average weight of oysters meat (g)	Concerning Cd*		Concerning Pb*	
			Men	Women	Men	Women
Oyster from Chaiya	at start	5.78	117	97	-	-
	3	13.29	39	33	-	-
	6	17.32	27	23	547	456
	9	22.41	12	10	233	194
Oyster from Kradae	at start	5.78	117	97	-	-
	3	19.62	30	25	-	-
	6	25.89	20	17	196	163
	9	30.02	16	13	158	132
Oyster from Tatong	at start	5.78	117	97	-	-
	3	18.73	27	22	-	-
	6	24.44	19	16	150	125
	9	28.85	14	12	96	80

Note: \*The unit is oysters/week

**Table 33:** Calculation results of safe daily uptake of oysters (oysters/meal/day)

Oyster culture stations	Exposure time (months)	Average weight of oysters meat (g)	Concerning Cd*		Concerning Pb*	
			Men	Women	Men	Women
Oyster from Chaiya	at start	5.78	17	14	-	-
	3	13.29	6	5	-	-
	6	17.32	4	3	281	235
	9	22.41	2	1	120	100
Oyster from Kradae	at start	5.78	17	14	-	-
	3	19.62	4	4	-	-
	6	25.89	3	2	101	84
	9	30.02	2	2	81	68
Oyster from Tatong	at start	5.78	17	14	-	-
	3	18.73	4	3	-	-
	6	24.44	3	2	77	64
	9	28.85	2	2	49	41

Note: \*The unit is oysters/meal/day

## 7. Economic Impact Evaluation

According to the statistical report on fishery by the Department of Fisheries of 2012, 4,804 tons of oysters were generated in Bandon Bay per year by oyster farms with a total farm area of 4,580 rai (7.328 km<sup>2</sup>) in Bandon Bay, Surat Thani province. This implied that there were some estimated 20,100,418 oysters from Bandon Bay delivered to the market, generating an annual income of 236,741,000 Baht, Department of Fisheries (2012). If heavy metals, especially Pb and Cd, accumulate in the oysters, this will impact the economy insofar as the chances of oysters farms in the area to sell their product will diminish. It was found that Pb and Cd accumulated in oysters raised in Bandon Bay, but the degree of accumulation of such heavy metals varied depending on the growth period and the culture location as mentioned before. The economic impact was evaluated considering the highest average values of Pb and Cd accumulation rates observed in this study and applying the contamination limits of the EC Standard (1.5, and 1.0 mg/kg wet weight for Pb and Cd respectively), based on the average oyster wet weight found in this study and the production rate as well as the market price obtained by the field survey in Bandon Bay. Table 34 presents the calculation results. These indicate that there were no problems in terms of Pb and Cd accumulation in oysters when cultured for 6 months (after use 6 months old oyster) (i.e. not exceeding the standard). Therefore, oysters raised for 6 months culture were acceptable to the market but could generate an income of about 180,063,000 Baht (due to lower size and price achievement). In contrast, if the oysters were rejected by the market due to exceeding the limit for Cd contamination the entire revenue of 236,837,200 Baht could be lost. Hence, it is recommended to consider selling the oysters after 6 months of cultivation to avoid a stronger heavy metal contamination. This may generate less income but maintain the opportunity to sell produce accepted by the market.

**Table 34:** Results of the evaluation of the economic impact of oyster contamination

Cultivation time (months)	Estimated Cd contained in oyster (mg/kg/individual)	Estimated Pb contained in oyster (mg/kg/ individual)	Price of oysters (kg)	Estimated weight of oyster harvest (tons)	Estimated income generated (Baht)
3	0.489	0.135	46.4	3,463	160,683,200
6	0.978	0.270	48.6	3,705	180,063,000
9	1.467*	0.405*	49.3	4,804	0** (236,837,200)
EC Standard	1.00	1.50			

Noted \* : > standard value

\* \*: rejected by the market

## 8. Recommendations for Measures to Control the Heavy Metal Contamination Problem in Bandon Bay

Heavy metal contamination in Bandon Bay is a complex matter and has accumulated continuously, illustrated by the example of Cd. This problem should be a serious concern for local planners and environmental experts, oyster farmer as well as stakeholder in the area. Without action, the problem will aggravate and become critical in the foreseeable future. Based on the results of the present study, some recommendations for measures are given to counter this problem as follows.

1) Continuous quality monitoring, in particular heavy metal contamination in the aquatic culture area in Bandon Bay should be implemented and provide information to the aquatic culture farmers in Bandon Bay. In addition, routine heavy metal contamination monitoring of oysters (biomonitoring) is recommended. The types of heavy metals to focus on should be Cd and Pb. The information obtained should be used for an effective surveillance of the Bandon Bay.

2) Zoning of aquatic cultures in Bandon Bay should be enforced more strongly, in particular separating cockle cultures from oyster culture areas. The

strategy to use this approach to implementation should also consider compensations when damage has occurred (whereby damages should be compensated only if a farm is in the determined zone). This could help reduce conflicts related to culturing activities, in particular harrowing which seriously affects seawater quality due to resuspension of particles from the sediment into the seawater column.

3) A comprehensive protocol for oyster cultivation defining specific areas and culture times should be recognized and implemented (for example, the oyster cultivation period should be less than 9 months). This approach would help reduce the impact of heavy metal contamination.

4) The study results indicated that there were about 10.4 and 47.1 tons of Cd and Pb discharging into Bandon Bay, respectively. The sources generating these amounts in the inland were non-point and point sources. Therefore, control of Pb and Cd discharges into Bandon Bay should be actively and strongly implemented. Non-point sources, in particular mining effluent/runoff and chemical fertilizer used in agricultural areas in the inland should be determined and controlled. Moreover, governmental organizations should use relating laws to strictly control the quality of effluent from domestic areas, industries and shrimp farms. Implementation of wastewater treatment, in particular for domestic wastewater from cities located along Bandon Bay should be a priority to address. This approach could reduce the heavy metal discharge from point sources into Bandon Bay.

5) More research on mechanisms/methods to remove heavy metals from sediment and reduce heavy metal accumulation in oysters, in particular concerning Pb and Cd, is recommended for further investigation. In addition, an appropriate technology to solve the heavy metal contamination in the area should be investigated. It is also recommended to deeply investigate the comparison of heavy metal phenomena in aquaculture area and non aquaculture area in Bandon Bay.

## CHAPTER 4

### CONCLUSION

The conclusions of this study are as follows. The results from secondary data estimation presented that the quantity of Cd, Cr, Pb, Cu, Mn and Zn discharging from inland to Bandon Bay were 10.4, 26.2, 47.1, 66, 156 and 423 ton per year, respectively as well as the determination of the point sources and non – point sources of heavy metals and amount estimated of them discharging from inland to Bandon Bay. The results presented that domestic wastewater must be emphasized since it is largest amount wastewater. The investigation from 7 points along the coastal area during 2011-2012 found that heavy metals concentration in seawater was lower than seawater quality for coastal aquaculture, except Fe and Cu. The average concentrations of heavy metals in sediments of Bandon Bay were lower than the standards of heavy metals in sediment of the Canadian Sediment Quality Guidelines for the Protection of Aquatic Life of Heavy Metal, except Cr and As.

The study implied that cockle harvesting in the bay was a significant impact to seawater quality. In addition, based on laboratory experiments investigation, it was observed that association of heavy metals between seawater and sediments was caused from adsorption and desorption reactions during mixing of resuspended particles from sediment in seawater and made changes of the heavy metal concentration in seawater. It was estimated that desorption rates of Cd were 0.103 and 0.122  $\mu\text{g/l}$  per hour, while the adsorption rate of Pb was 0.148  $\mu\text{g/l}$  per hour when sediment were mixed in seawater. In addition, the oysters grew at the farm in Kradae gave the highest growth comparing with the oysters grew in farms at Tatong and Chaiya. The accumulation rate of Cd in oysters were 0.103 - 0.280 mg/kg per month (wet weight), but for Pb were 0.03 -0.065 mg/kg per month (wet weight). Therefore, the accumulation rates of cadmium reflected that the oysters could be used as biological index providing the hazard contamination of Cd and Pb in the ecosystem in Bandon Bay ( use for Cd in better than Pb ). Moreover, it could reflect environmental quality background of Cd contamination in seawater the area. The

higher Cd accumulation rate in oyster was found, the higher Cd contaminated in seawater might be occurred.

Cd and Pb contamination and accumulation profiles in Bandon Bay were presented. It consisted of estimated load input of Cd and Pb to Bandon Bay at 10.4 ton and 47.1 ton, respectively. These amounts of Cd and Pb could be accumulated in seawater and sediment in Bandon Bay. However, the self pollution of heavy metals from sediment, particularly Cd could occur and affect the seawater quality. In the other hand, self purification of heavy metals influenced on sediment, especially Pb. Those were from the manmade activity to disturb sediment surface, especially cockle harvesting. The main mechanism of self pollution and purification of Cd and Pb in seawater ecosystem of Bandon Bay were from adsorption and desorption reactions. In addition, it was determined that removal of Cd and Pb from Bandon Bay via oyster harvesting used for human food were estimate to be 1.150 and 0.294 kg per year, respectively.

Ecological and health risk assessment for heavy metals pollution in Bandon Bay were simply determined. Ecological risk of heavy metals pollutants, focusing on Pb and Cd were estimated by using hazard quotients for risk. The risk study were done in 3 area included of Pb and Cd in seawater, sediment and in oyster accumulation. The results implied the there were risk in term of Cd and Pb contaminated in sediment and Cd contaminated in oyster. Based on the specific area concerned, it was found tht the area of Chaiya, Kradae and Tatong got risk, in particular Pb and Cd contaminated in sediment. These reflected that the area Chaiya Kradae and Tatong aere as hot spot for heavy metals pollution problem in Bandon Bay. For basic health risk analysis, it reflected that health risk might be occurred if no limit of oyster uptake. From the calculation, it was found that for Thai people, 1 person could uptake only 14 and 12 oyster/week for men and women, respectively when hazard of Cd were concerned, but for Pb were found to be 96 and 80 oysters/week for men and women respectively. In addition, it could say that for one meal consumption/day of oyster, it could say that 2 oyster could be taken without danger, based on the Joint FAO/WHO Food Standard criteria.



In term of economic impact, it was found that if do nothing, heavy metals contamination in oysters problem might give loss of 236,837,200 Baht per year due to market reject. However, the oysters were grown for 6 months with used 6 months old oyster to culture, the income might be received about 180,063,000 Baht per year.

Finally, recommendations for heavy metals contamination problem in Bandon Bay were addressed. Those were as follows;

- Sediment quality monitoring, in particular Cd and Pb contamination in the aquatic culture area in Bandon Bay, as well as use of oysters as biomonitoring for Cd and Pb contamination were recommended to implement.

- Zoning of aquatic culture in Bandon Bay should more strongly enforce in particular separately cockle culture and oysters.

- The good practice protocol for oyster cultivation considering with specific places and time for culture should be concerned with risk impact to agriculture.

- The generation sources of Pb and Cd from inland to Bandon Bay from non - point sources and point sources should be seriously controlled to limit the Pb and Cd discharge in effluent.

- More research dealing with mechanism/methods of heavy metals removed from sediment and reduction of heavy metals accumulation in oysters are recommended to further more investigation. In addition, the depth investigation with comparison of heavy metal phenomena in aquaculture and non-aquaculture areas in Bandon Bay is recommended to further study.

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## APPENDIX

**Table 1:** Results of seawater quality at Bandon Bay determined in 2011-2012.

Sampling points	Depth (m)	Chlorophyll a (µg/l)	Temperature (°C)	pH	Salinity (ppt)	DO (mg/l)	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)
11-Feb.-2011									
Oyster farm at Chaiya	0.50	1.94	30.30	7.77	25.00	5.75	16.2	4,196	2,133
Pumreang canal mouth	0.50	6.04	30.80	8.01	20.00	6.75	14.0	4,241	2,010
Tapi River mouth	4.00	1.76	27.20	7.27	8.00	4.65	35.6	2,033	1,386
Kradae canal mouth	2.50	3.93	27.60	7.75	15.00	5.23	26.0	5,054	1,559
Oyster farm at Kradae	1.50	9.16	28.20	7.42	15.00	5.68	36.8	3,230	1,453
Oyster farm at Tatong	3.50	8.46	28.10	7.64	10.00	6.25	19.2	2,174	1,498
Tatong canal mouth	2.00	7.95	28.10	7.61	15.00	5.18	18.6	4,040	1,978
24-Apr.-2011									
Oyster farm at Chaiya	1.20	0.62	26.8	8.10	23.00	6.40	75.8	9,696	5,795
Pumreang canal mouth	0.80	ND	27.2	8.10	20.00	5.78	94.4	10,705	2,583
Tapi River mouth	1.50	ND	30.0	7.66	5.00	4.23	225.0	19,482	8,274
Kradae canal mouth	0.80	ND	30.0	8.10	5.00	3.73	111.6	19,047	4,865
Oyster farm at Kradae	1.20	ND	31.5	8.34	8.00	4.68	78.2	19,576	6,990
Oyster farm at Tatong	3.00	ND	31.0	8.25	10.00	5.25	60.0	8,772	7,108
Tatong canal mouth	2.00	ND	29.5	8.14	15.00	5.15	92.6	17,508	3,548
8-Jun.-2011									
Oyster farm at Chaiya	1.80	1.69	30.8	7.69	25.00	6.03	30.8	9,175	1,324
Pumreang canal mouth	0.80	3.89	30.2	6.88	28.00	5.03	26.0	18,954	2,199
Tapi River mouth	1.20	2.37	29.0	7.33	8.00	4.38	49.2	4,124	546.0
Kradae canal mouth	1.50	5.91	29.0	7.55	20.00	4.33	61.8	8,242	422.0
Oyster farm at Kradae	0.80	4.75	27.0	7.23	20.00	4.73	73.0	8,744	382.0
Oyster farm at Tatong	3.00	1.44	28.0	7.14	18.00	5.30	3.20	7,639	237.0
Tatong canal mouth	1.50	3.15	27.0	6.74	20.00	4.03	36.6	12,881	717.0
2-Aug.-2011									
Oyster farm at Chaiya	2.50	2.01	26.7	7.69	20.00	6.03	34.6	9,010	1,991
Pumreang canal mouth	0.80	1.01	27.2	6.88	20.00	5.03	27.2	14,047	2,114
Tapi River mouth	1.50	4.26	28.3	7.33	0.00	4.38	33.8	2,049	782.0
Kradae canal mouth	1.60	4.42	27.3	7.55	8.00	4.33	62.8	9,054	1,407
Oyster farm at Kradae	0.50	6.17	27.6	7.23	10.00	4.73	40.2	13,169	1,382
Oyster farm at Tatong	3.00	2.91	28.6	7.14	12.00	5.30	25.4	10,175	2,117
Tatong canal mouth	1.00	4.91	28.0	6.74	12.00	4.23	31.0	18,090	1,392

**Table 1:** Results of seawater quality at Bandon Bay determined in 2011-2012. (CONT.)

Sampling points	Depth (m)	Chlorophyll a ( $\mu\text{g/l}$ )	Temperature ( $^{\circ}\text{C}$ )	pH	Salinity (ppt)	DO (mg/l)	SS (mg/l)	TDS (mg/l)	TDVS (mg/l)
15-Oct.-2011									
Oyster farm at Chaiya	2.50	2.01	29.7	7.69	20.00	6.03	31.00	14,210	1,998
Pumreang canal mouth	0.60	1.01	29.2	6.88	20.00	5.03	21.20	12,515	2,499
Tapi River mouth	1.20	6.29	26.9	7.33	2.00	4.38	51.40	3,656	1,103
Kradae canal mouth	1.00	5.40	27.0	7.55	5.00	4.33	87.80	11,901	1,481
Oyster farm at Kradae	0.80	9.96	26.7	7.23	10.00	4.73	77.40	15,806	1,470
Oyster farm at Tatong	1.80	3.25	28.1	7.14	12.00	5.30	36.40	10,238	1,926
Tatong canal mouth	2.50	5.05	27.7	6.74	15.00	4.23	30.00	13,824	2,059
25-Jan.-2012									
Oyster farm at Chaiya	1.80	3.57	28.0	7.35	12.00	5.60	27.80	13,162	1,433
Pumreang canal mouth	2.50	4.47	27.0	7.73	15.00	5.50	21.20	12,093	1,103
Tapi River mouth	0.50	5.04	31.8	8.10	20.00	6.20	52.20	3,850	668.0
Kradae canal mouth	0.80	9.63	31.2	7.89	20.00	5.20	70.80	11,149	1,054
Oyster farm at Kradae	1.50	9.49	30.5	7.40	5.00	5.50	39.40	12,010	1,055
Oyster farm at Tatong	1.20	3.81	29.0	8.16	5.00	5.50	40.40	11,939	1,077
Tatong canal mouth	0.80	8.48	28.0	8.12	12.00	5.50	29.60	12,999	1,419



**Table 2:** Heavy metal (dissolved) concentrations in seawater at Bandon Bay as determined in 2011-2012.

Sampling points	Fe (µg/l)	Mn (µg/l)	Cu (µg/l)	Ni (µg/l)	Zn (µg/l)	Cd (µg/l)	Cr (µg/l)	Pb (µg/l)	As (µg/l)	Hg (µg/l)
11-Feb.-2011										
Oyster farm at Chaiya	566.67	3.00	6.00	0.33	31.07	0.50	ND	ND	ND	0.015
Pumreang canal mouth	818.50	5.00	11.17	0.33	19.83	0.67	ND	ND	ND	0.015
Tapi River mouth	528.00	4.00	10.00	0.83	28.17	0.50	ND	ND	ND	0.013
Kradae canal mouth	816.33	4.00	8.33	0.50	30.83	0.67	0.50	ND	ND	0.015
Oyster farm at Kradae	257.33	4.00	6.50	0.83	40.67	0.83	0.67	ND	ND	0.015
Oyster farm at Tatong	245.17	2.50	9.83	0.50	28.83	0.50	0.33	ND	ND	0.018
Tatong canal mouth	258.00	3.00	11.50	0.50	11.00	0.20	ND	ND	ND	0.016
24-Apr.-2011										
Oyster farm at Chaiya	567.50	4.00	6.50	0.50	19.17	0.50	ND	ND	ND	ND
Pumreang canal mouth	598.83	5.00	7.17	0.50	37.67	1.33	ND	ND	ND	ND
Tapi River mouth	159.67	4.00	6.67	0.50	98.33	0.83	ND	ND	ND	0.420
Kradae canal mouth	120.67	3.33	5.17	0.83	23.67	0.83	ND	ND	ND	ND
Oyster farm at Kradae	108.50	3.50	4.33	0.83	16.50	1.00	0.67	ND	ND	0.015
Oyster farm at Tatong	126.00	4.66	6.83	0.67	25.33	0.83	0.33	ND	ND	0.031
Tatong canal mouth	105.17	3.00	4.50	0.50	21.67	0.20	ND	ND	ND	0.003
8-Jun.-2011										
Oyster farm at Chaiya	442.77	4.00	5.50	0.33	48.67	1.00	ND	ND	ND	ND
Pumreang canal mouth	426.33	5.00	6.17	0.33	28.17	0.50	ND	ND	ND	ND
Tapi River mouth	487.83	2.50	7.67	0.50	77.83	0.50	ND	ND	ND	ND
Kradae canal mouth	129.83	3.33	6.17	0.50	42.83	1.00	ND	ND	ND	0.003
Oyster farm at Kradae	113.00	3.50	6.67	1.00	56.33	0.83	ND	ND	ND	0.002
Oyster farm at Tatong	216.83	4.67	6.83	1.00	35.50	0.67	ND	ND	ND	0.004
Tatong canal mouth	426.33	3.00	9.50	0.50	32.33	0.50	ND	ND	ND	0.002

**Table 2:** Heavy metal (dissolved) concentrations in seawater at Bandon Bay as determined in 2011-2012. (CONT.)

Sampling points	Fe (µg/l)	Mn (µg/l)	Cu (µg/l)	Ni (µg/l)	Zn (µg/l)	Cd (µg/l)	Cr (µg/l)	Pb (µg/l)	As (µg/l)	Hg (µg/l)
2-Aug.-2011										
Oyster farm at Chaiya	782.63	4.00	8.83	0.27	20.75	3.83	0.17	ND	ND	ND
Pumreang canal mouth	723.17	4.30	11.57	0.25	29.30	2.58	0.17	ND	ND	ND
Tapi River mouth	238.13	4.00	5.67	0.43	43.48	0.50	0.15	ND	ND	ND
Kradae canal mouth	354.58	3.33	5.33	0.42	37.50	0.58	0.35	0.35	ND	ND
Oyster farm at Kradae	454.60	3.50	7.08	0.25	27.57	0.48	0.16	ND	ND	ND
Oyster farm at Tatong	246.82	4.67	8.33	0.25	24.37	0.91	0.16	ND	ND	ND
Tatong canal mouth	266.87	3.00	10.80	0.23	23.68	0.22	0.20	ND	ND	ND
15-Oct.-2011										
Oyster farm at Chaiya	246.82	5.00	8.83	0.25	20.75	1.98	0.17	ND	ND	ND
Pumreang canal mouth	258.47	0.87	11.57	0.30	24.30	1.17	ND	ND	ND	ND
Tapi River mouth	159.69	6.17	10.67	0.58	40.15	0.75	ND	ND	ND	ND
Kradae canal mouth	1054.70	3.83	7.53	0.42	24.17	1.17	0.27	0.23	ND	ND
Oyster farm at Kradae	238.13	4.17	8.72	0.32	25.72	1.74	0.20	ND	ND	ND
Oyster farm at Tatong	750.83	3.17	12.67	0.35	23.45	0.74	0.42	ND	ND	ND
Tatong canal mouth	454.60	4.00	13.38	0.28	22.52	0.21	0.25	ND	ND	ND
25-Jan.-2012										
Oyster farm at Chaiya	1338.83	2.70	13.17	0.25	20.75	1.83	0.20	ND	ND	ND
Pumreang canal mouth	268.40	1.22	9.13	0.30	19.80	0.98	ND	ND	ND	ND
Tapi River mouth	1203.50	2.62	11.67	0.33	44.17	0.33	ND	ND	0.67	0.003
Kradae canal mouth	1094.00	3.83	11.28	0.28	23.50	1.00	ND	0.25	0.83	ND
Oyster farm at Kradae	892.17	2.45	12.67	0.32	27.57	1.00	0.30	ND	ND	ND
Oyster farm at Tatong	1475.50	3.32	12.33	0.33	24.37	1.50	ND	ND	ND	ND
Tatong canal mouth	1425.33	3.90	13.50	0.31	23.68	1.00	0.20	ND	ND	ND

**Table 3:** Heavy metal (total) concentrations in seawater at Bandon Bay as determined in 2011-2012.

Sampling points	Fe (µg/l)	Mn (µg/l)	Cu (µg/l)	Ni (µg/l)	Zn (µg/l)	Cd (µg/l)	Cr (µg/l)	Pb (µg/l)	As (µg/l)	Hg (µg/l)
11-Feb.-2011										
Oyster farm at Chaiya	2011.2	5.00	7.50	0.33	45.00	0.83	0.50	ND	ND	0.022
Pumreang canal mouth	1008.0	5.00	25.33	0.67	36.50	0.67	0.50	1.92	ND	0.018
Tapi River mouth	668.67	4.67	23.33	1.00	63.00	0.67	1.00	0.50	ND	0.014
Kradae canal mouth	3033.67	5.00	11.17	1.17	38.17	1.17	0.50	5.50	ND	0.017
Oyster farm at Kradae	2059.83	7.50	9.67	1.00	65.67	1.00	1.00	4.67	ND	0.018
Oyster farm at Tatong	904.33	5.00	20.00	0.67	38.67	0.67	0.67	0.67	ND	0.019
Tatong canal mouth	2113.33	7.00	24.50	0.67	16.83	0.67	0.50	1.28	ND	0.025
24-Apr.-2011										
Oyster farm at Chaiya	707.33	5.00	10.00	0.67	40.00	0.50	0.33	ND	ND	0.019
Pumreang canal mouth	960.00	8.00	19.83	0.67	48.50	1.50	ND	1.23	ND	0.004
Tapi River mouth	2128.33	5.33	14.50	0.50	102.83	0.83	0.50	1.97	ND	0.544
Kradae canal mouth	1803.67	4.50	6.67	1.33	23.67	1.17	ND	1.17	ND	ND
Oyster farm at Kradae	1120.33	8.83	5.50	0.83	16.50	1.33	0.83	1.83	ND	0.015
Oyster farm at Tatong	1095.67	5.50	19.67	1.17	27.00	1.50	0.33	2.67	ND	0.032
Tatong canal mouth	1580.00	5.00	18.67	1.33	31.50	0.50	ND	1.83	ND	0.006
8-Jun.-2011										
Oyster farm at Chaiya	840.83	5.00	12.50	0.50	62.00	1.17	ND	ND	ND	0.002
Pumreang canal mouth	630.83	5.00	19.67	0.50	51.83	0.50	ND	2.13	ND	0.003
Tapi River mouth	508.00	3.67	25.00	0.50	112.33	0.50	ND	0.50	ND	0.002
Kradae canal mouth	543.50	5.00	14.00	1.33	49.67	1.50	ND	5.17	ND	0.004
Oyster farm at Kradae	1031.00	7.50	13.17	1.23	63.17	0.83	0.83	5.33	ND	0.002
Oyster farm at Tatong	462.33	5.00	15.00	1.17	49.50	0.83	ND	0.67	ND	0.004
Tatong canal mouth	1722.33	7.00	14.50	1.33	47.00	1.00	ND	0.78	ND	0.003

**Table 3:** Heavy metal (total) concentrations in seawater at Bandon Bay as determined in 2011-2012. (CONT.)

Sampling points	Fe (µg/l)	Mn (µg/l)	Cu (µg/l)	Ni (µg/l)	Zn (µg/l)	Cd (µg/l)	Cr (µg/l)	Pb (µg/l)	As (µg/l)	Hg (µg/l)
2-Aug.-2011										
Oyster farm at Chaiya	1417.92	5.00	13.93	0.27	45.18	4.17	0.37	0.63	ND	ND
Pumreang canal mouth	1054.70	5.00	24.10	0.27	36.57	3.23	0.35	0.48	ND	ND
Tapi River mouth	581.46	4.33	24.02	0.52	91.18	0.68	0.37	0.48	1.5	0.002
Kradae canal mouth	750.83	4.50	13.95	0.42	42.33	1.33	0.35	3.83	ND	0.043
Oyster farm at Kradae	522.83	8.33	13.40	0.28	35.72	0.98	0.20	4.17	ND	ND
Oyster farm at Tatong	2087.08	5.00	19.70	0.35	35.75	0.92	0.25	0.70	ND	ND
Tatong canal mouth	1520.83	5.00	25.88	0.23	47.18	1.27	0.20	0.75	ND	ND
15-Oct.-2011										
Oyster farm at Chaiya	567.17	6.17	14.43	0.27	24.18	2.80	0.18	0.57	ND	ND
Pumreang canal mouth	289.27	4.37	19.10	0.17	33.23	1.43	ND	0.47	ND	ND
Tapi River mouth	232.58	7.50	22.32	0.75	82.85	0.88	0.27	0.42	ND	0.003
Kradae canal mouth	1141.83	5.83	8.95	0.45	37.33	1.28	0.40	4.17	ND	ND
Oyster farm at Kradae	245.83	4.50	13.07	0.25	27.57	2.73	0.40	3.17	ND	ND
Oyster farm at Tatong	834.83	5.17	17.70	0.35	24.37	0.93	0.55	0.57	ND	ND
Tatong canal mouth	608.33	6.17	20.88	0.32	23.68	1.77	0.53	0.62	ND	ND
25-Jan.-2012										
Oyster farm at Chaiya	1838.8	5.17	10.17	0.53	25.77	2.67	ND	0.37	ND	ND
Pumreang canal mouth	301.7	2.13	18.00	0.75	37.08	1.13	ND	0.45	ND	ND
Tapi River mouth	1703.5	3.17	18.00	0.62	83.00	0.50	0.30	0.47	1.67	0.039
Kradae canal mouth	1594.0	4.57	16.00	0.27	31.67	1.00	ND	3.25	2.00	ND
Oyster farm at Kradae	1392.2	3.92	17.00	0.25	42.67	1.50	ND	4.00	2.17	ND
Oyster farm at Tatong	1992.2	5.17	23.17	0.55	32.33	1.67	0.25	0.43	2.33	ND
Tatong canal mouth	1925.3	6.17	25.33	0.73	37.00	1.00	0.20	1.07	ND	ND

**Table 4:** Heavy metal concentrations in sediments of Bandon Bay during 2011-2012.

Sampling points	Fe (%) dry weight	Mn (mg/kg) dry weight	Cu (mg/kg) dry weight	Ni (mg/kg) dry weight	Zn (mg/kg) dry weight	Cd (mg/kg) dry weight	Cr (mg/kg) dry weight	Pb (mg/kg) dry weight	As (mg/kg) dry weight	Hg (mg/kg) dry weight
11-Feb.-2011										
Oyster farm at Chaiya	0.85	261.09	2.02	ND	13.46	0.30	19.74	10.33	7.05	0.04
Pumreang canal mouth	0.71	395.01	4.37	ND	35.11	0.30	11.23	11.16	5.82	0.02
Tapi River mouth	2.73	406.00	10.48	3.08	43.14	0.66	17.92	9.56	24.30	0.17
Kradae canal mouth	2.69	674.99	17.52	5.74	55.29	1.46	24.19	14.73	90.88	0.12
Oyster farm at Kradae	2.54	620.98	13.24	8.54	38.96	1.22	28.56	11.85	97.81	0.10
Oyster farm at Tatong	2.55	691.86	12.49	14.45	49.38	0.50	26.69	13.71	46.51	0.32
Tatong canal mouth	2.19	578.65	9.24	4.90	34.12	0.50	22.22	11.39	16.42	0.12
24-Apr.-2011										
Oyster farm at Chaiya	0.96	265.51	7.73	55.03	15.61	0.90	341.00	13.36	5.77	0.04
Pumreang canal mouth	1.11	653.79	12.13	77.86	31.24	1.00	114.43	17.63	10.77	0.02
Tapi River mouth	1.94	452.45	8.09	164.2	37.36	1.09	172.70	8.79	12.72	0.20
Kradae canal mouth	2.50	388.92	24.10	121.5	36.52	2.24	212.13	12.51	50.10	0.11
Oyster farm at Kradae	2.71	693.53	24.77	27.23	68.48	2.91	59.40	33.93	71.50	0.10
Oyster farm at Tatong	2.59	741.76	14.90	32.80	47.18	1.23	86.10	20.06	16.77	0.22
Tatong canal mouth	1.13	811.53	16.70	24.70	55.18	1.25	63.10	33.90	20.03	0.15
8-Jun.-2011										
Oyster farm at Chaiya	0.56	209.59	4.53	7.08	16.62	1.64	32.09	13.17	8.37	0.03
Pumreang canal mouth	0.38	305.23	13.26	6.48	20.31	1.89	19.27	12.00	7.41	0.03
Tapi River mouth	1.97	303.37	7.99	17.18	51.81	1.67	23.08	16.32	24.28	0.18
Kradae canal mouth	2.99	663.34	16.53	11.55	47.67	2.52	25.12	22.09	73.70	0.15
Oyster farm at Kradae	1.69	538.47	23.09	15.05	35.65	2.08	33.22	21.38	56.17	0.10
Oyster farm at Tatong	3.02	753.81	9.62	22.52	44.03	1.41	27.73	19.57	19.93	0.17
Tatong canal mouth	1.63	464.89	23.37	12.60	23.58	1.76	20.62	15.25	16.45	0.11

**Table 4:** Heavy metal concentrations in sediments of Bandon Bay during 2011-2012.

(CONT.)

Sampling points	Fe (%) dry weight	Mn (mg/kg) dry weight	Cu (mg/kg) dry weight	Ni (mg/kg) dry weight	Zn (mg/kg) dry weight	Cd (mg/kg) dry weight	Cr (mg/kg) dry weight	Pb (mg/kg) dry weight	As (mg/kg) dry weight	Hg (mg/kg) dry weight
2-Aug.-2011										
Oyster farm at Chaiya	0.67	117.7	1.70	2.37	11.24	1.16	32.43	11.11	5.70	0.01
Pumreang canal mouth	0.88	389.6	6.86	ND	12.66	1.44	19.10	5.75	5.23	0.02
Tapi River mouth	2.32	423.6	8.32	10.11	28.64	1.34	28.94	14.69	22.65	0.09
Kradae canal mouth	2.80	477.2	12.39	6.48	26.80	2.47	25.90	10.72	62.34	0.09
Oyster farm at Kradae	1.69	588.5	19.94	15.29	30.36	2.33	32.24	18.29	66.28	0.04
Oyster farm at Tatong	2.46	638.4	4.91	21.38	26.12	1.43	29.25	10.69	16.10	0.09
Tatong canal mouth	1.72	536.1	17.45	8.02	14.62	1.75	31.75	8.05	18.87	0.05
15-Oct.-2011										
Oyster farm at Chaiya	0.85	159.53	ND	4.07	10.76	1.48	30.54	7.42	3.30	0.03
Pumreang canal mouth	0.78	329.64	6.14	ND	14.38	1.57	25.70	9.25	1.92	0.03
Tapi River mouth	1.63	579.90	9.43	9.28	34.96	1.43	26.52	11.16	27.25	0.08
Kradae canal mouth	2.61	605.17	10.46	8.93	35.52	2.56	21.17	10.68	47.00	0.09
Oyster farm at Kradae	2.18	587.96	17.78	10.71	39.62	2.37	31.74	17.11	59.57	0.05
Oyster farm at Tatong	2.45	590.70	7.42	18.83	48.60	1.41	27.25	14.16	13.75	0.11
Tatong canal mouth	1.63	397.77	18.07	8.12	28.49	1.67	31.49	8.10	10.51	0.06
25-Jan.-2012										
Oyster farm at Chaiya	0.63	139.17	4.40	ND	9.57	0.61	18.06	9.24	4.88	0.08
Pumreang canal mouth	0.53	242.88	8.36	ND	12.40	0.60	11.24	8.45	1.59	0.10
Tapi River mouth	1.63	327.20	14.08	6.68	26.07	0.89	21.67	19.45	25.83	0.09
Kradae canal mouth	2.82	438.88	11.81	5.52	33.47	1.40	24.28	18.20	42.33	0.12
Oyster farm at Kradae	2.01	532.80	13.22	8.26	45.47	1.49	22.78	18.36	47.21	0.10
Oyster farm at Tatong	2.48	634.21	11.52	15.52	46.51	1.03	27.89	19.00	17.64	0.12
Tatong canal mouth	1.97	558.75	9.95	8.05	41.74	0.84	21.95	17.37	11.10	0.08

**Table 5:** Heavy metal concentrations in oysters exposed to 3 farms in Bandon Bay.

Sampling points	Exposure time (months)	Cadmium (mg/kg)						Lead (mg/kg)					
		Dry weight			wet weight			Dry weight			wet weight		
Oyster farm at Chaiya	at start	4.07	4.18	4.07	0.69	0.73	0.72	ND	ND	ND	ND	ND	ND
	3	6.56	6.41	6.73	0.92	0.91	0.94	ND	ND	ND	ND	ND	ND
	6	7.73	7.59	7.58	1.03	1.01	1.01	0.35	0.40	0.40	0.05	0.05	0.05
	9	8.01	7.95	7.88	1.66	1.56	1.63	0.45	0.40	0.40	0.09	0.08	0.08
Oyster farming at Kradae	at start	4.07	4.18	4.07	0.69	0.73	0.72	ND	ND	ND	ND	ND	ND
	3	5.28	5.35	5.33	0.82	0.82	0.82	ND	ND	ND	ND	ND	ND
	6	6.30	6.25	6.37	0.91	0.94	0.95	0.69	0.59	0.64	0.10	0.09	0.10
	9	6.61	6.62	6.68	1.02	1.02	1.02	0.65	0.69	0.65	0.10	0.11	0.10
Oyster farming at Tatong	at start	4.07	4.18	4.07	0.69	0.73	0.72	ND	ND	ND	ND	ND	ND
	3	5.88	5.90	5.87	0.95	0.96	0.95	ND	ND	ND	ND	ND	ND
	6	6.61	6.61	6.59	1.02	1.03	1.04	0.89	0.79	0.85	0.14	0.12	0.13
	9	6.86	6.97	6.94	1.16	1.18	1.18	0.94	1.05	1.10	0.16	0.18	0.19