TOTAL PETROLEUM HYDROCARBON (TPH) IN SEAWATER, SEDIMENT, PLANKTON AND OYSTERS AT ANG SILA COAST, CHONBURI PROVINCE

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TOTAL PETROLEUM HYDROCARBON (TPH) IN SEAWATER, SEDIMENT, PLANKTON AND OYSTER AT ANG SILA COAST, CHONBURI PROVICE

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ABSTRACT

This research was conducted to investigate the level of total petroleum hydrocarbon (TPH) and the effect of seasonal variation on its distribution pattern during the wet season (September, 2006 and August, 2007) and the dry season (November, 2006 and May, 2007) in seawater, sediment, plankton and oyster. The levels of TPH in all samples were determined by gas chromatography mass spectrometry.

The results indicated that TPH concentrations were highest in sediment (0-8.50 µg/g) followed by plankton (0.07- 4.05 µg/g) oyster (0 – 3.94 µg/g) and seawater (0-87.95 µg/l). The major type of petroleum hydrocarbon in samples was n-alkanes ranging from $C_{14} – C_{34}$. The effect of seasonal variation on the levels of TPH showed that TPH concentrations in seawater in the dry season were significantly higher than in the wet season. On the other hand TPH concentrations in sediment and plankton in the wet season were significantly higher than in the dry season. However, the season was not effected on TPH accumulation in oysters. Investigation of polycyclic aromatic hydrocarbons (PAHs) (i.e.; phenanthrene, pyrene and benzo[a]pyrene) compounds in seawater, sediment, plankton and oysters found no traces. Relationship of TPH concentration in all samples showed that the correlation coefficient (r) of TPH concentration in most samples was poorly positive (r =0.078-0.595) except the correlation coefficient (r) obtained from seawater and sediment in November 2006 and May 2007 and sediment and oysters in May 2007 were highly positive (r = 0.584-0.902) at the level of 0.05.

Data on TPH in the marine environment is needed because they pose a risk to human and marine organisms. Therefore, the results obtained from this study contribute to the database for Ang Sila coast, Chonburi province.

KEY WORDS: PETROLEUM HYDROCARBON/ ANG SILA COAST/ ACCUMULATION/
MARINE POLLUTION/ GAS CHROMATOGRAPHY MASS SPECTROMETRY

107 pp.

สารปิโตรเลียมไฮโดรคาร์บอนรวมในน้ำทะเล ตะกอนดิน แพลงก์ตอน และหอยนางรม บริเวณชายฝั่งอ่างศิลา จังหวัดชลบุรี (TOTAL PETROLEUM HYDROCARBON (TPH) IN SEAWATER, SEDIMENT, PLANKTON AND OYSTER AT ANG SILA COAST, CHONBURI PROVICE)

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บทคัดย่อ

งานวิจัยครั้งนี้มีวัตถุประสงค์เพื่อศึกษาปริมาณของสารปิโตรเลียมไฮโดรคาร์บอนรวม และปัจจัยของฤดูกาลระหว่างฤดูน้ำมาก (เดือนกันยายน พ.ศ. 2549 และเดือนสิงหาคม พ.ศ. 2550) กับฤดูน้ำน้อย (เดือนพฤศจิกายน พ.ศ. 2549 และเดือนพฤษภาคม พ.ศ. 2550) ที่มีผลต่อปริมาณการสะสม ในตัวอย่าง น้ำทะเล ดินตะกอน แพลงก์ตอน และหอยนางรม โดยวิเคราะห์หาปริมาณสารปิโตรเลียมไฮโดรคาร์บอนรวมในตัวอย่างทั้งหมดโดยใช้แกสโครมาโตกราฟ แมสสเปกโตรเมตรี

ผลการศึกษาพบว่า ปริมาณสารปิโตรเลียมไฮโดรคาร์บอนรวมพบมากที่สุดในดินตะกอน (0-8.50 ไมโครกรัมต่อกรัม) รองลงมาคือ แพลงก์ตอน (0.07- 4.05 ไมโครกรัมต่อกรัม) หอยนางรม (0-3.94 ไมโครกรัมต่อกรัม) และ น้ำทะเล (0-87.95 ไมโครกรัมต่อลิตร) ตามลำดับ สารนอร์มัลเคนที่พบส่วนใหญ่อยู่ระหว่าง $C_{14} – C_{34}$ สำหรับปัจจัยของฤดูกาลพบว่าในตัวอย่างน้ำทะเลในฤดูน้ำน้อยมีปริมาณสารปิโตรเลียมไฮโดรคาร์บอนรวมสูงกว่าในฤดูน้ำมาก ในตัวอย่างดินตะกอนและแพลงก์ตอนพบว่าในฤดูน้ำมากมีปริมาณสูงกว่าในฤดูน้ำน้อย ในขณะที่ตัวอย่างหอยนางรมพบว่าฤดูกาลไม่มีอิทธิพลต่อการสะสมของสารปิโตรเลียมไฮโดรคาร์บอนรวม สำหรับสารโพลิไซคลิกอะโรมาติกไฮโดรคาร์บอน ได้แก่ ฟีแนนทรีน ไพรีน และเบนโซเอไพรีน ไม่พบในตัวอย่างที่ทำการศึกษา ความสัมพันธ์ของปริมาณสารปิโตรเลียมไฮโดรคาร์บอนรวมระหว่างตัวอย่างทั้งหมดพบว่า ส่วนใหญ่มีค่าของสัมประสิทธิ์สหสัมพันธ์ (r) ในเชิงบวกค่อนข้างน้อย (r = 0.078-0.595) ยกเว้นความสัมพันธ์ระหว่างสารปิโตรเลียมไฮโดรคาร์บอนรวมในน้ำทะเลกับดินตะกอนในเดือนพฤศจิกายน พ.ศ. 2549 และเดือนพฤษภาคม พ.ศ. 2550 และ ระหว่างดินตะกอนกับหอยนางรมในเดือนพฤษภาคม พ.ศ. 2550 มีค่าสัมประสิทธิ์สหสัมพันธ์ (r)ในเชิงบวกที่สูงกว่า (r = 0.584-0.902) ที่ระดับนัยสำคัญ 0.05

ข้อมูลของสารปิโตรเลียมไฮโดรคาร์บอนในสิ่งแวดล้อมทางทะเลนั้นเป็นสิ่งจำเป็นต่อมนุษย์และสิ่งมีชีวิตในทะเลในด้านความเสี่ยงอันตราย ซึ่งข้อมูลที่ได้จากการศึกษาครั้งนี้จะเป็นข้อมูลพื้นฐานของพื้นที่ชายฝั่งอ่งศิลา จังหวัดชลบุรี

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CHAPTER I
INTRODUCTION

1.1 Statement of the problem

Petroleum consists of crude oils and a wide variety of refined-oil products that the elemental composition varies over a narrow range: 82-87% carbon, 12-15% hydrogen, the balance being oxygen, nitrogen, and sulfur (1). Pollution of the sea by petroleum hydrocarbons arises from multiple sources, notably spill from oil tanker, discharges during marine transportation, leakages from drilling discharges, urban and river runoff, atmospheric deposition, and natural seeps (2, 3). Out of these, about 65.2% is discharged of municipal and industrial wastes, urban and river runoffs, oceanic dumping and atmospheric fallout; 26.2% derives from discharges related to transportation (e.g., dry docking, tanker accidents, de-blasting) and remaining 8.5% comes from fixed installations (e.g., coastal refineries, offshore production facilities, marine terminals) (4).

Petroleum hydrocarbons as important component organic input have received much attention because most of them are toxic, mutagenic and carcinogenic. In aquatic environment, due to then low water solubility and hydrophobic properties, hydrocarbons are commonly found to be transported to the sediment and biota (5, 6, 7). Petroleum can adversely affect living organisms by physical (smothering, reduced light), habitat (altered pH, decreased dissolved oxygen and decreased food availability) and toxic actions (8). Moreover, petroleum hydrocarbons can impact on human use by reducing economic and recreational values on either a short- or long-term basis and by changes of esthetics of the marine environment (9).

Ang Sila coast, Chonburi province located on the Eastern part of Gulf of Thailand. This area has fishery, fishing ports, mariculture (i.e.; Oyster (*Saccostrea cucullata*) and Asian Brown Mussel (*Perna viridis*)), seafood restaurants and seafood market. Many fishing boats stop at fishing ports around Ang Sila coast. Most of activities become major sources of petroleum hydrocarbons released to the marine environment. Bivalves especially oyster is a major commercial species in Ang Sila coast. It has a high potential to uptake petroleum hydrocarbons from water, sediment and food because of its characteristics; sessile, filter feeding and low metabolism organisms.

Ang Sila coast is important to fishery, mariculture and tourism and activities carried out within this area lead to oil pollution. In order to prevent and protect our marine resources from these activities, oil pollution must be controlled. This study was performed to investigate the level of petroleum hydrocarbons in seawater as well as accumulation in marine sediment and coastal organisms including seasonal variation for petroleum hydrocarbon level in marine environment and biota. The data on contamination level of total petroleum hydrocarbons in biota is needed because they pose a risk to human consumption. Therefore, the results obtained from this study contribute to the regional database for Ang Sila coast.

1.2 Objectives of the study

1. To study the level of total petroleum hydrocarbon (TPH) in seawater, sediment, plankton and oyster at Ang Sila coast, Chonburi province.
2. To investigate the seasonal variation of the distribution pattern of TPH in marine environment.

1.3 Scope of the study

1. All samples (i.e.; seawater, sediment, plankton, oyster) were collected from Ang Sila coast, Chonburi province. There are three fishing port sites (i.e., Wat Komut Ratthanaram, Ban Ang Sila and Ta Hoi). The sampling sites were designed based on the distance from fishing ports (e.g., 25 m, 500 m and 1000 m far from the fishing port) as well as the existing activities (See the detailed in Figure 3.1 in Chapter III).
2. Sampling periods were carried out four times: the wet season (September, 2006 and August, 2007) and the dry season (November, 2006 and May, 2007).

1.4 Research diagram

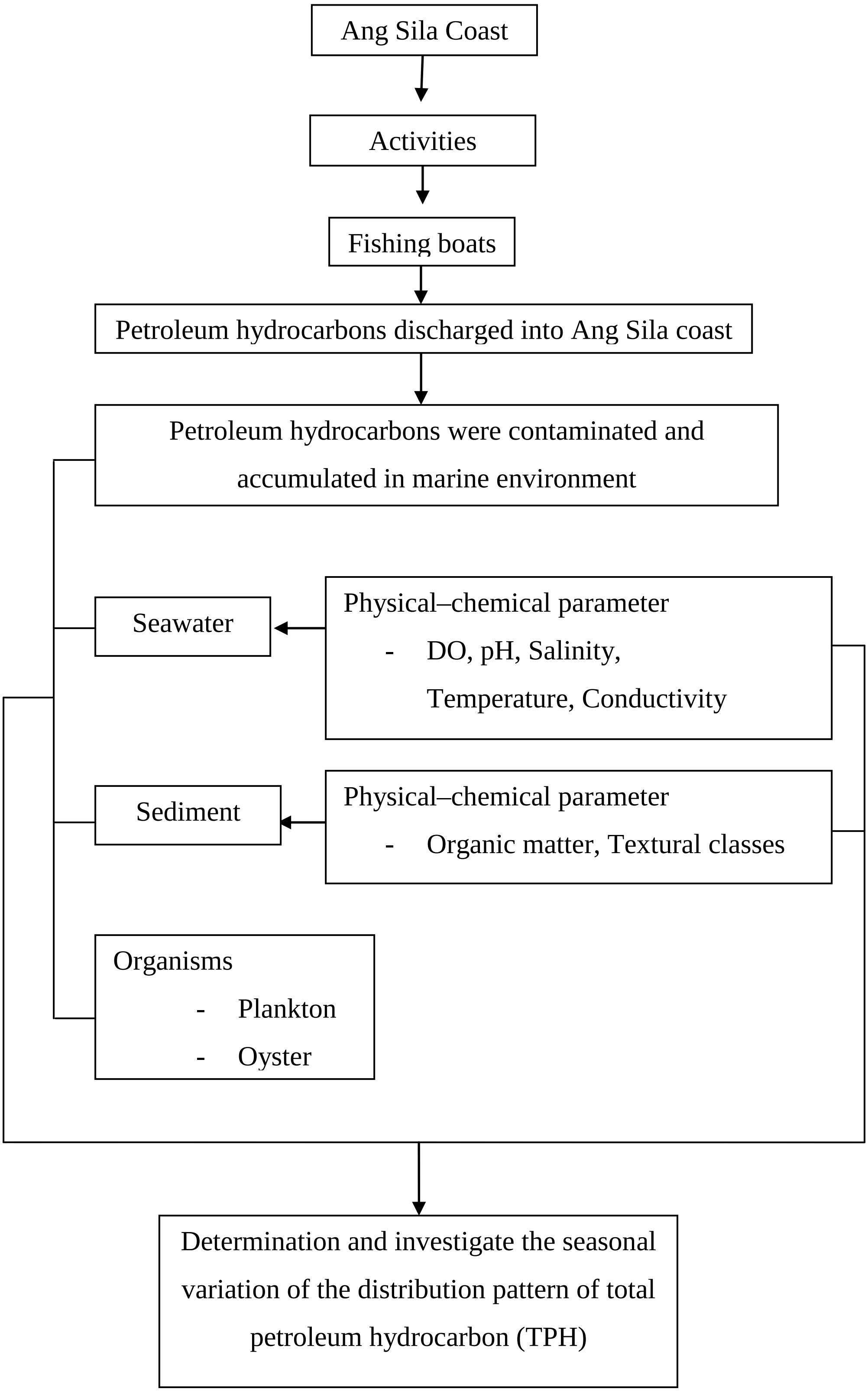

Figure 1-1 Research Diagram

1.5 Conceptual framework

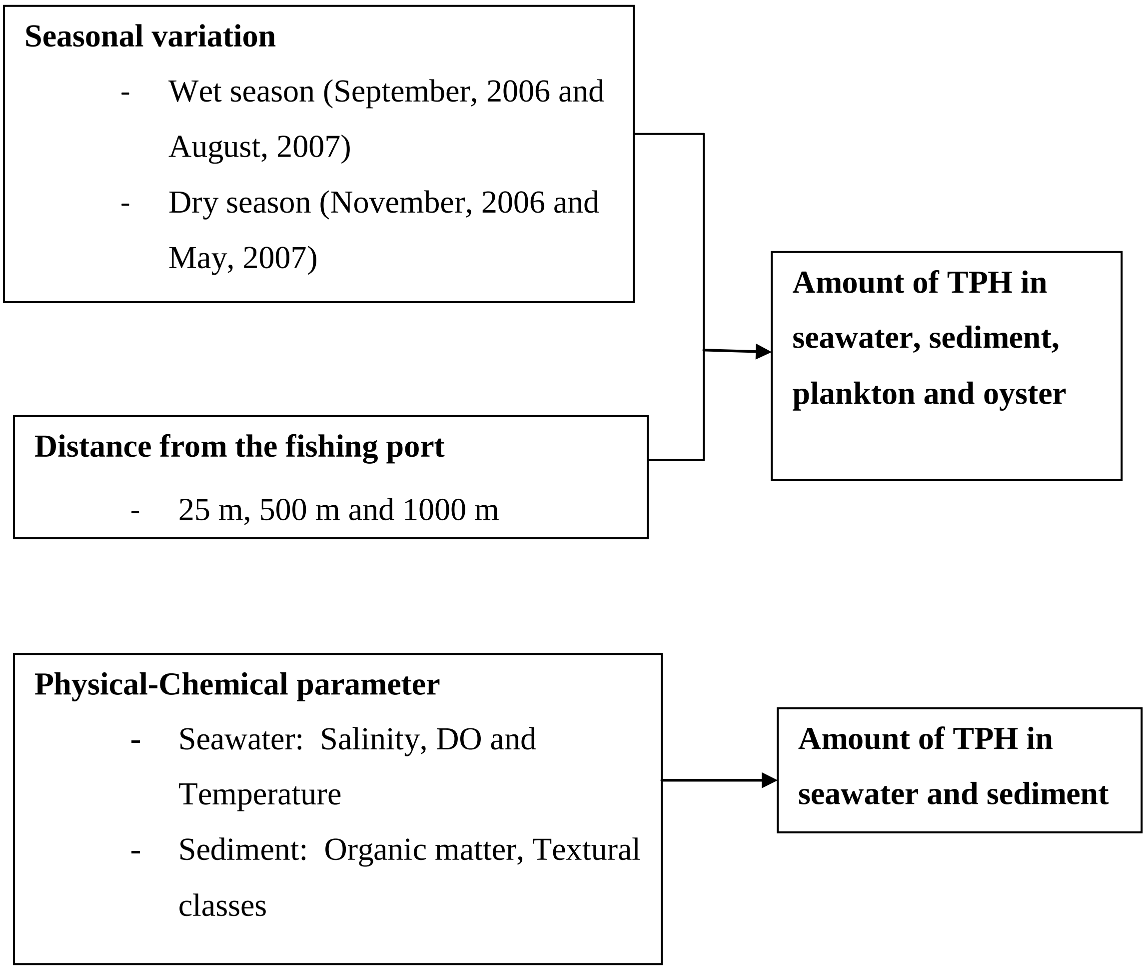

Figure 1-2 Conceptual Framework

CHAPTER II

LITERATURE REVIEW

2.1 Characteristic of study site

Ang Sila coast is located in Ang Sila sub-district, Muang district, Chonburi province which is located on the Eastern coast of Gulf of Thailand. The area of Ang Sila sub-district is approximate 18 km^2 and divided into 5 villages with a population of 21,021 (10). The fishery and aquaculture (i.e. Asian Brown Mussel (*Perna viridis*) and Oyster (*Saccostrea cucullata*)) were the major local careers in Ang Sila. The port areas have become major sources of pollutants releasing to the marine environment. Either accidental or intentional oil spills have prevailed. Petroleum hydrocarbons emitted directly to marine environment through seepage of diesel oil from fishing boats. Generally, fishing ports were contaminated with petroleum hydrocarbon more than recreation beach and aquaculture sites. It appeared that degree of contamination of coastal onshore waters increased from Chanthaburi to Trat, Chonburi and Rayong, respectively (11).

The bathymetric of the shore is flat plain. Sea-bottom of Ang Sila is soft mud (12). Ang Sila is under the influence of the predominant monsoon (13) as follows:

- Northeast monsoon in the cool season during the period of November to February.
- Southwest monsoon in summer during the period of March to May and the rainy season during period of June to October.
-

2.2 Compositions of petroleum hydrocarbons

Petroleum hydrocarbons consist of a very large number of compounds that by definition are found in crude oil as well as other sources of petroleum such as natural gas, coal, and peat. Analysis of crude oils from around the world shows that elemental composition varies over a narrow range: 82-87% carbon, 12-15% hydrogen and the balance being oxygen, nitrogen and sulfur (1). Hydrocarbons can be classified into four types as follows:

1. Alkanes (Parafins)

Alkanes occur in most petroleum as the most abundant series of hydrocarbons. Alkanes are saturated hydrocarbons with straight (n-alkanes) or branched chains (iso-alkanes). The general formula of alkanes is C_nH_{2n+2}. Crude oils often contain homologous series of n-alkanes extending C_2 to beyond C_{60} with a smooth distribution between odd and even numbered carbon chain lengths. Crudes contain parallel homologous series of isomers including series of isoprenoid alkanes (14).

2. Cycloalkanes (Naphthenes)

Cycloalkanes, saturated hydrocarbons with ring structure, are found in all crude oil in quantities ranging from 30 to 60 % and present in the fractions from C_5 upwards. The general formula of cycloalkanes is C_nH_{2n} (9). Allmost all of the cycloalkanes present in crude oil are derivatives of cyclopentene and cyclohexane (1).

3. Aromatic Hydrocarbons

Aromatic hydrocarbons are complex mixtures including mono and polyalkyl-benzenes, napthalenese and polyaromatics with multiple alkyl-substitution. The general formula of aromatic hydrocarbons is C_nH_{2n-6R}, where R is the number of the aromatic rings. The principal aromatic compounds of crude oils are benzene, toluene, the isomer of xylene, ethyl benzene and 1,3,5 trimethylbenzene (15).

The fuse-ring compounds including di-aromatics (naphthalenes) and tri-aromatics (phenanthrenes and anthracene) are solid at room temperature and found in the asphalt. These large aromatic hydrocarbons may be divided into two classes depending on the solubility in pentane. The component of asphalt soluble in pentene is called resins and insoluble one is called asphaltenes (15).

4. NSO's

NSO's are the compounds containing the heteroatoms nitrogen, sulfur, or oxygen. In principle, NSO's could include compounds containing any functional group of these elements (1).

Type of molecular structures found in petroleum hydrocarbon is shown in Figure 2-1

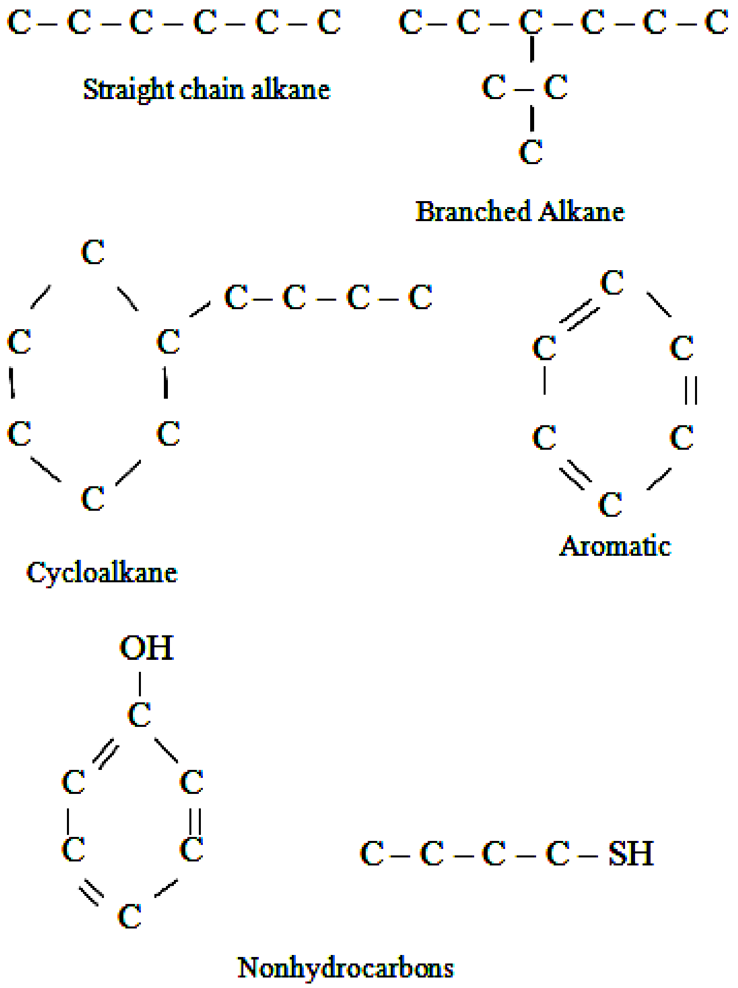

Figure 2-1 Type of molecular structures found in petroleum hydrocarbon (8)

2.3 Origin of hydrocarbons in the marine environment

Hydrocarbons enter the marine environment via three general processes (16)

1. **Biosynthesis (Biogenesis Hydrocarbons)**

Marine organisms can 1) synthesize their own hydrocarbons, 2) obtain from their food sources, or 3) convert precursor compounds obtained with their food. These hydrocarbons may be released during metabolism or upon the death and decomposition of the organism. Normal alkanes in organisms often exhibit a characteristic predominance of odd-numbered homologous over even-numbered ones. Odd carbon preference may be expressed by the ratio between the total weight of odd-carbon homologous and the weight of the even-carbon homologous. This ratio is known as the Carbon Preference Index (CPI) (17, 18, 19) and is calculated as follows:

$$CPI_{x\text{->}y} = \left(\frac{\left(\sum_{n=x}^{n=y} HC_{odd}\right)}{\left(\sum_{n=x}^{n=y} HC_{even}\right)}\right)\begin{matrix} D \\ \\ N \end{matrix}$$

Where D= number of even-numbered homologous between x and y, inclusive; and n= number of odd-numbered homologous between x and y, inclusive.

Marine algae are characterized by n-alkanes where predominant at C_{15}, C_{17}, C_{19} and C_{21}. In marine phytoplankton, the normal alkanes with 15, 17, 19 and 21 carbon atoms are most abundant (20, 21, 22, 23). Some bacteria are found to contain even- and odd- carbon-numbered C_{25} to C_{32} n-alkanes.

2. **Geochemical Processes**

There are a number of geochemical processes introducing hydrocarbons into the marine environment. The natural seepage of oil is an obvious example of this category. Weathering of ancient sediments and associated ancient hydrocarbons to the marine environment by fluvial or aeolian processes can result in introduction of an assemblage of hydrocarbons and other processes, forest fires and early diagenesis of organic matter deposited to surface sediments, must also be considered (16).

Submarine and coastal land oil-seeps release petroleum hydrocarbons to the marine environment. Weathering of soil and sediments and transports of some of the hydrocarbons in these sediment to the marine environment should also be considered as an input, although probably small when compared to other sources because of a slow degradation of the hydrocarbons during the weathering process. There are chemical synthesis processes which are sources of hydrocarbons. Forest fires inject hydrocarbons into the atmosphere. There are also chemical reactions occurring during the diagenesis of organic matter in sediments which yield hydrocarbons (16).

3. Anthropogenic Inputs (Petroleum Contamination)

The oil entering the sea from anthropogenic activities, most (65.2%) originates from discharges of municipal and industrial waste, urban and river runoff, ocean dumping, and atmospheric fallout. An additional 26.2% of the oil derives from discharges related to transportation (e.g., tanker accidents, deballasting, and dry docking). Only about 8.5% of the anthropogenic input is attributable to release from fixed installations (e.g., coastal refineries, offshore production facilities, marine terminals). The total oceanic input of petroleum hydrocarbons from man’s activities is approximately 2.115 million tons (mt)/year, which far exceeds that from natural source (0.25 mt/yr) such as oil seeps (8).

2.4 Sources of oil pollution in the marine environment of Thailand

Potential sources of oil pollution in the marine environment are as follows (24):

1. **Tanker and ship transportation**

There are 301 and 7 vessels monthly international tanker and ship vessel traffic including coastal tanker passing through the Gulf of Thailand and the Western shoreline, respectively. It is anticipated that when Lam Chabang and Map Ta Phut Deep Sea Ports in the Eastern Sea Board in operation, the vessels landing to the ports were about 180 and 51 vessel/month, respectively

Oil may spill from oil vessels when they are involved in an accident or when oil tankers are cleaned, water discharging and so on. However, the most of oil spill were from oil vessels.

2. **Refineries**

There are three refineries and tank farms in Thailand. One of the refineries (Bangchak Refinery) is along the Chao Phraya River and the other two are located on the shoreline of Sri Racha district, namely Thai Oil and Esso Refineries. Oil contamination may occur during oil transportation activities, tanker cleaning and deballasting by crude oil tanker and accidential discharges.

3. **The offshore petroleum exploration and production**

The activities may cause oil pollution from discharges from drilling mud during the exploration periods and accidential oil discharge during production processes.

4. **Ship-breaking Industry**

The demolishing processes may cause oil pollution. Oil can escape from machinery spaces, ballast tanks and fuel tank.

2.5 Environment fates

Petroleum hydrocarbons contamination in the aquatic environment is controlled by their characteristics and site condition as well. The fates of petroleum hydrocarbons in aquatic environment are mainly undergo the following patterns (25).

1. Physical

1.1 Spreading

As soon as the oil is spilled, it spreads over the sea surface. The rate of spreading and thickness of the slick is dependent on a number of factors including sea state, wind conditions, volume spilled and the viscosity of the oil. The viscosity of the oil depends largely on the ambient temperature and the composition of the oil. Light oils such as benzene tend to spread thinly and more quickly than heavy waxy oils. Once the light components of a medium weight oil dissolve or evaporate (usually after the first few days of a spill) the oil becomes more viscous and the rate of spreading reduces considerably. At temperatures below their pour point, oils rapidly solidify and remain as a solid mass on the sea surface

The weather plays an important factor in the spread of the oil with the wind determining the strength and direction of the spread, the state of the sea and temperature of the water. With time, wind and wave action spreads the oil in a linear direction parallel to the wind direction. Tidal streams and currents can also spread the oil quickly over large areas making an effective clean up operation difficult. Oil has been reported to travel downwind at a rate of 3-4% of the prevailing wind. The more severe the weather conditions, the more rapid the spreading and breaking up of the oil.

1.2 Evaporation

Immediately after an oil spillage, the process of evaporation begins. It is the single most important weathering process in the first several days of an oil spill. The more volatile components of an oil will evaporate to the atmosphere with the rate dependent on ambient temperatures and wind speed. In this process components of the oil which are volatile and of low molecular weight are lost changing the properties and composition of the remaining oil. The rate of evaporation is proportional to the initial spreading of the oil as a larger surface area will allow the lighter components to evaporate quickly. The overall amount of oil which is lost to evaporation depends on the type of oil and its constituents. Research has shown that for a light, volatile crude oil, evaporative loss is very pronounced with up to 40% being lost due to this process. The volatile, lighter hydrocarbons, such as benzene, are, in large concentrations, toxic to hydrocarbon degrader populations. Therefore when these components are lost the biodegradation of the heavier compounds occurs more rapidly.

Evaporation reduces the volume of the oil, its flammability and toxicity but increases the viscosity and density of the residue. The residue of the crude oil may have a specific gravity of about 1 and loaded with suspended matter, it may reach that of sea water increasing the probability of the oil sinking.

Although the total amount of oil lost to evaporation is difficult to measure, estimates can be made based on the type of oil spilled and the surface area exposed to the atmosphere.

1.3 Dispersion

Dispersion of oil can be enhanced by a rough sea state through the mechanical action of the waves and turbulence at the waters surface which removes oil from the surface. The wave action breaks up the oil into progressively smaller slicks and it eventually becomes mixed into the water column. Although the larger droplets will probably rise again to the sea surface to coalesce, the smaller droplets, with greater water-oil surface area, will remain in the water column until decomposition is complete. Typically, smaller volumes of oil are dispersed more readily. Light oils and those which have low viscosities disperse quickly. Oils that remain fluid and spread unhindered by other weathering processes may disperse completely in moderate sea conditions within a few days.

Dispersion can be aided by the use of dispersant chemicals. The treatment is to produce droplets to remove the oil from the surface where it will cause harm. Once the droplets have been formed they can be ingested by zooplankton and incorporated into faecal pellets which then sink.

2. Chemical

2.1 Emulsification

In some sea conditions, Beaufort Force 3 (wind speed 7 to 10 knots) a water-in-oil emulsion is first produced due to physical mixing of the water and oil promoted by turbulence at the sea surface. Due to its appearance, the resulting emulsion is often termed as ‘chocolate mousse’ and with its increased viscosity and volume, such a consistency may prevent air (oxygen) reaching the oil embedded in the mousse thus reducing the degradation process. The mousse is a water-in-oil emulsion containing up to 80% water so volume is increased. The formation of this water-in-oil emulsion is the main reason for the persistence of light and medium crude oils on the sea surface. With increase in spreading and mixing, the water-in-oil emulsion becomes an oil-in-water emulsion.

Mousse formation and stability depends greatly upon the type of oil. This emulsion is usually formed in oils which have a combined Nickel/Vanadium concentration greater than 15 ppm or an asphaltene content greater than 0.5%. However the stability of an emulsion decreases with increasing temperature and so, the reverse of this process can occur for example, if an emulsion is heated by sunlight.

Once emulsification has occurred, the clean up operation is made more difficult due to the increased volume of oil and the problem of its disposal.

2.2 Dissolution

The rate and extent to which an oil dissolves depends upon its composition, spreading, water temperature, turbulence and degree of dispersion. Some components of oil (namely the low-molecular-weight aromatics) such as benzene and naphthalene are water-soluble and when finely dispersed in the water column dissolve readily into sea water. However, most components of spilled oil are not particularly water-soluble and those which are, tend to be the first to be lost through evaporation.

The process of evaporation is 10-100 times faster than the process of dissolution. Oil contains very small amounts of these compounds making dissolution a relatively unimportant degrading process in comparison to others.

2.3 Oxidation/Photooxidation

Hydrocarbons by themselves are considered to be relatively resistant to oxygen. However in contact with water and light, they are oxidised more quickly.

Oxidation (electron loss, thus increasing the oxidation state of an atom or atoms within a molecule) is the degradation process whereby oil, both on the surface and in the water column, reacts chemically with oxygen. This process can affect oil in a wide range of states including dissolved hydrocarbons, dispersed oil droplets and water-in-oil emulsions. Oxidation breaks down the oils to form soluble products or can leave persistent compounds called tars. Sunlight can act as a catalyst for this process (photo-oxidation) and so the rate of oxidation depends largely upon light intensity and duration. Other factors include the viscosity of the oil and, aeration or exposure to oxygen, hence the importance of climatic conditions.

Direct photolysis (photo-oxidation - whereby a chemical absorbs solar radiation and is subsequently transformed) accounts for the degradation of a significant amount of the higher weight PAHs, since many of them absorb light in ultraviolet or visible wavelengths (300 and 500 nm) found in solar radiation (Lee, 2003). The photo-oxidation process produces compounds which tend to have increased water-solubility thus leading to uptake across biological membranes and are often more toxic than the original compounds. However, the process of oxidation is very slow and even in strong sunlight, thin films of oil break down at no more than 0.1% per day.

However, this behavior is not characteristic to all the products of photo-oxidation. Some products of this process have increased stability and contribute to the formation of water-in-oil emulsions. These products, with their increased density and viscosity are insoluble and can prove to be particularly persistent to degradation forming tar balls which sometimes strand shorelines. These tar balls usually consist of a solid outer crust of oxidised oil and sediment particles, surrounding a softer less weathered interior.

2.4 Sedimentation

Due to the relatively high density of sea water, very few oils are dense enough to sink in the marine environment. However, near the coast, oil may mix with debris, sediment or organic matter and bond sufficiently to form tar balls which subsequently sink. Adhesion to heavier particles most often takes place when the oil reaches the shoreline and strands on the beach. These layers of oil can be covered over by subsequent sediment deposition or alternatively uncovered during periods of erosion. Therefore this sediment is not permanently removed from the marine environment.

The oil is buried by sediment, the decomposition rate drops considerably. Oxidation processes slow down due to reduced light intensity together with microbial activity which can lead to anaerobic conditions within the sediment.

Within the water column, the sedimentation process is assisted by biological removal. Ingestion of the oil particles by zooplankton removes the oil from suspension. It then becomes incorporated into faecal pellets which sink to the seabed.

Oil adsorbed to particles also causes clays and silts in suspension to flocculate and therefore to sink.

Due to hydrophysical processes, the oil can become incorporated into the sediments where it may block the interstitial spaces and reduce the permeability of and oxygen penetration into the sediments. This can result in anaerobic conditions which will reduce the rate of or completely inhibit aerobic biodegradation. Hence the half life of oil goes from days to weeks in the water column to months to years in sediments.

3. Biological

Biodegradation

Biodegradation is the key process in the removal of oil from the environment. It is particularly important for the non-volatile components of the oil which are particularly resistant to the other processes of weathering. Biodegradation is assisted by the marine micro-organisms in sea water which are capable of metabolising oil compounds. These micro-organisms including bacteria, moulds, yeasts, uni-cellular algae and protozoa can utilize the oil by degrading it through progressive and sequential reactions to form water soluble compounds and eventually carbon dioxide and water.

As there is no one single strain of bacteria with the metabolic capacity to degrade all the components found within crude oil, degradation is carried out in stages by different groups of organisms. The intermediates produced by this process are often more toxic than the original compounds and it often takes longer for these to be broken down. Once the toxic lighter compounds are lost then microbes can more easily degrade the remainder.

The rate of biodegradation in the marine environment varies considerably and depends largely upon several factors including the composition of the oil, surface area of the oil, the availability of nutrients (such as nitrogen and phosphorus), the ambient temperature and the levels of oxygen present.

Chemical, physical, and biological fates of petroleum and PAHs in water are illustrated in Figure 2-2.

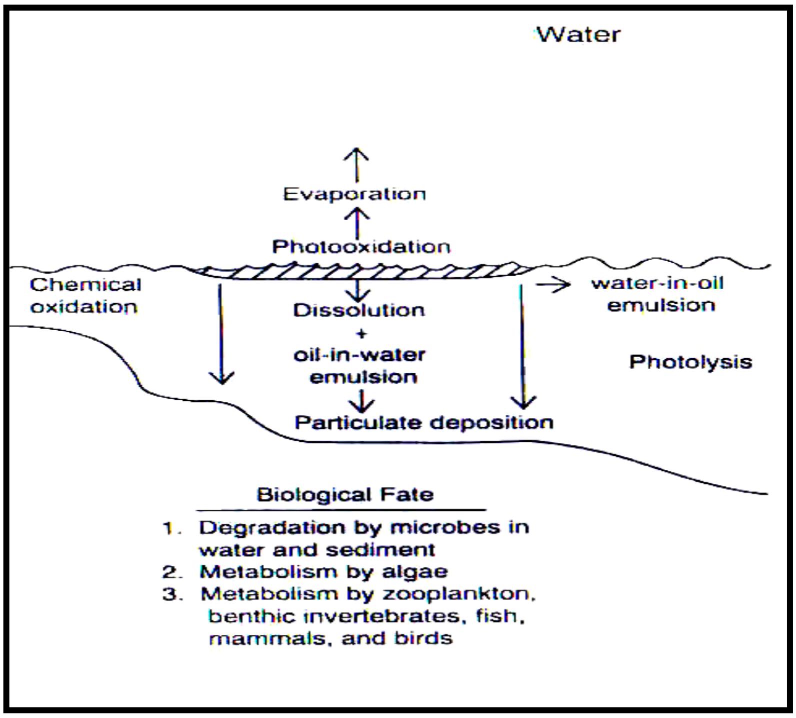

Figure 2-2 Physical, chemical and biological fates of petroleum to aquatic system (26)

2.6 Effects of petroleum hydrocarbons in marine environment

1. Toxicity of petroleum hydrocarbon

Water-soluble components of crude oils and refined products include a variety of compounds that are toxic to a wide spectrum of marine plants and animal. Aromatic compounds are more toxic than aliphatics, and middle-molecular-weight constituents are more toxic than high-molecular-weight tars. Low-molecular-weight compounds are generally unimportant because they are volatile and rapidly lost to the atmosphere. A spillage of diesel fuel, with a high aromatic content, is therefore much more damaging than bunker fuel and weathered oil, which have a low aromatic content. A spillage of petrol or other 'white spirit' may present a serious fire hazard, but has little impact on marine organisms in the water (26).

Anthropogenic PAHs affect living organisms through their toxicity. The mechanism of toxicity for PAHs seems to be interference with cellular membrane function and enzyme systems associated with the membrane. Although unmetabolized PAHs can have toxic effects, a major in concern in animals is the ability of reactive metabolites, such as epoxides and dihydrodiols of some PAHs to bind to cellular proteins and DNA. The resulting biochemical disruptions and cell damage lead to mutation, developmental malformations, tumors, and cancer. Four-, five-, and six ring PAHs have greater carcinogenic potential than do the two-, three-, and seven-ring PAHs (26).

In water the toxicity of individual PAHs to plants and animals increase as molecular weight (MW) increase up to MW 202 (fluoranthene, pyrene). Beyond MW 202, a rapid decline in solubility reduces potential PAH concentrations to less-than-lethal levels. However, sublethal effects can result from exposure to these very low concentrations of high-MW compounds. Environmental concentrations of PAHs in water are usually several orders of magnitude below levels that are acutely toxic to aquatic organisms. Sediment PAH concentrations can be much higher than water concentrations, but the limited bioavailability of these PAHs greatly reduces their toxic potential (26).

2. Marine organisms' impact

2.1 Plant

Differences in species' sensitivity to petroleum are responsible for the wide variation in community response for phytoplankton and microbes. Laboratory studies have revealed that the effects of oil on natural phytoplankton assemblages are not only dependent on the species investigated, but also on temperature, light intensity, nutritional physiology of the algae, and the type of oil. The lack of mobility and generally close proximity of some phytoplankton to oil floating on the sea surface can have hazardous consequences; however, the high turn over rates and patchy distribution of phytoplankton population levels that existed prior to a spill. While high concentrations of petroleum hydrocarbons are toxic to nearly all phytoplankton, low concentrations may actually increase primary production (8).

The effects of petroleum on marine plants, such as mangroves, seagrasses, saltmarsh grasses, and algae, have which caused death, reduced growth, and impaired reproduction in the large plants. Microalgae were either stimulated or inhibited, depending on the type and amount of oil present and the species of algae; the response was expressed as changes in biomass, photosynthesis activity, and community structure (26).

Individual PAHs, mostly two- and three-ring compound, at low concentrations (5-100 ppb) can stimulate or inhibit growth and cell division in aquatic bacteria and algae. At high concentrations (0.2-10 ppm) the same PAHs interfere with cell division of bacteria, cell division and photosynthesis of algae and macrophytes and can cause death (26).

2.2 Invertebrate

Invertebrates in the water column (zooplankton), while obviously sensitive to dispersed oil, usually recover relatively rapidly and return to pre-spill conditions faster than benthic invertebrates. Even low concentrations of oil and dispersants have been shown to adversely affect the fertilization, embryonic development, and feeding of copepods (8). Mortality and sublethal effects are caused by smothering; contact by adults, juveniles, larvae, egg, and sperm with dissolved oil or suspended oil particles; ingestion of oil or contaminated food and water; and, possibly, by chemical change in water, including oxygen depletion and pH change (26).

Petroleum on marine invertebrates is acute and chronic effects of various crude and refined oils on numerous responses. Among the findings are reduced survival, altered physiological function, altered cellular structure and function, inhibited reproduction, altered behavior, and changes species population and community composition (26).

Shellfish often remain contaminated for extended periods due to oil spills. For example, shellfish beds in Falmouth, MA, remained closed to shellfish for more than 8 years following the Florida oil spill. Oyster in the Aber-Benoit and in the Baie de Morlaix (Carantec) of France contained significant levels of residual aromatic hydrocarbons 7 years after the Amoco Cadiz oil spill. The oil caused a number of sublethal effects, such as necrosis, inflammation, and atrophy of gonadal cells (8).

Individual PAHs compounds, in short-term exposure trials (24-96 h) on selected aquatic invertebrate, had LC_{50} values ranging from 0.3 to 5.6 ppm. Egg and larval stages of invertebrates are more sensitive than juveniles or adults to dissolved PAHs. Sublethal effect include reduced reproduction, inhabited embryo and larval development, delayed emergence of insect larvae, decreased respiration and heart rate, abnormal blood chemistry, and lesions (26).

2.3 Fish

Oil pollution in coastal waters represents a serious treat to recreational and commercial fisheries. Many coastal regions sustain valuable fisheries resources that may be at risk during large oil spills. Because of their mortality, juvenile and adult fish generally are able to avoid oil slicks in open seas. However, the rapid advection of large volumes of oil into estuaries and embayments can trap fish populations, culminating in substantial mortality (8).

Egg, larvae, and early juvenile stages of fish are most sensitive to oil. The contact of egg masses and ichthyoplankton with surface oil can be lethal. Apart from the lethal effects of oil on embryos and larvae, sublethal effect on these early life stages commonly include abnormal development, reduced growth, premature and delayed hatching of eggs, and cellular abnormalities (8). Adult fish tolerate much higher concentrations of petroleum hydrocarbons than eggs and larvae. Sublethal effects of oil typically manifested in adult fish are changes in heart and respiratory rates, gill hyperplasia, enlarged liver, reduce growth, fin erosion, impaired endocrine system, behavioral modification, as well as alternations in feeding, migration, reproduction, swimming activity, schooling, and burrowing behavior. A variety of biochemical, blood, and cellular changes also may arise (3, 8).

Individual PAHs compounds in short term exposure trials (24-96 h) on selected species of fish had LC_{50} values ranging from less than 1 to more than 100 ppm. The primary target organ for the toxic action is the liver. Sublethal effect on eggs, larvae, juvenile, and adult fish are similar to those caused by exposure to petroleum (8).

2.4 Birds

Birds can affected by petroleum through external oiling, ingestion, egg oiling, and habitat changes. External oiling disrupts feather structure and causes matting of feathers and eye irritation. Deaths often result from hypothermia and drowning. Birds spend much of their time in the water. Diving ducks, auks, penguins, and sea ducks appear to be particularly vulnerable, because they spend a considerable amount of time on the sea surface (26).

Bird embryos are highly sensitive to petroleum. Contaminated nest material and oiled plumage are mechanisms for transferring oil to the shell surface. Small quantities (1-20 μl) of some types of oil are sufficient to cause death, particularly during the early stages of incubation (26).

Petroleum spilled in avian habitats can have immediately and long-term effects on the birds. Fumes from evaporating oil, a shortage of food, and clean-up activities can reduce the use of an effects area. Long-term effects are more difficult to document, but severely oiled wetlands and tidal mud flats are likely to have altered plant and animal communities for years after a major spill (26).

The limited information available on the effects of individual PAHs on birds come mostly from studies of the effects of petroleum on eggs. Experiments have show the PAH fraction of crude and refined oil is responsible for the lethal and sub lethal effects on bird embryos consisting primary of two- and three-ring PAHs for 7 months had a 25 % increase in liver weight and 30% increase in hepatic blood flow. The four-ring and higher aromatic fraction of crude oils was responsible for weight loss in young herring gulls (*Larus argentatus*) orally dosed with crude oils (26).

2.5 Mammals

Marine mammals that rely primarily on fur for insulation, such as the sea otter, polar bear, Alaska fur seal, and newborn hair seal pups are the most likely to die after contact with spilled oil. Oil fur becomes matted and loses its ability to trap air or water. Adult hair seals, sea lions and cetaceans (whales, porpoises, and dolphins) depend primarily on layers of fat for insulation, thus oiling causes much less heat loss. However, skin and eye irritation and interference with normal swimming can occur. Skin absorption of oil has been reported for seals and polar bears (26).

The metabolism and effects of some PAHs have been well documented in laboratory rodents and domestic mammals, but not in wild mammals. Acute oral LD_{50} values for selected PAHs in laboratory rodents range from 50-2000 mg/kg^2. Target organs for PAHs toxic action are tissues of the hematopoietic system, skin, small intestine, kidney, and mammary gland; the immune system can also be adversely affected. Unsubstituted PAHs are rapidly metabolized; hence, accumulate dose not occur (26).

Because PAHs toxicity occurs at levels that can also induce cancer, concerns about the carcinogenic potential predominate. Consequently, PAHs that are not carcinogenic are less studied than those that are carcinogenic. Alkalated PAH and metabolites of unsubstituted PAHs can induce cancerous and noncancerous neoplasm in most of the epithelial tissues of laboratory and domestic mammals. Species differences in sensitivity to carcinogenic appear to be largely a function of difference in levels of mixed function oxygenase (MFO) activity. Interactions among PAHs and between PAHs and other substances found in mammals have been reported investigations involving mixture of PAHs are needed to accurately determine the potential hazard to all organisms of exposure to multiple PAHs from polluted environments (26).

3. Public health risk

Some petroleum hydrocarbons are toxic to human being and there are a few cases on record of children being made seriously ill or even drying after inadvertently swallowing kerosene (paraffin). But humans have an extremely low taste threshold for petroleum hydrocarbons and the taste is particularly repulsive. There is therefore little risk of humans unknowingly receiving measurable dose of these toxins from contaminated food or drinking water.

Oil includes polycyclic aromatic hydrocarbons (PAHs) some of which are know carcinogens. In the early 1970s there was a fear that PAHs behaved in much the same way as chlorinated hydrocarbons like DDT, that is they were resistant to bacterial attack and were excreted only slowly, if at all, by animals. As a result, it was concluded that these compounds might concentrate in the tissues of marine organisms with the concentrations increasing up the food chain to therefore be exposed to relatively large amounts of these carcinogens ever in the absence of overt oil pollution. Fortunately these fears have proved to be groundless. There is little evidence that petroleum hydrocarbons accumulate in marine organisms, and seafood contains small concentrations of PAH (as measured by benzo[a]pyrene, a potent carcinogen) (27).

4. Commercial damage

4.1 Fisheries

Fixed installation where fish or shellfish are held in intensive mariculture are particular vulnerable to damage from accidental oil pollution because the animals cannot escape. A slick of oil drifting through such an installation may inflict commercial damage quite incommensurate with the size of the spillage. Japan, where mariculture is more varies and more advanced than in most other countries, has had many such unfortunate experiences.

In open sea and as a rule in inshore water, adult fish of commercial importance appear to be able to avoid areas affected by floating oil and are rarely killed. During the period when oil from a blow-out in the offshore oilfield at Santa Barbara, California, contaminated coastal water, spotter planes used by the local fishing fleets to detect fish shoals, found them in normal abundance in areas of clear water between the streamers of oil.

Since fish eggs and larvae are more sensitive than adults to toxins and are commonly in surface water where they are likely to encounter high concentrations of petroleum hydrocarbons, they are expected to be particularly vulnerable to damage by oil pollution. Many commercial species of fish and shellfish produce enormous quantities of eggs, and even massive addition juvenile mortality may have no influence on the stock of adults which from the basis of fishery (27).

4.2 Tainting

As serious losses are resulting from deaths of fish and shellfish, the most important commercial damage is from tainting. Light oils and the middle-boiling range of crude oil distillates are the most potent source of taint, but all crude oils, refined products, refinery effluents, wastes from petrochemical complexes, the exhaust from outboard motors burning oil-petrol mixture, and a host of other sources can impart an unpleasant flavour to fish and seafood which is detectable at extremely low levels of contamination. ‘Oily’ or ‘petroleum’ flavours are generally repulsive to humans and fish tainted in this way is unmarketable. Low levels of contamination may produce indefinite, but certainly detectable ‘off-flavours’ which are at least damaging to the market.

The concentrations of oil in water necessary to cause tainting in finfish vary widely with the oil and the fish: fatty fish like salmon contract a taint much more readily than non-fatty species. In the natural environment, finfish rarely become tainted from floating oil because they avoid contaminated areas. The chief risk to commercial fisherman comes from fouling of fishing gear and this may result in tainting of the whole catch. In chronically polluted water, fish are either excluded or, generally, are fished.

Shellfish may be affected in a variety of ways. Stranded oil contaminates the shells of mollusks without damaging them, but even a small quantity of oil on a few shells of mussels, cockles, or winkles can taint the whole catch if, as if commonly the case, they are boiled before eating. Since oil can be retained on shells for a considerable time, this source of tainting is very persistent.

A commoner form of shellfish tainting that affects all filter-feeders results from the uptake of fine droplets of emulsified oil in the tissues. Tainting in this way is common and bivalves are the principle subjects. The oily taste is lost within three to four weeks if the source of contamination is removed and the shellfish are transferred to uncontaminated water.

The fishing industry is vulnerable to irrational moves in a way that few others are, and even the suspicion that fish may be tainted or contaminated is sufficient to depress the market (27).

4.3 Tourism

Tourists prefer their bathing beaches free from oil and most coastal resorts put a good deal of effort into removing tar and oily residues from their amenity beaches. This oil pollution, mostly resulting from casual discharges, is a nuisance but not necessarily a heavy financial burden on the resort because the beaches are cleared of little, plastics and other debris regularly in the course of preserving the local amenities and removing odd patch of tar adds little to the cost of beach cleaning.

Severe pollutions resulting from a major accident in the vicinity of a resort is a different matter. It may well be beyond the means of the local community to deal with it and is generally treated as a national emergency calling for a national response.

It is commonly said that oil pollution of beaches is harmful to the tourist industry, but although tourists may grumble there is little evidence that they actually stay away from beaches and resorts subject to minor oil pollution. Even large-scale pollution as from a tanker wreck dose not apparently deter tourists who have been know to flock to view a disaster or potential disaster (27).

2.7 Relevant research

1. Studies of petroleum hydrocarbons accumulation in Thailand

Petroleum-derived n-parafins in seawater and sediments were studies in the Gulf of Thailand during May and November 1977 using GC technique (28). No significant seasonal differences were noted. During May and June, the range of concentration of C_{10} to C_{30} n-parafins was 20.5- 329 µg/l (mean 110.9 µg/l) while in September to November, the range was between 23.4 and 428 µg/l (mean 151.4 µg/l). A higher maen concentration (233 µg/l) was recorded near a major oil refinery in Chonburi Province. Sediments from the Upper Gulf of Thailand contained higher mean concentrations of n-parafins in the dry season (3.7 µg/g wet wt) than in the wet season (2.9 µg/g wet wt). The annual mean concentration of parafins in sediments of the Lower Gulf was 1.2 µg/g, while at the Chonburi area were more contaminated n-parafins with mean concentration of 7.9 µg/g wet wt.

Petpiroon (10) studied concentration of dissolved petroleum hydrocarbons in seawater samples (1 m depth) collected from coastal area of Pattaya to Trat in November-December 1987 and April 1988. Forty sampling stations were select along the coastline to represent beneficial uses of the coastal resources such as recreation beaches, aquaculture and fishing ports. These were compares with 21 sampling stations both nearshore (5-20 km) and offshore (25-90 km). The results indicated that onshore waters were more polluted by dissolved petroleum hydrocarbon than nearshore and offshore waters. Concentration of dissolved petroleum hydrocarbons in onshore waters ranged 0.018 – 5.286 µg/l with the mean of 0.320 µg/l. The maximum value was found at Ban Nang Faeb, Tambon Map Ta Phut. The highest mean found at Rayong Province was 0.908 µg/l, for Chonburi, Trad and Chantaburi were 0.658, 0.468 and 0.397 µg/l, respectively.

Petroleum hydrocarbons in bivalves *Perna viridis* and Green mussel collected from Ang Sila, Srichang Island and Sriracha were studied using GC technic

(29). Total aromatic hydrocarbons in both species varied from 34.97-74.08 μg/g dry weight.

Petroleum hydrocarbons in marine environment were collected around ship-breaking industry area, Map Ta Phut, Rayong (14). These were analyzed for dissolved/dispersed petroleum hydrocarbon by fluorescence spectrometry (UVF). Petroleum hydrocarbon concentrations were found to be higher in the two scraping period in June and November 1989. Sediments and bivalve, *Donax* sp. tissue samples were gas chromatographic analysis, using flame ionization detector. The results of sediment sample analyses showed n-alkane ranging from C_{15}-C_{30}. The average total aliphatics are 0.35 and 0.36 μg/g (dry wt) for October and June samples. The average aromatics are 0.33 μg/g in October and 0.69 μg/g in June. *Donax* sp. Tissue contained total n-alkane (C_{15}-C_{26}) ranging 6.18-14.91 μg/g in October and 10.84-38.94 μg/g in June. PAH found include acenaphthene, acenaphthylene, dibenzothiophen, phenanthrene, anthracene, 1-mrthylphenanthrene, fluoranthrene, pyrene and benzo(a)pyrene.

Petroleum hydrocarbons in water at 1m-depth, sediments and green mussel Perna varidis samples collected from the mouth of Chao Phraya River was carried out by fluorescence spectroscopy (UVF) and gas chromatography (GC) (30). The results of water samples analysis, by UVF method, showed the average petroleum hydrocarbons was 18.02 μg/l (chrysene equivalents) in May and 6.01 μg/l in September 1993. The results of sediment sample analysis by GC analysis, showed n-alkanes ranging from C_{14}-C_{34}. Total n-alkanes average 5.20 and 5.82 μg/g. (dry wt) for May and September respectively. The sediment samples contained Polycyclic Aromatic Hydrocarbons (PAHs) from 2-6 rings. Concentrations of total PAHs averaged 1.93 μg/g in May and 2.14 μg/g in September. Mussel samples contained n-alkanes (C_{15}-C_{25}) ranging from 0.85-0.98 μg/g (dry wt) with the average of 0.94 μg/g.

Tappatat (31) studied petroleum hydrocarbons in water and sediments in coastal area of Rayong Province, Thailand during February to December 1994. Petroleum hydrocarbons in water were analyzed by fluorescence spectroscopic method, whereas those of surface sediments were analyzed by gas chromatographic technique. Concentrations of hydrocarbons in seawater were found to be 0.05-11.84 μg/l chrysene equivalents. The average concentrations were 1.94, 1.12, and 1.09 μg/l for industrial, urbanized and aquacultural sites, respectively. Average petroleum hydrocarbons for near-shore, 5 and 10 km offshore areas were found to be 2.85, 0.67 and 0.63 μg/l, respectively. Fluorescence spectra of the samples revealed that contamination was mostly from diesel oil.

Total n-alkanes in surface sediments were 0.11-14.37 μg/g dry wt, with the average of 2.52 μg/g. Comparison of total n-alkanes in the three areas of studied showed the highest value to be around the industrial site, followed by urbanized aquacultural sites, respectively. Total n-alkanes was found to decrease with distance away offshore. PAHs content in the sediments ranged from trace-1.66 μg/g dry wt, with the average of 0.28 μg/g. Total PAHs in urbanized area was found to be the highest, as compared to industrial and aquacultural sites.

Hydrocarbon contents both in seawater samples and surface sediments were not significantly different with respect to land-use purposes. However, hydrocarbon contents in the nearshore area were significantly different from those of the 5 and 10 km offshore areas at the significant level of 0.5.

Major sources of hydrocarbon contamination in nearshore sediments, particularly around industrial and urbanized sites, were found to be mostly anthropogenic in origin, being diesel as well as used lubricating oils from industrial and boating activities. Hydrocarbon found in 5 km offshore area derived from biogenic (phytoplankton and higher plants) and anthropogenic source. In 10 km offshore area, hydrocarbons were mostly from biogenic sources with little contribution from anthropogenic sources.

Distribution of hydrocarbons with depth of deposition in 4 dated sediment cores was also studied. Nearshore sediments, from 1 km offshore station was found to be contaminated by hydrocarbons from pyrogenic sources at much earlier dates when compares with sediments from stations located more than 20 km offshors. PAHs were found mostly in upper layers of sediment cores whereas hydrocarbons in much deeper sediments derived mainly from bacterial activities.

Suwanangosoom (9) studied the accumulation of total petroleum hydrocarbon (TPH) in the marine food chain around Phe Bay, Rayong province, Thailand during June and September 2000. The average contamination levels of TPH in seawater and sediment were 0.61±0.26 µg/l and 1.53±2.39 µg/g, respectively. Concentrations of TPH in some marine organisms were decreased in order of benthic invertebrate > plankton > clam > demersal fish. The relationships among these different compartments in this study were roughly estimated as bioconcentration factor (BCF), bioaccumulation factor (BAF) and dietary accumulation based on the ratio of petroleum hydrocarbons in marine organisms to natural environment. The calculated BCF of marine organism to seawater were found to be the highest in benthic invertebrate followed by plankton and green mussel (*Perna viridis*). The highest value of BAF of marine organism to sediment were found on benthic invertribrate followed by *P. veridis*, *M. lusoria*, *Sillago* spp. *N. hexodon* and *S. taeniopterus*, respectively. Dietary accumulation from plankton were also calculated from green mussel and dermersal fish samples. . The highest value of bioaccumulation factors of marine organism to sediment were found on benthic invertribrate followed by *P. veridis*, *M. lusoria*, *Sillago* spp. *N. hexodon* and *S. taeniopterus*, respectively. The results from this study indicated that higher accumulation of TPH was found in marine organism when compared with seawater and sediment.

Total Petroleum hydrocarbon (TPH) in seawater around Sichang Island and vicinity was monitored between 1996-1998 and 2007 (32). There were 4 sampling stations around Sichand Island and 1 sampling station at Siracha. Analytical method was Fluorescent Spectrophotometry with Chrysene reference. TPH was trend to decreased with maximum total average as 8.716 ug/l as Chrysene in June 1996. Average TPH in April 2007 was 0.778 ug/l as Chrysene with maximum at Siracha as 1.322 ug/l as Chrysene. TPH average around Sichang Island and vicinity in April 2007 was slightly higher than Standard Coastal Seawater, PCD 2006, for water resource type 1-3 as 0.5 ug/l as Chrysene but in range of standard for water resource type 4, as 1.0 ug/l as Chrysene. Average TPH Siracha was higher than type 4 coastal seawater standard but in level of type 5-6 coastal seawater standard, 5 ug/l as Chrysene.TPH in seawater around Sichang Island was in coastal seawater standard type 4 and Siracha was in type 5-6.

2. Studies of petroleum hydrocarbon accumulation in other countries

Seasonal distribution and contamination levels of dissolved and/or dispersed total petroleum hydrocarbons (PHCs) and total polycyclic aromatic hydrocarbons (PAHs) coastal waters were studied at the Alang–Sosiya ship scrapping yard, Gulf of Cambay, India, 2003 (33). Alang–Sosiya situated on the Gulf of Cambay is one of the largest ship-breaking yard in the world. The concentrations of PHCs were ranged from 257-1,437 µg/l in summer (May), 453-2,325 µg/l in monsoon (August) and 550-3,540 µg/l in winter (December). The concentrations of PAHs were ranged from 78-719 µg/l in summer (May), 99-889 µg/l in monsoon (August) and 120-1,565 µg/l in winter (December). The concentrations of petroleum hydrocarbons are higher in the winter than in the monsoon and summer. The concentrations of total PHCs and PAHs are about three times higher in the winter and two times in the monsoon or summer at Along–Sosiya and about twice in all seasons at two stations one on either side 5 km away from it as compared to the reference station at Mahuva, 60 km away towards the south. Further, the levels of PHCs are correlated with salinity and compared with those of other regions.

Zanardi, Bícego, Miranda and Weber (34) studied distribution and origin of hydrocarbons in water and sediment in Sáo Sebastiáo, SP, Brazil. This study describes the dissolved/dispersed petroleum hydrocarbons (DDPH) in surface water and the origin and distribution of aliphatic and aromatic hydrocarbons in samples from the surface bottom sediments. The main objective was to verify the anthropogenic contribution on the adjacent inner shelf of Sáo Sebastiáo, taking into account the distribution of hydrographic properties and knowledge of the main circulation. The DDPH concentration range of the 20 samples was from 0.35 to 2.50 µg/l, characterizing this region as slightly affected by the contribution of petroleum hydrocarbons. Considering sediment hydrocarbon results, sites located in the inner shelf were divided into three groups: one with mainly biogenic hydrocarbons, a second one with biogenic and petroleum hydrocarbons and a third with significant contribution of petroleum hydrocarbons. These results show an influence of human activities in the Sáo Sebastiõ Channel on the surrounding area of the inner.

The abundances and compositions of aliphatic hydrocarbons (AHC) and polyaromatic hydrocarbons (PAH) were investigated in the water and bottom sediments of the southwestern Amur Bay in the Sea of Japan (35). The water contained from 0 to 129 g/l AHC (averaging 42.2 g/l) and from 5 to 85 ng/l PAH (averaging 18 ng/l). The bottom sediments contained 168–2098g/g AHC and 7.2–1100 ng/g dry mass PAH. It was shown that the input of anthropogenic HC is better recorded by molecular markers than the distribution of AHC and PAH concentrations. The discovery of elevated HC concentrations in the bottom water layer suggests that the bottom sediments induced secondary contamination of the water body.

Samples of subsurface seawater (1m) were collected in the South West Atlantic (36). These were analyzed for natural levels of dissolved/dispersed petroleum hydrocarbons by fluorescence. Concentrations ranged from 0.07 to 0.75 µg/l oil equivalents.

The levels and distributions of petroleum hydrocarbons in coastal waters and sediments of the United Arab Emirates (U. A. E.) along the Arabian Gulf and the Gulf of Oman were investigated (37). Oil concentrations in the waters of the U. A. E. were below the 15 µg/l and ranged from 1.6 to 13 µg/l. Petroleum hydrocarbons showed different pattern of distribution in the Arabian Gulf and the Gulf of Oman with more or less similar values. Horizontal distribution of petroleum hydrocarbons at the Arabian Gulf showed significant differences between most sites. At the Gulf of Oman, similar oil concentrations were measured at different sites. Meanwhile, vertical distributions of petroleum hydrocarbons indicated higher concentrations at surface layers of the Arabian Gulf compared to bottom layers. Whereas, more or less similar concentrations were measured at the Gulf of Oman. The concentration of petroleum hydrocarbons in marine sediments varied from 2.5 to 8.2 µg/l (dry wt), with higher concentrations at the Arabian Gulf compared to the Gulf of Oman. The pattern of distribution for petroleum hydrocarbons in marine sediments resembled to some extent the distribution of organic carbon in marine sediments. The study revealed that the concentrations of petroleum hydrocarbons in waters and sediments of the investigated area are not high compared to other areas of the world.

Chouksey, Kadam and Zingde (5) reported petroleum hydrocarbon (PHc) contamination in water, sediment and biota of the coastal area of Bassein–Mumbai in relation to relatively less polluted sites (Dabhol and Ratnagiri) off the west coast of India. To facilitate inter-comparison three standards have been used though the results are reported in terms of SAM (Residue of Saudi Arabian Mix crude). The concentration of PHc in water off Bassein–Mumbai varies widely (2.9–39.2 µg/l) as compared to the average baseline (2.8 µg/l) with higher values generally confined to creeks and estuaries. The higher concentration of PHc in the bottom water of shallow areas is attributed to the contribution from the sediment-associated petroleum residue. High concentration of PHc in the surficial sediment of inshore area Ratnagiri (107.7 ppm, dry wt) is perhaps the remnants of an oil spill that occurred in the Bombay High region on May 17, 1993. The majority of values of PHc concentration in the surficial sediment of the Bassein–Mumbai region exceed 15 ppm (dry wt) against the expected background (<3 ppm, dry wt) and the trend is indicative of transfer of PHc loads from the inshore areas to the open-shore sediments. A minor peak in most cores in the top 10 cm sediment probably results from biological transfer of PHc lower into the sediment by benthic organisms. Excess of PHc retained in the sediment of the Bassein–Mumbai region over the biogenic background is estimated at 40,000 t. The PHc residues (1.8–10.8 ppm, wet wt) in fish caught off Bassein–Mumbai do not suggest bioaccumulation.

Abdullah (38) studied hydrocarbon pollution in the sediment of some Malaysian coastal areas. A study was carried out at some selected coastal areas of Malaysia to determine the present status of hydrocarbon pollution. Five site were chosen and these include Pulau Langkawi and Pulau Ketam in the west coast, Tanjung Piai in the south, and Pulau Tioman and Kemaman in the east coast of Peninsular Malaysia. The levels of total hydrocarbon in the sediments are found to vary from 18.2 to 847.4 mg/kg with sediments from Pulau Langkawi and Tanjung Piai recorded the highest values (691.2 to 847.4 mg/kg) while Kemaman and Pulau Ketam recorded the lowest values (18.2 to 59.8 mg/kg). It was noted that these values are related not only to possible sources of hydrocarbon but also to the physical characteristics of the sediments analysed. Sandy sediment generally contains less hydrocarbon than clay sediment. Further analyses of the sediment extract indicate that the sources of the hydrocarbon pollution are predominantly petrogenic with significant contribution from biogenic hydrocarbon.

The composition and spatial distribution of aliphatic and polycyclic aromatic hydrocarbons (PAHs) were investigated in biota and coastal sediments from four countries surrounding the Gulf (Bahrain, Qatar, United Arab Emirates and Oman) (39). The levels of total petroleum hydrocarbons (TPH), aliphatic unresolved mixture and PAHs in sediments and biota were relatively low compared to world-wide locations reported to be chronically contaminated by oil. Only in the case of the sediments collected near the BAPCO oil refinery in Bahrain, having concentrations of 779 µg/g total petroleum hydrocarbon equivalents and 6.6 µg/g ∑PAHs, can they be categorized as chronically contaminated. Some evidence of oil contamination was also apparent in sediments and bivalves around Akkah Head and Abu Dhabi in the UAE, and near Mirbat in Oman. Contaminant patterns in sediments and biota indicated that the PAHs were mainly from fossil sources, with the exception of the high PAH concentrations in sediments near the BAPCO refinery that contained substantial concentrations of carcinogenic PAH combustion products.

A total of 20 surficial sediment samples, obtained from Hong Kong coastal waters, were analyzed for petroleum hydrocarbons (PHCs) and a suite of 15 polycyclic aromatic hydrocarbons (PAHs) (40). The results indicate that Hong Kong coastal sediments are often seriously polluted with petroleum related hydrocarbons. This is especially so in heavily urbanized or industrialized localities, such as Kowloon Bay (Victoria Harbour), Tsing Yi North and Tolo Harbour. Petroleum hydrocarbon pollutants in marine sediments are believed to be mainly derived from the transportation of oil, shipping activities, spillages, and industrial, stormwater and wastewater discharge. The ratio of unresolved complex mixture (UCM) to n-alkanes, carbon preference index (CPI), and n-C_{16} values indicate that the main contribution to petroleum hydrocarbon contamination is *via* oil and its products. Pollutant sources appear to be stable and continuing when compared with previous data.

CHAPTER III

MATERIALS AND METHODS

3.1 Study site

Samples were collected from three fishing port areas around Ang Sila coast, Chonburi province. Three fishing ports are namely Wat Komut Ratthanaram, Ban Ang Sila and Ta Hoi. The sampling sites were designed based on the distance from fishing ports as well as the existing activities. The sampling sites were divided into three groups. The details of sampling sites are shown in Figure 3-1 and described as follows:

1. About 25 meters from fishing ports: The sampling points at this site were located about 25 meters far from Wat Komut Ratthanaram fishing port, Ban Ang Sila fishing port and Ta Hoi fishing port. These sites are around the fishing port and near-shore. The beach is muddy flat and rock. Restaurants, market, and fishing village were situated around the coast at this site. Seawater, sediment, wild oyster and plankton were collected.

2. About 500 meters from fishing ports: The sampling points at this site were located about 500 meters far from Wat Komut Ratthanaram, Ban Ang Sila fishing port and Ta Hoi fishing port. These sites have oyster farming. Seawater, sediment, farmed oyster and plankton were collected.

3. About 1,000 meters from fishing ports: The sampling points at this site were located about 1000 meters far from Wat Komut Ratthanaram, Ban Ang Sila and Ta Hoi fishing port. These sites have oyster farming. Seawater, sediment, farmed oyster and plankton were collected.

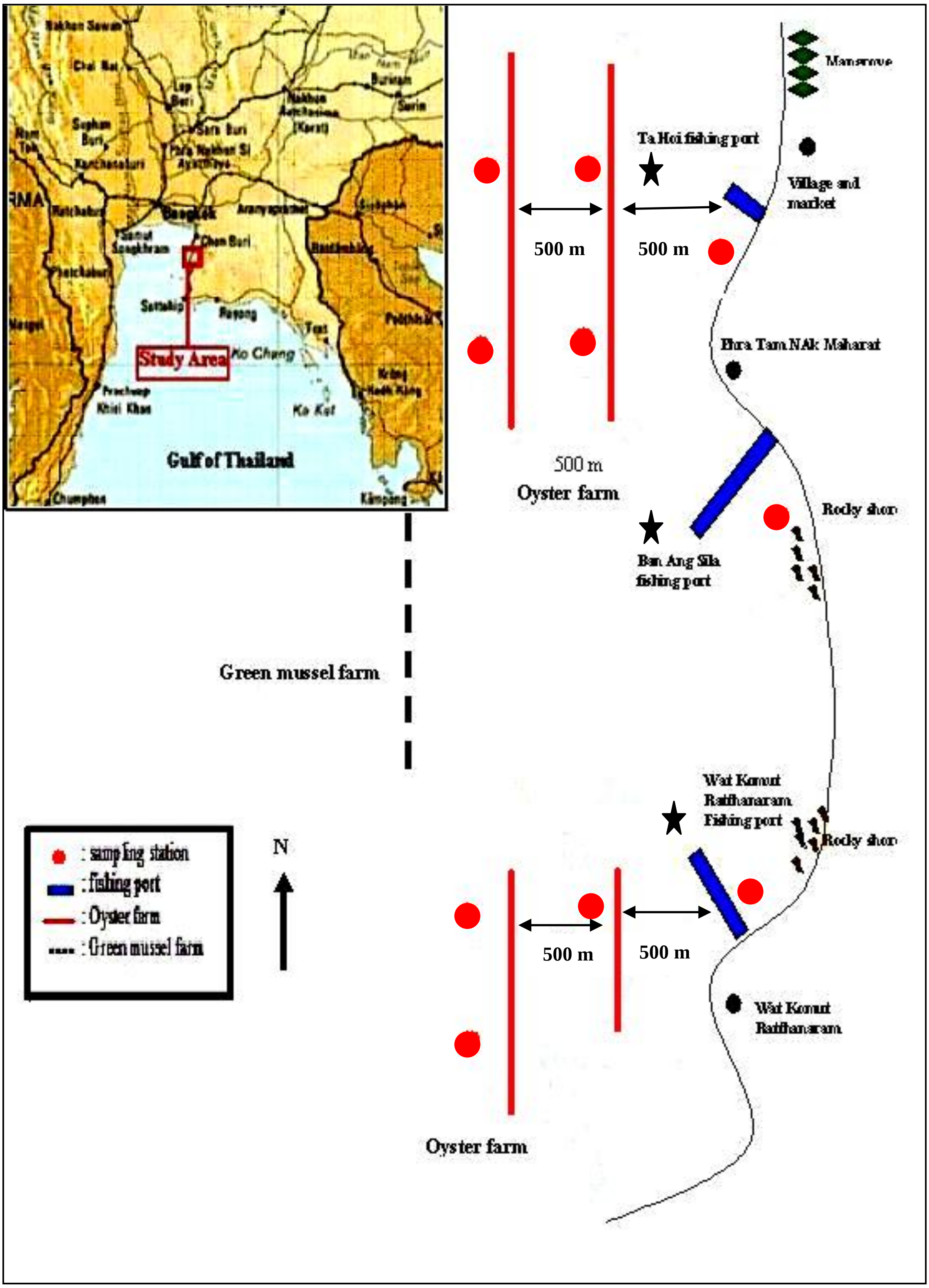

Figure 3-1 The schematic diagram of the sampling points in Ang Sila coast (not to scale)

Source: 41

3.2 Sampling period

All samples (seawater, sediment, oyster, plankton) were collected during the designed sampling period i.e., wet season (September 2006 and August 2007) and dry season (November, 2006 and May 2007).

3.3 Materials, equipments and chemicals

1. Materials

1) Separatory funnel 250 ml
2) Conical flask size 250 ml
3) Vial size 1.5 and 10 ml
4) Erlenmeyer flask (250 ml)
5) Pipette (1, 5, 10 ml)
6) Glass fiber filter (Whatman GF/C)
7) Centrifuge tube
8) Amber-glass bottle (500 ml)
9) Amber-glass jars
10) Polyethylene bag

2. Equipments

1) Incubator shaker
2) Ultrasonic bath
3) Rotary Evaporator
4) Centrifuge
5) Gas chromatography mass spectrometry (GC-MS)
6) pH meter
7) DO meter
8) Conductivity meter
9) Plankton net (mesh size 37 μm)
10) Water sampler
12) Stainless steel wire cage

3. Chemicals

1) Hexane
2) Sodium sulphate anhydrous
3) Dichloromethane (DCM)
4) Acetone
5) Standard: Phenanthrene, Pyrene and Benzo(a)pyrene
6) Diesel oil (commercial grade)

3.4 Sample collection and sample preparation

1. Seawater

The collection procedure was described below:

Seawater samples were collected by grab water sampler at 1 meter depth from water surface. Seawater samples were kept in polyethylene beaker for analysis of some parameters in the field. Their characteristics that were analyzed in the field are listed in Table 3-1.

For total petroleum hydrocarbons (TPH) analysis, seawater samples were collected by Drop-bottle technique (42). A device of seawater collection consists of a weighted bottle holder with a clean amber-glass bottle of 500 ml capacity. Prior to use, the bottle should be thoroughly cleaned and rinsed with detergent, tap water, acetone or methylene chloride, and hexane (nanograde), respectively.

The setup apparatus was thrown as far as possible away from the vessel to avoid seawater that have been disturbed or contaminated by the vessel. The bottle immediately sank to 1 meter depth from the water surface and slowly filled with seawater (43). The samples were stored in the dark and cool place (4 °C) prior to use for TPH analysis.

2. Sediments

Sediments were collected for organic matter, particle distribution, and TPH analysis. The collection procedures are described as follows

About 1 kg of sediment samples were collected by hand-scooping at surface bottom. The samples were kept in polyethylene bag and taken to laboratory. They were stored at 4 °C for further analysis of organic matter and particle size distribution.

For TPH analysis, sediment samples were collected by hand-scooping at surface bottom and immediately placed in a wide mouth glass jars. Prior to use, the jar should be thoroughly cleaned and rinsed with detergent, tap water, acetone or methylene chloride, and hexane (nanograde), respectively. The samples were stored at 4^o C for further TPH analysis (modified from 44).

3. Plankton

Plankton were collected by the 37 μm mesh size plankton net with a 30 cm diameter; net 70 cm length and collection buckle 25 ml which included the phytoplankton and zooplankton. The nets were cleaned with cotton soaked up with hexane before use. Samples were collected at the sea surface. Each sampling site was horizontal towed for about 10 minutes (modified from 45). The volume of the seawater filtered by the net in each sampling point was calculated from readings of the flow meter attached to the net. The samples were kept in polyethylene bottle and stored at -20^o C for further TPH analysis**.**

4. Oyster

Oyster samples were collected by hand. The samples divided into two groups as follows:

- Wild oyster were collected for two sizes i.e., small size (< 5 cm shell length) and big size (≥ 5 cm shell length).
- Farmed oyster were collected for two groups of ages i.e., 3 months and 9 months.

Samples were covered with aluminum foil (clean with hexane before use), kept in polyethylene bag and stored in deep freeze at -20^o C for further analysis of TPH.

3.5 Samples analysis

Before analysis of TPH and PAHs, all glassware were washed with detergent and rinsed several times with tap water, distilled water, acetone and hexane, respectively.

1. Seawater

1.1 Seawater characteristics

Characteristics of seawater that were analyzed in the field are listed in Table 3-1.

Table 3-1 Parameter of seawater that were analyzed in the field

Parameter	Analytical Equipments	Model
pH	pH meter	SevenGo Mettler-Toledo
Conductivity	Conductivity meter	SevenGo Mettler-Toledo
Salinity	Conductivity meter	SevenGo Mettler-Toledo
Water Temperature	DO meter	YSI Model 52 dissolved oxygen meter
Dissolved Oxygen	DO meter	YSI Model 52 dissolved oxygen meter

1.2 TPH analysis

The extraction of TPH in seawater was conducted using liquid-liquid extraction method (modified from 42). The procedures of TPH extraction are described as follows.

One hundred ml of seawater are removed from the sample bottle and added in 250 ml separatory funnel. Sixty ml of hexane are added and the funnel is shaken vigorously for some seconds. The screw cap loosened to allow hexane vapour to escape and the shaking continued for 5 min. After shaking, the funnel is placed in rack to allow the hexane phase separated from the seawater. The hexane phase (extracted solution) is then drained into conical flask size 250 ml. Forty ml of new hexane is added to the separatory funnel and the extraction process was repeated.

After extraction, extracted solution from 1st and 2nd were combined and added to 250 ml conical flask. A few grams of anhydrous Na_2SO_4 are added to break any emulsion and to remove excess water. The extracted solution was concentrated by using a rotary evaporator at 60 °C. The reduced extracted solution is carefully kept in cleaned 10 ml vial glass. This concentrate was finally added with hexane (GC grade) to make a final volume of 5 ml. The sample is then ready for analysis of TPH by using GC-MS.

2. Sediment

2.1 Particle size distribution and texture

Analytical method for particle size distribution was given in appendix A.

2.2 Organic matter

Analytical method for organic matter was given in appendix B.

2.3 TPH analysis

Prior to analyze, the sediment sample were air-dried for 3-4 days. The air- dried sediments were gently homogenized with a mortar and pestle and then passed through a 2 mm sieve.

Air-dried sediment samples were homogenized and extracted with dichloromethane (DCM) by incubator shaker (modified from 46). The procedures of TPH extraction are described as follows.

Five gm of sediment samples (dry weight) were added in 250 ml flask and 60 ml of DCM were used as extraction solvent. The flask was sealed with a foil-line cap and shaken for first extraction with incubator shaker at 200 rpm/28°C for 90 min.

After extraction, extracted solution was transferred to 250 ml conical flask. The new 40 ml of DCM were added to the flask and extraction process was repeated. The extracted solutions from 1st and 2nd were combined and transferred to 250 ml conical flask. The combined extracted solutions were evaporated to remove DCM by rotary evaporator at 60 °C. The final volume was adjusted to 5 ml by hexane

(GC grade) and kept in 10 ml vial. The sample is then ready for, analysis of TPH by using GC-MS.

3. Plankton

TPH analysis

Plankton samples were concentrated in pre-combusted (105°C 4h) by Whatman GF/C filters. Then plankton was freeze-dried by freeze dryer about 24 hours.

One gm of plankton (dry weight) was place in a centrifuge tube containing 15 ml of dichloromethane (DCM). The tube was sonicated for 10 min, centrifuged (2,500 rpm, 10 min) and subsequently washed twice 10 ml of DCM (modified from 47). The combined extracted solutions transferred to conical flask and evaporated by rotary evaporator at 60 °C. Adjusted final volume to 5 ml with hexane (GC grade) and kept in 10 ml vial. The sample is then ready for analysis of TPH using by GC-MS.

4. Oyster

TPH analysis

Before analysis, the oyster tissues were carefully picked from their shells, homogenized and freeze-dried by freeze dryer about 48 hours then ground into a fine powder by mortar.

One gram of homogenized oyster tissues was extracted with 5 ml of dichloromethane (DCM) by sonication in the ultrasonic bath for 15 min, centrifuged (2,500 rpm, 10 min) and extracted solution was separated. The extraction procedure was repeated three times, each time with 5 ml of DCM (modified from 48). The combined extracted solutions of 1st, 2nd and 3rd extraction were transferred to 250 ml conical flask. The combined extracted solutions were evaporated by rotary evaporator at 60 °C. Then adjusted the final volume to 5 ml with hexane (GC grade) and kept in 10 ml vial. The sample is then ready for analysis of TPH by using GC-MS.

3.6 Determinations of total petroleum hydrocarbon (TPH) by gas chromatography mass spectrometry (GC-MS)

The determinations of TPH in samples (i.e., seawater, sediment, plankton and oyster) were conducted using GC-MS. The GC-MS analyses were conducted on an Agilent gas chromatography 6890N equipped with MS5975 inert XL mass selective detector. The capillary column used was 30 m × 0.25mmID, 0.25 µm film thickness. The operation conditions were: carrier gas (He) 1 ml/min; make up gas 50 ml/min; sample injection 1 µl in a splitless mode; inlet temperature 280 ºC; and detector temperature 300 ºC. The two steps of oven temperature program were as follows:

Initial temperature 100 °C

Initial time 0.00 min

Step	Rates (°C/ min)	Final temperature (°C)	Holding time (min)
1	25	220	0
2	5	300	1.2

Total running time: 22 minutes

The GC-MS data were acquired and processed with HP Chemstation software equipped with a GC-MS Data library. The mass spectrometer scanned 50 – 450 Daltons per seconds; electron energy was 70 eV.

Identifications and quantifications of 3PAH compounds were base on matching their retention time with an individual of PAH standard. The 3PAH compound were phenanthrene [Phe, 178 m/z], pyrene [Pyr, m/z 202] and benzo[a]pyrene [BaP, m/z 252]. N-alkanes and other compound identifications were performed using the m/z of mass chromatography and mass spectra database (NIST98). The levels TPH were quantified the peak area of chromatogram using the diesel calibration curve with an external standard technique (49) (the detail in appendix C).

3.7 Calculation of Carbon Preference Index (CPI)

Carbon Preference Index (CPI_1) means the ratios between total weight of ood-carbon homologues and weight of the even-carbon homologous (17, 18, 19).

$$CPI_1 = \frac{\text{odd carbon number homologs}}{\text{even carbon number homologs}}$$

Moreover, Columbo *et al.* (99) presented CPI_2 is given by the ratio $2(C_{27}+C_{29})/(C_{26}+2(C_{28})+C_{30}$.

3.8 Statistical analysis

One-Way Analysis of Variance (One-Way ANOVA) in the statistical programme “SPSS for Windows 12.0” (50) was used to evaluate variability following Scheffe test (at 0.05 level) for comparison between TPH concentration of the distance of 25 m, 500 m and 1000 m from fishing ports. T-Test for comparison the concentrations of TPH between wet season and dry season for each sample. The relationship of TPH concentrations among samples were explained by correlation coefficient. Statistic explanation such as average±SD, minimum value and maximum value were used to explain results as well.

CHAPTER IV

RESULTS AND DISCUSSION

The study of total petroleum hydrocarbon (TPH) seawater, sediment, plankton and oyster were collected from three fishing ports areas around Ang Sila coast, Chonburi province during the wet season (September, 2006 and June, 2007) and the dry season (November, 2006 and May, 2007). Sampling sites were designed based on the distance from the fishing ports (i.e.; 25 m, 500 m and 1000 m) as well as the existing activities. The results of this study are presented and discussed as follows.

4.1 Physical and chemical parameters of seawater

The physical and chemical parameters were influence on TPH concentration in seawater. The physical and chemical parameters of dissolved oxygen (DO), pH, temperature, conductivity and salinity were investigated and presented in Table 4-1.

Table 4-1 Physical and chemical parameters of seawater

Fishing port sites	Distance from fishing port (m)	Physical and Chemical parameters of seawater																			
		Wet season										Dry Season									
		September 2006					August 2007					November 2006					May 2007				
		DO (mg/l)	pH	Temp (°C)	Conduc-tivity (µS/m)	Salinity (ppt)	DO (mg/l)	pH	Temp (°C)	Conduc-tivity (µS/m)	Salinity (ppt)	DO (mg/l)	pH	Temp (°C)	Conduc-tivity (µS/m)	Salinity (ppt)	DO (mg/l)	pH	Temp (°C)	Conduc-tivity (µS/m)	Salinity (ppt)
Wat Komut Rattha-naram	25	7.6	8.80	31.1	25.0	11.2	5.4	7.89	29.2	41.8	24.8	7.5	7.89	29.0	49.6	30.1	4.4	8.14	30.1	45.6	29.6
	500	6.7	8.61	31.5	19.9	11.2	5.6	8.11	31.0	44.2	24.8	6.9	7.50	28.9	49.7	30.1	4.3	8.05	30.0	45.8	29.6
	1000	7.2	8.71	30.9	25.1	11.2	4.8	8.19	30.9	43.3	24.8	7.6	7.76	29.0	50.1	30.1	4.2	8.13	30.4	45.5	29.6
Ban Ang Sila	25	5.5	8.81	30.7	23.1	11.2	5.3	8.17	29.2	42.2	24.8	7.9	7.57	29.0	48.7	30.1	5.2	8.26	30.4	45.4	29.6
	500	7.0	8.64	31.3	21.8	11.2	4.1	8.02	29.9	42.1	24.8	7.0	7.45	29.2	50.2	30.1	5.6	8.15	30.9	45.4	29.6
	1000	7.5	8.61	31.0	25.0	11.2	4.3	8.15	30.4	40.8	24.8	8.1	7.78	29.1	50.8	30.1	4.2	7.88	30.2	41.2	29.6
Ta Hoi	25	6.3	8.57	31.8	20.5	11.2	4.6	8.08	29.3	41.8	24.8	7.1	7.95	29.0	49.3	30.1	4.5	8.07	30.7	44.3	29.6
	500	5.8	8.43	31.3	23.0	11.2	4.2	7.89	29.8	41.6	24.8	8.0	7.60	29.0	49.5	30.1	4.9	8.10	30.9	39.6	29.6
	1000	7.2	8.77	30.8	26.2	11.2	4.3	8.12	29.9	39.8	24.8	6.4	7.42	29.4	50.6	30.1	4.2	7.94	30.4	42.0	29.6
Minimum		*5.5*	*8.43*	*30.7*	*19.9*	*11.2*	*4.1*	*7.89*	*29.2*	*39.8*	*24.8*	*6.4*	*7.42*	*28.9*	*48.7*	*30.1*	*4.2*	*7.88*	*30.0*	*39.6*	29.6
Maximum		*7.6*	*8.81*	*31.8*	*25.0*	*11.2*	*5.6*	*8.19*	*30.9*	*44.2*	*24.8*	*8.0*	*7.95*	*29.4*	*50.8*	*30.1*	*5.6*	*8.26*	*30.9*	*45.8*	29.6
Mean		*6.80*	*8.67*	*31.12*	*23.50*	*11.20*	*4.63*	*8.09*	*30.04*	*42.28*	*24.80*	*7.40*	*7.67*	*29.10*	*50.05*	*30.10*	*4.56*	*8.08*	*30.44*	*44.03*	*29.60*

Among the physical and chemical parameters, salinity was exhibited higher values (29-30 ppt) in the dry season (November 2006 and May 2007). The salinity of seawater in wet season (September 2006 and August 2007) was relatively low when compared to the dry season. The lower salinity is best explained by freshwater runoff entering the marine system accompanying by the rainfall in the wet season (mean of rainfall shown in appendix F). The conductivity was related to the salinity and exhibited the similar pattern. In the same year dissolved oxygen (DO) was not exhibited significant different in both seasons. However, it was noted that DO in year 2007 was relatively lower (4-5 mg/l) than DO presented in year 2006 (5-8 mg/l). This might be occurred by different time. In year 2006 the sample was collected in the afternoon whereas year 2007 the sample was collected in the morning. DO concentrations are usually highest in the late afternoon, because photosynthesis has been occurring throughout day (51). For the reason, oxygen is produced during photosynthesis and consumed during respiration and decomposition. Because it requires light, photosynthesis occurs only during daylight hours. Respiration and decomposition process, on the other hand, occur 24 hours a day. This difference alone can account for large daily variations in DO concentrations. During the night, when photosynthesis cannot counterbalance the loss of oxygen through respiration and decomposition, DO concentration may steadily decline. It is lowest just before dawn, when photosynthesis resumes (52). For the pH and temperature showed slightly difference between the wet and dry seasons.

According to Coastal Water Quality Standards in Thailand (53), the quality of seawater can be divided in to six classes as presented in Table 4-2. The activity in study area is contribute to class 5 (industries and ports) of the standards. However the results of DO, temperature, pH and salinity of seawater of the study area were in the limit of seawater quality standard in class 5.

Table 4-2 Coastal Water Quality Standards

Coastal Water Quality Standards	Parameters				
	DO (mg/l)	pH	Temp (ºC)	Salinity (ppt)	Conductivity (µS/m)
Class 1 Preservation Area	<<4	7.0-8.5	D>>1	D>>10%	-
Class 2 Coral Conservation	<<6		ND		
Class 3 Water for Coastal Farms	<<4		D>>1		
Class 4 Proximity Activities			D>>2		
Class 5 Industries and Ports					
Class 6 Community					

Remark: >> = not more than , << = not less than , D = change from natural condition, ND= not change from natural condition

Source: 53

4.2 Some characteristics of sediment

Some characteristics of texture classes, percentage of organic matter and organic carbon are presented in Table 4-3.

The texture classes of sediment were sandy clay loam and clay loam. The texture of sediment samples at the distances of 500 m and 1000 m from the fishing ports were mostly found as clay loam. Percentages of organic matter and organic carbon in sediment collected in the wet season range from 0.75-3.07 and 0.44-1.78, respectively and collected in the dry season range from 0.74-2.23 and 0.43-1.30, respectively. However, percentage of organic matter and organic carbon in clay loam sediment were found to be higher than those presented in sandy clay loam.

Table 4-3 Some characteristic of sediment

Fishing port sites	Distance from fishing port (m)	Wet season						Dry season					
		September 2006			August 2007			November 2006			May 2007		
		Texture name	OM (%)	OC (%)	Texture name	OM (%)	OC (%)	Texture name	OM (%)	OC (%)	Texture name	OM (%)	OC (%)
Wat Komut Rattha-naram	**25**	Sandy clay loam	1.66	0.96	Sandy clay loam	0.85	0.49	Sandy clay loam	1.24	0.72	Sandy clay loam	1.41	0.82
	500	Sandy clay loam	1.37	0.79	Clay loam	1.79	1.04	Sandy clay loam	1.60	0.93	Sandy clay loam	1.99	1.15
	1000	Clay loam	2.39	1.38	Clay loam	1.98	1.15	Sandy clay loam	1.77	1.02	Clay loam	2.10	1.22
Ban Ang Sila	**25**	Sandy clay loam	0.97	0.56	Sandy clay loam	0.75	0.44	Sandy clay loam	1.35	0.63	Sandy clay loam	2.23	1.30
	500	Clay loam	2.25	1.30	Sandy clay loam	1.05	0.61	Sandy clay loam	0.61	0.35	Clay loam	1.60	0.93
	1000	Clay loam	3.07	1.78	Sandy clay loam	1.32	0.76	Sandy clay loam	1.09	0.63	Clay loam	1.06	0.61
Ta Hoi	**25**	Sandy clay loam	1.35	0.78	Sandy clay loam	1.16	0.67	Sandy clay loam	1.30	0.75	Sandy clay loam	1.89	1.09
	500	Clay loam	2.46	1.43	Sandy clay loam	1.05	0.61	Sandy clay loam	1.28	0.67	Clay loam	0.74	0.43
	1000	Sandy clay loam	1.87	1.09	Sandy clay loam	1.26	0.73	Sandy clay loam	0.97	0.56	Clay loam	1.02	0.59
Mean		-	*1.98*	*1.12*	-	*1.33*	*0.77*	-	1.27	0.74	-	1.53	0.90

4.3 Total petroleum hydrocarbon (TPH) around Ang Sila coast, Chonburi province

The concentrations of TPH in seawater, sediment, plankton and oyster during the wet season (September, 2006 and June, 2007) and the dry season (November, 2006 and May, 2007) are presented in Table 4-4. The samples were analyzed by GC-MS for accumulation and distribution of TPH. TPH in all sample are found n-alkanes compounds.

Table 4-4 TPH concentration in samples

Fishing port sites	Distance from fishing port (m)	TPH Concentration ± SD															
		Wet Season								Dry Season							
		September 2006				August 2007				November 2006				May 2007			
		Seawater (µg/l)	Sediment (µg/g)	Plankton (µg/g)	Oyster (µg/g)	Seawater (µg/l)	Sediment (µg/g)	Plankton (µg/g)	Oyster (µg/g)	Seawater (µg/l)	Sediment (µg/g)	Plankton (µg/g)	Oyster (µg/g)	Seawater (µg/l)	Sediment (µg/g)	Plankton (µg/g)	Oyster (µg/g)
Wat Komut Rattha-naram	25	0.75±0.14	0.19±0.04	NS	0.45^{bw} ND^{SW}	22.27±692	0.01±0.00	0.12	ND^{bw} ND^{SW}	80.41±10.97	1.34±0.04	NS	ND^{bw} ND^{SW}	44.08±13.21	0.09±0.04	0.07	ND^{bw} 0.26^{SW}
	500	68.85±573	0.40±0.19	NS	ND^{F}	ND	0.02±0.00	0.36	ND^{F}	1.49±0.19	1.01±0.12	NS	ND^{F}	2.90±0.28	ND	0.26	ND^{F}
	1000	1.88±2.18	4.42±0.80	NS	ND^{F}	3.24±3.68	0.08±0.02	1.56	0.18	NO	0.68±0.14	NS	ND^{F}	8.04±9.30	ND	0.18	ND^{F}
Ban Ang Sila	25	11.59±072	0.19±0.01	NS	ND^{bw} ND^{SW}	ND	0.03±0.00	0.62	ND^{bw} ND^{SW}	87.95±9.72	1.44±2.20	NS	ND^{bw} ND^{SW}	28.60±21.99	0.18±0.05	0.25	0.55^{bw} 3.94^{SW}
	500	ND	8.30±0.05	NS	ND^{F}	ND	0.01±0.00	4.05	ND^{F}	12.88±0.82	0.59±0.10	NS	ND^{F}	ND	0.03±0.00	0.04	ND^{F}
	1000	2.88±0.45	4.29±0.08	NS	ND^{F}	ND	0.01±0.00	2.74	ND^{F}	0.20±0.00	0.60±0.02	NS	ND^{F}	0.38±0.01	ND	0.21	ND^{F}
Ta Hoi	25	ND	0.15±0.02	NS	NS	2.21±1.26	0.18±0.14	3.94	NS	83.12±13.90	0.87±0.31	NS	NS	15.26±3.15	0.03±0.01	0.15	NS
	500	ND	8.50±0.37	NS	ND^{F}	ND	0.01±0.00	0.30	0.17	30.88±5.04	0.99±0.00	NS	ND^{F}	41.09±25.65	ND	0.50	ND^{F}
	1000	ND	7.51±0.87	NS	ND^{F}	ND	0.01±0.00	0.37	ND^{F}	ND	0.96±0.06	NS	ND^{F}	ND	0.02±0.00	0.28	0.15
Minimum		*ND*	*0.15±0.02*	-	*ND*	*ND*	*0.01±0.00*	*0.12*	*ND*	*ND*	*0.59±0.10*	-	*ND*	*ND*	*ND*	*0.07*	*ND*
Maximum		*68.85±573*	*8.50±0.37*	-	*0.45*	*22.27±692*	*0.18±0.14*	*4.05*	*0.18*	*87.95±9.72*	*1.44±2.20*	-	*ND*	*44.08±13.21*	*0.18±0.05*	*0.50*	*3.94*
Mean		*8.78±2141*	*3.40±3.65*	-	-	*3.77±6.96*	*0.042±0.06*	*1.56±1.52*	-	*32.99±38.61*	*0.94±0.30*	-	-	*14.91±17.48*	*0.072±0.07*	*0.21±0.14*	-

^{SW} = wild oyster size < 5 cm; ^{bw} = wild oyster size ≥ 5 cm; ^{F} = farmed oyster; NS = No Sample; ND = Non Detectable

4.3.1 The concentration of TPH in seawater

The concentrations of TPH in seawater are presented in Table 4-4. The results revealed that TPH concentrations in the dry season were significant higher than in the wet season during 2006-2007 (appendix E).

In the wet season, TPH concentrations were in the range of 0-68.85 µg/l. TPH concentrations in most of the samples were non detectable. In September 2006, TPH concentrations in samples were in the range of 0-68.85 µg/l. TPH concentrations in seawater at the distance of 500 m from Wat Komut Ratthanaram fishing port was found to be the highest as compared to the other two sites at the same distance. In August 2007, TPH concentrations in samples were in the range of 0-22.7 µg/l. However, TPH concentrations in August 2007 were lower than those presented in September 2006. The low concentration levels of TPH in the wet season illustrated that they were being diluted. The high input of fresh waters and river discharges during the wet season dilute the petroleum hydrocarbons effectively into the seawater (mean of rainfall in appendix F).

In the dry season, TPH concentrations were in the range of 0-87.95 µg/l. In November 2006, TPH concentrations in samples were in the range of 0-87.95 µg/l. The highest TPH concentration in November 2006 was found in seawater collected from Ban Ang Sila fishing port. However it was noted that TPH content was decreased with distance away from offshore for all fishing ports. In May 2007, TPH concentrations in samples were in the range of 0-44.08 µg/l and they were lower than the presented in November 2006. The high water-residence time could be an important factor influencing the accumulation and retention of hydrocarbons in seawaters in the dry season (33).

The distribution pattern implied that the high concentrations of TPH were found in samples at the distance of 25 m from the fishing port possibly contributed to most activities produced from fishing boats such as oil spilled from machine and fuel tank. This study was corresponded to Petpiroon (10) who reported that fishing ports were generally more contaminated than recreation beach and aquaculture site. Similar result was reported by Tappatat (31) who found that concentration of TPH in aquaculture site (1.09 µg/l) was found to be lower than industrial (1.94 µg/l) and urbanized (1.12 µg/l), respectively.

Coastal water quality standards of Thai Environment Regulation stated that TPH concentration of seawater for preservation area, for coral conservation and for coastal farm (classes 1-3) was 0.5 µg/l as Chrysene; seawater for recreation (class 4) was 1 µg/l as Chrysene and seawater for industries and ports and for community (classes 5-6) was 5 µg/l as Chrysene (53). Considerations of the results from this study, TPH concentrations in seawater at the distance of 25 m from all the fishing ports were not met the criteria of Standard of Coastal Seawater in the categories of classes 5-6 except the results obtained from Wat Komut Ratthanaram and Ta Hoi in September 2006 and Ban Ang Sila and Ta Hoi in August 2007. TPH in seawater at the distance of 500 m and 1000 m from all the fishing ports were lower than those in the categories of classes 5-6 except the results obtained at the distance of 500 m from Wat Komut Ratthanaram in September 2006, Ban Ang Sila in November 2006 and Ta Hoi in May 2007 and at the distance of 1000 m from Wat Komut Ratthanaram in May 2007.

However, the plausible explanation for low concentration of petroleum hydrocarbon residues in seawater is the effect of several processes such as evaporation, photooxidation and biodegradation (54). Additionally in aquatic environment, petroleum hydrocarbon has low solubility and hydrophobic properties (5, 6, 7). Moreover, physical and chemical parameter of seawater could significantly influence the natural fate and distribution of the petroleum hydrocarbons such as high seawater temperature contributes to the increasing of evaporation of petroleum hydrocarbon (55), water temperature, oxygen levels and salinity were influenced the biodegradation rates (8) and salinity can substantially affect the water solubility of many compounds especially the solubility of hydrophobic organic contaminants (56).

Comparing the concentration of petroleum hydrocarbon in the previous studies (see Table 4-5) the results showed that the levels of TPH obtained from this study were lower except the results in Gulf of Thailand.

Table 4-5 Contamination of petroleum hydrocarbons in seawater of petroleum hydrocarbons in Thailand

Area	Type	Method	Concentration	References
Phe Bay,Rayong province	TPH	UVF	0.61±0.26 µg/l	9
Eastern coastral area from Pattaya to Trat	TPH	UVF	0.55 µg/l (coastal) 0.30 µg/l (near shore and off shore)	10
Gulf of Thailand	n-alkane	GC	110 µg/l (May and June) 151 µg/l (September and November)	28
The mouth of Chao Phraya River	TPH	UVF	18.02 µg/l (May) 6.01 µg/l (September)	30
Rayong province	TPH	UVF	1.94 µg/l (industrial) 1.12 µg/l (urbanized) 1.09 µg/l (aquaculture sites)	31

Comparison to petroleum hydrocarbons in seawater collected in other countries (Table 4-6), it can be concluded that the concentrations were lower than concentrations obtained from this study except Alang-Sosiya ship scrapping yard in India. However the TPH concentration at the Alang-Sosiya ship scrapping yard where the world's largest ship scrapping zone on the Gulf of Cambay, India illustrated the higher level than those presented in costal area such as Bassein–Mumbai, São Sebastião, The South West Atlantic and The United Arab Emirates (U. A. E.).

Table 4-6 Contamination of petroleum hydrocarbons in seawater in other countries

Area	Type	Method	Concentration	References
Bassein–Mumbai, India	TPH	UVF	2.9-39.2 µg/l	5
Alang-Sosiya ship scrapping yard, Gulf of Cambay, India	TPH	UVF	257-1437 µg/l (May) 453-2325 µg/l (August) 550-3540 µg/l (December)	33
São Sebastião, SP, Brazil	dissolved/disperse petroleum hydrocarbons (DDPH)	UVF	0.35-2.50 µg/l	34
The southwestern Amur Bay in the Sea of Japan.	aliphatic hydrocarbon	IR - spectroscopy	0-129 µg/l	35
The South West Atlantic	DDPH	UVF	0.07-0.75 µg/l	36
The United Arab Emirates (U.A.E.) along the Arabian Gulf and the Gulf of Oman	TPH	UVF	1.6-13 µg/l	37

4.3.2 The concentration of TPH in sediment

The concentrations of TPH in sediment were presented in Table 4-4. The results revealed that TPH concentrations in the wet season were significant higher than in the dry season in year 2006 whereas in year 2007 this result showed no significant difference (appendix E).

In the wet season, TPH contents were in the range of 0.01-8.50 µg/g. In September 2006, TPH concentrations of samples were in the range of 0.15-8.50 µg/g. The highest level of TPH was at Ta Hoi fishing port followed by Ban Ang Sila fishing port and Wat Komut Ratthanaram fishing port, respectively. The lowest concentration was found in sediment samples at distance of 25 m. In August 2007, TPH concentrations of samples were in the range of 0.01-0.18 µg/g and they were slightly different among the three fishing ports.

For the dry season, TPH contents were in the range of 0-1.44 µg/g. In November 2006, TPH concentrations of samples were ranged from 0.59-1.44 µg/g. TPH concentrations in sediment collected in November 2006 were higher than presented in May 2007. In May 2007, TPH concentrations of samples were in the range of 0-0.18 µg/g. TPH concentration in sediment collected at the distance of 1000 m from all the fishing port were non detectable.

The multiple comparisons of TPH concentrations in sediment according to the distance from the fishing ports (i.e., 25 m, 500 m and 1000 m) revealed that the TPH concentration were significantly different in September 2006; November 2006 and May 2007 whereas the value was not significantly different in August 2007 (appendix D).

The sediment is composed of high clay and silt with potentially containing more oil or hydrocarbon than sandy sediment (38). As indicate in the Table 4-3, the high values of TPH concentration found in sediment samples at the distance of 500 m and 1000 m from the fishing ports may be related to the high clay and silt content (clay loam texture) of the sediment. Similarly the sandy clay loam of sediment samples at the distance of 25 from the fishing ports may contribute to lower values of TPH concentration at this area. This study was corresponded to Ocean Affairs Board (57) who reported that courser sediment such as sand and gravel allows greater penetration of oil derived hydrocarbons than finer sediments. The highest concentration of oil can generally associate with silt sediment possibly because sediments have a greater area for adsorption of oil. Courser sediments although allowing greater oil penetration also have high biodegradation rates relative to fine sediment, possibly because of greater aeration and nutrient flow to subsurface. Similar to the study of Abdullah (38) who noted that the hydrocarbon content of the sediment is related to the physical characteristics of the sediment i.e. sandy sediment contains less hydrocarbon than sediment consist of high clay and silt.

Moreover, petroleum hydrocarbons could be absorbed by suspended and dissolved materials (i.e., dentritus, humic material, fine grained clays) (58) that, upon deposition, contribute to build up contaminants in the sediment and directly related to sediment’s organic content (26). Many researchers have observed that petroleum hydrocarbon in sediments is mainly adsorbed with the organic matter (9, 14, 26, 37, 58). Organic carbon is often a positive correlation between the total organic carbon content and levels of hydrophobic contaminants in sediment (59). In this study the correlation coefficient (r) between organic carbon and TPH concentration in sediment was significant positive correlation (r = 0.67) in September 2006 whereas the correlation coefficients (r) in November 2006 (r = 0.18), May 2007 (r = 0.38) and August 2007(r = 0.31) were not significant.

According to Ghadban *et al.* (60) who found that a relationship between percentage of total organic carbon and petroleum hydrocarbon can be considered when petroleum hydrocarbons are present in high concentration. However, the pattern of distribution for petroleum hydrocarbons in sediments from this study resembled to some extent the distributions of organic carbon in marine sediment (Table 4-7). This is supported by the significant positive correlation between the TPH concentration in sediment and corresponding values of organic carbon which implying that the increased in petroleum hydrocarbons contaminated from fishing boats would resulted in an increase of organic carbon content. However, several factors that might contribute in the concentration of total organic carbons such as the water circulation, total petroleum hydrocarbons, inorganic carbon, sediment grain size and biological productivity are discussed (60).

Table 4-7 Concentration of TPH (µg/g) and percentages of organic carbon in sediment

Fishing port sites	Distance from fishing port (m)	September 2006	
		Org. carbon (%)	TPH Conc. (µg/g)
Wat Komut Ratthanaram	25	0.96	0.19
	500	0.79	0.40
	1000	1.38	4.42
Ban Ang Sila	25	0.56	0.19
	500	1.30	8.30
	1000	1.78	4.29
Ta Hoi	25	0.78	0.15
	500	1.43	8.50
	1000	1.09	7.51

TPH concentrations in sediment (0-8.50 µg/g (ppm)) were higher than those in seawater (0-87.95 µg/l (ppb)). This might be occurred by hydrocarbon contaminants in sediments which hydrocarbon were not affected by weathering processes such as evaporation, photooxidation and water washing (61, 62). Additionally the polar characteristic of the suspended clay/silt particles and hydrocarbon, the intensive mixing of the oil and water and the eventual setting of these particles within the sediment would show higher concentration in the deeper sediment based on contaminant loading within the water column (63, 64).

Comparison of various studies of petroleum hydrocarbons in sediment in other areas of Thailand (Table 4-8), the results showed that the study in the lower Tha Chin River (65) and the lower Chao Phraya River (30) were higher than the results obtained from this study. The concentrations of petroleum hydrocarbons in other regions (10, 14, 28, 31) showed slightly different from this study.

Table 4-8 Contamination of petroleum hydrocarbons in sediment in Thailand

Area	Type	Method	Concentration	References
Phe Bay Rayong province	TPH	UVF	1.18 ±1.86 µg/g (June) 1.88±3.02 µg/g (September)	10
Ship –breaking industry area, Rayong province	n-alkane	GC	0.35 µg/g (October) 0.36 µg/g (June)	14
Gulf of Thailand	n-alkane	GC	3.7 µg/g (Dry season) 2.9 µg/g (Wet season)	28
The lower of Chao Phraya River	n-alkane	GC	5.20 µg/g (May) 5.82 µg/g (September)	30
Coastal area, Rayong province	n-alkane	GC	0.11-14.37 µg/g	31
The lower Tha Chin River	n-alkane	GC	20.99±7.85 µg/g (March) 15.39±3.15 µg/g (August)	65

Comparison of petroleum hydrocarbons in sediments collected in other countries (Table 4-9), it can be concluded that the concentrations of TPH from this study were similar to those presented in the United Arab Emirates (U. A. E.). Meanwhile, the concentration was found to be lower when compared to the coastal area such as Bassein–Mumbai, some Malaysian coastal area, the Gulf (Bahrain, Qatar, United Arab Emirates and Oman) and Hong Kong coastline and higher than that of costal area such as the southwestern Amur Bay. These coastal have port areas, refineries and industrials have become major sources of petroleum hydrocarbons to the marine coastal. Especially, Hong Kong coastline where the international shipping hubs in the South China Sea was highest contaminated.

Table 4-9 Contamination of petroleum hydrocarbons in sediment in other countries

Area	Type	Method	Concentration	References
Bassein–Mumbai, India	TPH	UVF	107.7 µg/g	5
The southwestern Amur Bay in the Sea of Japan	aliphatic hydrocarbon	IR-spectroscopy	7.2-1100 ng/g	35
The United Arab Emirates (U. A. E.) along the Arabian Gulf and the Gulf of Oman	TPH	UVF	2.5-8.2 µg/g	37
Some Malaysian coastal area	n-alkane	UVF	18.2-847 µg/g	38
The Gulf (Bahrain, Qatar, United Arab Emirates and Oman).	TPH	UVF	779 µg/g	39
Hong Kong coastline	TPH	GC	4.5-1996 µg/g	40

4.3.3 The concentrations of TPH in plankton

The concentrations of TPH in plankton were collected by the 37 µm mesh size plankton net which included the phytoplankton and zooplankton during the wet season (August, 2007) and the dry season (May, 2007). The concentrations of TPH in plankton are presented in Table 4-4.

The seasonal distributions of TPH were compared between the wet season and dry season. TPH concentrations in the wet season were significant higher than those in the dry season (appendix E).

In the wet season, TPH concentrations in plankton were in the range of 0.12-4.05 µg/g. Its concentration in plankton collected from 500 m and 1000 m from Ban Ang Sila fishing port and 25 m from Ta Hoi fishing port were higher than the others. In the dry season, TPH concentrations in plankton were in the range of 0.07-0.50 µg/g and they were slightly different among the three fishing ports. Petroleum hydrocarbons were that accumulated in plankton was possibly due to the uptake from surrounding contaminated seawater around fishing port. (9)

However, multiple comparisons of TPH concentrations in plankton according to the distance from the fishing ports (i.e., 25 m, 500 m and 1000 m) revealed that the TPH concentration were not significantly different between the wet and dry seasons (appendix D).

Comparative with the research of Suwangosoom (9) who reported that the concentrations of TPH in plankton at Phe Bay, Rayong province was performed by fluorescence spectrometry. The levels of TPH in plankton were 24.30 µg/g which they were higher than the results of this study.

4.3.4 The concentration of TPH in oyster

The oyster samples divided into two groups as wild oyster which were collected for two sizes (i.e., small size (< 5 cm shell length) and big size (≥ 5 cm shell length)) and farmed oyster. The number of wild oyster at Ta Hoi fishing port was too few to be collected. The concentrations of TPH in oyster are presented in Table 4-4.

The seasonal accumulations of TPH were compared between the wet and dry seasons. Both years 2006 and 2007, TPH concentrations in oyster samples were not significantly different between the wet and dry seasons (appendix E).

Moreover TPH concentrations in most of samples were non detectable. A low levels of TPH presented in oyster were related to the low concentration of TPH in seawater.

Additionally the seasonal, size and the distance from fishing port have no effected on TPH accumulation in oyster.

Comparison to the previous studies (Table 4-10), the results showed that the concentration of petroleum hydrocarbon in oyster and mussel at Ang Sila, Srichang Island and Sriracha (29), mussel and clam at Phe Bay (9), *Donex* sp. at Ship –breaking industry area, Rayong province (14) and mussel at the lower of Chao Phraya River (30) were higher than the results obtained from this study.

Table 4-10 Contamination of petroleum hydrocarbons in bivalves in Thailand

Sample	Area	Type	Method	Concentration	References
Mussel (*Perna viridis*) Clam (*Meretrix lusoria*)	Phe Bay Rayong province	TPH	UVF	16.97±17.33µg/g 7.97±8.41 µg/g	9
Donax sp.	Ship –breaking industry area, Rayong province	n-alkanes	GC	6.18-14.91µg/g (October) 10.84-38.94µg/g (June)	14
Mussel (*Perna viridis*)	The lower of Chao Phraya River	n-alkanes	GC	1.93 µg/g (May, 1993) 2.14 µg/g (September, 1993)	30

4.4 Typical of petroleum hydrocarbon in samples around Ang Sila coast, Chonburi province

4.4.1 Typical of petroleum hydrocarbon in seawater

The major type of petroleum hydrocarbons in seawater was n-alkanes ranging from $C_{18} – C_{34}$. The n-alkanes in seawater samples were exhibited the similar pattern between the wet and dry season.

The short-chain n-alkanes ($C \leq 20$) in seawater were generally non-detectable throughout the study at all sampling sites. The long-chain n-alkanes ($C \geq 20$) were predominant in seawater. Considerable amount of the long-chain n-alkanes in seawater were lower than those in the sediments. Other studies have reported that the lighter and aliphatic hydrocarbons are probably affected immediately by evaporation and dissolution processes (66, 67, 68, 69, 70, 71). Similar processes may have resulted in low or non detectable levels of the lighter-end aliphatic hydrocarbon ($C \leq 20$) than in the present study.

The example of chromatogram of aliphatic hydrocarbon in seawater is shown in Figure 4-1.

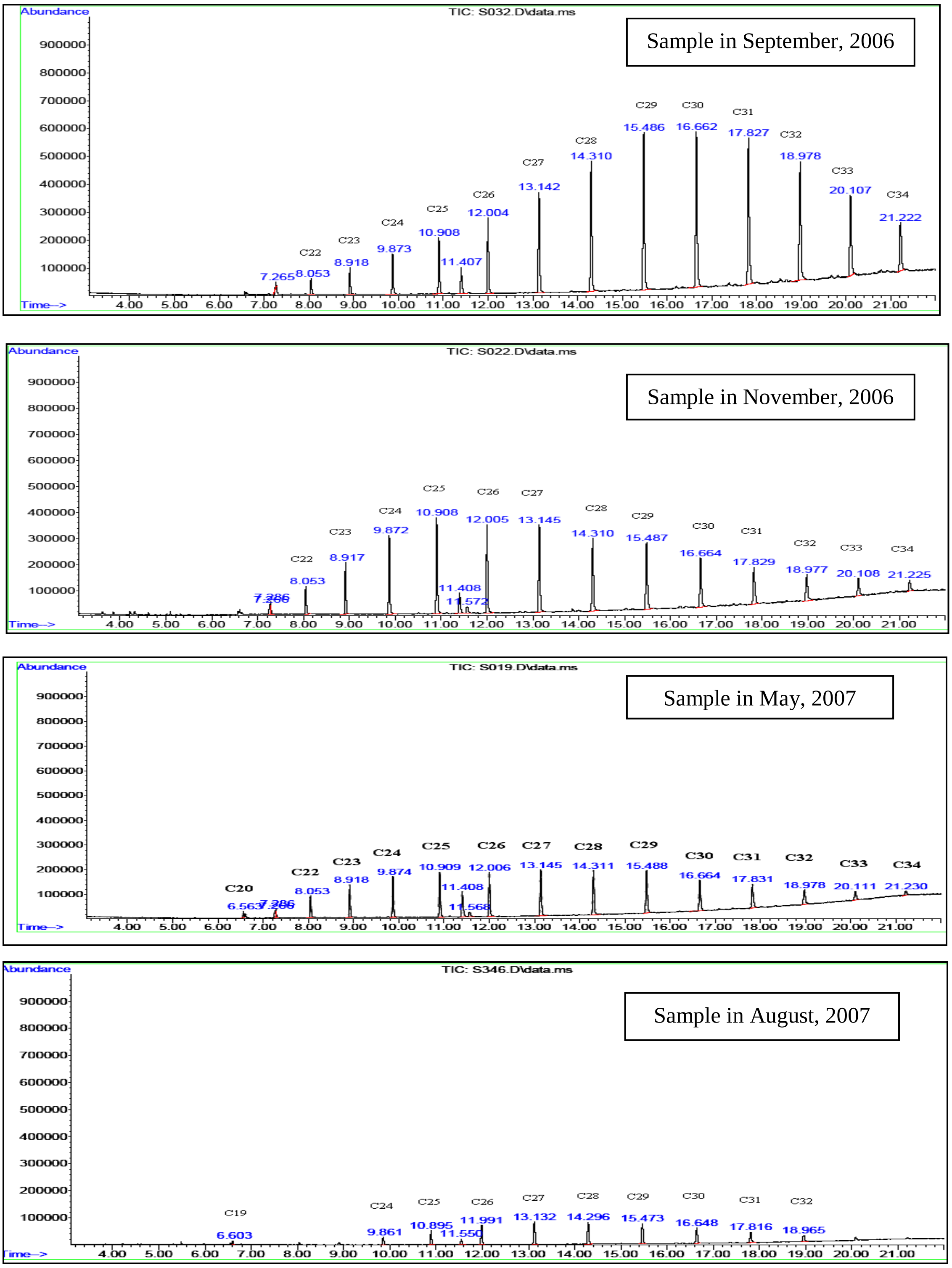

Figure 4-1 The example of chromatogram of aliphatic hydrocarbon in seawater

4.4.2 Typical of petroleum hydrocarbon in sediment

Petroleum hydrocarbon in sediment composed mainly of n- alkanes from C_{14} – C_{34}. This study was corresponded to the previous researches. Nookyoo (30) found that the n- alkanes with carbon atom ranging from C_{14} – C_{34} were presented in sediment sample collected from the lower Chao Phraya River. Sunwanich (65) found that sediment samples at Tha Chin River showed n-alkanes ranging from C_{14} – C_{32} and Sarin (72) found that sediment samples at the Gulf of Thailand showed n-alkanes ranging from C_{15} – C_{34}. The n-alkanes in sediment samples were exhibited the similar pattern between the wet and dry seasons.

The short-chain ($C \leq 20$) n-alkanes were generally non-detectable throughout the study at all sampling points. The long-chain n-alkanes ($C \geq 20$) are predominant in sediment. This might be occurred by higher-weight aromatic and aliphatics in seawater absorb to suspended particles because of their low water solubility while lower-weight hydrocarbons and more polar oil components remained dissolved in the water (73).

Several processes increase oil density leading to its settlement to the sea floor. These include: (1) evaporation and dissolution of lower-molecular weight compounds, (2) photooxidation and subsequent dissolution of oxygenated materials, (3) formation of viscous and higher density water-in-oil emulsion, (4) incorporation of particulates and agglomeration of oil particulate mixtures and (5) incorporation of higher density microorganisms and macroorganism (e.g., banacles) (57). The density of parent oil, which can vary appreciably, has much to do with its capacity to sink (8). Similar processes may have resulted in high levels of the high molecular weight compounds ($C \geq 20$) in sediment samples in this study.

The example of chromatogram of aliphatic hydrocarbon in sediment is shown in Figure 4-2.

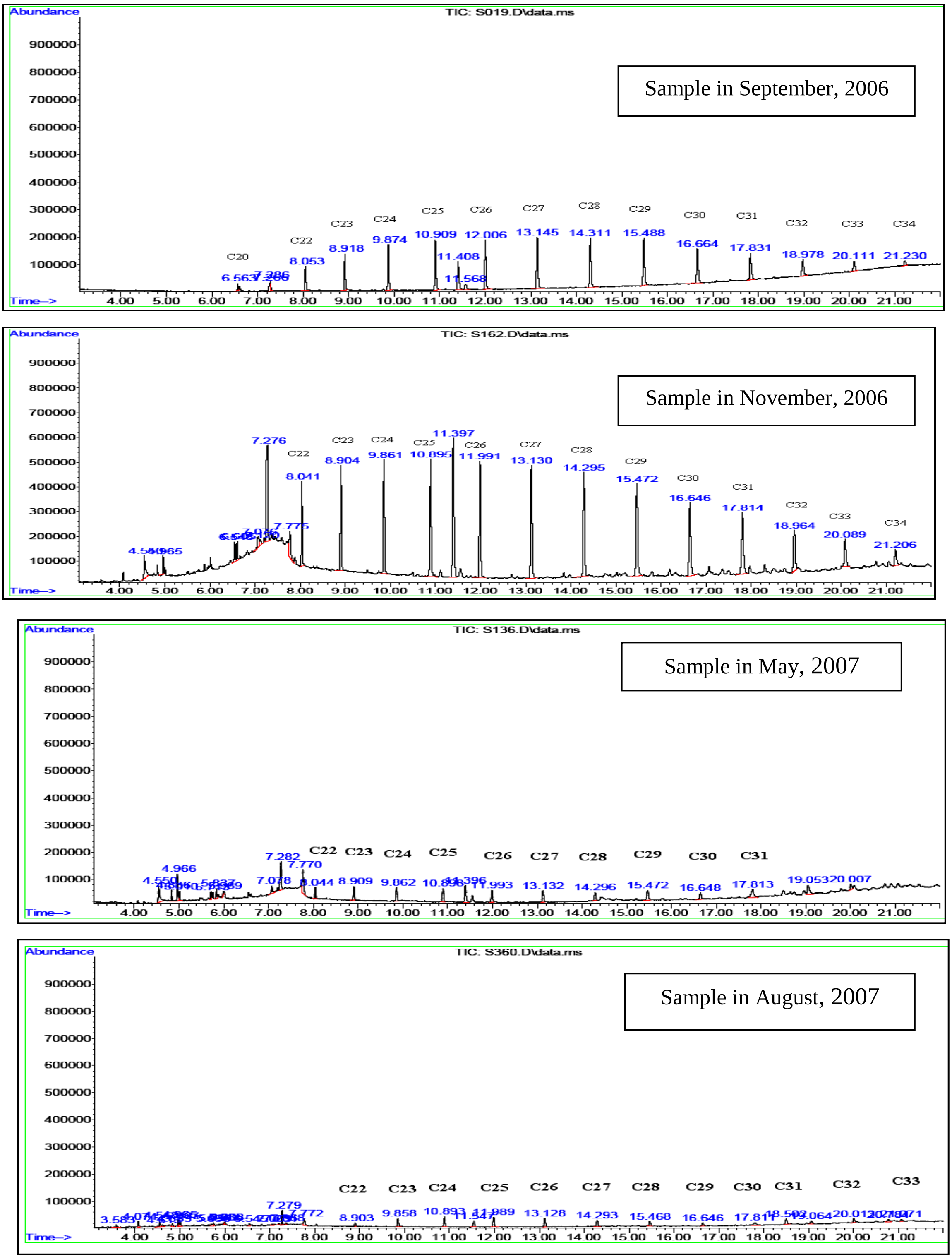

Figure 4-2 The example of chromatogram of aliphatic hydrocarbon in sediment

Petroleum contains several homologous series with adjacent members usually present in nearly the same concentrations and this resulted in the approximately unity for even- and odd-numbered alkanes (16). In contrast, it was observed that the biogenic hydrocarbons exhibit a very strong odd-carbon predominance (16, 19) Carbon Preference Index (CPI_1) means the ratios between total weight of ood-carbon homologues and weight of the even-carbon homologous (17, 18, 19). The $CPI_{1,}$ an index of the predicates of biologically synthesize n-alkanes (98), indicated the relative contribution of n-alkanes from natural sources (biogenic/terrestrial; CPI>1) compare to anthropogenic ones (petroleum pollution, and highly degrade organic matter; CPI≈1).

Moreover, Columbo *et al.* (75) presented that CPI_2 is given by the ratio $2(C_{27}+C_{29})/(C_{26}+2(C_{28})+C_{30}$. Petrogenic hydrocarbons show values around 1, while vascular plants and uncontaminated sediment ranged from 3-6.

As shown in Table 4-11 the CPI_1 values were ranged from 0.36 – 1.86 and the CPI_2 values ranged from 0.78- 2.17. As indicated in Table 4-11 that CPI index from all fishing ports was shown the values around 1 and more than 1 therefore the n-alkanes in sediment were contributed from a petroleum and biosynthesis hydrocarbons. However, the season and the distance from the fishing ports were not indicated the sources of n-alkanes in this study.

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Table 4-11 CPI_1 and CPI_2 values of sediment

Fishing port sites	Distance from fishing port (M)	Wet season				Dry season			
		September 2006		August 2007		November 2006		May 2007	
		CPI_1	CPI_2	CPI_1	CPI_2	CPI_1	CPI_2	CPI_1	CPI_2
Wat Komut Ratthanaram	25	0.91	1.04	-	-	0.99	1.20	0.94	1.13
	500	1.12	1.02	0.96	1.08	0.87	1.13	-	-
	1000	1.24	0.94	1.48	1.40	0.45	1.39	-	-
Ban Ang Sila	25	0.94	1.09	0.75	1.21	0.97	1.11	0.90	1.11
	500	1.54	0.78	0.31	1.09	0.91	1.14	-	-
	1000	0.79	2.17	-	-	1.12	0.99	-	-
Ta Hoi	25	0.91	0.85	0.88	1.05	0.67	1.30	-	-
	500	1.47	0.82	-	-	0.97	1.12	-	-
	1000	1.02	1.06	1.10	0.96	1.16	0.90	-	-
Minimum		*0.79*	*0.78*	*0.36*	*0.96*	*0.45*	*0.90*	*0.90*	*1.11*
Maximum		*1.54*	*2.17*	*1.86*	*1.40*	*1.16*	*1.39*	*0.94*	*1.13*
Mean		*1.12*	*1.07*	*0.99*	*1.17*	*0.90*	*1.14*	*0.92*	*1.12*

4.4.3 Typical of petroleum hydrocarbon in plankton

Resolved petroleum hydrocarbon in plankton consisted mainly of C_{22} – C_{29} n- alkanes in the dry season (May 2007) and mainly of C_{16} – C_{29} n-alkanes in the wet season (August 2007). The dominant peaks in the wet season were C_{17}, C_{19} and C_{21} n-alkanes which are normally found in marine phytoplankton that often exhibit this nature (16, 21). Most of hydrocarbons were derived from phytoplankton. This may relate to the activity at Ang Sila coast where subject to more restricted water circulation and eutrophication with the development of plankton bloom in the wet season (June, August and September) (76).

For the dry season, n-alkanes in plankton were similar to n-alkanes that found in seawater. This might be occurred by plankton uptaked petroleum hydrocarbon from seawater (9).

The example of chromatogram of aliphatic hydrocarbon in plankton is shown in Figure 4-3.

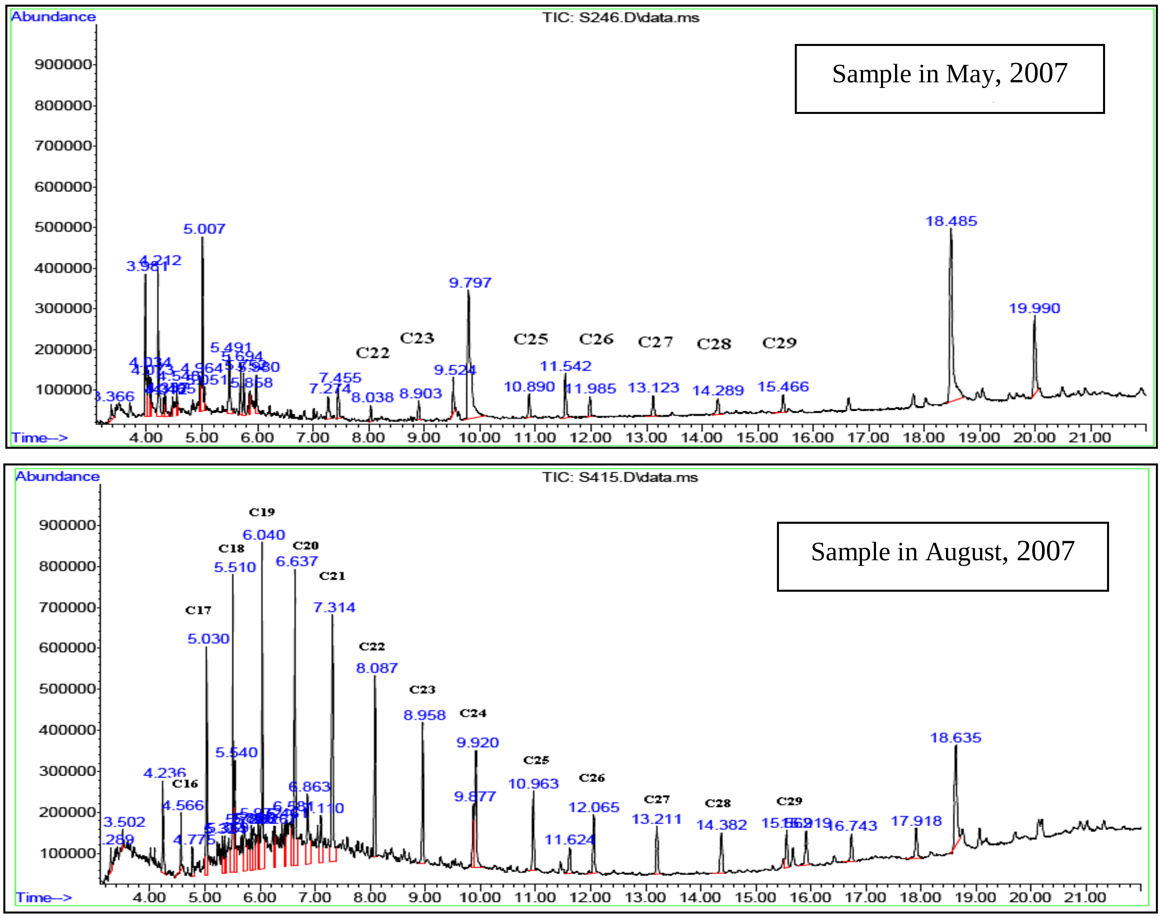

Figure 4-3 The example of chromatogram of aliphatic hydrocarbon in plankton

4.4.4 Typical of petroleum hydrocarbon in oyster

In wild oyster samples, resolved petroleum hydrocarbon consisted mainly of C_{24} – C_{34} n-alkanes. Figure 4-4 shows representative chromatograms of long-chain alkanes ($C \geq 20$) that were found in wild oyster samples. This might be occurred by the short-chain n-alkanes which were more prone to degradation than long-chain ones (77).

The rest of compounds found in farmed oyster were alcohol, fatty acid, lipid and cholesterol are showed in Figure 4-5. The low or non detectable of aliphatic hydrocarbon in farmed oyster can be explained that petroleum hydrocarbons in seawater were presented in low levels. Farmed oyster are by suspended culture with roped in the seawater were derive petroleum hydrocarbon as filter feeding.

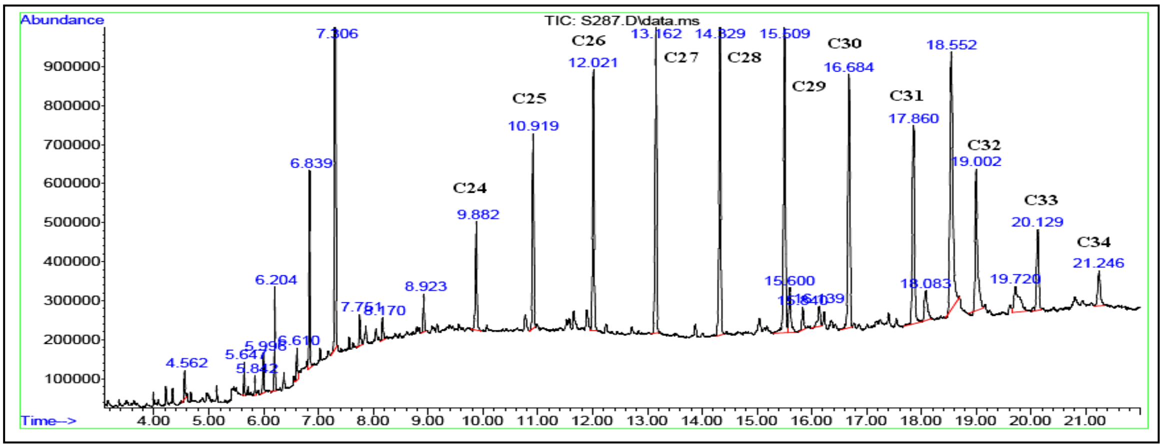

Figure 4-4 The example of chromatogram of aliphatic hydrocarbon in wild oyster

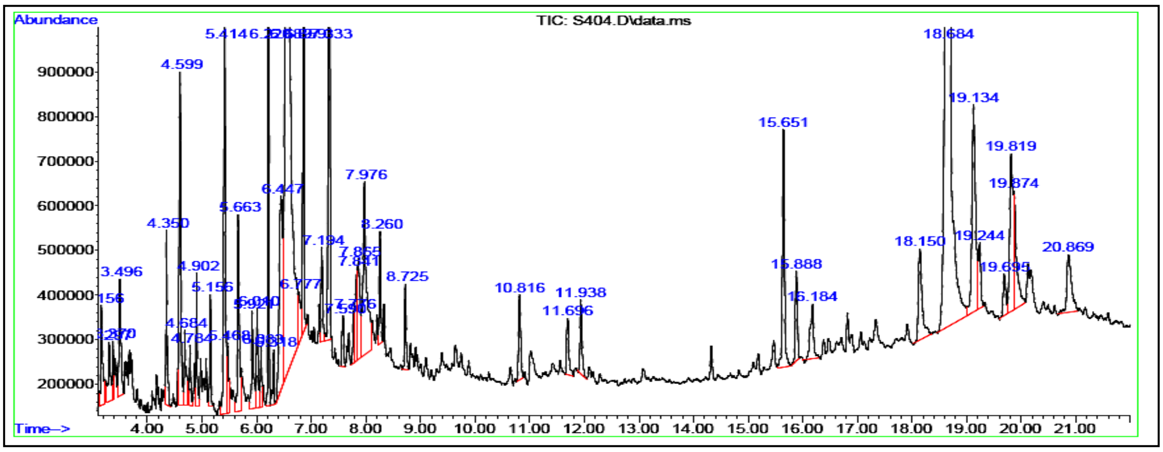

Figure 4-5 The example of chromatogram of other compounds in farmed oyster

4.4.5 Other organic compounds in samples

Other chemical compounds such as 2,4-Bis(dimethylbenzyl)-6-t-butylphenol used industrially in antioxidant formulations for plastic and rubber polymer manufacturing including dibutyl phthalate; phenol,2,6-bis(1,1-dimethylethyl)-4- and 1,2-Benzenedicarboxylic acid were plasticizer (78) were found in seawater sediment and plankton (Table 4-12). Furthermore, Butylated hydroxytoluene is used as an antioxidant food additive (E number E321) as well as in cosmetics, pharmaceuticals, jet fuels, rubber, petroleum products, and embalming fluid (79). These chemical compound have an effect to the environment as for dibutyl phthalate persists in the environment, and damages the hormone systems of animals. It is strongly suspected that humans eating these animals will be harmed as well (80). This may be suggested that other chemical compounds found in samples were implied from urban waste in the study site. For the naturally compound found in plankton and oyster whereas the cholesterols were found in sediment. These sterols must have originated from marine fauna (81).

Table 4-12 Other organic compounds in samples

Type	Name of compound	Formula	Found
Chemical	Butylated Hydroxytoluene	$C_{16}H_{22}O_4$	seawater, sediment and plankton
	Dibutyl pthalate	$C_{15}H_{24}O$	
	Phenol,2,6-bis(1,1-dimethylethyl)-4	$C_{23}H_{32}O$	
	1,2-Benzenedicarboxylic acid	$C_{24}H_{38}O_4$	
	2,4-Bis(dimethylbenzyl)-6-t-butylphenol	$C_{28}H_{34}O$	
Natural	**Alcohal**		plankton and oyster
	Tetradecanol	$C_{14}H_{30}O$	
	1-Hexadecanol	$C_{16}H_{34}O$	
	9-Hexadecanol-ol,(z)-	$C_{16}H_{32}O$	
	Octadecanal	$C_{18}H_{36}O$	
	1-Heptatriacotanol	$C_{37}H_{76}O$	
	Fatty acid		plankton and oyster
	Tetradecanoic acid	$C_{14}H_{28}O_2$	
	Hexadecanoic acid	$C_{16}H_{30}O_2$	
	Oleic acid	$C_{18}H_{34}O_2$	
	Lipid		plankton and oyster
	9-Octadecanamide,(z)	$C_{18}H_{35}NO$	
	Chlorophyll		plankton
	Phytol	$C_{20}H_{40}O$	
	Cholesterol		sediment, plankton and oyster
	Choresta-4-6-dien-3-ol,(3β)	$C_{27}H_{44}O$	
	Cholesterol margarate	$C_{44}H_{78}O_2$	

4.5 Polycyclic aromatic hydrocarbons (PAHs) around Ang Sila coast, Chonburi province

Identifications and quantifications of PAH compounds in samples were base on matching their retention time with an individual peak of PAHs standard. The results revealed that the three of PAH (i.e.; phenanthrene, pyrene and benzo[a]pyrene) compounds in seawater, sediment, plankton and oyster were not found. Chromatograms of PAHs and samples are shown in Figure 4-6.

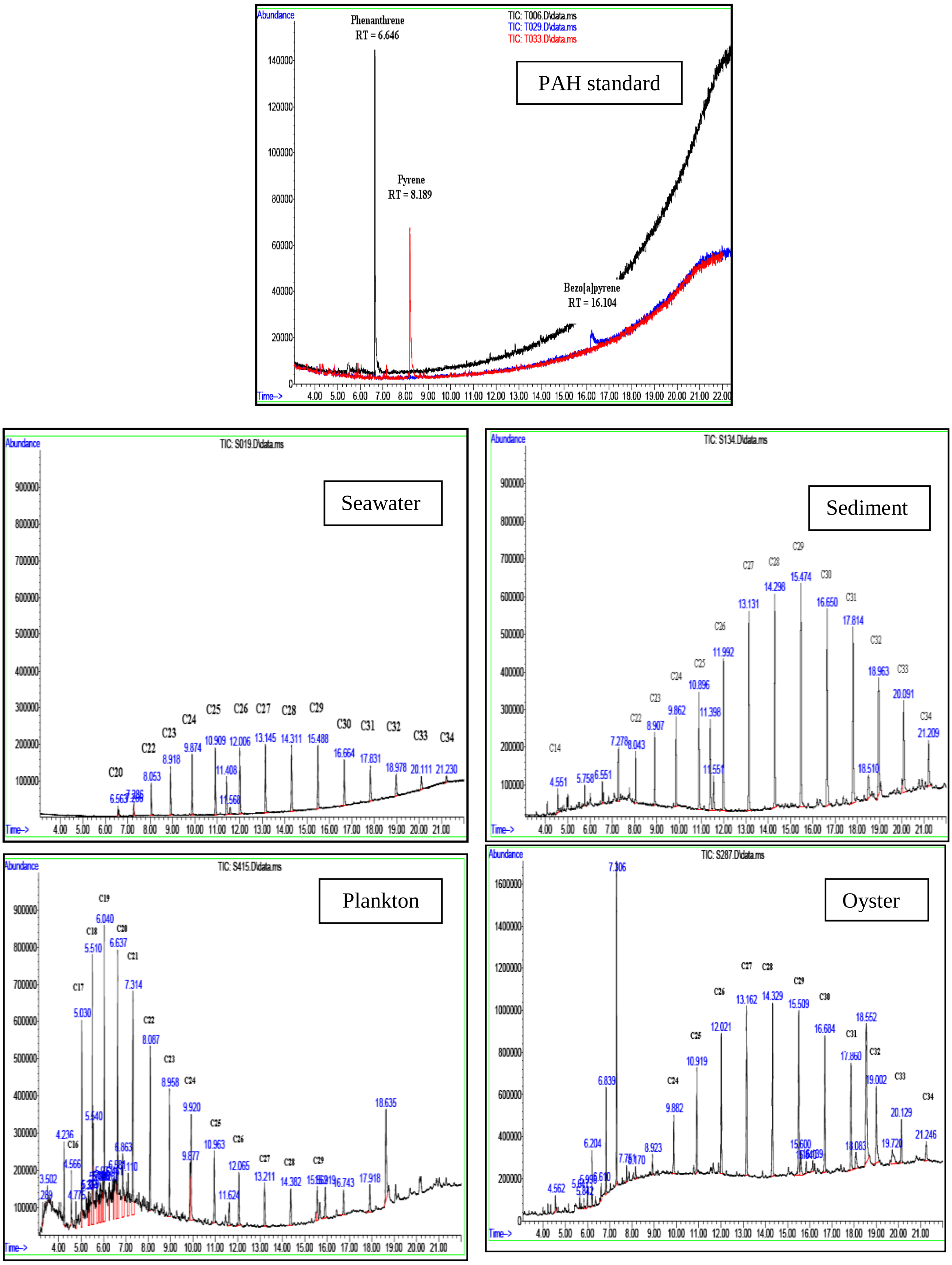

Figure 4-6 Chromatogram of PAH standard and samples

4.6 Relationship of the TPH concentrations in all samples

The relationship between TPH concentration in all samples followed the correlation coefficient that are presented in Table 4-13.

Table 4-13 Correlation coefficient of TPH concentration in all samples

Season	Month	Relationship of TPH concentration in all samples					
		Seawater and sediment	Seawater and plankton	Seawater and oyster	Sediment and plankton	Sediment and oyster	Plankton and oyster
Wet	Sep-06	0.393	NS	0.170	NS	0.415	NS
	Aug-07	0.078	0.334	0.266	0.507	0.595	0.137
Dry	Nov-06	0.584*	NS	NC	NS	NC	NS
	May-07	0.592*	0.191	0.310	0.310	0.902*	0.061

Remarks: * = Correlation is significant at the 0.05 level

NC = Statistics cannot be computed, because of TPH in oyster samples were non detectable.

NS = No Sample

Table 4-13 shows the positive correlations of TPH concentrations between seawater and sediment but significant value was found in the dry season. This results suggested that increase of TPH concentration in seawater caused increasing of TPH in sediment. While, the correlations of TPH concentrations between seawater and plankton, seawater and oyster, sediment and plankton, sediment and oyster, and plankton and oyster were poorly correlated. Except, in May 2007 the correlation of TPH concentrations between sediment and oyster showed positively significant.

4.7 TPH accumulation in marine food chain around Ang Sila coast, Chonburi province

Concentrations of TPH in marine environment of Ang Sila coast decreased in order of sediemt (0-8.50 µg/g) > plankton (0.07- 4.05 µg/g) > oyster (0 – 3.94 µg/g) > seawater (0-87.95 µg/l). When petroleum hydrocarbons enter the marine environment a variety of processes occur which result in their distribution to different environment phases and exposure of biota (Figure 4-7). Many publications suggested that pattern of distribution for a lipophilic chemicals in aquatic system is tranfer from low level trophic biota to higher level trophic biota to aquatic birds and marine mammal (26, 82). However, bioavailability and organic physiology are the two important variables that have major effect on contaminant body burden, Physiological factors, including lipid levels and the rate of uptake and elimination (metabolism, diffusion and excretion) are also affected contaminant body burden (83).

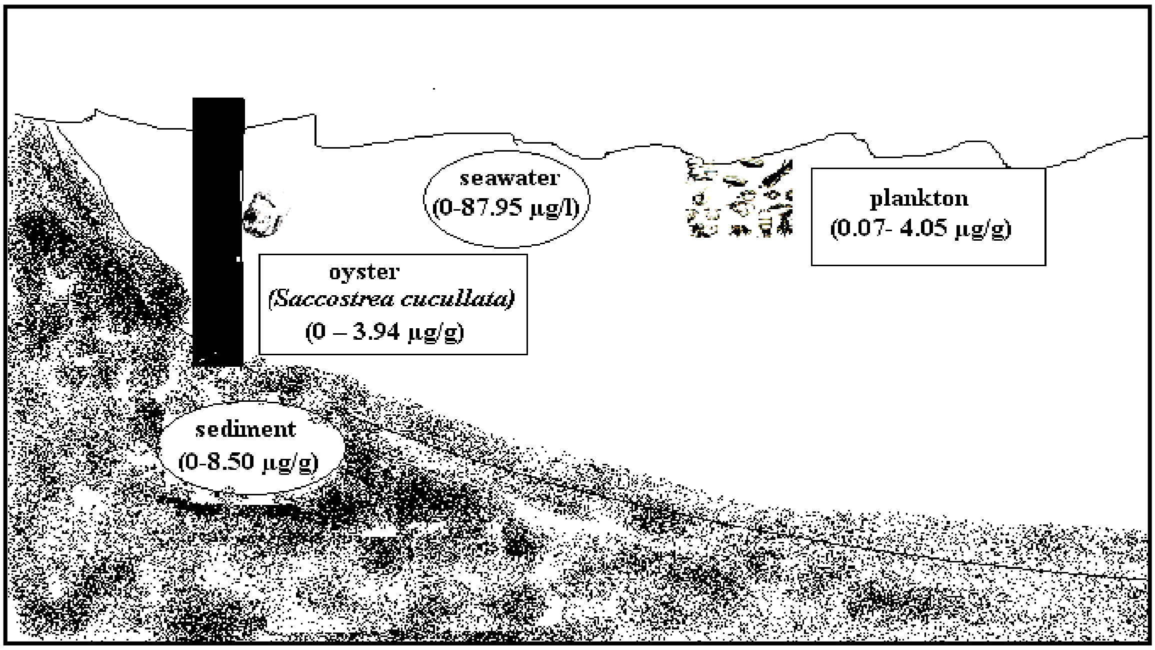

Figure 4-7 Diagrammatic representation of the distribution of petroleum hydrocarbon in marine environment of Ang Sila coast, Chonburi provice

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The concentrations of TPH in seawater, sediment, plankton and oyster were studied at Ang Sila coast, Chonburi province during the wet season (September, 2006 and June, 2007) and the dry season (November, 2006 and May, 2007). According to the results of this study, it can be concluded as follows.

1. **TPH concentration and typical of petroleum hydrocarbon in seawater**

TPH concentrations in seawater in the dry season were significantly higher than in wet season during 2006-2007. TPH contents in the wet season and the dry season were in the range of 0-68.85 µg/l and 0-87.95 µg/l, respectively. The distribution pattern implied that the high concentrations of TPH were found in samples at the distance of 25 m from the fishing ports which possibly contributed to most activities produced from fishing boats. The major type of petroleum hydrocarbons in seawater was n-alkanes ranging from $C_{18} – C_{34.}$

2. **TPH concentration and typical of petroleum hydrocarbon in sediment**

TPH concentrations in sediment in the wet season were significantly higher than in the dry season in the year 2006 whereas in year 2007 this result was not showed significantly different. TPH contents in the wet season and the dry season were in the range of 0.01-8.50 µg/g and 0-1.44 µg/g, respectively. Petroleum hydrocarbon in sediment composed mainly of n- alkanes from $C_{14} – C_{34}$. Additionally, the n-alkanes in sediment were contributed from a petroleum and biosynthesis hydrocarbons

3. TPH concentration and typical of petroleum hydrocarbon in plankton

TPH concentrations in plankton in the wet season were significantly higher than in the dry season. TPH contents in the wet season (August 2007) and the dry season (May 2007) were in the range of 0.12-4.05 µg/g and 0.07-0.50 µg/g, respectively. Resolved petroleum hydrocarbon in plankton consisted mainly from C_{22} – C_{29} n-alkanes in the dry season and mainly of C_{16} – C_{29} n-alkanes in the wet season. The dominant peaks in the wet season was C_{17}, C_{19} and C_{21} n-alkanes which normally found in marine phytoplankton For the dry season, n-alkanes in plankton were similar to n-alkanes found in seawater.

4. TPH concentration and typical of petroleum hydrocarbon in oyster

In both the wet and the dry season, TPH concentration in most of samples were non detectable and not showed significantly difference between the wet season and the dry season. The season, size and the distance from fishing port were not effected on TPH accumulation in oyster. Resolved petroleum hydrocarbon in wild oyster consisted mainly from C_{24} – C_{34} n-alkanes whereas most compounds found in farmed oyster were alcohol, fatty acid, lipid and cholesterol.

5. PAHs around Ang Sila coast, Chonburi province

The three of PAH (i.e.; phenanthrene, pyrene and benzo[a]pyrene) compounds in seawater, sediment, plankton and oyster were not found.

6. Relationship of the TPH concentrations in all samples

The correlation of TPH concentrations in most of samples were poorly positive except the correlations obtained from seawater and sediment in November 2006 and May 2007 and sediment and oyster in May 2007 were highly positive significant at the level of 0.05.

7 TPH accumulation in marine food chain around Ang Sila coast, Chonburi province

Concentrations of TPH in marine environment of Ang Sila coast decreased in the order of sediment (0-8.50 µg/g) > plankton (0.07- 4.05 µg/g) > oyster (0 – 3.94 µg/g) > seawater (0-87.95 µg/l).

5.2 Recommendations

1. The accumulation of TPH in marine organisms should be studied in various species (e.g., fish and benthos) to obtain the accumulation in marine food chain.
2. The environment factors (e.g., wind, current and tidal) affecting accumulation should be considered.

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APPENDIX

APPENDIX A

Particle size distribution (Globe, 2003)

Method

1) Prepare the dispersing solution by mixing 50 g of Sodium Hexametaphosphate (or other soil dispersing agent) in 1 L of distilled water. Stir or shake until the dispersing agent has completely dissolved.

2) Weigh 25 g of dried, sieved soil and pour it into a 250 ml or larger container.

3) Add 100 ml of the dispersing solution and 50 ml of distilled water to the beaker. Stir vigorously with a spoon or stirring rod for at the least one minute. Be sure the soil is thoroughly mixed and does not stick to the bottom of the beaker. Do not let any of the soil suspension spills out the top. Rinse any soil off the spoon or stirring rod into the container using a little distilled water.

4) While the soil suspension is sitting, measure the distance between the base and the 500 ml mark of the cylinder. Place the meter stick inside the cylinder to get this measurement. Read the temperature at which your hydrometer has been calibrated (such as 15.6° C [60° F] or 20° C). This value is found on the body of the hydrometer.

5) Complete the top section of Particle Size Distribution Data Sheet

6) After at least 24 hours, stir the suspension in the container and pour into a 500 ml graduated cylinder. Use a squirt bottle to the rise all soil out of the container and into the cylinder.

7) Add enough distilled water to the cylinder to the 500 ml mark.

8) Securely cover the top of the cylinder using plastic wrap or other cover. Place your hand over the mouth of the cylinder and mixed the soil suspension vigorous by rotating the cover cylinder hand overhand at the least 10 times. Be sure that the soil is thoroughly mixed suspension and that no soil suspension leak out of the top of the cylinder.

9) Gently set the cylinder down in a safe a place and immediately begin timing with a stop watch or clock that has a second hand.

10) Record the time that the cylinder was set down to second.

11) After 1 minute and 30 second has passed, carefully lower (do not drop) the hydrometer into the cylinder and let it float in the soil suspension. Carefully steady the hydrometer to stop its bobbing motion.

12) At exactly 2 minute after the cylinder was set down, read the line on the hydrometer that is closest to the surface of the soil suspension and record the number on the Particle Size Distribution Data Sheet.

13) Remove the hydrometer, rinse it away from the cylinder, dry it and gently put it down in safe place.

14) Suspend the thermometer in the suspension for about one minute.

15) At the end of a minute, life the thermometer from the suspension enough so that you can read the temperature and record the result on the Particle Size Distribution Data Sheet.

16) Rinse the thermometer off and dry it.

17) Leave the cylinder undisturbed for 24 hours. After 24 hours, take another hydrometer and temperature reading. Record the results on the Particle Size Distribution Data Sheet. (The 24-hour hydrometer reading should be 24 hours from the initial timing start.)

18) Discard the soil suspension by pouring it into a special pail and spill the contents outside in a special for discarding soil materials.

APPENDIX B

Organic matter (Walkley and Black, 1947)

Method

1. Prepare reagent and solution

1) Potassium Dichromate solution 1 N

Dissolve 49.04 g of potassium dichromate ($K_2Cr_2O_7$) was baked at 105 ºC in the distilled water and dilute the solution to a volume of 1,000 ml.

2) Ferrous Ammonium Sulphate slution 0.5 N

Dissolve 20 g of ferrous ammonium sulphate [$Fe(NH_4)_2(SO_4)_2 . 6H_2O$] in the distilled water then add sulfuric acid (conc. H_2SO_4) 2.5 ml. Pour the distilled water in the solution until the volume about 100 ml.

3) O-phenanthroline indicator solution (0.025 M)

Dissolve 0.7 gram of ferrous sulfate ($FeSO_4 . 7 H_2O$) and O-phenanthroline 1.48 gram in the distilled water. Dilute the solution to a volume of 100 ml.

4) Sulfuric acid (conc. H_2SO_4)

2 Analysis

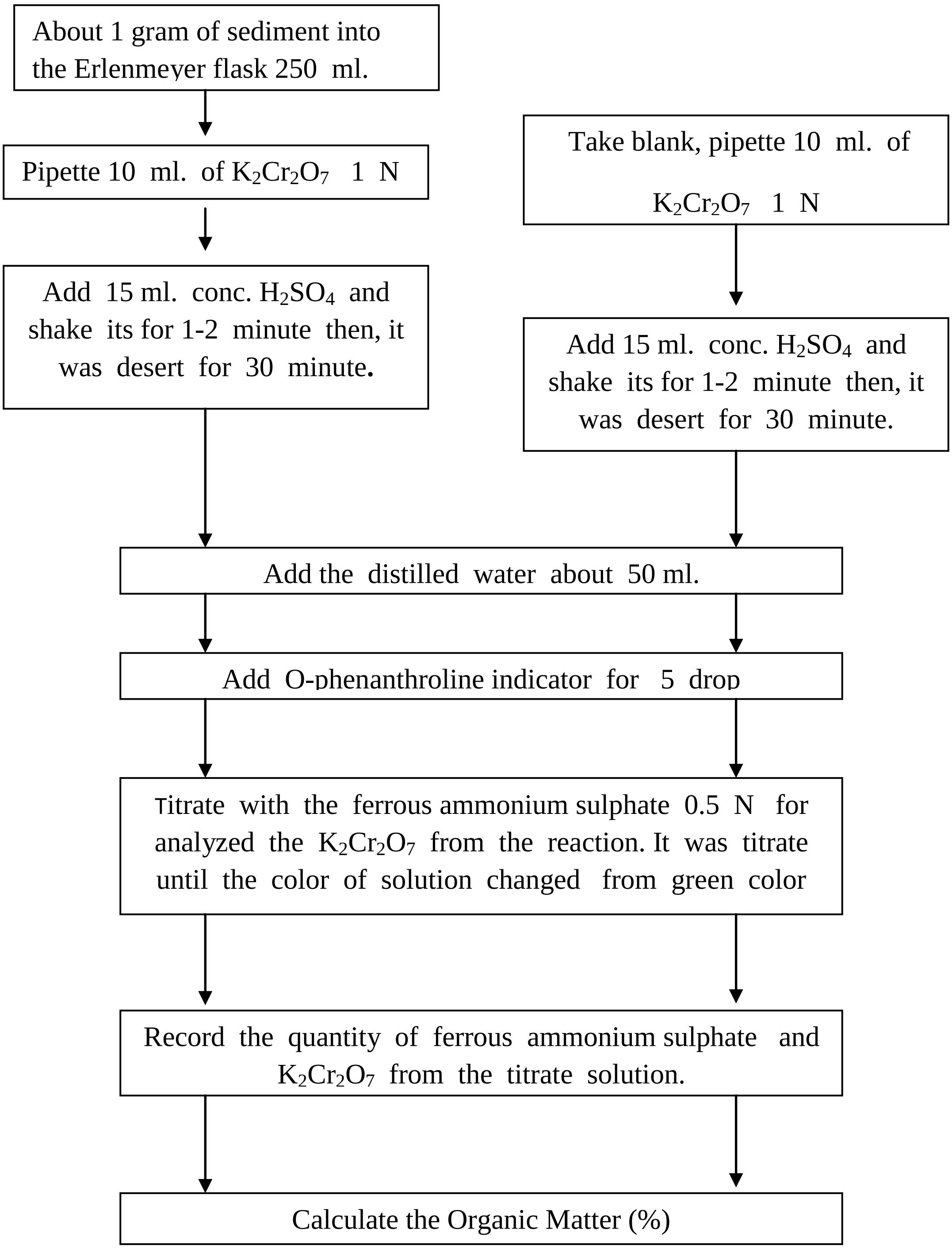

Figure B Procedure of organic matter analysis

3 Calculate

$$\% \text{ Organic carbon} = \frac{(B-T)N}{B} \times \frac{100}{77} \times \frac{3}{10^3} \times \frac{100}{X} \times 10$$

$$\% \text{ Organic matter} = \% \text{ Organic carbon} \times 1.724$$

or

$$\% \text{ Organic matter} = \frac{(B-T)N}{B} \times \frac{100}{77} \times \frac{100}{58} \times \frac{3}{10^3} \times \frac{100}{X} \times 10$$

When

N = The concentration of potassium dichromate

B = The quantity of ferrous ammonium sulfate which titrate with blank (ml)

T = The quantity of ferrous ammonium sulfate which titrate with soil sample (ml)

X = weight of soil sample (g)

APPENDIX C

Calculation of total petroleum hydrocarbon concentration

1. Preparation of Diesel oil

The stock standard solution were prepared by accurately weighting 0.01 g of diesel oil and dissolved in hexane (GC grade). Diesel oil solution was prepared at concentrations of 1 mg/l, 5 mg/l, 10 mg/l, 50 µg/ml and 100 mg/l.

2. Diesel oil calibration

Diesel oil calibration achieved by performing a linear least squares regression of the instrument response versus the mass of the analysis chromatographed. Make certain that the sample to the responses from the target compounds in the calibration standards. Sample peak areas (or peak heights) are compared to peak areas (or heights) of the standards. The example of chromatogram in diesel oil and the calibration curve of diesel oil were shown in Figure C-1 and C-2, respectively.

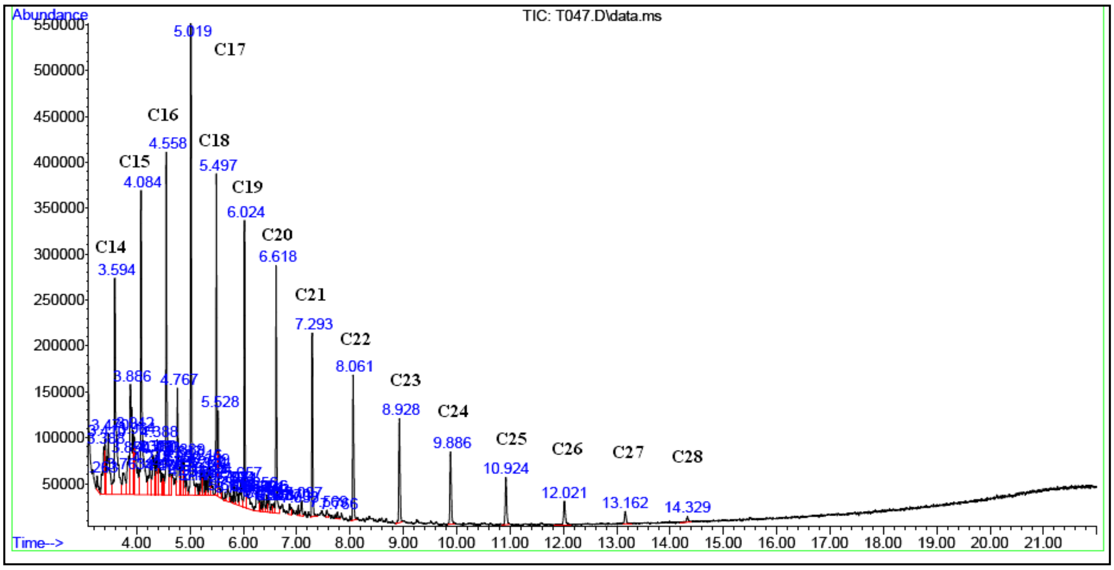

Figure C-1 Example of chromatogram in diesel oil

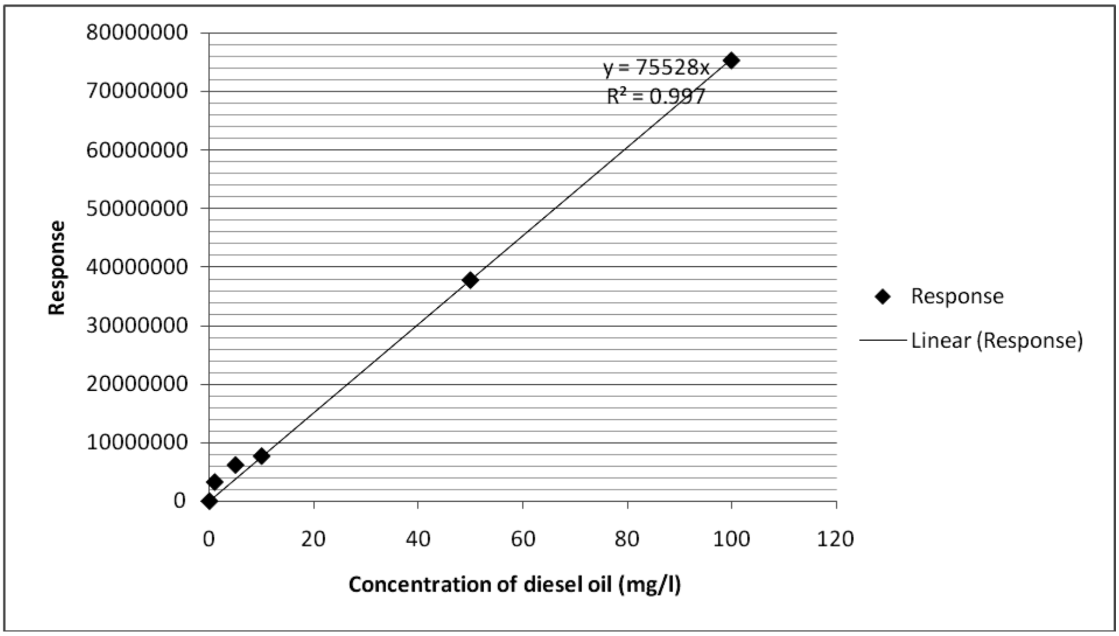

Figure C-2 The calibration curve of diesel oil

Using diesel oil calibration, the mass of the analysis in the sample aliquot introduced into the instrument is calculated as:

$$X_s = \frac{(A_s - b)}{a}$$

where:

X_s= Calculated mass of the analyte (in nanograms) in the sample aliquot introduced into the instrument.

As = Peak area or height of analyte.

a = Regression coefficient or the slope of the line.

b = The y-intercept.

3. Calculations

The calculation of sample results depends on the type of diesel oil calibration and the linear least squares regression.

3.1 Seawater concentration by µg/l

$$\text{Concentration } (\mu g/l) = \frac{(X_S)(V_t)(D)}{(V_i)(V_s)}$$

Where:

X_s= Calculated mass of the analysis (in nanograms) in the sample aliquot introduced into the instrument.

V_t = Total volume of the concentrated extract (in µL).

V_i = Volume of the extract injected (in µL). The nominal injection volume for samples and calibration must be the same.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, then D=1. The dilution factor is always dimensionless.

Vs = Volume of the aqueous sample extracted or purged, in milliliters (ml)

3.2 Sediment and Biota concentration by µg/kg

$$\text{Concentration } (\mu g/kg) = \frac{(xs)(Vt)(D)}{(Vi)(Ws)}$$

Where:

X_s= Calculated mass of the analysis (in nanograms) in the sample aliquot introduced into the instrument.

V_t = Total volume of the concentrated extract (in µL).

V_i = Volume of the extract injected (in µL). The nominal injection volume for samples and calibration must be the same.

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, then D=1. The dilution factor is always dimensionless.

Ws = Weight of sample extracted (in grams).

APPENDIX D

TableD-1 Multiple comparisons of seawater in September 2006 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	-18.836667	11.328640	.278	-49.19882	11.52549
	1000.00	2.454583	10.596973	.974	-25.94661	30.85578
500.00	25.00	18.836667	11.328640	.278	-11.52549	49.19882
	1000.00	21.291250	10.596973	.163	-7.10994	49.69244
1000.00	25.00	-2.454583	10.596973	.974	-30.85578	25.94661
	500.00	-21.291250	10.596973	.163	-49.69244	7.10994

TableD-2 Multiple comparisons of seawater in November 2006 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	61.467500(*)	5.884050	.000	45.69752	77.23748
	1000.00	82.549167(*)	5.504025	.000	67.79770	97.30063
500.00	25.00	-61.467500(*)	5.884050	.000	-77.23748	-45.69752
	1000.00	21.081667(*)	5.504025	.005	6.33020	35.83313
1000.00	25.00	-82.549167(*)	5.504025	.000	-97.30063	-67.79770
	500.00	-21.081667(*)	5.504025	.005	-35.83313	-6.33020

* The mean difference is significant at the .05 level.

TableD-3 Multiple comparisons of seawater in August 2007 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	13.906667	9.677467	.377	-12.03014	39.84347
	1000.00	24.453750(*)	9.052441	.048	.19209	48.71541
500.00	25.00	-13.906667	9.677467	.377	-39.84347	12.03014
	1000.00	10.547083	9.052441	.520	-13.71458	34.80874
1000.00	25.00	-24.453750(*)	9.052441	.048	-48.71541	-.19209
	500.00	-10.547083	9.052441	.520	-34.80874	13.71458

* The mean difference is significant at the .05 level.

TableD-4 Multiple comparisons of seawater in August 2007 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	7.249167	3.776834	.189	-2.87321	17.37155
	1000.00	6.534792	3.532904	.210	-2.93383	16.00341
500.00	25.00	-7.249167	3.776834	.189	-17.37155	2.87321
	1000.00	-.714375	3.532904	.980	-10.18299	8.75424
1000.00	25.00	-6.534792	3.532904	.210	-16.00341	2.93383
	500.00	.714375	3.532904	.980	-8.75424	10.18299

TableD-5 Multiple comparisons of sediment in September 2006 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	-5.766667(*)	1.675254	.011	-10.25655	-1.27678
	1000.00	-4.120917	1.567057	.055	-8.32082	.07899
500.00	25.00	5.766667(*)	1.675254	.011	1.27678	10.25655
	1000.00	1.645750	1.567057	.586	-2.55416	5.84566
1000.00	25.00	4.120917	1.567057	.055	-.07899	8.32082
	500.00	-1.645750	1.567057	.586	-5.84566	2.55416

* The mean difference is significant at the .05 level.

TableD-6 Multiple comparisons of sediment in November 2006 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	.291167	.181761	.303	-.19598	.77831
	1000.00	.621792(*)	.170022	.007	.16611	1.07747
500.00	25.00	-.291167	.181761	.303	-.77831	.19598
	1000.00	.330625	.170022	.181	-.12506	.78631
1000.00	25.00	-.621792(*)	.170022	.007	-1.07747	-.16611
	500.00	-.330625	.170022	.181	-.78631	.12506

* The mean difference is significant at the .05 level.

TableD-7 Multiple comparisons of sediment in May 2007 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	.141000(*)	.031102	.001	.05764	.22436
	1000.00	.145250(*)	.029093	.000	.06728	.22322
500.00	25.00	-.141000(*)	.031102	.001	-.22436	-.05764
	1000.00	.004250	.029093	.989	-.07372	.08222
1000.00	25.00	-.145250(*)	.029093	.000	-.22322	-.06728
	500.00	-.004250	.029093	.989	-.08222	.07372

* The mean difference is significant at the .05 level.

TableD-8 Multiple comparisons of sediment in August 2007 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	.055000	.036867	.351	-.04381	.15381
	1000.00	.024833	.034486	.775	-.06759	.11726
500.00	25.00	-.055000	.036867	.351	-.15381	.04381
	1000.00	-.030167	.034486	.688	-.12259	.06226
1000.00	25.00	-.024833	.034486	.775	-.11726	.06759
	500.00	.030167	.034486	.688	-.06226	.12259

TableD-8 Multiple comparisons of plankton in May 2007 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	-.109667	.118571	.668	-.47464	.25531
	1000.00	-.052083	.110913	.897	-.39349	.28932
500.00	25.00	.109667	.118571	.668	-.25531	.47464
	1000.00	.057583	.110913	.876	-.28382	.39899
1000.00	25.00	.052083	.110913	.897	-.28932	.39349
	500.00	-.057583	.110913	.876	-.39899	.28382

TableD-9 Multiple comparisons of plankton in August 2007 according to distance from fishing port

Multiple Comparisons

Dependent Variable: TPH
Scheffe

(I) Distance	(J) Distance	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
25.00	500.00	-.013333	1.405307	1.000	-4.33904	4.31237
	1000.00	-.002083	1.314545	1.000	-4.04841	4.04424
500.00	25.00	.013333	1.405307	1.000	-4.31237	4.33904
	1000.00	.011250	1.314545	1.000	-4.03508	4.05758
1000.00	25.00	.002083	1.314545	1.000	-4.04424	4.04841
	500.00	-.011250	1.314545	1.000	-4.05758	4.03508

APPENDIX E

TableE-1 t-test analysis for comparison of seawater between wet and dry season in 2006

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Sep06	8.78250	20	20.883562	4.669706
	Nov06	31.08925	20	36.983428	8.269746

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 Sep06 - Nov06	-22.306750	46.236413	10.338776	-43.946057	-.667443	-2.158	19	.044

TableE-2 t-test analysis for comparison of seawater between wet and dry season in 2007

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	May07	14.61650	20	18.955040	4.238476
	Aug07	8.68225	20	24.686915	5.520162

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 Aug07 - May07	-5.93425	21.65687	4.842625	-16.06998	4.20148	-1.225	19	.235

Table E-3 t-test analysis for comparison of sediment between wet and dry season in 2006

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Sep06	3.55170	20	3.629161	.811505
	Nov06	.84110	20	.399193	.089262

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Sep06 - Nov06	2.71060	3.690313	.82517	.98348	4.437720	3.285	19	.004

Table E-4 t-test analysis for comparison of sediment between wet and dry season in 2007

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Aug07	.04040	20	.064248	.014366
	May07	.05060	20	.084541	.018904

Paired Samples Test

		Paired Differences					t	df	Sig. (2-tailed)
		Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
					Lower	Upper			
Pair 1	Aug07 - May07	-.01020	.115278	.025777	-.064152	.043752	-.396	19	.697

Table E-5 t-test analysis for comparison of plankton between wet and dry season in 2007

Paired Samples Statistics

		Mean	N	Std. Deviation	Std. Error Mean
Pair 1	Aug07	1.56150	10	1.517917	.480008
	May07	.21140	10	.135679	.042905

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
Pair 1 Aug07 - May07	1.350100	1.587336	.501960	.214588	2.485612	2.690	9	.025

APPENDIX F

Mean of rainfall at Meung district, Chonburi province

Table F Mean of rainfall (mm) (Thai Meteorological Department, 2007)

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
2006	0	81.5	34.4	126.6	205.6	87.3	106.3	136.5	217.2	301.6	20.9	0
2007	2.8	0.3	14.8	234.1	238.6	216.1	220.7	51.9	189	-	-	-
1976-2006	10.9	20.6	44.8	69.5	171.2	144.7	131.2	155.2	267.3	201.9	51.3	4.3

APPENDIX G

Biological detail of oyster collected from Ang Sila coast

Table G-1 Biological detail of oyster collected from Ang Sila coast in September 2006

Sampling Point	Type	n	Size or Age	Shell length (cm) [average(rang)]
P1	Wild	60	<5 cm	5.23(5.0-7.0)
	Wild	60	≥5 cm	4.08(3-4.8)
P2	Wild	60	<5 cm	4.02(3.0-4.9)
	Wild	60	≥5 cm	5.14(5.0-5.8)
P3	NS		NS	NS
P4	Farm	60	9month	4.10(3.0-6.8)
P5	Farm	60	9 month	4.59(3.5-7.0)
P6	Farm	60	3 month	4.01(3.1-5.6)
P7	Farm	60	9 month	4.20(3.5-6.5)
P8	Farm	60	9 month	4.76(3.5-8.6)
P9	Farm	60	NS	NS
P10	Farm	60	3 month	3.55(2.2-5.9)

Table G-2 Biological detail of oyster collected from Ang Sila coast in November 2006

Sampling Point	Type	n	Size or Age	Shell length (cm) [average(rang)]
P1	Wild	60	<5 cm	4.33(3.9-4.9)
	Wild	60	≥5 cm	5.28(5.0-7.0)
P2	Wild	60	<5 cm	3.90(2.7-4.8)
	Wild	60	≥5 cm	5.14(5.0-7.5)
P3	NS		NS	NS
P4	Farm	60	3month	2.99(2.2-4.6)
P5	Farm	60	9 month	4.20(3.5-6.5)
P6	Farm	60	9 month	4.89(3.9-8.0)
P7	Farm	60	9 month	4.58(3.1-8.9)
P8	Farm	60	3 month	3.50(2.7-5.7)
P9	Farm	60	3 month	3.11(2.2-6.1)
P10	Farm	60	9 month	5.45(4.0-7.5)

Table G-3 Biological detail of oyster collected from Ang Sila coast in May 2007

Sampling Point	Type	n	Size or Age	Shell length (cm) [average(rang)]
P1	Wild	60	<5 cm	3.99(3.0-4.9)
	Wild	60	≥5 cm	5.36(5.1-6.3)
P2	Wild	60	<5 cm	4.26(3-4.9)
	Wild	60	≥5 cm	5.55(5.1-7.5)
P3	NS		NS	NS
P4	Farm	60	9month	4.81(3.0-6.7)
P5	Farm	60	9 month	4.99(3.0-6.4)
P6	Farm	60	9 month	4.70(3.5-5.5)
P7	Farm	60	9 month	4.85(3.0-8.0)
P8	Farm	60	9 month	5.03(3.0-9.0)
P9	Farm	60	9 month	4.52(3.0-9.5)
P10	Farm	60	3 month	3.70(2.2-5.6)

Table G-4 Biological detail of oyster collected from Ang Sila coast in August 2007

Sampling Point	Type	n	Size or Age	Shell length (cm) [average(rang)]
P1	Wild	60	<5 cm	4.18(3.0-4.8)
	Wild	60	≥5 cm	5.25(5.0-6.3)
P2	Wild	60	<5 cm	4.47(3.5-4.9)
	Wild	60	≥5 cm	5.58(5.0-7.3)
P3	NS		NS	NS
P4	Farm	60	3month	4.21(3.0-5.5)
P5	Farm	60	9 month	4.90(2.5-7.0)
P6	Farm	60	9 month	4.47(3.0-6.5)
P7	Farm	60	9 month	5.19(3.0-7.0)
P8	Farm	60	9 month	4.69(3.3-6.7)
P9	Farm	60	9 month	4.86(3.0-6.5)
P10	Farm	60	9 month	4.60(3.0-7.0)

BIOGRAPHY

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