Pollution Level and Health Risk Assessment for the Total Petroleum Hydrocarbon in the Marine Environment, and Aquatic Products From the Southern Sea Area of Zhejiang Province, China

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Abstract

In order to evaluate the pollution level and risk of total petroleum hydrocarbon (TPH), seawater, sediments, and organisms were sampled from the southern sea area of Zhejiang province (Yangtze River Delta, China) between 2017 and 2019. Petroleum hydrocarbons were widely present in the aquatic environment as well as in products, and their concentrations were highly variable. The average value of PI exceeded 1 from 2017 to 2018, 45.46% to 69.19% samples for seawater and 56.87% to 50.00% samples for sediment were polluted. The results showed significant differences in the TPH concentration in various aquatic organism species. The average TPH value in aquatic organisms order was bivalve>shrimp>crab>fish, further reflecting the ability to accumulate and metabolize TPH exists differently among aquatic organisms within the same culturing pond environment. It is relatively safe to eat aquatic products based on the exposure risk index far below threshold values in this study. Therefore, it will be prudent to undertake regular monitoring of TPH to ensure effective ecosystem functioning as well as seafood safety in Zhejiang southern ocean.

1. Introduction

Total petroleum hydrocarbon (TPH) is a complex mixture of short and long-chain aliphatic hydrocarbons and aromatic compounds. TPH is commonly present in coastal environments due to exploitation, transportation, oil leaks and other human activities (Daskalou et al., 2009; ATSDR., 1999). The rapid expansion of urbanization, and extensive industrial activities during the past decades have led to the increase in the consumption of petroleum and its products around the world. According to the annual maritime transport statistics, there are on average 4.63 million tons of oil spilled every year. This seriously affects the marine environment, fishery resources, and the ecological communities composition (Muniz et al., 2015; Ukpaka et al., 2020). In addition, some compounds of polycyclic aromatic hydrocarbons (PAHs) are considered

to be the most toxic components in crude oil, with carcinogenic, teratogenic, and mutagenic effects in aquatic animals and human (Ali et al., 2014; Bo et al, 2017; Mirjani et al., 2021).

There are a lot of studies focusing on the analysis of these TPHs in water (Mishra and Kumar, 2015), sediment (Li et al., 2019) or organism (Zakir et al., 2012). However, research data has only focused on one or two aspects of water-sediment-organism systems; and as such, has been unable to determine the true exposure routes of TPH in polluted marine regions. Furthermore, petroleum pollutants may influence human health through bio concentration and amplification of the food chain. Petroleum hydrocarbons the main pollutants in petroleum pollution affect effect marine life by interfering with the ability to breed, reproduce, grow, and perform other vital functions (Rico-Martinez et al., 2013). As a result the entire seawater-sediment-organism system needs to be considered in order to obtain an accurate understanding of marine pollution from TPH.

Zhejiang Province is located in the south of the Yangtze River Delta on the southeast coast of China. The coastal sea area is vast, with a total coastline of more than 6400 kilometers and a territorial sea area of

115,000 square kilometers. Zhejiang is a major province of marine fisheries. The total marine fishing and aquaculture production reached 120.89 million tons in 2019. The marine fisheries economy plays an important role in Zhejiang's national economy. The integrated ecological mixed culturing mode of seawater ponds along the south coast of Zhejiang is typical of the farming model in Zhejiang province. This model is characterized by multispecies comprehensive breeding based on different nutritional organisms for polyculture. However, in the past two decades, with the rapid economic development of the Yangtze River Delta region, Zhejiang coast has been damaged by a large amount of land-based industrial and domestic pollution, coupled with marine aquaculture, fishing and marine transport pollution, the pollution level of the sea area shows an increasing trend year by year (Mei et al., 2016).

To understand the migration and transformation of TPH in the aquatic culturing environment and marine organism, this paper has systematically summarized TPH pollution status, spatial distribution and risk level. Therefore, in this study an attempt has been made to: 1) Determine the concentrations and potential sources of TPH in the coastal environment (surface seawater and sediment) and aquatic organisms; 2) Explore the TPH pollution characteristics of typical pond culturing mode in the southern Zhejiang ocean, and find the relationship between TPH and lipid content in aquatic organisms; 3) Evaluate the risks of TPH in coastal areas by as a result of the pollution index method, and the health risk evaluation method. Most importantly, this is the first study that has focused on the accumulation and transportation of TPH in an entire seawater-sediment-organism system. This is critical to the control and management of these pollutants within a complex marine environment.

2. Material And Methods

2.1. Sample collection

A total of 98 surface seawater samples and 81 surface sediments were collected at 25 monitoring stations representing environmentally different coastal aquaculture areas of southern Zhejiang province from 2017 to 2019. In general, the environmental (seawater and sediment) and aquatic products of the station site were taken from the same location. The station position of the sampling point is shown in Fig.1. The water samples were collected from the surface seawater with a throw-floating oil-free glass water collector from each survey station. Then the water samples were collected in 500 mL brown narrow-necked glass sample bottles, 5 mL of sulfuric acid solution acidified water samples were added to have the $\text{pH} \leq 2$. The grab-type bottom mud sampler was used to collect surface sediments (0 - 5 cm) at each survey station. The surface sediment samples were then sealed in polyethylene bags and placed in a foam box with ice cubes before they were brought to the laboratory in cold containers. To determine the physio-chemical characteristics of the sediment samples, samples were air-dried at room temperature in the laboratory, and then slightly crushed, homogenized, and passed through a 180 μm stainless steel sieve. The marine organism samples were sixteen species in total, which is made up of five shellfish species, five crustacean species, and six fish species. There were a total of 79 shellfish samples, 116 crustacean samples, and 63 fish samples taken from the coast of southern Zhejiang province. Five

shellfish species including: *Tegillarca granosa*, *Sinonovacula constricta*, *Moerella iridescens*, *Cyclina sinensis* and *Meretrix meretrix*. Five crustacean species including: *Litopenaeus vannamei*, *Scylla serrata*, *Portunus trituberculatus*, *Cratosquilla oratoria* and *Parapenaeopsis hardwickii*. Six fish species including: *Larimichthys crocea*, *Nibea albiflora*, *Pagrus major*, *Acanthopagrus schlegelii*, *Lateolabrax japonicas* and *Hapalogenys nitens*. The aquatic samples were initially stored in an icebox until there were delivered to the laboratory and kept on -20°C for further analysis.

Based on a typical integrated ecological mixed culturing mode of seawater ponds, five main culturing zones were monitored again in 2019. The five monitor areas included Wenyang town of Leqing city (WY), Qingjiang town of Leqing city (QJ), Yanpu town of Cangnang county (YP), Gere two village of Ruian city (GX) and Damen town of Dongtou district (DM).

2.2. Sample treatment and analysis

The surface seawater samples were extracted with hexane solvent in triplicate following China's marine monitoring standards of GB 17378.4-2007. The concentrations of TPH in the extracts were quantified by ultra-violet fluorescence spectroscopy (T9-Spectrofluorophotometer, Persee, China) at wavelength 225 nm (An et al., 2009; Li et al., 2010). The detection limit for this method for TPH is 0.01 mg L⁻¹. The standard used was Crude Oil (1000 µg mL⁻¹) from the National Marine Environmental Monitoring Center in China.

The surface sediment samples were then extracted with hexane solvent in triplicate following China's marine monitoring standards of GB 17378.5-2007. The concentrations of TPH in the extracts were quantified by ultra-violet fluorescence spectroscopy (T9-Spectrofluorophotometer, Persee, China) at a wavelength of 225 nm. The detection limit for this method for TPH is 1.0 mg kg⁻¹.

After thawing at room temperature in the laboratory, the shells of aquatic products were removed and homogenized, they were then extracted with anhydrous ethanol solution in triplicate following China's marine monitoring standards of GB 17378.6-2007. The concentrations of TPH in the extracts were quantified by fluorescence spectroscopy (960-fluorophotometer, INESA analytical Instrument, China). Fluorescence conditions were as follows: excitation at 310 nm and emission at 360 nm (Zakir, et al., 2012). The detection limit for this method for TPH is 1.0 mg kg⁻¹.

The lipid content in aquatic organisms was determined as reported by Sun et al. (2016). 5 g of each aquatic product sample was extracted using ethyl acetate (20 ml) in an ultrasonic bath for 30 min. The extraction was repeated once. The solvent was evaporated to dryness from the combined extract using a rotary evaporator and lipid content determined gravimetrically.

2.3. Quality assurance/quality control (QA/QC)

All analytical data were subjected to strict quality assurances and quality controls. Analysis of a reagent blank, spiked blank, matrix spike and sample duplicate were processed with every batch of 12 samples.

The average recovery of the target was 94.5 % to 105 % for seawater samples and aquatic products and 91 %-100 % for sediment samples. The relative standard deviations (RSD) were 3.5 % and 3.2 %. The standard material and blank samples were measured every 10 samples, to ensure the accuracy of the measured samples. The relative percentage analysis difference between duplicate samples was ≤ 15 .

2.4. Judgment standards and evaluation methods

2.4.1. Single pollution index (PI) and Nemerow pollution index (NPI)

The PI method is used to evaluate the pollution status of the coastal environment and aquatic products in southern Zhejiang. When evaluating the pollution status of petroleum hydrocarbon, the PI method is generally used (Kowalska et al., 2018; Cao et al., 2020), and the calculation formula is:

$$P_i = C_i / C_{i0}$$

Where P_i , C_i , C_{i0} represents the evaluated results, the actual measured data, and evaluation standard of petroleum hydrocarbon respectively. The evaluation standard of TPH is 0.05 mg L^{-1} in surface seawater (GB11607-1989 and GB 3097-1997), 500 mg kg^{-1} in surface sediment (GB 18668-2002) and 15 mg kg^{-1} in aquatic products (GB2762-2012) respectively. PI classifies the environment and aquatic products into three categories: The non polluted type when $PI < 0.5$; the moderately polluted environment and aquatic products, when it varies between 0.50 and 1; and the highly polluted environment and aquatic products, when $PI > 1$.

The NPI method takes into account the average and the highest value of PI, and more comprehensively reflects the degree of the environment's pollution, and can highlight the role of pollutants with TPH. The calculation formula is as follows (Nemerow, 1974):

$$NPI = \sqrt{\frac{(\bar{P}_i)^2 + (P_{i\max})^2}{2}}$$

For NPI, pollution levels are safe when $NPI \leq 0.7$; pollution levels are low when $0.7 < NPI \leq 1.0$; pollution levels are low when $1 < NPI \leq 2.0$; pollution levels are moderate when $2 < NPI \leq 3.0$; and pollution levels are high when $NPI > 3$.

2.4.2. Biota-sediment accumulation factor

The accumulation of organic pollutants in aquatic organisms can be expressed by the Biota-sediment accumulation factor (BSAF) (Shen et al., 2011), and the calculation formula is as follows:

$$BSAF = C_i / C_w$$

Where C_i , C_w , BSAF are the amount of TPH pollutants contained in the aquatic products (mg kg^{-1}), TPH concentration in sediment (mg kg^{-1}), and biota-sediment accumulation is the factor of petroleum

hydrocarbon.

2.5. Human health risk assessment

2.5.1. Average daily intake of EDI

The average daily intake EDI is a commonly used health assessment method. The daily allowable intake of EDI can be used to assess the health effects of aquatic products from the southern coast of Zhejiang Province. The calculation formula of EDI is

$$EDI = C \times M / BW$$

where C is the average concentration of the chemical contaminants (ng g^{-1} wet weight) in the aquatic products; M is the average daily consumption of aquatic products of Zhejiang coastal residents which is 141 g; BW represents an average adult weight of 60 kg.

2.5.2. Risk characterization

Due to the complex composition of TPH, which is mainly composed of hydrocarbons with only a small part of poly-cyclic aromatic hydrocarbons which are carcinogenic, so it characterizes its non-carcinogenic risk, that is, exposure risk index (ERI), or hazardous quotient (HQ) (Pinedo et al., 2014; Pinedo et al., 2013; In-Sun and Jae-Woo., 2010).

The calculation formula of ERI is

$$ERI = EDI / RfD$$

Where EDI is average daily intake EDI (ng/kg bw/d); RfD is oral reference dose for non-carcinogenic effects. The value of the oral intake reference (RfD) is $4.3 \text{ mg kg}^{-1} \text{ d}^{-1}$ according to the U.S. EPA Risk Assessment Information System (USEPA, 2004).

2.6. Statistical analyses

In this study, TPH levels in seawater were presented as mg L^{-1} , TPH contents in sediments were presented as dry weight, and TPH content in aquatic products were presented as mg kg^{-1} . Statistical analysis of all results was carried out by using Microsoft Excel and Software Package for Social Sciences (SPSS) version 24.0. The data obtained were analyzed on Microsoft Excel by using descriptive statistics while the independent-samples Kolmogorov-Smirnov Test was carried out with SPSS, and used to establish the relationship between the parameters. At $P < 0.05$, the difference is significant.

3. Results And Discussion

3.1.1. Concentrations of TPH in surface seawater and sediment

The concentration of TPH in the surface seawater and sediment in this study are shown in Table 1. The concentration of TPH in the environment of sampling points showed varying levels of exposure. TPH contents in the surface seawater of the study area ranged from no detected (ND) to 0.299 mg L⁻¹ and ND to 0.217 mg L⁻¹ between 2017 and 2018, with the average of 0.056 mg L⁻¹ and 0.053mg L⁻¹ respectively. The exposure levels of TPH in sediment ranged from 3.990 to 1862.502 mg kg⁻¹ dry weight (DW) and 13.570 to 1777.590 mg kg⁻¹ DW between 2017 and 2018, with the average of 531.931 mg kg⁻¹ DW and 752.173 mg kg⁻¹ DW respectively. Overall, the average content of TPH does not change much from year to year. It shows that the sediment in the culturing area has an accumulation effect on petroleum hydrocarbons and is even polluted by petroleum hydrocarbons. It can be seen that the marine environment has been revealed various degrees of contamination with TPH in aquatic culturing of the southern Zhejiang oceans. Petroleum hydrocarbon pollutants mainly come from human activities. The transportation of oil, shipping and industrial activities, urban runoff, and wastewater discharge are likely to be the main sources of TPH contamination in the environment (Sogbanmu et al., 2019; Adeniji et al., 2017). The highest mean TPH value of 0.112 ug L⁻¹ was found in WY station, which is located just mouth of Yueqing Bay. The harbor activities and reclamation were the major sources of pollution. TPH will migrate and transform after entering the water environment and becoming deposited in sediments (Bi et al., 2017). Then it will affect the main aquatic area in WY station. Therefore, understanding the source of pollution for petroleum hydrocarbons is the fundamental guarantee for effective prevention and control of the hazards of TPH. The seawater of Tianjin Bohai Bay was reported to have ubiquitous TPH in the range of 23.7 to 508 µg L⁻¹ during 1996-2005 (Li et al., 2010). Li et al (2019) reported TPH in the range of 50.05 mg kg⁻¹ to 428.50 mg kg⁻¹ with an average of 176.25 mg kg⁻¹ in the surface sediments of Yangtze Estuary and the adjacent sea areas during 2011-2016.

3.1.2. Concentrations of TPH in aquatic products

Marine organisms including shellfish, crustaceans, and fish, were investigated to generate the baseline data on TPH in marine organisms. All of the studied organisms are commercially important seafood for the coastal residence of southern Zhejiang. The ranges of TPH are illustrated in Fig. 2 for each marine species. The results show that the concentration of TPH varies greatly among the five different shellfish species. The average value of TPH in the shellfish samples varies between ND to 222.333 mg kg⁻¹ wet weight (ww), with an average total content of 18.486 mg kg⁻¹ ww. There are significant differences in the TPH concentration in different intra-species. The average concentrations were in the shellfish decreased in the order of *Sinonovacula constrictus* (34.904 mg kg⁻¹ ww) > *Tegillarca granosa* (18.880 mg kg⁻¹ ww) > *Meretrix meretrix* (15.502 mg kg⁻¹ ww) > *Cyclina sinensis* (2.744 mg kg⁻¹ ww) > *Moerella iridescens* (ND). The concentration of TPH varied greatly in five different crustacean species. The average value of TPH in the crustacean samples varied between ND to 54.245 mg kg⁻¹ ww. The TPH average concentrations of six crustaceans in order are: *Portunus trituberculatus* (27.612 mg kg⁻¹) > *Scylla serrata* (21.813 mg kg⁻¹) > *Litopenaeus vannamei* (20.352 mg kg⁻¹) > *Cratosquilla oratoria* (17.662 mg kg⁻¹) > *Parapenaeopsis hardwickii* (16.450 mg kg⁻¹). The average value of TPH in the fish species samples varies between ND to

45.711 mg kg⁻¹ ww, with an average total content of 11.352 mg kg⁻¹ ww. The average content of TPH in the muscle tissues of the six fish species is as follows: *Hapalogenys nitens* (19.122 mg kg⁻¹) > *Pagrus major* (17.422 mg kg⁻¹) > *Acanthopagrus schlegelii* (9.389 mg kg⁻¹) > *Larimichthys crocea* (9.140 mg kg⁻¹) > *Lateolabrax japonicas* (8.596 mg kg⁻¹) > *Nibea albiflora* (7.393 mg kg⁻¹).

The concentration of TPH in our study showed contrasting variation between some of the species. The enriched TPH capacity were in order from greatest to least as follows: bivalve > cephalopods > crustaceans > fish from southern Shandong peninsula (Zhang et al., 2010) > Zhejian ocean (Lin and Zhang et al., 2001) , Bengal bay (Zakir et al., 2012) similar with the trend of the present results. Zhong (2005) this study showed that the order of TPH content in different shellfish was *Sinonovacula constricta* (15.60 mg kg⁻¹) > *Saccostrea cucullata* (11.70 mg kg⁻¹) > *Perna viridis* (10.90 mg kg⁻¹) > *Grassostrea Gigas* (8.93 mg kg⁻¹) > *Arca ganosa* (8.04 mg kg⁻¹) > *Ruditapes philippinarum* (7.95 mg kg⁻¹). So, the enrichment of marine organisms to petroleum hydrocarbons is a passive process, there are differences in the capability of marine organisms to enrich petroleum hydrocarbon compounds. Moreover, the maximum value was recorded in bivalve (*Sinonovacula constricta*) in the present study.

3.2. Evaluation of TPH content in the aquaculture environment and aquatic products

3.2.1. Pollution level assessment for environment

The evaluation and source tracking of petroleum pollution in seawater and sediment is important for the estimating the health status of the coastal environments (Yuan et al., 2014; Khudur et al., 2018). In this study, the PI for each sample was calculated to evaluate the degree of pollution in the environment. The results of the PI are shown in Fig. 3. The average value of PI exceeded 1 from 2017 to 2018, indicating that the aquatic environment was polluted by petroleum. For seawater, 54.55 % to 40.91 % samples were found without pollution, 15.91 % to 13.64 % samples were moderately polluted and 29.55 % to 45.55 % of samples were classified as highly polluted. For sediment, 43.14 % to 50 % samples were found without pollution, 15.69 % to 9.52 % samples were moderately polluted and 41.18 % to 40.48 % of samples were classified as highly polluted.

Furthermore, this paper documents for the first time the spatial evaluation of TPH in an aquatic culturing area by the method of PI and NPI (Table 2). The NPI of TPH in the environment of six monitoring zones shows a spatial distribution trend as follows: WY > YP > GX > QJ > DM. The highest value was observed in Yueqing Bay mouth, near harbors and outfall where shipping activities and land-based wastewater discharges are the major sources of pollution in the area (Zhou et al., 2015). Yueqing Bay is a typical semi-enclosed system among the environmentally most impacted coastal ecosystems. The coastal aquaculture industry is greatly influenced by urbanization and industrialization. The range of TPH concentration along Yueqing Bay during 2013-2014 year was reported to vary from 0.006 to 0.398 mg l⁻¹, with an average value of 0.062 mg l⁻¹ (Liu et al., 2019).

3.2.2. Assessment of TPH pollution in aquatic products

In this study carried out in coastal areas of southern Zhejiang, the average single pollution index of TPH for three main commercial aquatic products (shellfish, crustacean and fish) were 1.26, 1.41 and 0.76, respectively. The PI ranged from 0.02 to 14.82, 0.02 to 3.62, 0.02 to 1.90, showed 'slight' to 'heavy' pollution. As shown in the Fig. 4, the mean PI (0.5) indicated slight or low pollution levels, accounting for 55.70 % of shellfish, 25.86 % of crustacean, 33.87 % of fish. 15.19 % of shellfish and 11.21 % of crustacean and 35.48 % of fish were contaminated (moderate pollution levels), 29.11 % of shellfish, 62.93 % of crustacean and 30.65 % of fish were contaminated (heavy pollution levels).

3.2.3. Biota-sediment accumulation factor

In order to have a better understanding of the accumulative effects of TPH in aquatic products, BSAF is calculated to reveal the distribution of TPH between the aquatic organisms and the surrounding surface sediments (Li et al., 2021). As shown in Fig. 5, the BSAF values of almost all sample points from typical pond culturing mode were less than 1. The mean values of BSAF in descending are as follows:

Sinonovacula constricta > *Scylla serrata* > *Litopenaeus vannamei* > *Tegillarcagranosa* > *Cyclina sinensis* > *Meretrix meretrix*. The average content of TPH is higher in *Sinonovacula constricta* than other aquatic species. Furthermore, the accumulation capacity of *Sinonovacula constricta* to petroleum hydrocarbon was significantly higher than that of other bivalves, and the TPH accumulation capacity of *Scylla serrata* in crustaceans was higher than that of *Litopenaeus vannamei*. Previous studies showed that organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were considerable. Bioaccumulation occurs from sediment to biota when BSAF are close to, or greater than 1 (Yang et al., 2019). The BSAF values of aliphatic hydrocarbons dramatically varied from 0.829 in *Cyprinus carpio* to 17.3 in *Silurus asotus* (Wang et al., 2019), due to the differences in selective excretion abilities and elimination mechanisms among different species (Wang et al., 2018).

3.3. Relationships between TPH in aquatic products and lipid content

The relationship between lipid content and concentration of TPH in main pond culturing was present Table 3. The present study observed the correlation between TPH concentration and lipid content of aquatic products. They found they were significantly positive in the pond mixed culturing mode by linear regression method analysis, with a correlation coefficient of 0.778 to 0.921 ($P < 0.05$). It is shown that the lipid content plays a major role in the accumulation of organic pollutants in marine organisms (Li et al., 2019). The main components of petroleum hydrocarbon are fatty hydrocarbons and aromatic hydrocarbon chemicals, which are lipid-friendly and easy to be absorbed and accumulated by fatty tissues in marine organism (Gobas et al., 1999; Shriadah., 2001). The TPH concentration and lipid content in different tissues of dolphins (*Sousa chinensis*) (Gan et al., 2010) and *chiromantes dehaani* (Tang et al., 2014) were positively correlated.

The integrated ecological mixed culturing mode of seawater ponds along the south coast of Zhejiang makes full use of the principle of mutual benefit and symbiosis of ecological habits of various cultured species. Looking at the average TPH value in aquatic organisms in order: Bivalve > shrimp > crab > fish,

further reflects that the ability to accumulate and metabolize TPH exists differently among aquatic organisms in the same culturing pond environment. Petroleum hydrocarbon in bivalve will accumulate and remain for longer. Pollutants in bivalve are not easy to discharge due to the defects in the oxidation system of bivalves, and its physiological metabolism capacity is very limited (Sun et al., 2020).

The present study found that the level of TPH in gonad tissue in *Scylla* was 1.6 to 2.5 times higher than that of muscle, and that the correlation between lipid and gonad was higher than that of muscle (Fig. 6). The concentration of organochlorine pesticides (OCPs) in commercial Pacific salmon organs in Russia's far eastern seas increased in the following order: muscle<live<eggs<male gonads (Tsygankov et al., 2019). The concentration of OCPs and PCBs in *Nibeaalbi flora* organs from Quanzhou Bay increased in the following order: muscle<live<gonads, and PAHs concentration increased in the following order: muscle<gonads<live (Zhang et al., 2019).

2.4. Human health risk assessment of TPH in aquatic products

Petroleum hydrocarbons are easily migrated from the surrounding environment to aquatic organisms via bioaccumulation. Further, they constitute a great hazard to humans through consumption of contaminated seafood (Abha and Singh., 2012; Joshua et al., 2019). The Food and Drug Administration of Zhejiang Province published a 2008 survey report on 'the dietary structure of urban and rural residents in Zhejiang Province' the investigation report states Zhejiang Province's per capita consumption of fish and shrimp is 108.5 g d⁻¹ (93.43 g d⁻¹ in country and 121.54 g d⁻¹ in urban areas respectively) through 22 survey districts in Zhejiang Province (11 urban and rural survey points each) and a total of 9,798 people. Meanwhile, Taking into account the abundance of seafood in Zhejiang coastal areas, residents consume more seafood than in inland areas. They consume more seafood by a factor of 1.3, and the per capita consumption of seafood by coastal residents is estimated at 141 g d⁻¹ (rural and urban, respectively, 121.5 g d⁻¹ and 158 g d⁻¹) (Mei et al., 2016). The EDI values of coastal urban residents and rural populations in Zhejiang province were 0.045 (shellfish), 0.051 (crustacean) and 0.025 (fish) respectively. ERI through consumption of three major aquatic products were 0.010 (shellfish), 0.012 (crustacean) and 0.006 (fish) respectively. So the calculated EDIs were far below the acceptable daily intakes. Exposure risk index were far below threshold values. This means that it is safe to eat aquatic products on the southern Zhejiang coast from the point of view of the health hazards of petroleum hydrocarbons in this study.

4. Conclusions

This study conducted a comprehensive investigation of TPH in terms of the seawater-sediment-organism system in the southern sea area of Zhejiang province, China. TPH pollution status in seawater in southern Zhejiang aquatic culture area has been polluted more than half, and the sediment also has a certain accumulation of TPH. The culture aquatic organism was also polluted by TPH with different degrees among three species, the pollution degree of crustacean was more serious than that of shellfish and fish. The study revealed a strong relationship between the lipid content and the TPH concentration in aquatic products. Although the EDIs or ERIs were below the threshold values, the potential for these pollutant to

threaten human health as a result of consuming seafood harvested in coastal residents still cannot be ignored. Therefore periodical monitoring and assessment of TPH contamination and its bioaccumulation in marine organisms is recommended from public health view point.

Declarations

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Statements & Declarations

Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

The author confirms:

1. That the work described has not been published before;
2. That it is not under consideration for publication elsewhere;
3. That its publication has been approved (tacitly or explicitly) by the responsible authorities at the institution where the work is carried out.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author contributions

All authors contributed to the study conception and design. The first draft of the manuscript was written by Yuan Hu and all authors commented on previous versions of the manuscript. The conception of the study was contributed to Jilin Xu. The experiment was performed by Kailun Xu and Yinuo Zheng. The analysis and manuscript preparation was contributed by Rongmao Lu. The analysis with constructive discussions was helped to perform by Chaosheng Zhou and Aiyin Ke. All authors read and approved the final manuscript.

Availability of data and materials

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"National Food Safety Standard Limits of Contaminants in Foods" (GB2762-2012)

Tables

Table 1 Concentration, frequencies and exceeding standard rate of TPH in environment

Medium	parameters	Time	
		2017 year	2018 year
Seawater	Range (mg L ⁻¹)	ND~0.299	ND ~0.217
	Mean (mg L ⁻¹)	0.056	0.053
	Frequency (%)	52.27	69.57
Sediment	Range (mg kg ⁻¹)	3.99~1862.50	13.57~1777.59
	Mean (mg kg ⁻¹)	531.93	752.17
	Frequency (%)	100	100

Table 2 Comparison of PI and NPI between different districts

Station	Medium	PI range	Average PI	NPI	Pollution level
YP	Seawater	0.05~4.34	1.43	5.22	high
	Sediment	0.10~3.44	1.87	3.83	high
GX	Seawater	0.05~4.03	0.84	4.24	high
	Sediment	0~3.73	0.76	3.62	high
DM	Seawater	0.1~1.34	0.35	0.47	safe
	Sediment	0.1~1.24	0.41	0.43	safe
WY	Seawater	0.1~5.61	0.72	8.00	high
	Sediment	0.05~3.70	1.80	4.24	high
QJ	Seawater	0.05~3.11	0.813	2.59	high
	Sediment	0~2.23	0.74	1.38	moderate

Table 3 The relationship between lipid content and concentration of TPH in main pond culturing

Marine species	Sampling location	Concentration(mg kg ⁻¹)	Lipid (%)	correlation coefficient	Significant value
Shrimp	WY	10.68±2.67	1.15±0.08	0.921	<0.05
	YP	20.50±6.62	1.51±0.35		
	GX	5.15±1.54	0.85±0.17		
Crab	WY	6.45±1.99	0.91±0.17	0.778	<0.05
	YP	8.06±3.63	1.02±0.18		
	GX	6.28±1.62	0.97±0.14		
Bivalve	WY	25.62±6.82	2.05±0.80	0.823	<0.05
	YP	24.07±7.75	1.80±0.42		
	GX	18.63±4.02	1.90±0.28		
Fish	YP	7.24±2.27	9.10±1.72	0.893	<0.05
	GX	7.57±4.53	8.75±4.06		

Figures

Figure 1

Location of the southern sea area of Zhejiang province (A) and sampling location of monitoring stations (B).

Figure 2

Box plots for TPH concentrations in various organisms of southern Zhejiang ocean. The lower and upper hinges and the line in the box indicate the 25th, 50th and 75th percentile values, respectively. Asterisks are outliers.

Figure 3

Pollution index of TPH in environment in aquatic culturing area of southern Zhejiang ocean

Figure 4

PI value in commercial aquatic products

Figure 5

The BSAF of aquatic products from typical pond culturing

Figure 6

Comparison with TPH values between muscle and gonad in *Scylla*