# DIOXIN AND DIOXIN-LIKE PCBs IN FISH AND SEAFOOD OF HONG KONG

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## Abstract

This study determined the concentrations of polychlorinated biphenyl, polychlorinated dibenzo-p-dioxins and dibenzofurans in common fish and seafood on the Hong Kong markets. The total TEQ ranged from 0.055 pg WHO-TEQ/g of red shrimp to 2.14 pg WHO-TEQ/g and the fish with high or moderate fat content contains relatively higher level of such organochlorinated contaminants. TCDF, 23478PeCDF,HpCDD,OCDD are found to be the most abundant congeners and PCB contribution to total TEQ of most fish species is over 50%.

## Introduction

The dioxin and dioxin-like polychlorinated biphenyls (DL-PCBs) are a group of highly concerned persistent organic pollutants (POPs) for their toxicological effects. They accumulate through the food chain and the dietary intake is the main source of human exposure to such high toxic contaminants [1]. Therefore, the assessment of human exposure to such hazardous contaminants is normally carried out by the assessment of the dietary intake from the food chain. There are three approaches for assessing the dietary intakes recommended by World Hygiene Organization, including Total diet study (TDS), duplicate portion study (DPS) and selective study of individual food. Since the dilution effect of TDS and DPS, the selective study of individual food is the most commonly used approach of dioxin dietary intake of most researchers and was adopted in this study. The objective is to measure the concentrations of PCDD/F and dioxin-like PCBs in common seafood available in Hong Kong market for the future assessment of potential risk to local human consumers combining the data from other animal origin.

Based on food consumption survey conducted by HKSAR[2], seafood is one of the five categories of food origin of local people and were analyzed. The result of toxic equivalent (TEQ) levels of all samples is compared to the legislation of Europe Commission[3].

## Materials and methods

### Sample collection

Seafood were purchased from local market of Hong Kong during from 2008 to early 2009 with clear label of the origin and species. Totally 32 species of seafood, including 25 fish species, 2 shrimp species, 3 bivalves 1 cephalopods and 1 crab were obtained and the detail is shown in table 1. The mussel tissues of individual species were collected from the sample, pooled and kept frozen in refrigerator until analysis.

Table 1. Details of the analyzed fish and seafood

| Categories | Species | Number of samples | Average body mussel weight (g) |
|---|---|---|---|
| Fish | Cod (US) | 2 | 321 |
| | Ferring (Norway) | 2 | 406 |
| | Mackerel (Japan) | 2 | 357 |
| | Halibut (Greenland) | 2 | 374 |
| | Black Carp (China) | 2 | 427 |
| | Salmon (Norway) | 2 | 387 |
| | Eel (Japan) | 2 | 214 |
| | Shark（indonesia） | 2 | 762 |
| | Sarding (US) | 3 | 242 |
| | Golden Thread （China） | 5 | 187 |
| | Pacific Saury (Japan) | 2 | 238 |
| | Red snapper ( Vietnam) | 2 | 284 |
| | Crucian Carp (China) | 2 | 386 |
| | Carp (China) | 2 | 367 |
| | Grasscarp (China) | 2 | 268 |
| | Yellow croaker (US) | 5 | 325 |
| | Snakehead （China） | 2 | 325 |
| | Bigeye （China） | 3 | 154 |
| | Bass(China) | 2 | 421 |
| | Flounder(vietnam) | 3 | 324 |
| | *Acanthopagrus australis(China)* | 2 | 214 |
| | Tuna (Japan) | 2 | 541 |
| | Weever (China) | 2 | 254 |
| | Grouper（China） | 2 | 342 |
| | Pomfret ( Burma) | 2 | 235 |
| bivalve | Oyster (China) | 1000g | 41 |
| | Crab (Japan) | 951g | 18 |
| | Scallop (China) | 560g | 21 |
| Cephalopod | Squid(Japan) | 674g | 34 |
| shrimp | White shrimp (Vietnam) | 543g | 9.8 |
| | Red shrimp (Thailand) | 456g | 8.7 |

**Chemical analysis**

The determination of PCDD/F is according to the method described elsewhere with modification and USEPA 1613 for environment matrices was also used as references [5-7]. Approximately 20g of freeze-dried solid samples was extracted by Soxhlet extraction by 1:1 n-hexane and dichloromethane

after injection of 20ul $C^{13}$ labelled PCDD/Fs and PCBs as internal standards. The extract was cleaned up by acidic silica gel, acidic alumina, florisil, active carbon and GPC before the injection into the instrument. The instrument analysis is performed by high resolution gas chromatograph/ high resolution mass spectrum (HRGC/HRMS) in selective ion mode (SIM) mode operating positive EI ionization at a resolution > 10000. The HRMS is MacroMass Autospec Ultima coupled with HP 6890 GC equipped with a DB-5MS column (60 m, 0.25 mm id, 0:1 lm film thickness).

To assure the quality assurance/ quality control (QA/QC) of the study, a blank sample, a duplicate sample and a fortification sample is analyzed for each batch. Peaks were identified by retention times of the internal standards if the S/N > 3 and were quantified if the target/qualifier ratios were within 15%. $C^{13}$ labelled recovery standards were spiked to calculate the recovery of internal standard and any samples lower than 40% was discarded. To assure the trueness of the result, the analytical procedures were applied to international proficiency test samples held by Norwegian Institute of Public Health. The Z-score of the PCDD/F and PCB TEQ of cream and eel are 1.17 and 0.14, respectively. This satisfactory result indicates that the analytical procedure applied is applicable to the analysis of dioxin and dioxin like PCBs.

## Results and Discussions

The total TEQ of edible tissues of all fish and seafood species is shown in Figure 1. The total TEQ ranged from 0.055 pg WHO-TEQ/g of Thailand red shrimp to 2.14 pg WHO-TEQ/g. This range of TEQ is comparable to the report of Finland and Germany[8, 9]. Among all samples, the Cod(US) 2.16 pg WHO-TEQ/g, Ferring (Norway) 1.96 pg WHO-TEQ/g , Mackerel(Japan) 1.80 pg WHO-TEQ/g and Hallibut (GreenLand ) 1.72 pg WHO-TEQ/g, were found to be the most contaminated species among all fish and seafood. Although they are still lower than the European Union action level for fish product ( 3 pg WHO-TEQ/g for dioxin and 3 pg WHO-TEQ/g for DL-PCB)[3], they may still be dangerous for consumers to take relatively large amount. Considering the fact that the fat content of this four species is 21%, 15% 33$ and 26%, respectively, high fat content may contribute to the high dioxin-like compound levels. Other researchers also report the relatively high contamination of such sea fish species which contains high or moderate level of fat.[9, 1011]

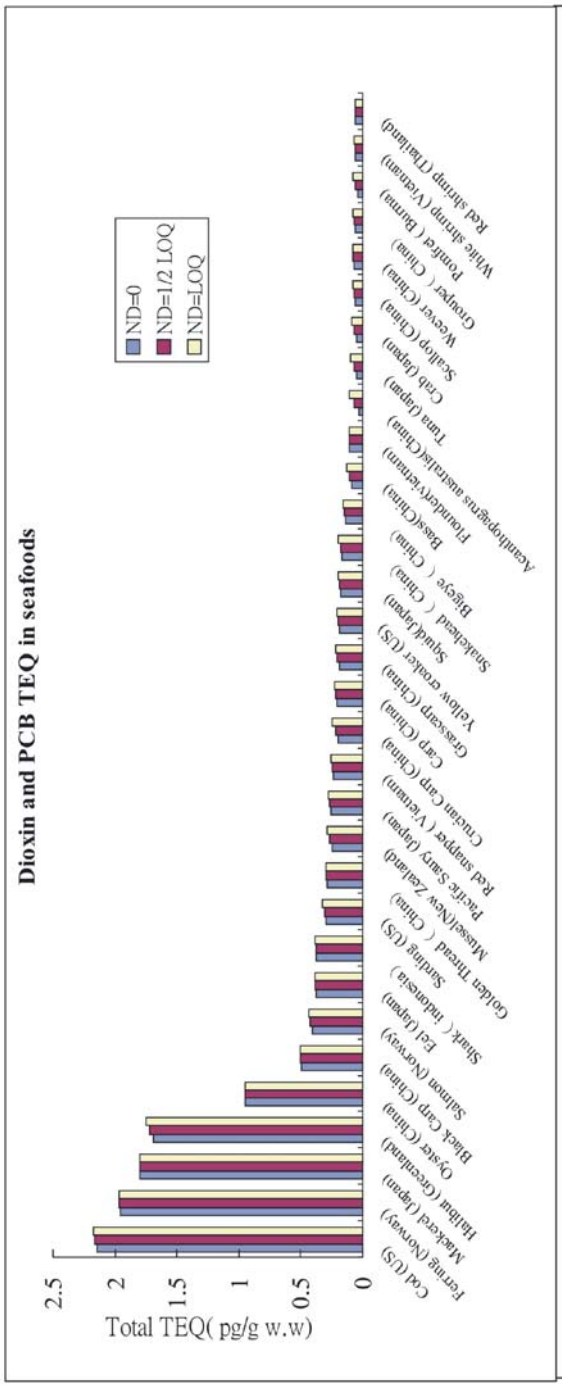


Fig.1. Total TEQs of fish & seafood of Hong Kong

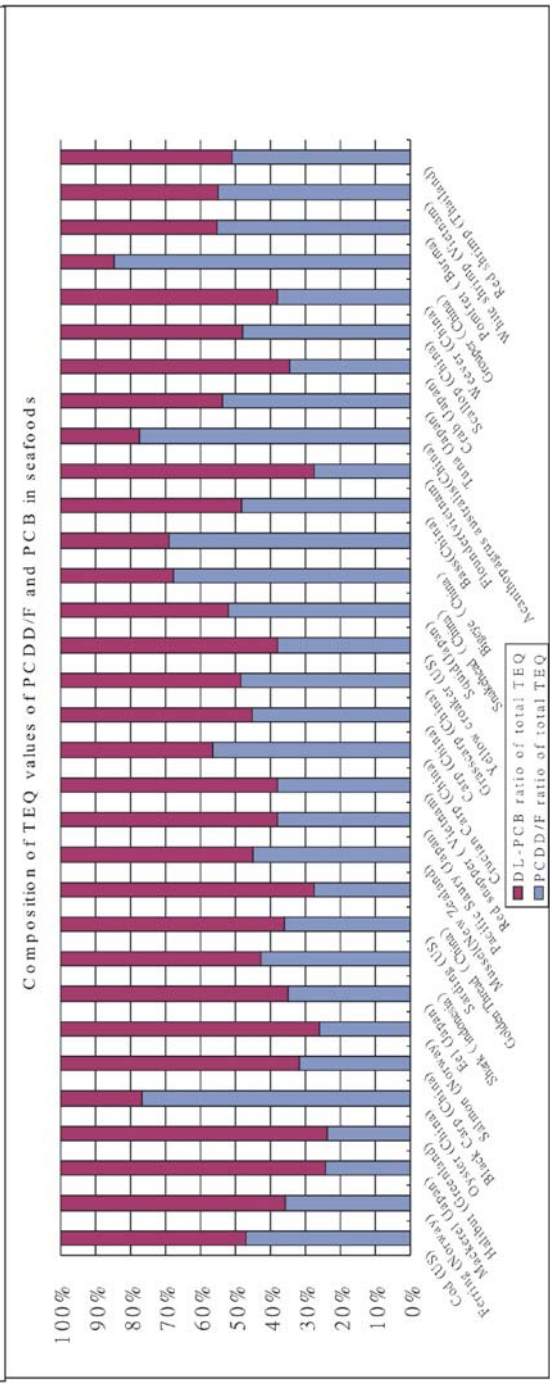


Fig.2. Composition of TEQ values of PCDD/Fs and DL-PCBs in fish & seafood of Hong Kong

Among all the congeners of PCDD/F, OCDD is the most abundant one and can be detected in all species. OCDD dominates in bivalves take 72-82% of total concentration while the total TEQ of such species is low due to the low TEF of OCDD. TCDF, 2,3,4,7,8-PeCDF and HpCDD in most fish species are most commonly seen. They contribute 51-65% of PCDD/F concentrations and 58-72% of TEQ of PCDD/Fs. Although TCDD and PeCDD were only seen in Ferring and Mackerel, it contributes to total

TEQ because the half limit of quantitation is used. The concentrations of all PCBs are approximately 100-1000 times higher than PCDD/Fs and therefore make PCB ubiquitous compounds in all samples. The contribution of PCB to total TEQ (PCDD/F+PCB) is shown in figure 2. In most fish species, it is shown that PCBs contribute more than PCDD/F to total TEQ. As expected, PCB118 and PCB105 are the two most abundant PCB congeners but PCB126 contribute 65% of PCB TEQ due to the highest TEF factor. The result of this investigation is comparable to those of previous studies around the world[12-15].

**Acknowledgement**

This work is supported by the Hong Kong Baptist University Faculty Research Grant (FRG)

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