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Halogenated Contaminants in Farmed Salmon, Trout, Tilapia, Pangasius, and Shrimp

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Polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans (PCDD/Fs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane diastereomers (HBCDs), and perfluorinated compounds (PFCs) were analyzed in popular farmed fish such as salmon, trout, tilapia, and pangasius and in farmed shrimp. The samples originated from southeast Asia, Europe, and South America. Results show the following: (i) Carnivorous species contained higher contaminant concentrations than omnivorous species. (ii) Contaminant concentrations generally decreased per species in the following order of salmon > trout ≫ tilapia ≈ pangasius ≈ shrimp. (iii) Most contaminant concentrations decreased in the following order of PCBs ≈ dichloro-diphenyl-trichloroethanes (DDTs) ≫ hexachlorobenzene ≈ pentachlorobenzene ≈ dieldrin ≈ PBDEs ≈ α-HBCD ≈ perfluorooctane sulfonate (PFOS) ≫ World Health Organization toxic equivalents (WHO-TEQ) [PCDD/Fs and dioxin-like (dl)-PCBs]. (iv) Contaminant concentrations were very low (mostly <1 ng/g wet weight) and far below the European and Dutch legislative limits. (v) Contaminant concentrations in farmed shrimp, pangasius, and tilapia were lower than those in wild fish, whereas contaminant concentrations in farmed salmon and trout were higher than those in lean wild marine fish. From the five species investigated, salmon is predominantly responsible (97%) for human exposure to the sum of the investigated contaminants. The contribution of trout, tilapia, pangasius, and shrimp is small (3%) because contaminant concentrations and consumption volumes were much lower.

Introduction

During the last decades, the world production of aquaculture has grown considerably (*1*). Therefore, human consumption of farmed fish and crustaceans has also increased. This is true for well-known species such as salmon, trout, and shrimp as well as for new species like pangasius and tilapia (*1*). Recent reports have shown that commonly consumed farmed salmon and trout can be contaminated with a range of contaminants, including polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans (PCDD/Fs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) (*2*−*6*). However, almost no information is available on the contamination of farmed shrimp and new species like tilapia and pangasius, and this information is urgently needed because of the rapidly growing consumption of these species worldwide. Pangasius (*Pangasius hypopthalmus*, also known as swai, tra, basa, sutchi catfish, Siamese shark, striped catfish, shark catfish, and iridescent shark) is an omnivorous fish that is primarily farmed in the Mekong delta in Vietnam. Virtually all fish is processed (filleted) in Vietnam and is shipped deep-frozen to Russia, North America, and Europe (*1, 7*). The fish is sold frozen or 'refreshed' (meaning that the fillets are thawed and sold thawed). Tilapia is the common name for *Oreochromis mossambicus* and *Oreochromis niloticus*. Tilapia is farmed in southeast Asia and South America (*1*) in rice fields, floating net cages, and ponds. However, tilapia is also successfully (commercially) farmed in recirculation systems (e.g., in The Netherlands). Tilapia is offered fresh and deep frozen. Both pangasius and tilapia are omnivorous fish, and their diet is dominated by proteins and lipids from vegetable sources, which may suggest that their contaminant concentrations are low. However, there is no comprehensive data to confirm this hypothesis. Therefore, together with the Dutch Food and Consumer Product Safety Authority (VWA), the following objectives were identified for this study: (i) Determine the contamination levels of PCBs, OCPs, PCDD/Fs, and dioxin-like (dl)-PCBs in new farmed species (tilapia and pangasius). (ii) Determine the contamination levels of PBDEs, perfluorinated compounds (PFCs), and hexabromocyclododecane diastereomers (HBCDs) in all investigated species (salmon, trout, shrimp, tilapia, and pangasius).

Materials and Methods

Sampling and Sample Pretreatment. The fish species were selected for sampling on the basis of information on trade flows of farmed fish in The Netherlands (*7*). From that study, it became clear that the current top five farmed fishery product species consumed in The Netherlands are salmon, trout, shrimp, tilapia, and pangasius. Consumption volumes are listed in Table 1.

The investigated species, number of samples, and contaminants are listed in Table 1. PCDD/Fs and dl-PCBs were not investigated in salmon and trout because there is already a substantial amount of information available in the literature (*2, 6, 8*−*10*), and the concentrations commonly observed are below the maximum residue limits (MRLs) of the European Union (EU) (*11*).

The fish and shrimp samples were purchased between October 2007 and January 2008 from various suppliers from different places in The Netherlands. These included supermarkets, fish stores, week markets, and suppliers for restaurants. One shrimp sample was obtained directly from a farm in The Netherlands. The fish samples were purchased fresh (cooled) or frozen. All samples were stored at −20 °C in their original packaging. Pangasius and tilapia samples were purchased as whole fillets. Salmon was purchased as parts of the whole fillets. Trout was purchased as a whole fish but with the intestines removed (degutted). The trout samples were filleted. One trout sample was bought as a fillet. For each sample, generally 10 or more fillets were purchased, and these were pooled. Shrimp were purchased in a variety of physical states such as cooked, raw, frozen,

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cooled, decapitated, etc. (Table S1 of the Supporting Information). If the heads were still attached, they were removed prior to pooling the individuals. Twenty-five or more individuals were pooled per sample. Each pooled sample was ground using a kitchen machine (type AL2−3, Krefft Gmbh, Gevelsberg, Germany) equipped with a rotary knife and sieve with 10 mm diameter holes. Subsequently, the samples were further ground (to reduce particle size) and homogenized (Warring blender) and stored in glass containers at −20 °C until analysis. Detailed sample information, including laboratory information management system (LIMS) identities, sample weights, physical state at purchase, etc., was recorded and can be found in Table S1of the Supporting Information.

Chemical Analysis. Analytical methods are summarized below. Detailed information can be found in Table S2 and pp S5−S7 of the Supporting Information.

Lipid Determination. Lipid determination was performed according to a modified Bligh and Dyer method (*12*). This method determines the triglycerides as well as the more polar lipid constituents such as phospholipids and cholesterol.

PCDD/Fs and dl-PCBs. All 29 WHO PCDD/F and dl-PCB congeners (*13*) were analyzed in a selection of samples (Table 1). After addition of ^{13}C-labeled PCDD/Fs, ^{13}C-labeled non-ortho-PCBs, and ^{13}C-labeled mono-ortho-PCBs internal standards (IS), the samples were extracted by accelerated solvent extraction (ASE). A comprehensive cleanup and fractionation was performed by the Power-Prep system (Fluid Management Systems, Waltham, MA). The purified extracts were analyzed by gas chromatography coupled to a high resolution mass spectrometer (GC-HRMS) operated in electron ionization (EI) mode (resolution 10000).

PCBs and OCPs. The seven indicator PCBs (CB 28, 52, 101, 118, 138, 153, and 180) and 21 OCPs [hexachlorobutadiene (HCBD), pentachlorobenzene (QCB), hexachlorobenzene (HCB), α-hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, aldrin, telodrin, isodrin, dieldrin, endrin, α-endosulfan, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, and *p,p′*-DDT] were analyzed. The samples were Soxhlet extracted with dichloromethane (DCM)/acetone (7:3, v/v). The coextracted lipids were removed by Al_2O_3 column chromatography, followed by silica column cleanup and fractionation. The two resulting fractions were, after a concentration step, analyzed on a dual column GC−electron capture detection (ECD) system equipped with a CP-Sil-8 CB and CP-Sil-19 CB column (Varian, Bergen op Zoom, The Netherlands). CB 103 was added as an IS after extraction to correct for errors made during the cleanup and GC analysis.

PBDEs and HBCDs. Twenty-three PBDE congeners (28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 208, 206, and 209) and the three major HBCD diastereomers (α-, β-, and γ-diastereomers) were Soxhlet extracted from the samples using DCM/acetone (7:3, v/v). After extraction, the following IS were spiked to the sample extract: $^{13}C_{12}$-α-, β-, and γ-HBCD, $^{13}C_{12}$-deca-BDE, and BDE 58. These IS covered the whole analytical procedure except the sample extraction. The lipids were removed from the crude extract by acidic (H_2SO_4) silica column cleanup. The eluate was fractionated over a neutral silica column into two fractions containing PBDEs and α- and γ-HBCD (first fraction) and β-HBCD (second fraction). The fractionation was performed for cleanup reasons as the second fraction also contained many polar compounds that may interfere in the GC analysis. Only the first fraction (containing the PBDEs) was analyzed by GC-electron capture negative ionization (ECNI)-MS, equipped with a CP-Sil-8 CB column. Deca-BDE was analyzed on a short column (15 m DB-5) in order to prevent degradation due to long residence times in the GC oven at high temperatures (*14*). After analysis of the PBDEs,

TABLE 1. Investigated Farmed Fish and Shrimp Samples and Species

investigated species		Dutch consumption estimate (tons/yr)[a]	origin	number of samples investigated					
common names	Latin name			PFC	PBDE	HBCD	WHO-TEQ	PCB	OCP
salmon, Atlantic salmon	*Salmo salar*	8700	Norway, Scotland, Chile	7	7	7	–	7	7
pangasius, swai, sutchi catfish, striped catfish, iridescent shark	*Pangasius hypophthalmus*	1700	Vietnam	7	7	7	5	7	7
tilapia	*Oreochromis mossambicus, Oreochromis niloticus*	1200	China, Ecuador, Indonesia, The Netherlands	7	7	6	5	7	7
trout	*Oncorhynchus mykiss, Salmo trutta*	900	Denmark, Italy, Turkey	5	5	5	–	5	5
shrimp	*Penaeus monoden, Penaeus vannamei, Litopenaeus vannamei*	1500	Bangladesh, mixed Asia[b], The Netherlands	6	6	6	5	6	6
Total		14000		32	32	31	15	32	32

[a] Dutch consumption (ton/yr) of farmed fish in 2006, representing approximately 18% of the total fish and shellfish consumption in The Netherlands (*7*). [b] Mixed origins were declared on the package label (Bangladesh/India, Indonesia/China, or Thailand/Malaysia/Indonesia).

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the first and second fractions were combined again and were carefully evaporated to dryness and redissolved in 100 μL of acetonitrile/water (75:25, v/v). The HBCD diastereomers were determined by liquid chromatography coupled to an electrospray ionization triple quadrupole mass spectrometry (HPLC-ESI-MS/MS) using a Zorbax eclipse column. The diastereomers were quantified using multiple reaction monitoring (MRM).

PFCs. The target compounds of this study were perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrA), perfluorotetradecanoic acid (PFTeA), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), and perfluorinated sulfonamide (PFOSA). Prior to extraction, $^{13}C_n$ analogues of PFHxA, PFOA, PFNA, PFDA, PFUnA, and PFOS were added as well as $^{18}O_2$−PFOSA. Subsequently, the samples were dried by mixing with Kieselguhr, which considerably improved the recoveries for the longer chain compounds (see page S6 of the Supporting Information for details). Extraction was similar to the method of Powley et al. (*15*), except for using methanol as the extraction solvent instead of acetonitrile. The PFCs were analyzed by HPLC-ESI-MS/MS and quantified using MRMs.

Quality Assurance. The quality of the analysis was assured routinely by analysis of procedural blanks, duplicate analysis of selected samples, internal reference materials, certified reference materials (CRMs) [mussel tissue standard reference material (SRM) 2978 for PCBs and OCPs and the candidate CRM BROC-01 for the PBDEs (*16*)], the use of (mass-labeled) internal standards (as mentioned in Chemical Analysis), and the participation in various interlaboratory studies (e.g., Folkehelsa www.fhi.no, QUASIMEME www.quasimeme.org), and the second worldwide PFC interlaboratory study). More information is presented on page S6 of the Supporting Information.

Results and Discussion

Contaminants in Farmed Fish and Shrimp. There is a clear distinction in the contaminant concentrations between the fish and shrimp samples, with concentrations decreasing in the following order of salmon > trout ≫ tilapia ≈ shrimp ≈ pangasius (Figure 1). For example, ∑7-PCB concentrations (the sum of CB 28, 52, 101, 118, 138, 153, and 180) in salmon are 3-fold higher than in trout and 100−200-fold higher than in the other species. The median concentrations [in pg/g wet weight (ww)] were salmon, 10860; trout, 3480; shrimp, 117; tilapia, 47; and pangasius, 47. This also generally holds true for the other contaminants.

∑9-PBDE represents the sum of the BDEs 28, 47, 99, 100, 153, 154, 183, and 209, which were recently recommended for monitoring by the European Food Safety Authority (EFSA) (*17*). BDE 49 was added because this congener was detected frequently at concentrations similar to those of BDE 100. ∑4-DDT represents the sum of *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, and *o,p′*-DDT. ∑7-PCB, OCP, and ∑9-PBDE concentrations in salmon and ∑7-PCB and ∑4-DDT concentrations in trout were >1 ng/g ww. Contaminant concentrations in all other species were generally <1 ng/g ww. The higher concentrations in the carnivorous fish (salmon and trout) are believed to be related to their diets, which substantially consist of fish oil and meal. Although the diets of these fish were not analyzed, it is known that fish oil and meal are contaminated with a range of contaminants (*4*). Farmed tilapia and pangasius feed on a higher proportion of vegetable lipids and proteins, resulting in lower contamination concentrations. Lipid contents of the samples are as follows: salmon 14.5 ± 3.7%; trout 6.6 ± 1.4%; shrimp 1.2 ± 0.5%;

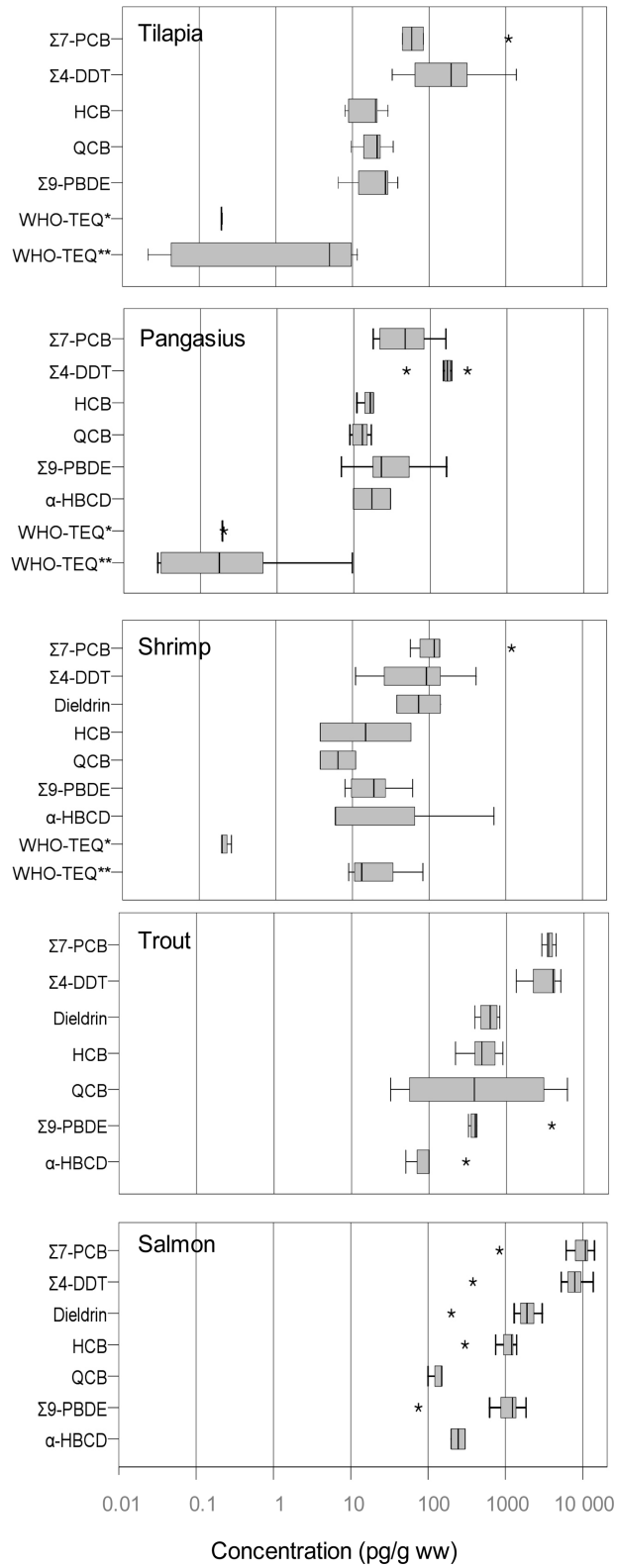

FIGURE 1. Contaminant concentrations in farmed fish and shrimp. Data for ∑7-PCB, ∑4-DDT, dieldrin, HCB, QCB, ∑9-PBDE, and α-HBCD are presented in pg/g ww. WHO-TEQ* data are presented as upperbound data (pg/g ww). WHO-TEQ data are presented as lowerbound data (in fg/g ww). ∑7-PCB values represent the sum of the indicator PCBs. ∑9-PBDE values are the sum of EFSA8$^+$ (see text for details). ∑4-DDT values represent the sum of *p,p′*-DDD, *p,p′*-DDE, *p,p′*-DDT, and *o,p′*-DDT. Vertical bars in the boxes represent the median. Outlying values are indicated in the plot by *.**

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pangasius 1.9 ± 0.9%, and tilapia 3.1 ± 1.2% (see Table S3 of the Supporting Information for lipid content per sample). In case the contaminant concentrations are expressed on a lipid weight basis, the concentrations in different fish samples will be closer to each other (data not shown), but salmon and trout remain the samples with the highest contaminant concentrations.

Per contaminant, the concentrations generally decrease in the following order of ∑7-PCB ≈ ∑4-DDT ≫ hexachlorobenzene (HCB) ≈ pentachlorobenzene (QCB) ≈ dieldrin ≈ ∑9-PBDE ≈ α-HBCD ≫ WHO-TEQ (PCDD/Fs and dl-PCBs). This order is observed in nearly all species. The ∑4-DDT concentrations were in the same range as the ∑7-PCB concentrations. Dieldrin, QCB, and HCB concentrations were lower. α-HCH, *β*-HCH, *γ*-HCH, HCBD, aldrin, telodrin, isodrin, endrin, *o,p′*-DDE, *o,p′*-DDD, α-endosulfan, cis-heptachlorepoxide, and trans-heptachlorepoxide were below the limit of detection (LOD) in all samples (or detected infrequently) and were, therefore, not included in Figure 1. Median ∑9-PBDE concentrations range from 12 pg/g ww (tilapia) to 1164 pg/g ww (salmon). The following PBDEs were not detected in any of the samples or only at low frequency: BDEs 17, 66, 71, 77, 85, 119, 126, 138, 156, 184, 191, 196, and 197; therefore, these were not included in Figure 1. ∑9-PBDE accounted for approximately 90% of the sum of all analyzed congeners. BDE 209 was observed in many samples and was the predominant congener in shrimp and most pangasius samples. The predominance of BDE 209 in farmed fish has not before been shown. The PBDE congener profile will be discussed later.

HBCDs were detected in 16 samples ranging from 6 to 1200 pg/g ww for the sum of the 3 diastereomers. In all cases, α-HBCD was the predominant diastereomer, which is commonly observed in fish samples (*18*). *β*- and *γ*-HBCD were hardly detected in any of the samples and are therefore not presented in Figure 1. No α-HBCD was detected in any of the tilapia, most of the pangasius, and some shrimp and salmon from Chile (LODs ranging from 10 pg/g ww for pangasius to 100 pg/g ww for salmon). The Dutch shrimp sample had a surprisingly high α-HBCD concentration (710 pg/g ww) as well as high *β*-HBCD concentration (520 pg/g ww). This was not observed in any of the other fish or shrimp samples, and it is unclear what could have caused this. These shrimp are farmed in a closed recirculation system rather than in natural ponds like the the Asian shrimp samples. Possibly, contaminants arise from the construction materials used in the recirculation system. In addition, ingredients for their feed may originate from other sources rather than those of the Asian shrimp feed. These suggestions on possible causes require further study. The PCDD/F and dl-PCB concentrations (expressed as WHO-TEQ concentrations (*13*)) in pangasius, tilapia, and shrimp were extremely low (all approximately 0.2 pg WHO-TEQ/g ww). On a lowerbound basis (presented in Figure 1 as WHO-TEQ**), concentrations ranged from <1 to 82 fg WHO-TEQ/g ww, and except for example OCDD, CB 77, and CB 126, nearly all congeners were <LOQ in most samples. The upperbound concentrations (WHO-TEQ*, Figure 1) were approximately 0.2 pg/g ww (Figure 1). Salmon and trout were not analyzed for PCDD/Fs and dl-PCBs in this study because a substantial amount of data show that these species meet the EU MRL of 8 pg total TEQ/g ww.

PFCs were not detected in most of the samples at all. Out of all PFC observations (33 samples × 13 PFCs analyzed), 41 values were above the LODs (Figure 2). When detected, PFC values ranged from 10 pg/g ww [PFNA in shrimp from M-AS 1 (mixed Asia 1)] to 600 pg/g ww (PFOS in shrimp from The Netherlands, Figure 2). The highest concentrations were found for PFOS. All other PFC concentrations were much lower. PFUnA and PFTrA were detected at higher frequencies

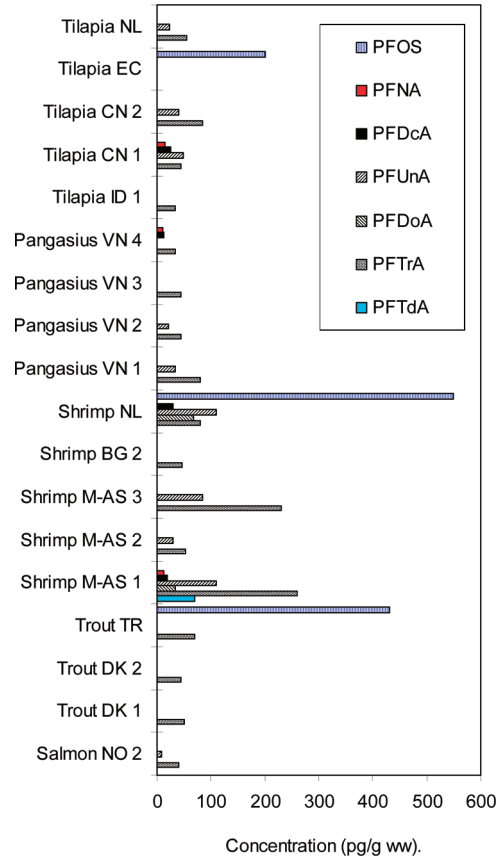

FIGURE 2. PFCs in farmed fish and shrimp. Country codes: NO = Norway, DK = Denmark, TR = Turkey, M-AS = Asia, mixed origins, BG = Bangladesh, NL = Netherlands, VN = Vietnam, EC = Ecuador, ID = Indonesia, and CN = China. Where no bars are shown, concentrations were below the LOD.

than PFOS, which is not commonly observed. Possibly, the higher LOD for PFOS (0.2−0.8 ng/g ww) caused this uncharacteristic observation as this may have resulted in more nondetects compared to PFUnA and PFTrA (LOD of 0.01−0.1 ng/g ww). PFUnA and PFTrA concentrations were not associated with a specific species; salmon and trout do not show the highest concentrations compared to other species (as was found for PCBs, OCPs, PBDEs, and α-HBCD). The reasons of the specific accumulation patterns require further study. Accumulation of PFCs in biota may be comparable to that of short- and medium-chain length fatty acids (*19*) because it is different than the accumulation of neutral lipophilic contaminants such as PCBs.

Comparison to Other Farmed Fish. In this study, the ∑7-PCB and OCP concentrations in salmon are at the lower end of the range reported by Hites et al. (*2*). Their results were based on the sum of 197 congeners. The ∑7-PCBs account for approximately 30−35% of the sum of 197 congeners. Accounting for this difference, the PCB results in our study are comparable to those of Hites et al. (*2*). Also in agreement with the Hites study, PCB and OCP concentrations in salmon from Chile were lower (10- to 20-fold) than those from Europe (Figure 1, low outlying values in the salmon data set). The ∑7-PCB and OCP results are lower than those reported by Jacobs et al. (*4*). Orban et al. (*20*) recently reported the first data on PCBs and OCPs in two pangasius samples. Although they reported many values <LOQ, the PCB and DDT concentrations of the lowest contaminated sample were similar to our results. The concentrations in the other sample were higher (820 pg/g ww for the sum of PCBs and 2610 pg/g ww for the sum of DDTs) (*20*).

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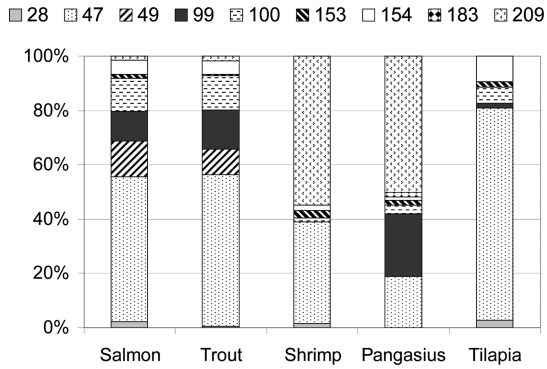

FIGURE 3. ∑9-PBDE profiles. The profile is based on mean lowerbound concentrations of each species. The ∑9-BDE concentrations were 1045 (salmon), 333 (trout), 21 (shrimp), 50 (pangasius), and 16 (tilapia) pg/g ww. The outlying high value of BDE 209 in trout from Turkey was excluded to prevent an uncharacteristically high BDE 209 contribution to the PBDE profile of trout (see PBDE Profiles for details).

In the present study, the PBDE concentrations in salmon are at the low end of those reported earlier for European salmon (*4, 21*). The PBDE concentrations in trout are much lower than those reported in farmed trout by Zenneg et al. (740−1300 pg/g ww) (*3*), except for the trout sample from Turkey that had a high BDE 209 concentration (3500 pg/g ww, see outlying ∑9-PBDE value in Figure 1 and discussion in PBDE Profiles).

In an earlier Dutch study, total HBCD was analyzed in two farmed salmon samples by GC-ECNI-MS. In that study, the Norwegian salmon showed lower concentrations, whereas the Scottish sample had approximately 3-fold higher HBCD concentrations (1.3 ng/g ww) (*22*). To our knowledge, no information has been published on the α-HBCD contamination of farmed shrimp, trout, tilapia, and pangasius.

Apart from farmed fish, the Dutch population consumes wild fish and shellfish such as herring, cod, sole, pike-perch, mussels, and shrimp. WHO-TEQ concentrations in farmed fish are lower than those earlier reported by van Leeuwen and de Boer (*22*) in Dutch wild marine and freshwater fish (1.5-fold lower than that in cod and coalfish to 260-fold lower than that in wild eel). This is even more pronounced when the concentrations of farmed fish are expressed in a lowerbound basis (Figure 1). The concentrations of ∑7-PCBs in that earlier study (*23*) ranged from 0.2 (shrimp) to 1739 ng/g ww. The farmed fish samples in this study are at the low end of that range. The same holds true for PBDEs. In an earlier Dutch study on wild fish (*22*), the concentrations ranged from 0.1 (haddock and mussels) to 149 (eel) ng/g ww for the sum of 7 BDEs, whereas the concentrations in the current study are at the low end of that range (Figure 1).

HBCD concentrations in the present study [0.006 (shrimp) to 1.2 ng/g ww (shrimp) for the sum of three diastereomers] are at the low end of those in wild fish [0.2 (coalfish and mussels) to 230 (wild eel) ng/g ww] (*22*). An earlier survey on PFCs in Dutch wild fish showed PFOS concentrations of 5.9−150 ng/g ww (eel and pike-perch) and <1−51 ng/g ww in marine fish (*24*), which are all substantially higher than the concentrations in the present study. Similar to the present study, PFNA, PFUnA, and PFDoA were also detected in Dutch wild fish (livers) (*24*).

Summarizing, the PBDE, WHO-TEQ, PCB, and OCP concentrations for farmed salmon and trout in this study are generally equal to or lower than those reported in earlier studies. Concentrations in farmed salmon and trout were higher than those in lean marine fish. Contaminant concentrations in farmed shrimp, pangasius, and tilapia were substantially lower than those in farmed salmon and trout and lower than in most wild fish.

PBDE Profiles. BDE 47 was predominant in salmon, trout, and tilapia. BDEs 28, 49 (salmon and trout), 99, 100, 153, and 154 were also detected frequently. Meng et al. found a similar PBDE profile in farmed tilapia from China (*25*). BDE 209 was detected in a limited number of salmon and trout samples (4 out of 12). In all tilapia samples, the concentration of BDE 209 was below the LOD. The most remarkable observations were the frequent detection of BDE 209 (in 12 out of 13 shrimp and pangasius samples) and the relative high BDE 209 concentration in shrimp and pangasius (56 and 50%, respectively). Such a high BDE 209 concentration has not before been reported in fish. One trout sample showed a high BDE 209 concentration (3500 pg/g ww) compared to that of other trout samples in which the BDE 209 concentration was close to the LOD (<19−22 pg/g ww). Reanalysis of the sample (starting from sample extraction onward) confirmed the high concentration. The BDE 209 concentration was uncharacteristically high compared to that of BDE 47, 99, or 100. This high observation was excluded from Figure 3 as it would have strongly affected the profile. The trout

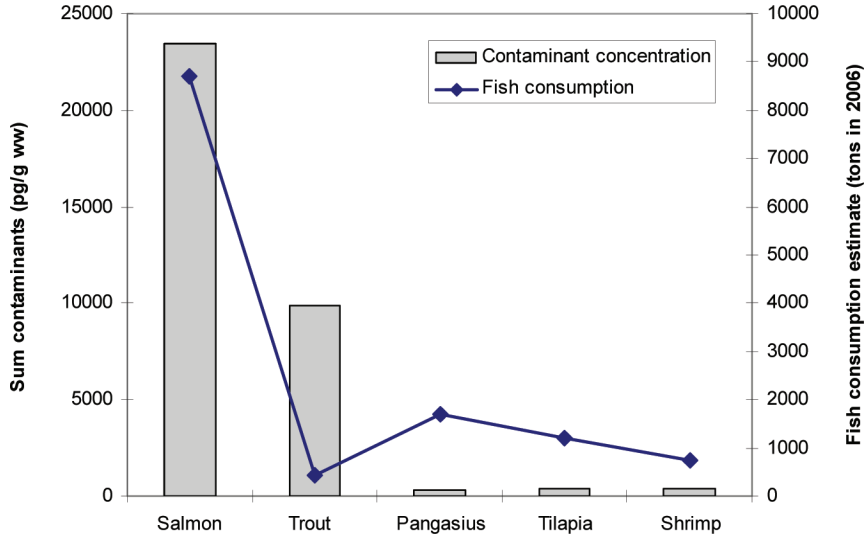

FIGURE 4. Total contaminant concentrations (WHO-TEQ, PCBs, OCPs, PBDEs, and α-HBCD) in relation to the Dutch consumption volumes of salmon, trout, pangasius, tilapia, and shrimp (data for 2006). The consumption volumes of trout and shrimp were corrected for nonedible parts.

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sample is nearly equal to the salmon profile, possibly because salmon and trout are closely related species (both belong to the Salmoninae subfamily).

It is not clear what caused the BDE 209 contamination of the shrimp, pangasius, and the trout sample from Turkey. Recently, Ashizuka et al. (*26*) also reported BDE 209 as the predominant congener in two out of three wild shrimp samples. They speculated that BDE 209 in particulate matter present in the digestive tract could have caused these elevated BDE 209 concentrations. This speculation possibly plays a role in this study as well as the fact that the digestive tracts were (whenever present) not removed from the shrimp. Shrimp are generally farmed in ponds (except the Dutch sample, which was farmed in a recirculation system), and particulate matter may have been present in the digestive tract. The reason for the predominance of BDE 209 in pangasius is unknown. No other data on PBDEs in pangasius are available in the literature. BDE 209 is a high-production chemical that is used in many polymer applications (*27*). Possibly, the contamination of the samples originates from direct contact with polymer materials (or recycled polymers) during harvesting, processing, packaging, and transportation. The analysis of BDE 209 is complex, and errors easily occur (*14, 28*). We have made considerable efforts to control the BDE 209 analysis (e.g., blank contributions) and to reach low detection limits. We, therefore, believe that the data discussed above are attributable to the fish samples themselves rather than being laboratory artifacts. Obviously, these high BDE 209 concentrations require further study, e.g., by analysis of BDE 209 in feeds, farming conditions, and possible post-harvesting contamination of the samples. Another remarkable observation was the absence of BDE 99 in all shrimp samples. Voorspoels et al. suggested that wild shrimp (*Crangon crangon*) lack the possibility for BDE 99 metabolization (*29*). The species in the present study (Table 1) are different and may have contaminant metabolization capacities, but we have found no information on his matter. BDE 183, although recommended for monitoring by EFSA because this and the earlier mentioned congeners are "predominantly found in feed, food, and human samples" (*17*), was below the LOD in all samples, including salmon and trout. Possibly, BDE 183 is not bioavailable for accumulation, or it may be debrominated in the intestinal tract (*30*).

Human Exposure. WHO-TEQ concentrations found in this study are far below the EU MRL of 8 pg total TEQ/g ww (*11*). The Dutch MRLs for the seven indicator PCBs in fish (40−120 ng/g ww per congener) (*31*) are easily met by the samples in this study. For the other contaminants, no EU or Dutch MRLs are available.

Recent studies have shown that fish contributes 28 and 12% to the exposure of Dutch citizens to PBDEs and PCDD/Fs and dl-PCBs (*32, 33*), respectively. In these studies, wild fish (e.g., herring, eel, plaice, sole, and cod) and farmed fish (i.e., salmon) were included. Herring, salmon, and eel showed the highest contaminant concentrations. Herring is a popular fish in The Netherlands and is an important contributor to contaminant exposure. However, in this study, we focus on the top five farmed fish consumed in The Netherlands. With new farmed species being consumed in increasing amounts, one might expect a change of the human exposure to contaminants. We have investigated this for WHO-TEQs, ∑7-PCBs, OCPs, ∑9-PBDEs, and α-HBCD from the five species in this study.

Preferably, one uses food consumption survey data to determine contaminant exposure. However, the data covering the Dutch population originate from 1997−1998 (*34*) and does not include consumption data of the new species such as pangasius and tilapia. Therefore, we used the estimates of a recent inventory on Dutch consumption volumes per species as sold in supermarkets, weekly markets, fish shops, etc. (Table 1) (*7*). For pangasius, tilapia, and salmon, this concerns almost exclusively edible parts. Trout is partly sold as whole fish (degutted). In order to arrive at the estimate for the edible parts, it was assumed 30% of whole trout consisted of fillets. The consumption volumes from Table 1 were corrected for this. For shrimp, the edible parts were assumed to be 50%. We summarized the concentrations of WHO-TEQs, PCBs, OCPs, PBDEs, and α-HBCD per fish sample (sum concentration) and calculated the means per species. By multiplying these mean sum concentrations with the (corrected) consumption volumes per species (Figure 4), we obtained an estimate of the human exposure per species. Salmon dominates the contaminant exposure from the investigated species (approximately 97%, data not shown), whereas trout, tilapia, pangasius, and shrimp together contribute approx 3%. This is caused by the following: (i) Salmon is still consumed in the highest quantities. (ii) Contaminant concentrations in salmon are much higher, 10-fold (QCB) to 200-fold (∑7-PCBs), than compared to those in pangasius, tilapia, and shrimp (Figure 4).

This is only a first estimation of the relative importance of contaminant exposure originating from new species such as pangasius and tilapia, but it clearly shows that the contribution from these species to the exposure is still minimal, compared to that of farmed salmon. Obviously, these results should also be viewed in relation to the degree of contamination and consumption of wild fish, and further investigations are needed to determine the relative importance of the different fish.

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Supporting Information Available

Sampling information and details on analytical methods are provided. This information is available free of charge via the Internet at http://pubs.acs.org.

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