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Levels of Polybrominated Diphenyl Ethers in Commercial Food in Siena Province (Tuscany, Italy)

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Abstract: This study reports on the presence and levels of polybrominated diphenyl ethers (PBDEs) in food items collected during the period 2004-2010 in commercial food shops in Siena (Southern Tuscany, Central Italy), in order to evaluate risk to humans due to food consumption. We have considered the following eight PBDE congeners to be of primary interest: BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183 and BDE209. The overall results clearly show a strong difference in concentration of PBDEs between seafood and food from the terrestrial trophic web. PBDE concentrations in commercial food from terrestrial origin vary from an average of 156 pg g^{-1} fat in chicken breast (6 pg g^{-1} fresh weight) to an average of 404 pg g^{-1} fat in butter (125 pg g^{-1} f.w.). In seafood, average values are comprised between 174 pg g^{-1} f.w. in hake to 692 pg g^{-1} f.w. in swordfish. In several samples of swordfish PBDE values are higher than 1 ng g^{-1} f.w. If we consider PBDE congeners individually, BDE47 is the predominant one in seafood, with percentages above 50% in all species. In commercial food of terrestrial origin, BDE47 is predominant in beef, pork, bacon, butter and sausage (27%-35%), followed by BDE209 (25%-28%). In chicken breast, eggs and cow's milk, BDE209 is predominant (28%-32%) followed by BDE47 (25%-30%). The level of PBDEs found in bluefin tuna and swordfish, considering their importance in the human diet, suggests the need for particular care in our food choices.

Key words*:* PBDEs, commercial food, Italy, bluefin tuna, swordfish.

1. Introduction

The purpose of this study was to assess the levels of polybrominated diphenyl ethers, a class of toxic contaminants that have adverse effects on the endocrine system, in commercial foods from the provinces of Siena (Southern Tuscany, Central Italy). Among the endocrine disruptors (EDCs), recent studies continue to show that several persistent organic pollutants (POPs) such as dichlorodiphenyltrichloroethane (DDT) and its metabolites, as well as polychlorobiphenyls (PCBs) continue to be found in foods in Italy, despite the restrictions on the use and production that have been in place for many years [1-7]. More recently, other pollutants with endocrine disruptor actions have been found in food products, posing a risk of adverse effects to human health and the environment; they include polybrominated diphenyl ethers (PBDEs). These contaminants are increasingly found in Mediterranean ecosystems, while there are serious shortcomings in terms of availability of data on aspects such as the contribution of various food products to human exposure [8-11]. Polybrominated diphenyl ethers (PBDEs) are a class of emerging substances used worldwide as flame retardants. They are hydrophobic, lipophilic, relatively resistant to biodegradation and show similar behavior to PCBs in aquatic and terrestrial ecosystems [12]. Moreover, they can cause acute toxicity in organisms [13]. The majority of emissions into the environment today are the result of the use and recycling of end products containing PBDEs. Production of these compounds is confined to only a few areas of the planet, especially Western Europe and the US, although emissions also occur during the production processes. However, their

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penetration into food webs has become ubiquitous; many studies have highlighted the presence of PBDEs in various areas of the planet, including the polar regions [10, 14-15], confirming that these compounds are persistent, subject to long-distance transport, and capable of bioaccumulating in the tissues of organisms. As a consequence of their increasing use, environmental levels of PBDEs have risen since their first application, and recent studies have reported that PBDE concentrations are increasing in the environment [16] and in animal and human tissues [9, 17-18]. In some areas PBDE levels in wildlife and humans have surpassed the levels of PCBs [19].

Effects of PBDEs in experimental animals include endocrine disruption, neurodevelopmental and behavioral outcomes, hepatic abnormalities, and possibly cancer [13, 20]. Although little human epidemiology has yet been done, early studies suggest effects on male reproductive hormones [21] and fertility [22], thyroid hormone homeostasis [23], cryptorchidism [24], and lower birth weight and length [25].

The most significant contributor to the dietary PBDE intake in humans is food and in particular seafood [26]. For this reason, this study reports on the presence and levels of PBDEs in commercial food in the Province of Siena (Italy), with a particular attention to food products of marine origin, in order to evaluate risk for humans due to food consumption. Published papers on the presence of PBDEs in food in Italy are scarce or nonexistent, although there is information available on their presence in the Mediterranean marine environment [8, 10-11], and their threat to human health is well known [20-25]. Based on the composition of the technical PBDE mixtures, the occurrence in the environment and in food, and the report of the Panel on Contaminants in the Food Chain (CONTAM Panel), we have considered the following eight PBDE congeners to be of primary interest: BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183 and BDE209. These eight PBDE congeners are the most abundant compounds present in the three commercial mixtures PentaBDE, OctaBDE and DecaBDE, and they are considered the most relevant for dietary PBDE exposure.

2. Materials and Method

2.1 Materials

Samples were collected in commercial shop in Siena (Tuscany, Italy) in the period 2004-2010. Aliquots of commercial food, frozen and stored at -20 °C, from a pool of several samples were analysed.

2.2 Methods

PBDEs were analyzed following a method described elsewhere, with some modifications [1, 9]. Briefly, samples were homogenized with anhydrous sodium sulfate salt and Soxhlet extracted with hexane:dichloromethane (40:60). Interferences were removed by fractionation by a multilayer silica gel column. After solvent evaporation, gravimetric lipid determination was performed. Eight BDE congeners (IUPAC numbers BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209) were identified and quantified using a GC/MS (ion trap mass spectrometer) from Thermo Finnigan (Trace GC 2000/GC Polaris), equipped with an AS2000 autosampler (Rtx-5MS capillary column, 30 m × 0.25 mm i.d., film thickness 0.25 μm; Restek). A 2 μL aliquot of sample in isooctane was injected in splitless injection mode with helium as the carrier gas. The injector temperature was 275 °C. The ramp program was as follows: the initial temperature of the oven was 80 °C, held for two minutes; it was increased to 200 °C at a rate of 25 °C min^{-1}, then to 300 °C at 4 °C min^{-1} and held for 10 min. The excitation voltages were 4.75 V for tri-and tetra-BDEs, 4.60 V for penta-BDEs, and 4.70 V for hexa-BDEs. The internal standard was CB1413C in isooctane, from Cambridge Isotope Laboratories; the PBDE calibration standard solution was from Wellington Laboratories, Inc. The compounds detected in the blanks were BDE99 and

BDE154. Detection limits, calculated as the mean blank + 3SD, were 4 pg g^{-1} fresh tissue. Throughout this manuscript PBDEs are represented by their IUPAC numbers.

2.3 Data Analysis

All statistical analyses were performed using STATISTICA 7.1 (StatSoft Italia srl, 2005).

Concentrations are expressed as arithmetic means with standard deviations. Associations between dependent and independent variables were assessed by linear regression analysis. The sum of eight BDE congeners (Nos. 28, 47, 99, 100, 153, 154, 183 and 209) were considered to allow comparison with other works.

3. Results and Discussion

This study evaluated the presence and amount of polybrominated diphenyl ethers (PBDEs), calculated as the sum of eight congeners (IUPAC numbers BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209), in food items collected during the period 2004-2010 in commercial food shops in Siena (Tuscany, Italy), in order to assess risk to humans due to food consumption. Results of the average concentrations, the standard deviation and the range of PBDEs in the various types of food analyzed over the entire period are shown in Table 1 on a lipid basis (food of terrestrial origin), and in Table 2 on a fresh weight basis (seafood). PBDE concentrations in commercial food from the terrestrial trophic web vary from an average of 156 pg g^{-1} fat in chicken breast to an average of 404 pg g^{-1} fat in butter. The other values higher than 1 ng g^{-1} f.w. Standard deviation values are high in most cases, and this may be due to the natural variability usually found when analyzing samples of organisms belonging to different sex and age classes; in the case of fish, feeding habits and ecological behaviour may also contribute to very different accumulation levels of these pollutants in tissues. The overall results clearly show a strong difference in concentration of these contaminants between foods from the terrestrial trophic web and those from the marine trophic web; this difference is more evident if we compare results on a fresh weight base (Figs. 1 and 2).

These results clearly show a strong relationship between level of PBDEs and fat content in food of terrestrial origin (Fig. 3); this relationship is much less evident in seafood (Fig. 4), which also shows less homogeneous values. This may be determined by several factors, the principal of which is surely the fact that the marine environment is the ultimate repository of terrestrial matter with its associated array of man-made chemicals. For instance, a large proportion of persistent contaminants such as PCBs that have escaped into the global environment are found in coastal sediments and open-ocean waters, suggesting the role of the marine environment as a reservoir of persistent semi-volatile organochlorines [27, 28]. This is evident in the Mediterranean in general, and the Tyrrhenian Sea in particular, where much of the fish and seafood consumed in Siena is caught. Due to pressures from the human population and limited water exchange [29], this basin's sediments are subject to accumulation of persistent contaminants such as PBDEs-which have characteristics similar to those of PCBs-, and to their consequent release into the marine food chain. Another important factor in explaining this variability as well as elevated PBDE levels is position in the food web; several species of fish used for human consumption, such as bluefin tuna and swordfish are top predators, and are thus subject to bioaccumulation and biomagnifications of this type of contaminant [9, 26, 30].

For bluefin tuna and swordfish, a further evaluation was carried out during sample collection (Table 3). PBDE concentrations in tuna went from an average of 669 pg g^{-1} f.w. in the year 2004, to an average value of 437 pg g^{-1} f.w. in 2010. In swordfish, average values vary from 901 pg g^{-1} f.w. in 2004 to 528 pg g^{-1} f.w. in 2008 and 582 pg g^{-1} in 2010. It is interesting to note a significant decrease in levels of PBDEs in bluefin tuna

Table 1 Levels of PBDEs (pg g^{-1} fat) in commercial food in Siena.

Commercial food	n	Fat (%)	PBDEs pg g^{-1} fat			
			Mean	SD	min	max
Chicken eggs	8	13.6	277	223	76	734
Chicken breast	10	3.1	156	85	75	323
Beaf	10	8.2	254	106	123	444
Pork meat	10	9.5	247	122	89	443
Pork beacon	10	40.4	321	160	99	590
Pork sausage	10	21.5	280	107	110	427
Butter	6	72.1	404	105	239	541
Cow's milk	6	11.3	250	53	178	310

n: number of samples; SD: Standard deviation.

Table 2 Levels of PBDEs (pg g^{-1} f.w.) in commercial food in Siena.

Commercial food	n	Fat (%)	PBDEs pg g^{-1} f.w.			
			mean	SD	min	max
Hake	10*	3.2	174	120	54	412
Bluefin tuna	25	12.4	505	285	124	1,005
Swordfish	25	9.9	659	377	147	1,315
Eel	10*	15.6	408	225	146	720
Anchovy	10*	8.3	301	128	100	523
Sardine	10*	10.3	406	135	210	601
Sea bream (farmed)	15*	7.2	397	221	116	882
Sea bass (farmed)	15*	8.5	362	217	110	820

n: number of samples; n*: number of pool; SD: Standard deviation.

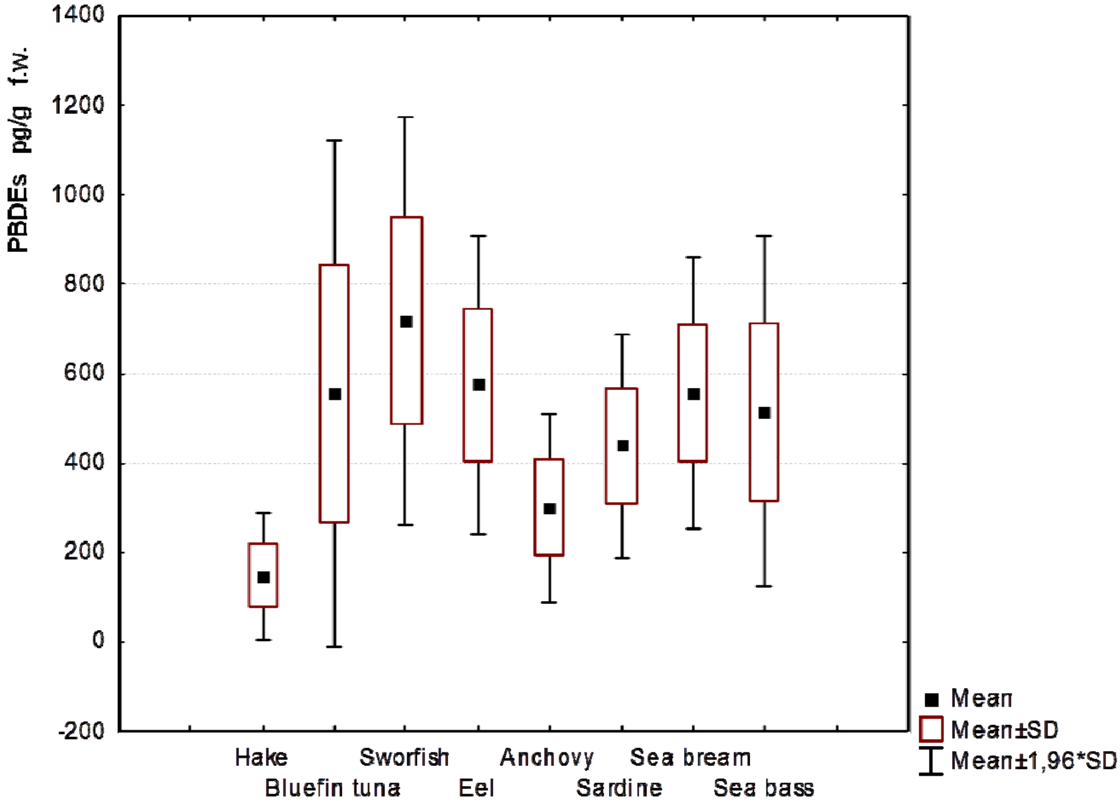

Fig. 1 Boxplot of PBDEs concentrations (pg/g f.w.) in seafood.

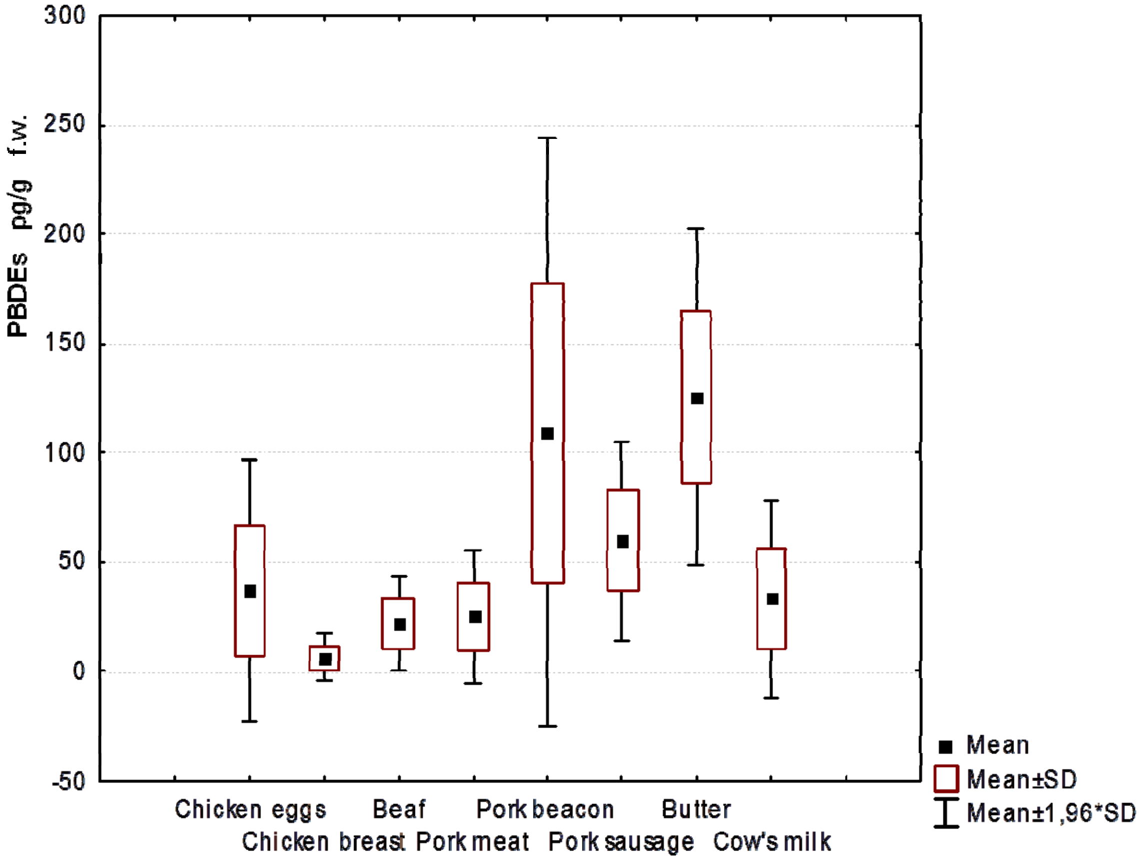

Fig. 2 Boxplot of PBDEs concentrations (pg/g f.w.) in food of terrestrial origin.

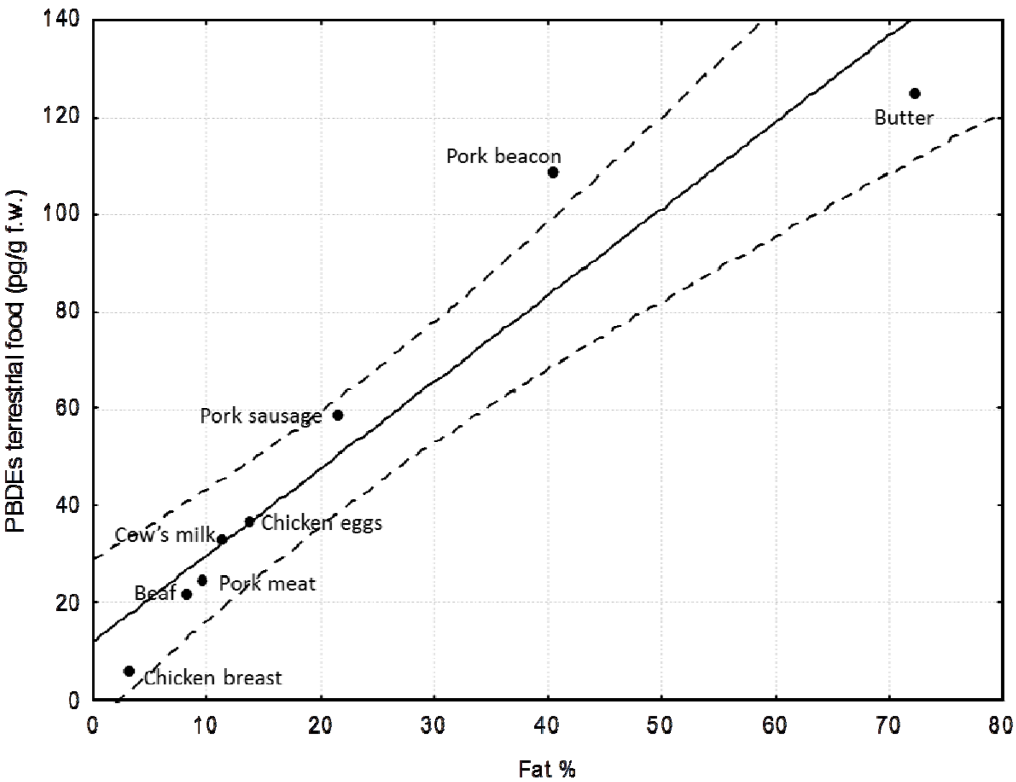

Fig. 3 Scatterplot: fat% vs. PBDEs (pg g^{-1} f.w.) in commercial food of terrestrial origin.

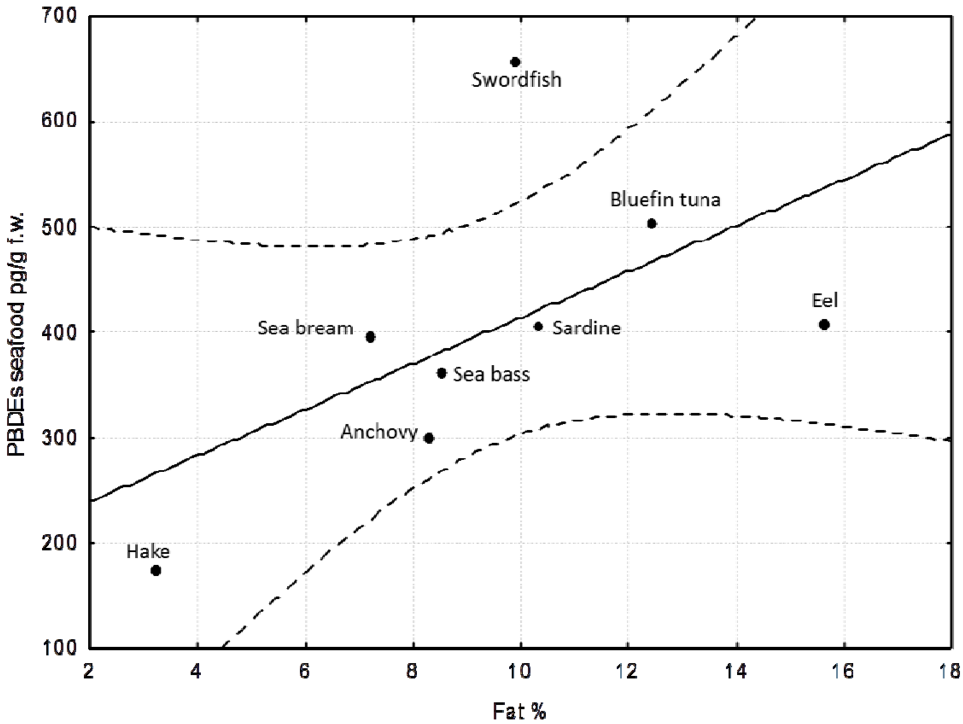

Fig. 4 Scatterplot: fat% vs. PBDEs (pg g^{-1} f.w.) in commercial seafood.

Table 3 Levels of PBDEs (pg g^{-1} f.w.) in commercial food, bluefin tuna and swordfish, in Siena in different years.

Commercial Food	n	PBDEs pg g^{-1} f.w.			
		mean	SD	Min	Max
Bluefin tuna 2004	5	669	410	124	1,005
Bluefin tuna 2005	5	547	217	234	810
Bluefin tuna 2007	5	409	299	167	923
Bluefin tuna 2008	5	462	145	312	689
Bluefin tuna 2010	5	437	325	187	891
Swordfish 2004	5	901	232	589	1,134
Swordfish 2005	5	705	343	280	1,221
Swordfish 2007	5	577	393	290	1,213
Swordfish 2008	5	528	476	166	1,315
Swordfish 2010	5	582	432	147	1,088

n: number of samples; SD: Standard deviation.

and swordfish found in the Sienese market between 2004-2005 and 2007-2010. This decrease is greater more substantial in swordfish, but variability is as well, with a very high standard deviation (Fig. 5). This decrease may be due to the fact that in the Mediterranean, the size of fish of these two species is gradually being reduced as a result of overfishing (younger, less polluted), but also to potential reproductive alterations in large pelagic fish in this basin resulting from high levels of accumulation of endocrine disruptors in these two species [7, 8, 10].

This results clearly indicate the presence of these contaminants in commercial food in Italy, particularly in seafood, confirming the penetration of these contaminants in the Mediterranean food chain. It is interesting to note that in the muscle tissue of 9 bluefin tuna caught in 2003 in the Southern Tyrrhenian Sea, the average concentration of PBDEs found was 15 ng g^{-1} f.w. [10] and in 17 swordfish caught in the samearea in 2005, the average concentration

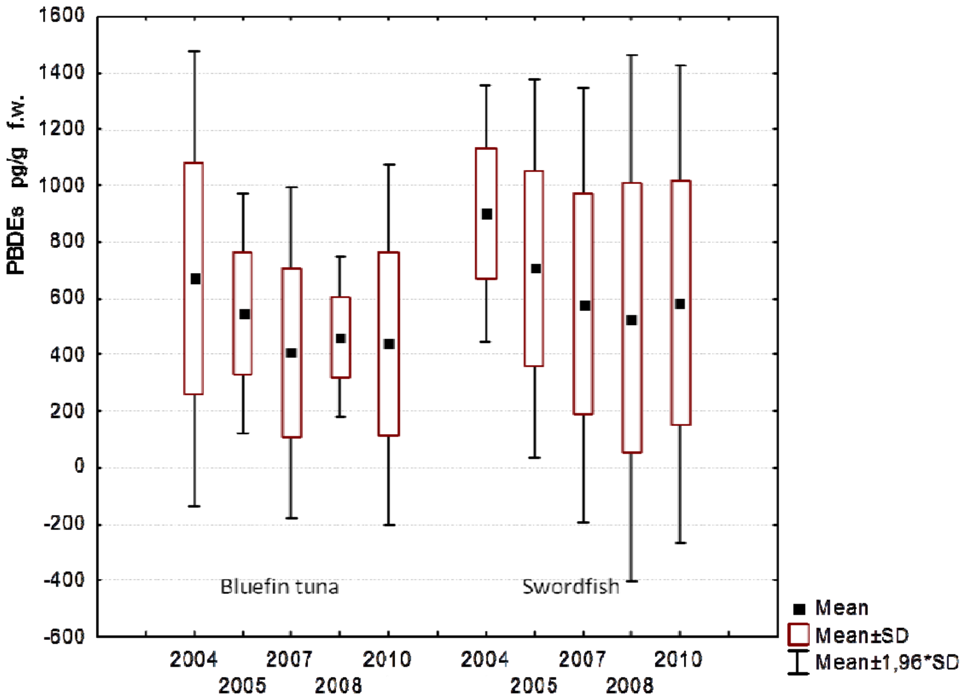

Fig. 5 Boxplot of PBDEs concentrations (pg/g f.w.) in commercial seafood, bluefin tuna and swordfish, in different years.

found was 612 pg g^{-1} f.w. [7]. In 2007 swordfish samples from the Ionian Sea, PBDE values ranged from 150 to 1,320 pg g^{-1} f.w., and in bluefin tuna from the same area PBDEs ranged between 120 and 1,150 pg g^{-1} f.w. (8). The values found in this study are comparable with PBDE concentrations in fish (88-1,019 pg g^{-1} f.w.) in Spain [26] and in Japan (17.7-1,720 ppt) [31].

If we consider PBDE congeners, BDE47 was the predominant one in seafood, with percentages above 50% in all species, followed by BDE100 and BDE209. BDE47 reached levels of 60% in farmed fish (sea bream and sea bass) and in eel (Fig. 6). BDE47 was predominant in swordfish collected in the year 2005 in the Southern Tyrrhenian [9] and in several species of fish from the Ionian Sea in 2007 (8).

A similar profile has been described in many aquatic species by several authors [30, 32-34]. BDE47 is the congener most used in penta-brominated commercial mixtures, which have been banned in Europe since 15 August 2004. Previous use, debromination processes [32] or long-range transport [35] from countries where penta-brominated mixtures are still in use may be responsible for this pattern. The predominance of BDE47 may also be due to preferential elimination or metabolic degradation of BDE99, following the debromination pattern [34]. In commercial food of terrestrial origin in Siena, BDE47 is predominant in beef, pork, bacon and sausage (27%-35%), followed by BDE209 (25%-28%). In chicken breast, eggs and cow's milk, BDE209 is predominant (28%-32%) followed by BDE47 (25%-30%). In butter, the trend is BDE47 > BDE99 > BDE209 (Fig. 7).

These results clearly highlight the now-consolidated presence of PBDEs in commercial food in Italy, and in particular in seafood. Higher average values (> 500 pg g^{-1} f.w.) detected in bluefin tuna and swordfish puts these species at particular risk and could also explain the higher endocrine disrupting chemical (EDC) levels observed in their tissues [1, 7, 10]. The first warning about toxicological risk to large Mediterranean pelagic fish due to endocrine disruptors (EDCs) was sounded with regard to swordfish [36]. The authors used vitellogenin (Vtg) and zona radiata proteins (Zrp) as

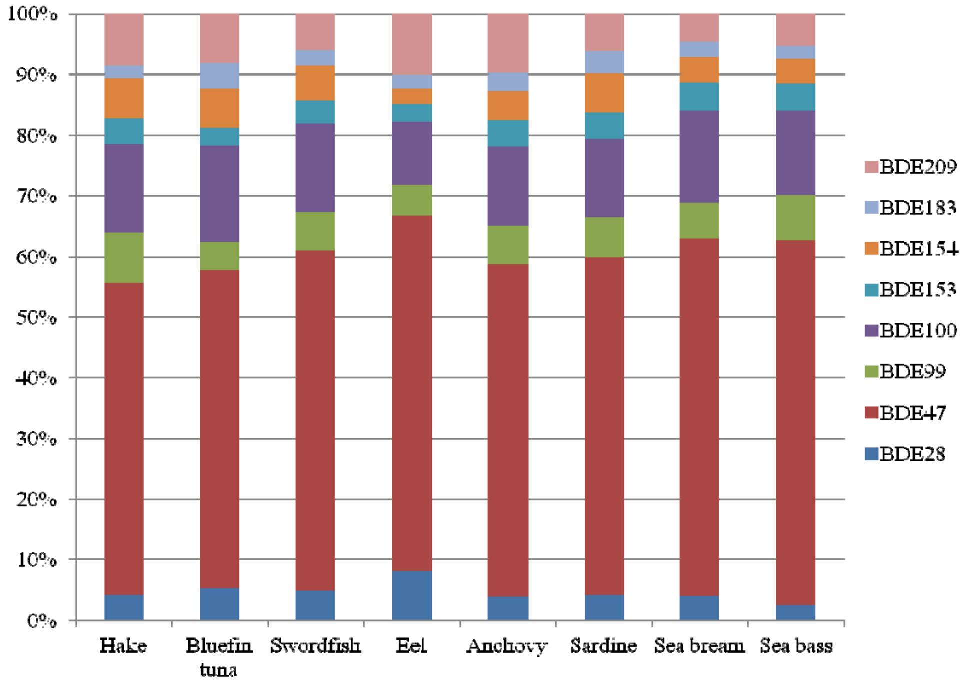

Fig. 6 Percentage of BDE congeners in seafood.

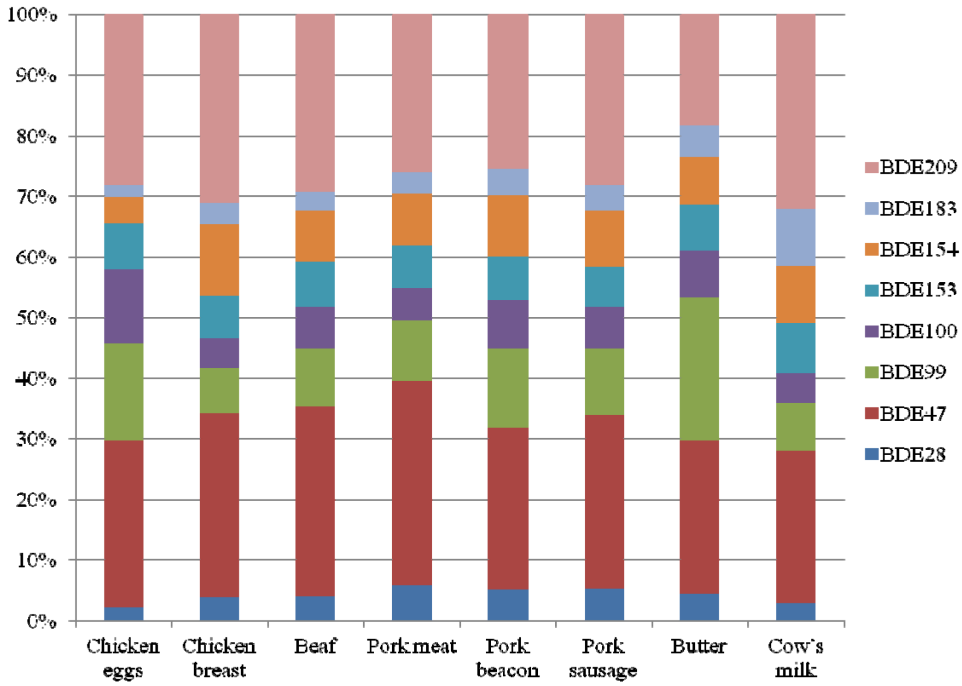

Fig. 7 Percentage of BDE congeners in commercial food from terrestrial trophic web.

diagnostic and prognostic biomarkers. Dramatic induction of these typically female proteins was detected by ELISA and Western blot in adult males. The importance of bluefin tuna and swordfish in the human diet in Italy suggests that we should be making our food choices with particular care, and it is advisable that pregnant and breastfeeding women as well as young children select fish from a wide range of species, without giving undue preference to large predatory fish such as swordfish and tuna.

4. Conclusions

The results of this study are consistent with previous studies that have reported now-generalized contamination by polybrominated diphenyl ethers (PBDEs) in commercial food. In particular, we evaluated the presence and levels of these contaminants in food products in the Province of Siena in Central Italy, in order to evaluate risk to humans due to food consumption. The overall results clearly show a strong difference in concentration of these contaminants between foods from the terrestrial trophic web and those from the marine trophic web. In seafood, values are higher, and in several samples of swordfish PBDE values are above 1 ng g^{-1} f.w. BDE47 was the predominant congener, with percentages above 50% in fish species. In commercial food of terrestrial origin, BDE47 is predominant in beef, pork, butter, bacon and sausage.

Levels of PBDEs in bluefin tuna and swordfish found in the Sienese market decreased over the course of the past six years. This is possibly due to the fact that in the Mediterranean, fish size in these two species is gradually being reduced as a result of overfishing (younger, less polluted). But it may also be due to potential reproductive alterations in large pelagic fish in this basin resulting from high levels of accumulation of endocrine disruptors. This puts these two species at the top of the food chain at particular risk, and their importance in the human diet suggests the need for particular care in our food choices.

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