POLYBROMINATED DIPHENYL ETHERS, ORGANOCHLORINE PESTICIDES, POLYCHLORINATED BIPHENYLS AND PERFLUORINATED COMPOUNDS IN COMPOSITE SAMPLES OF UNITED STATES FOOD

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Abstract

Introduction: The environment, food, and people have been shown to be contaminated with a variety of persistent organic pollutants. These chemicals can cause deleterious health effects; however, the levels of contamination of combinations of these chemicals have not been determined for US food.
Materials/Methods: Samples of 31 different food types were collected from 5 US grocery stores in Dallas, TX, USA (total of 310 samples) and pooled to make 31 composite samples. The food samples were analyzed for polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane, perfluorinated compounds, organochlorine pesticides, and PCBs.
Results: Food samples tested were found to be contaminated with a mixture of organic pollutants. Levels of PBDEs were highest in fish, dairy and meat foods, while perfluorooctanoic acid (PFOA) was found in vegetable based foods and fish at the highest levels. Organochlorine pesticides were detected in almost all food samples.
Conclusion: Many types of US food are contaminated with multiple organic pollutants. Research should be conducted to determine allowable levels of these chemicals in US foods as well as the health effects due to exposure to mixtures of these compounds. Regulation and monitoring of levels of toxic chemicals in the US food supply by government agencies are likely necessary.

Introduction

In recent years, concerns about health effects from the many chemicals that are currently ubiquitous in the environment have risen. This abstract will examine levels of persistent organic pollutants: polybrominated diphenyl ethers (PBDEs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and perfluorinated compounds (PFCs) in thirty-one foods common to the US diet.

PBDEs are flame retardant chemicals that are found in many types of plastics, foams, electronics, and fabrics. Commercially, they exist in three different mixtures: Penta, Octa, and Deca[1]. Every year approximately 67,000 metric tons are produced, during which PBDEs can enter the air, water, soil and biota[1]. In each media, they can accumulate and adhere to other particles. This process occurs in food products as well, making diet a significant source of exposure. The health effects of PBDE exposure are not well characterized. There have been preliminary studies that have associated elevated exposure with decreased thyroid function[2], endocrine disruption[3, 4], and impaired spermatogenesis[5]. PBDE production of Penta and Octa has been phased out in Europe and the United States, yet levels have not necessarily begun to decline[6]. We have previously described the levels of PBDEs in US food from analysis of individual samples[7-10]. There has been a rapid increase in PBDE body burden in the US and Europe the past 30 years as demonstrated by elevated levels in blood and nursing mothers' milk measured over this time[11-14].

While no longer produced in the US, PCBs are also still ubiquitous in the environment[15]. Originally they were used as coolants and lubricants in many electronic devices such as transformers and capacitors because they are good insulators and do not burn easily[16]. Because of their persistence and resistance to degradation, PCBs do not readily break down in the environment[17]. In humans, they also have a relatively long half life of elimination[18] During their original production, PCBs entered the water, air, and soil. In water, plankton and fish eat the organic-PCB particle complexes and other fish, leading to a large biomagnification effect up the food

web[19]. With respect to health effects PCBs have been associated with neurodevelopmental problems, growth abnormalities carcinogenicity, and, sometimes at high doses in sensitive persons, chloracne [20-23].

OCPs were first produced in the 1940s. Many individual products have since been banned by the USEPA; however, because of their persistence and continued global production, many of the pesticides are still ubiquitous in the environment. DDT is still considered useful in control of malaria in many countries. People are exposed to OCPs largely through diet. In human studies, occupationally exposed workers have developed liver damage, elevated serum lipids, and diabetes [24]. Organochlorines may also disrupt thyroid function during pregnancy, prostate cancer, and neurotoxicity [25, 26].

Perfluorinated compounds (PFCs) are directly released into the environment during manufacture and were used as a main component in aqueous fire-fighting foam[27]. The most commonly manufactured PFCs, perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) were widely used in Scotchgard™, a water and stain repellent, and Teflon®, used in no stick cooking utensils, respectively, before being phased out. PFCs have also been used as additives in a wide array of products, including in food packaging, floor polishes, medical inhalers, air fresheners, lubricants, electronic equipment and gasoline [27]. Calculations have suggested that the while the majority of historically released PFCs are in the ocean, large proportions of emissions exist in surface water [27]. Human pathways to exposure are not clearly defined, though it is thought that direct skin contact, through diet and drinking water, and perhaps dust are probable routes[28]. PFCs have been reported in serum in representative surveys of the US population in the periodic National Health and Nutrition Examination Survey (NHANES)[29].

This abstract explores diet as a mechanism of exposure for PBDES, organochlorine pesticides, PCBs, and perfluorinated compounds.

Materials and Methods

Sample Collection: Ten samples of thirty-one different food types (total of 310 samples) were collected from five grocery stores in Dallas, TX, USA on several separate occasions in January 2009 and April 2009. The collected samples included meat (ground beef, bacon, turkey, sausage, ham, chicken breast, roast beef, canned chili), fish (salmon, canned tuna, catfish, tilapia, cod, canned sardines in water, frozen fish sticks), dairy foods (butter, milk, cream cheese, American cheese, other cheese, ice cream, frozen yogurt, yogurt), vegetable based foods (olive oil, canola oil, margarine, cereal, apples potatoes, peanut butter), and eggs. The food samples were frozen (when required) and shipped to Eurofins GfA GmbH laboratory in Hamburg, Germany for analysis. Equal weights of each of the ten samples for each food type were homogenized and combined to make a composite sample for each analysis.

Chemical Analysis: Each sample was analyzed for a range of brominated flame retardants, perfluorinated chemicals, and pesticides. The brominated flame retardants included hexabromocyclododecane (HBCD) and the PBDEs (BDEs 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209). The perfluorinated chemicals included perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorobutane sulfonate (PFBS), perfluorohexansulfonate (PFHxS), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctanesulfonic acid (PFOSA), perfluorodecane sulfonic acid (PFDeS), and perfluorododecanoic acid (PFDoA). The pesticides included α-, β-, γ-, δ- , and ε-HCH, DDT and DDT metabolites, aldrin, dieldrin, endrin, isodrin, α and β-endosulfan, endosulfan sulfate, toxaphene 26, 50, and 62, heptachlor, mirex, α and γ chlordane, oxychlordane, transnonochlor, *cis* and *trans* heptachlorepoxid, and octachlorstyrene. The food samples were also analyzed for polychlorinated biphenyl congeners 28, 52, 101, 118, 138, 153, and 180. The analysis for these POPs in food has been described previously[30, 31].

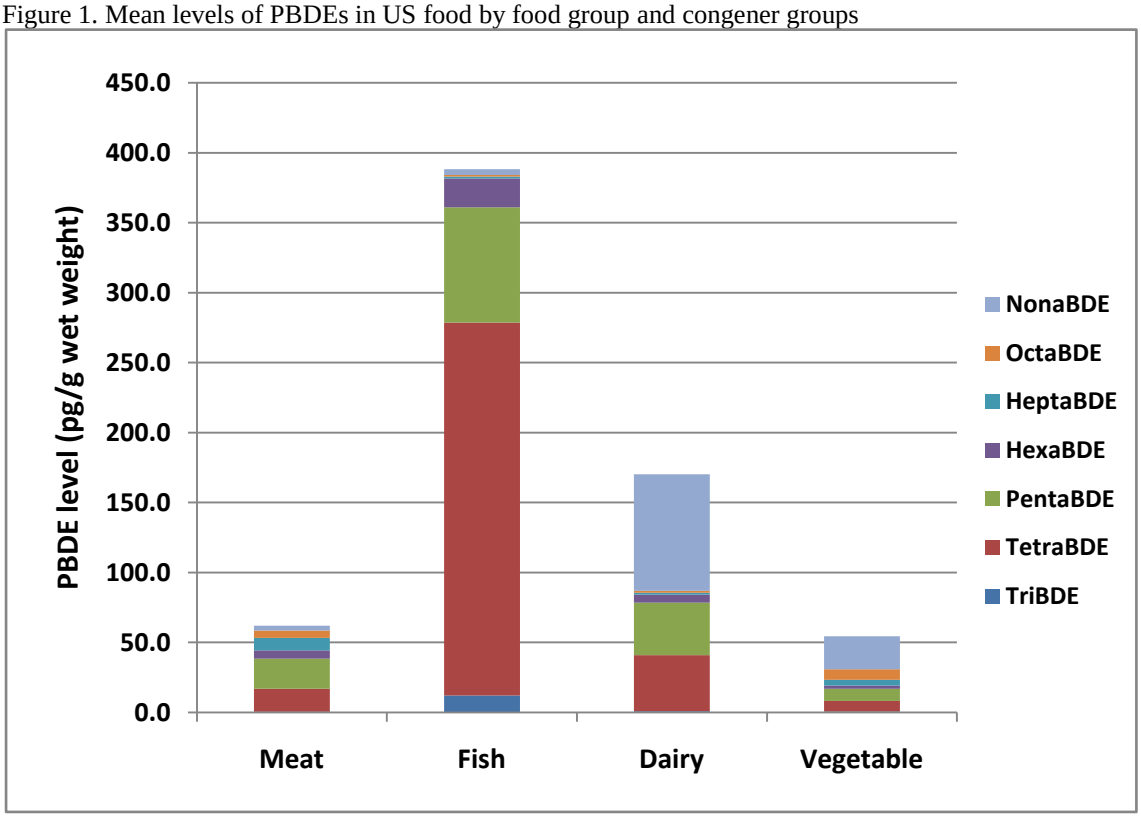
Results

Brominated Flame Retardants

Every sample measured had detectable levels of PBDEs except canola oil. For technical reasons BDE 209 was not detected above the limit of detection in any of the samples, and therefore was not included in any PBDE totals. For other PBDE congeners, non-detected PBDEs were estimated as half of the limit of detection. The highest total levels of PBDEs were measured in fresh salmon (930 pg/g wet weight [ww]), butter (1046 pg/g

ww), and canned sardines in water (1498 pg/g ww). In salmon and sardines, the majority of the detected PBDEs was the tetrabrominated congener BDE 47 (486 and 798 pg/g ww). Additionally, both salmon and sardines had detectable levels of tetrabrominated BDE 49 (139 and 259 pg/g ww). Two nonabrominated congeners, BDE 206 and 207, were detected at the highest levels in butter (260 and 395 pg/g ww). These congeners could be breakdown products from decabrominated BDE 209.

Figure 1. Mean levels of PBDEs in US food by food group and congener groups



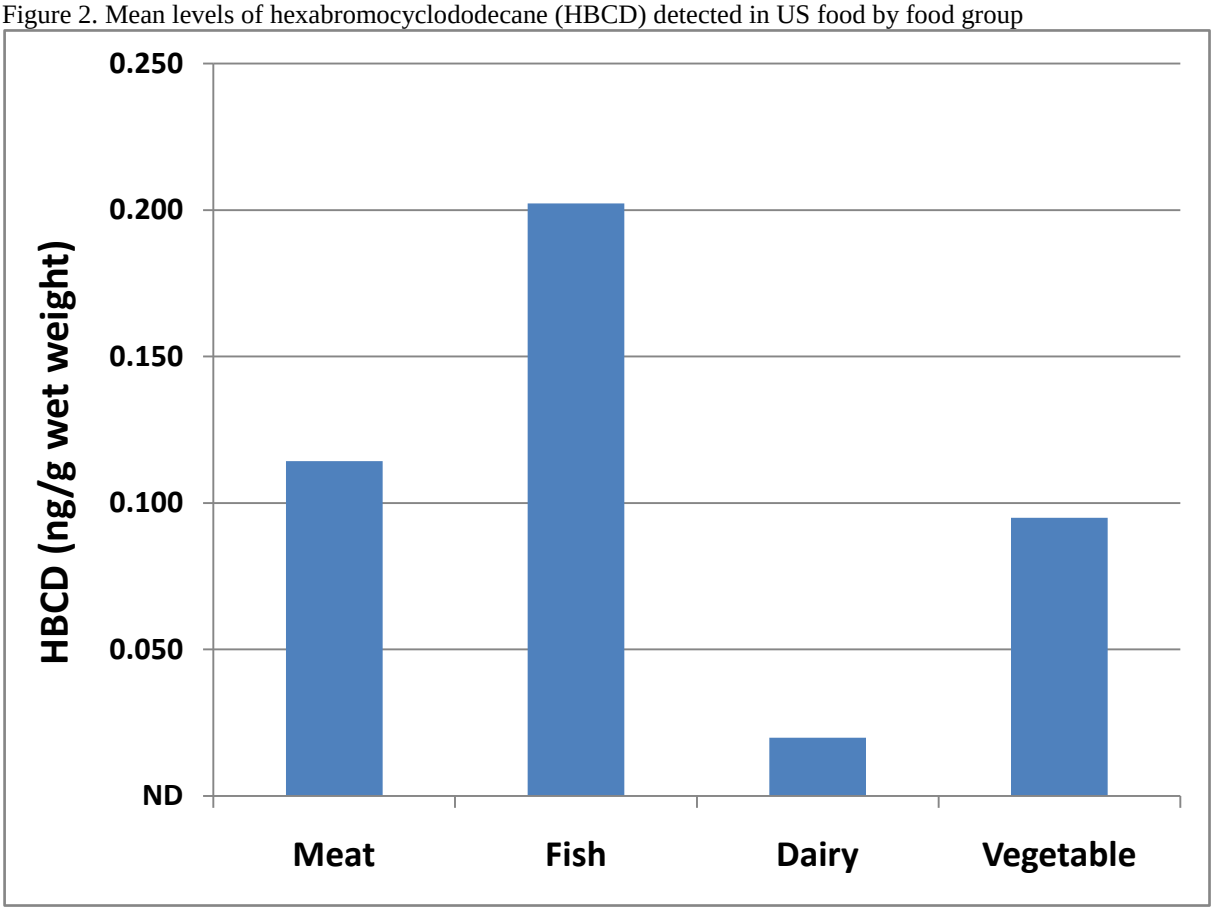
Total PBDE levels detected in food by food type are shown in Figure 1. In this study, the highest mean total PBDE levels were detected in fish, followed by dairy, meat, and vegetable based foods. In fish and meat, tetra and pentabrominated congeners comprised the bulk of the total. In dairy based foods, on average, nonabrominated congeners also made up a large portion of the total, driven by the elevated levels detected in butter. High detection limits for the nonabrominated congeners in olive oil, canola oil, peanut butter, and margarine skewed the contribution of nonabrominated BDEs to the total PBDEs in the vegetable based food samples.

HBCD was detected in 14 of 29 food samples tested (at the time of writing, results were not yet available for two samples, ground beef and cereal). The highest levels were detected in canned sardines (0.593 ng/g ww), salmon (0.352 ng/g ww) peanut butter (0.295 ng/g ww), bacon (0.192 ng/g ww), roast beef (0.188 ng/g ww), and tilapia (0.180 ng/g ww). The only dairy based food that had detectable levels of HBCD was cream cheese, 0.057 ng/g ww. When comparing mean HBCD levels by food group, as shown in Figure 2, fish had the highest detected levels, followed by meat, vegetable based foods, then dairy foods.

Perfluorinated Compounds

While the composite food samples were analyzed for twelve separate PFCs, the only detectable PFC in any of the samples was PFOA. PFOA was detected in 12 out of 21 samples (at the time of writing, data for ground beef, bacon, butter, whole milk, yogurt, margarine, cereal, eggs, apples, and peanut butter was not available). The highest levels of PFOA were detected in olive oil (1.8 ng/g ww), catfish (0.30 ng/g ww), salmon (0.23 ng/g ww), and fish sticks (0.21 ng/g ww). When comparing the mean levels of PFOA across different food groups, the highest levels were detected in vegetable based foods, then fish, meat and dairy foods.

Figure 2. Mean levels of hexabromocyclododecane (HBCD) detected in US food by food group



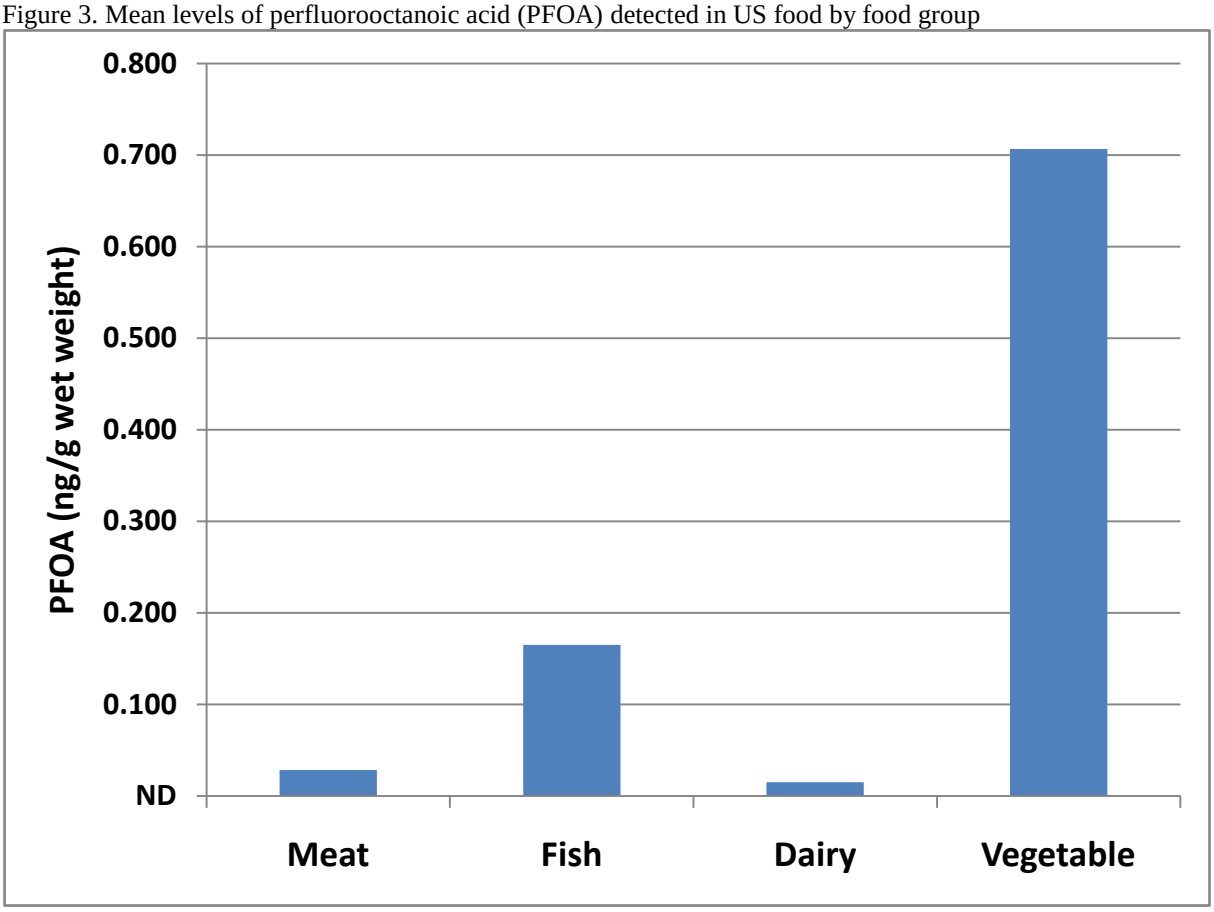
Organochlorine Pesticides

Organochlorine pesticides were detected in 25 of the 31 composite food samples tested (non-detectables included turkey, ham, chicken breast, canola oil, cereal, and potatoes). Of note were elevated levels of the persistent DDT metabolite p,p'-DDE in catfish (9.0 ng/g ww), cream cheese (5.7 ng/g ww), butter (5.1 ng/g ww), American cheese (4.8 ng/g ww) and salmon (3.5 ng/g ww). Salmon was contaminated with detectable levels of 27 of the 33 organochlorine pesticide compounds tested, including the highest levels of the insecticide toxaphene (total of 1.61 ng/g ww for the sum of toxaphenes 26, 50, and 62), which has been banned for over two decades in the US. Peanut butter was found to be contaminated with 18 of the 33 organochlorine pesticides tested, including α-HCH (0.2 ng/g ww), β-HCH (0.42 ng/g ww), γ-HCH (0.34 ng/g ww), δ-HCH (0.25 ng/g ww), dieldrin (0.93 ng/g ww), eldrin (0.82 ng/g ww), and hexachlorobenzene (0.73 ng/g ww). Apples were found to be contaminated with the insecticide endosulfan, including α-endosulfan (0.39 ng/g ww), β-endosulfan (0.57 ng/g ww), and endosulfan sulfate (1.3 ng/g ww).

Polychlorinated Biphenyls

The 7 non-dioxin-like marker PCBs were found above the limit of detection, which ranged from 0.02 to 2 ng/g, in 5 of the 31 composite food samples tested (ground beef, salmon, canned sardines, peanut butter, and ice cream). The highest total PCB levels were found in canned sardines (6.1 ng/g ww) and salmon (3.9 ng/g).

Figure 3. Mean levels of perfluorooctanoic acid (PFOA) detected in US food by food group



Discussion

This study of composite samples of 31 commonly consumed food types extends our previous work examining the levels of POPs in US foodstuffs. Our previous studies have established that there is a large amount of variability in the levels of POPs, particularly PBDEs, between different samples of the same food type. Here, we combined ten samples of the same food type, collected from five different grocery stores on two separate occasions in an attempt to determine what the average or mean levels of various POPs are in US food. Our most recent previous study of PBDEs in US food collected from three locations found the highest levels in meat, while this study found the highest levels in fish, which we had previously observed in our earlier market basket surveys. Also of interest were the elevated PFOA levels detected in food, rather than PFOS which is usually found in higher amounts in biologic samples. In this study, a wide variety of chemical contaminants, including PBDEs, HBCD, PFOA, pesticides, and PCBs were found in the food samples collected, often in the same samples. Results from this study suggest the need for increased monitoring and regulation of the US food supply, particularly when compounds that have been banned for decades, including PCBs and toxaphene, are still being found in appreciable quantities in US food.

Disclaimer: This abstract does not reflect NIEHS/NIH policy.

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