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Cooking fish is not effective in reducing exposure to perfluoroalkyl and polyfluoroalkyl substances

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ABSTRACT

Consumption of fish is considered a part of a healthy diet; however, health risks from fish consumption exist due to potential exposure to various contaminants accumulated in fish. Cooking fish can reduce exposure to many organic chemicals in fish. Similar results have been presented for low levels of perfluoroalkyl and polyfluoroalkyl substances (PFASs), a class of contaminants of emerging concern, in grocery store fish. We examined the effectiveness of three cooking methods (i.e., baking, broiling, and frying) on reducing PFAS levels in four sport fish species. Samples of Chinook salmon, common carp, lake trout and walleye were collected from four rivers in Ontario, Canada and skin-off fillets were analyzed for regular groups of PFASs such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), as well as perfluoroalkyl phosphonic acids (PFPAs), perfluoroalkyl phosphinic acids (PFPIAs) and polyfluoroalkyl phosphoric acid diesters (diPAPs), which are PFASs of emerging concern. Perfluorooctane sulfonate (PFOS) was the dominant PFAS detected and the concentrations were more than an order of magnitude higher than those reported for fish from grocery stores in Canada, Spain, and China. Although concentrations of PFOS in fish fillets generally increase after cooking, amounts of PFOS largely remain unchanged. Relatively minor differences in changes in the fish PFAS amounts after cooking depended on fish species and cooking method used. We conclude that cooking sport fish is generally not an effective approach to reduce dietary exposure to PFASs, especially PFOS.

1. Introduction

Fish consumption has been regarded as beneficial to human health due to the high-quality protein, minerals, antioxidants, vitamins and omega-3 polyunsaturated fatty acids (PUFAs) in fish (Domingo, 2007). Health benefits of fish consumption include optimal brain and retinal development and reduced risk of coronary heart disease (Egeland and Middaugh, 1997). Several health agencies such as the World Health Organization (WHO, 2002) and Health Canada (Health Canada, 2007a) recommend at least two servings of fish per week. While enjoying health benefits of fish consumption, humans are also subject to potential health risks from exposure to various contaminants accumulated in fish (Mozaffarian and Rimm, 2006). In order to minimize such health risks, various government agencies determine safe amounts of fish that can be consumed, and as necessary, issue fish consumption advisories (Bhavsar et al., 2011; Health Canada, 2007b; OMOE, 2011; U.S. EPA, 2010).

It has been demonstrated that cooking and removal of skin can reduce the concentrations of some organic contaminants, such as dioxins and polychlorinated biphenyls (PCBs) (Hori et al., 2005; Sherer and Price, 1993; Zhang et al., 2013). However, such practices have minimal impact on fish concentrations of some other contaminants, such as heavy metals. In fact, some studies have reported increases in concentrations of heavy metals after skin removal or cooking (Morgan et al., 1997; Perelló et al., 2008). The extent to which the concentration of a contaminant may be altered by cooking processes depends upon the type of tissue in which it accumulates. Neutral organic contaminants generally have a higher affinity for the fatty tissues of fish (Bertelsen et al., 1998), and loss of fat via skin removal or cooking is a major contributor to reducing concentrations of these contaminants (Bayen et al., 2005; Wilson et al., 1998). In contrast, heavy metals generally bind with tissue proteins (Hamza-Chaffai et al., 1995) and are less affected by fish processing methods.

Similar to heavy metals, binding to proteins is also considered to be the bioaccumulation mechanism for the ionizable perfluorinated compounds, a group of organic compounds with unique surface properties and low water and oil solubility (Conder et al., 2008; Haukas et al.,

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2007; Jones et al., 2003; Kelly et al., 2009). Historically, they have been used in diverse applications including surfactants and in aqueous film forming foam fire fighting agents (AFFF). The strong carbon-fluorine bonds of PFASs make them less susceptible to degradation and highly persistent in the environment (Lindstrom et al., 2011). The persistence makes it possible for PFASs to undergo long range transport to remote regions where no PFASs have been produced or used (Houde et al., 2011; Wania, 2007). Further, PFASs have been found in organisms at various trophic levels (Houde et al., 2011), and are considered endocrine disruptive, immunotoxic and tumorgenic in laboratory animals at relatively high doses (Betts, 2007). Because of their persistent nature, long range transport capability, bioaccumulation potential and toxicity, a group of PFASs including perfluorooctanesulfonic acid (also known as perfluorooctane sulfonate or PFOS), its salts and perfluorooctane sulfonyl fluoride were listed in Annex B of the United Nations Stockholm Convention on Persistent Organic Pollutants list in 2009 (UNEP, 2009).

In the past decade, increasing surveillance data of PFAS concentrations in fish have become available worldwide. In some parts of North America, surveillance of sport fish for PFASs has resulted in the issuance of restrictive fish consumption advisories (Delinsky et al., 2010; OMOE, 2011). However, in contrast to neutral organic contaminants such as PCBs and dioxins, little information on the effects of different cooking methods on PFAS levels in fish is available. A recent comparison of PFAS concentrations in raw fish with the corresponding cooked fish by Del Gobbo et al. (2008) showed a decline in PFAS concentrations after cooking. These findings are, however, in contrast to the unchanged or even increased concentrations of heavy metals in fish after cooking even though both PFASs and heavy metals bind to protein. Since the fish samples utilized by Del Gobbo et al. (2008) were obtained from grocery stores and the PFAS concentrations were relatively low (e.g., PFOS ranging 0.21–1.68 ng/g ww) compared to those for sport fish, it is possible that analytical uncertainty might have contributed to the proposed decline in the concentrations after the cooking. Therefore, more data on how different cooking methods affect PFAS concentrations in fish are needed to refine exposure assessments and ensuing fish consumption advice.

The goal of this study is to gather information on the effectiveness of three cooking methods (i.e., baking, broiling, and frying) to reduce PFC levels in four fish species sampled from rivers in Ontario, Canada, rather than from a grocery store. We considered Chinook salmon (*Oncorhynchus tshawytscha*), common carp (*Cyprinus carpio*), lake trout (*Salvelinus namaycush*) and walleye (*Sander vitreus*). In addition to perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), we also examined perfluoroalkyl phosphonic acids (PFPAs), perfluoroalkyl phosphinic acids (PFPIAs) and polyfluoroalkyl phosphoric acid diesters (diPAPs), which are PFASs of emerging concern. PFPAs and PFPIAs have been used as wetting and foam-dampening agents, while diPAPs have been used in food-contact paper products (Begley et al., 2005; Dupont, 2012; Mason Chemical Co., 2012). However, to date no submission has been made to the Food Directorate of Health Canada requesting the use of diPAPs in food packaging materials sold in Canada (Rulibikiye, Health Canada, personal communication).

2. Methods

2.1. Sample collection and preparation

Fish samples were collected in summer/fall of 2010/11 from four rivers in Ontario, Canada: Credit River (Chinook salmon, N = 5, 58–91 cm), Thames River (common carp, N = 5, 66–76 cm), Niagara River (lake trout, N = 4, 58–79 cm), and Welland River (walleye, N = 5, 46–62 cm). Relatively elevated concentrations of PFASs in fish from these locations were expected based on nearby industrial activities or previous monitoring work conducted by the Ontario Ministry of Environment (OMOE). The samples were measured for total length and weight, sexed and filleted (both sides, skin-off) in the field. The fillets were stored on ice and transported to the Ontario Ministry of the Environment's Sport Fish Contaminant Monitoring Program office in Toronto, Ontario, Canada where they were stored at −20 °C until further processing. The two fillets from each fish were partially thawed and segmented into 16 parts and classified into four groups (raw plus three cooking methods) as shown in the Supporting Information (SI) Fig. S1 in order to minimize influence of potentially varying PFAS levels in different parts of the fillets on the study results. Four subsamples from each fish were stored at −20 °C until further processing. Fillet samples for three cooking methods were then stored on ice and transported to the Health Canada laboratory in Ottawa, Ontario, Canada where they were stored at −20 °C until cooked. Raw and cooked fillets were later homogenized at the Toronto laboratory using a Buchi B-400 Mixer and stored again at −20 °C until chemical analysis.

2.2. Cooking details

Frozen fish fillets were allowed to warm to room temperature. The weights of large aluminum weighing dishes were measured, then 10 g canola oil was added to each dish and evenly distributed over the bottom of the dish using a silicone brush. We chose canola oil because it is typically used for cooking in Canada where the experiments were performed, and is the third most consumed vegetable oil in the world (Canola Council of Canada, 2013). The weight of the dish with the oil was measured and recorded. Each fish sample was then placed in its labeled weighing dish. The total weight (dish + oil + fish) was also measured.

2.2.1. Frying

An electric frying pan was set to 175 °C and given 10 min to reach test temperature. The aluminum dishes were placed in the frying pan and cooked uncovered. After 5 min, the fish fillets were carefully flipped with a plastic spatula and cooked for an additional 5 min.

2.2.2. Baking

A small toaster oven was preheated to 200 °C (measured using an oven thermometer). The aluminum dishes were placed in the oven and cooked uncovered for 15 min.

2.2.3. Broiling

The toaster oven was set to broil. The broiling temperature (measured using an oven thermometer) was set at 300 °C. The aluminum dishes were placed in the oven and cooked uncovered for 10 min.

2.2.4. Post-cooking

The samples were removed from heat and the internal temperature of the fish was immediately measured with a digital probe. The fish were allowed to cool before the total weight (dish + oil + fish) was measured. The fish was removed from its weighing dish, wrapped in aluminum foil, replaced in its original labeled bag and frozen to −20 °C for later analysis. The final weight of the dish with cooking juices and leftover canola oil was also measured. The weights of the cooking juices generated were calculated by subtracting pre-cooking weight of dish with oil from the final weight of the dish with juices and oil. Cooking juices and leftover canola oil were transferred to a polypropylene sample bottle and frozen for later analysis.

2.2.5. Blanks

Canola oil (10 g) was added to an unused aluminum weighing dish and evenly distributed over the bottom of the dish using a silicone brush. The dish was then baked at 200 °C for 15 min. The dish was allowed to cool, then the oil was transferred to a polypropylene sample bottle.