Endocrine disruptors in fish: Incidence of perfluoroalkyl substances in marine and lake species and their impact on food safety

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INTRODUCTION

Perfluoroalkyl substances (PFASs) are fluorinated compounds with high chemical, biological and thermal inertness, used for a wide range of industrial and chemical products. PFASs are included among the contaminants of emerging concern (CECs), which are able to bioaccumulate and to bio-magnify in higher trophic levels of a food chain, and are recognised as endocrine disruptors (EDs). The primary source of PFAS exposure is diet, and mainly fish. PFAS contamination levels in fish vary according to geographical area, trophic level, age and fish species. In addition, with the application of modern omics techniques, the toxicological potential of short-chain PFASs is also being progressively explored and, consequently, greater focus on the presence of these substances and the discovery of new compounds should be encouraged. The aim of this study was to investigate the presence of PFASs in the most consumed farmed sea fish (sea bass and sea bream) of the Mediterranean Sea in comparison with common lake fish from the major lakes of Northern Italy. Lastly, the investigation culminated in a risk assessment to verify compliance with the TWI according to the recent EFSA note.

METHODOLOGY

Overall, 176 samples were collected to evaluate the incidence of PFASs. In particular, sixty-eight sea fish divided into thirty-four sea basses (Dicentrarchus labrax) and thirty-four sea breams (Sparus aurata) from Italy, Croatia, Greece, and Turkey and lake fish including thirty-four whitefishes (C. lavaretus), thirty-six perches (Perca fluviatilis) and thirty-eight Mediterranean shads (Alosa agone) were collected from the major and representative lakes of Northern Italy (Lake Maggiore, Lake Garda, Lake Lecco and Lake Iseo).

Five grams of homogenised sample were weighed into a 50-mL polypropylene falcon tube and spiked with internal standards to have a concentration of 5 ng g-1 in matrix. Then, 10 mL of acetonitrile were added for PFAS extraction and protein precipitation. The supernatant was purified via STRATA PFAS cartridges. The UPLC-HRMS system consists of a Vanquish system (Thermo Fisher Scientific, Waltham, United States) coupled to a Thermo Q-Exactive Orbitrap™ (Thermo Fisher Scientific, Waltham, United States), equipped with a heated

electrospray ionisation (HESI) source. PFASs were separated via a Raptor 119 ARC-18 column (Restek, Bellefonte, United States).

RESULTS

All the method validation parameters satisfied the requirements indicated in the guidelines SANTE/12682/2019. In particular, the method showed high selectivity and high specificity. The recoveries ranged between 70 and 120 %. Repeatability and precision with CVs were lower than 20 %, in accordance with the tolerances indicated for these validation criteria. Considering PFAS distribution in fish, lake fish showed a slightly higher average concentration, especially for PFOS and for PFBS, the latter of which was not observed in sea bass and sea bream. As regards lake fish, Mediterranean shads (Alosa agone) were the most contaminated species in addition to those from Lake Garda and Lake Lecco. Briefly, Mediterranean shads from Lake Garda showed slightly higher concentrations for PFBA (8.09±7.94 ng g-1) and PFBS (1.12±2.28 ng g-1) than those from Lake Lecco, whereas those from Lake Lecco showed a higher average concentration for PFOS (9.91±6.47 ng g-1). As regards farmed sea fish, the average concentrations for sea basses and sea breams are comparable for PFBA, but different for PFOS, and were detected at higher frequencies and higher concentrations in sea bass, especially those from Turkey.

DISCUSSION

For lake fish, only PFBA was found at trace level (<LOQ). This is in line with the findings of Åkerblom et al. (2017), Junttila et al. (2019) and Mazzoni et al. (2020). As regards sea fish, a comparison with state-of-the-art articles showed that studies by Paiano et al. (2013), Miniero et al. (2014), and Barbosa et al. (2018) that searched PFASs in sea bream and sea bass from Italy found lower amounts of PFAS than those in our study. In relation to risk assessments, the tolerable weekly intake (TWI) of 4.4 ng/kg bw was calculated for the sum of PFOA, PFNA, PFHxS and PFOS (EFSA, 2020). Adopting a conservative approach, the TWIs calculated in consideration of the higher average concentrations obtained for PFOS (9.91 and 0.16 ng g-1 for Mediterranean shads and sea bass, respectively) were 2.80 and 0.04 ng for freshwater fish and sea bass. In both cases, the TWI never exceeded the threshold indicated by the most recent EFSA note. Monitoring the bioaccumulation of PFASs in fish as well as in foods must now be considered crucial from a food safety point of view, as recommended by EFSA, and it is important to assess the quality status of the environment due to the different possible sources of contamination.