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Differential biomagnification of PCB, PBDE, Hg and Radiocesium in the food web of the European hake from the NW Mediterranean

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ABSTRACT

Consumption of marine organisms represents one of the main exposure sources of contaminants for human populations. To obtain a global view of the contamination in commercial fish in the NW Mediterranean Sea, we analysed four types of priority contaminants (PCBs, PBDEs, Hg and ^{137}Cs) in the European hake, *Merluccius merluccius*, from the Gulf of Lions in relation with organism's trophic level (δ^{15}N). All contaminants presented a significant increase in concentration in hake muscle with trophic level. However, obvious differences between contaminants were evidenced. Biomagnification factors (BMF and FWMF) along the hake food web were higher for Hg and CB-153 than for BDE-47 and ^{137}Cs, and increase in contaminant concentration with trophic level occurred at different rates depending on contaminants. Such differences of biomagnification patterns can be related to physico-chemical properties of the different contaminants.

1. Introduction

Contaminants in marine environments are of high concern for both ecological and human health reasons. The consumption of marine organisms represents one of the main sources of persistent organic pollutants (POPs) and certain trace metals (including radionuclides) for human population (Johansen et al., 1996; Pompa et al., 2003). They have become widespread in the aquatic ecosystems mainly through atmospheric and river transport, and accumulate in sediments and biota (Rasmussen et al., 1990; Tolosa et al., 1997). They are susceptible to be transferred into organisms with different efficiencies and biomagnifed differently in food webs. Bioaccumulation and biomagnification of contaminants along trophic webs are complex phenomena ruled by both physico-chemical properties of compounds and ecological and biological factors of organisms (Fisk et al., 2001; Bodiguel et al., 2009). It is thus interesting to compare the fate, transfer processes and biomagnification patterns of various types of chemical contaminants in marine ecosystems.

Polychlorinated biphenyls (PCBs) are synthetic chemicals introduced into the environment since the 1920s and mainly used in electric appliances, heat transfer systems, and hydraulic fluids. Whereas their use in open applications was banned in many countries in the 1970s they were used in transformers up to 1990 (Tolosa et al., 1997; Bodiguel et al., 2009). Polybrominated diphenyl ethers (PBDEs) are a class of additive flame retardants used in electronic, automobiles, textiles, and building materials (de Witt, 2002). Both PCBs and PBDEs persist in the environment for long periods (Boon et al., 2002; Burreau et al., 2004, 2006) and bioaccumulate in the food web (Kidd et al., 1998; Bodiguel et al., 2008). Mercury (Hg) has both natural and anthropogenic origins (Cossa and Coquery, 2005). Hg biomagnifies along food webs and can have severe toxicological effects (Fitzgerald and Clarkson, 1991; Booth and Zeller, 2005). Radiocesium-137 is a man-made radionuclide (fission product, half-life 30.2 years) introduced in the environment by several ways, i.e. by the fallout arising from both atmospheric nuclear bomb testing (1945–1980) and the Chernobyl (1986) and Fukushima (2011) accidents, and releases from the nuclear industry. Although cesium is not an essential element for organisms, it easily enters food webs owing to its chemical similarity with K^+ (Rowan et al., 1998). Generally, PCBs, PBDEs and Hg are known to be highly particle reactive. Cesium isotopes are

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known to have a strong affinity for particles in freshwaters and to be mainly under dissolved form in marine waters due to competition with other cations. However in coastal areas, cesium isotopes have been shown to be good tracers of particle inputs from rivers (Charmasson, 2003). All these contaminants are susceptible to be transferred into organisms, bioaccumulated in organisms, and biomagnified along food webs. Food is the main pathway of contaminants in marine consumers accounting for 85–95% of contaminant uptake. In fish, this has been demonstrated for PCBs and other organic pollutants (Burreau et al., 2004; Elliot et al., 2009), for Hg (Hall et al., 1997; Amlund et al., 2007) and to a lesser extent for radiocesium (Zhao et al., 2001; Mathews and Fisher, 2009). Thus, the knowledge of trophic relationships is essential in understanding contaminant pathways along food webs and biomagnification processes. The most common way to define the trophic level of an organism is to determine its stable nitrogen isotope signature ($\delta^{15}N$) (Cabana and Rasmussen, 1994), as the ratio $^{15}N/^{14}N$ increases generally by 2–5‰ (mean = 3.4‰) from one trophic level to the next one (Vander Zanden and Rasmussen, 2001).

In the Western Mediterranean, the Gulf of Lions is greatly exposed to large contaminant discharges from the highly urbanised and industrialised watershed of the Rhone River (Radakovitch et al., 2008). Understanding the prevalence of contaminants in the Gulf of Lions is of particular interest as this highly productive area provides 90% of French Mediterranean fisheries, the European hake (*Merluccius merluccius* Linnaeus, 1758) being the most important commercial fish species in the demersal landings (Aldebert et al., 1993).

In the present study, four types of contaminants were taken into consideration (PCBs, PBDEs, Hg and ^{137}Cs). PCBs are composed of 209 congeners that differ in chlorination level, physico-chemical properties and toxicity (Paterson et al., 2006). CB-153 is the prevalent congener found in the European hake (Bodiguel et al., 2009) as well as in other fish species (Gerstenberger and Dellinger, 2002; Paterson et al., 2006; Matsuo et al., 2009). Thus, bioaccumulation and biomagnification of PCBs in the present paper were based on CB-153 concentrations, as the best illustration of PCBs contamination. Similar to PCBs, PBDEs present 209 congeners, based on the halogenation of the phenyl rings (Kelly et al., 2008). Amongst these congeners, BDE-47 is dominant in marine food webs (Burreau et al., 2006; Kelly et al., 2008; Mizukawa et al., 2009) and prevails in hake in the Gulf of Lions (Bodiguel et al., 2008). It was then chosen here to illustrate PBDEs contamination in the European hake trophic web. Contamination profiles of PCBs and PBDEs congeners in different tissues of the European hake are given in previous studies (Bodiguel et al., 2008, 2009), along with water and lipid percentages. As the present study focussed on the comparison amongst four contaminant types, only the dominant and most representative congeners, CB-153 and BDE-47, were taken into consideration here for these two types of POPs. Mercury is found as different chemical forms in the environment and in organisms (Morel et al., 1998), and concentrations in Hg_T were determined in the present study. In the Gulf of Lions, the presence of nuclear fuel reprocessing plant on the Rhone River till 1997 has generated long-term monitoring studies of man-made radionuclide concentrations in marine coastal organisms (Charmasson et al., 1999). ^{137}Cs was selected as a witness of anthropogenic radionuclide contamination in the hake food web in this area.

The main aims of the present study were to (1) determine the concentrations of PCBs, PBDEs, Hg and ^{137}Cs in the different size classes and sex of hake in the Gulf of Lions, (2) compare their bioaccumulation patterns in hake muscle, and (3) compare their biomagnification factors along the hake food web. This study allowed determining if the different contaminant classes behave similarly or not in the same fish species and the same food web.

2. Materials and methods

2.1. Sample collection

Sampling was conducted in the Gulf of Lions (NW Mediterranean, 42°15′-43°35′ N, 3°00′-6°00′ E) from 2004 to 2006 by trawling on the continental shelf between 20 m and 150 m, and with gill nets on the continental slope down to 600 m deep. Total length (TL cm), mass (g) and sex of individuals were recorded for hake, and digestive tract removed and fixed in 5% buffered formalin for diet analysis. Hake fish prey were also collected and measured. Samples of dorsal white muscle of hake and fish prey were collected for stable isotope and contaminant analyses, and kept frozen at −20 °C in appropriate vials before analyses. Phytoplankton, zooplankton and suprabenthic crustaceans were collected with different appropriate gears detailed in Sorbe (1999) and Harmelin-Vivien et al. (2008), and kept frozen at −20 °C before analyses.

2.2. Laboratory analyses

The method used for PCBs and PBDEs analysis and validation of the analytical method were described in Loizeau et al. (2001) and Bodiguel et al. (2008). Between 100 mg and 5 g dry weight (dw) of biological tissues were extracted with dichloromethane using a pressurised solvent extraction (ASE, Dionex Corp., CA) for the analysis of PBDEs and PCBs, or with hexane/acetone mixture (80:20) using SOXTEC, for only PCB analysis. The samples were spiked with recovery standards (BDE139, CB30, CB198 and CB209). The removal of co-extracted lipids was performed by gel permeation chromatography (GPC) on a laboratory prepared column (Bio Beads SX-3 200–400 Mesh, 460 mm × 26 mm column). The extracts were further purified and fractionated on a two layer silica/alumina column (H_2O 5% deactivated silica gel and alumina) using hexane and hexane/dichloromethane (9:1) as an eluent. The extracts were finally treated with sulphuric acid to further remove remaining lipids. PBDEs were analysed by GC/MS in electron capture negative ionisation mode (ECNI) using methane as the reagent gas. The column was a DB-1, 15 m × 248 μm i.d. × 0.10 μm film thickness (J&W Scientific), fitted with a 1–2 m deactivated non-polar retention gap column. The ionisation voltage was about 170 eV, set to the optimum by tuning. Spectra were recorded using selected ion monitoring at *m*/*z* 79, 81 and 161. The quantification was carried out using eight-level calibration curves in the 2–200 pg range. Polychlorinated biphenyls CBs were analysed by high resolution gas chromatography fitted with two electron capture detectors (ECD), using two columns of different polarities: a DB-5 (5% phenyl-methylpolysiloxane) column of 60 m × 0.25 mm (film thickness 0.25 μm), and a HT8 (8% phenyl–polysiloxane–carborane) column of 50 m × 0.25 mm (film thickness 0.25 μm). Hydrogen was the carrier gas at a linear velocity of 27.6 cm s^{-1}. Concentrations were calculated by external multi level calibration regression in the linear range of the response of the detector. Concentrations of CB-153 and BDE-47 were expressed in μg kg^{-1} dry weight (dw) for allowing comparison with other contaminants analysed, and were not lipid-normalised contrary to what is commonly done for PCBs and PBDEs (Paterson et al., 2006; Matsuo et al., 2009; Mizukawa et al., 2009). Quality assurance and quality control for PCB and PBDE analyses are described in details in Bodiguel et al. (2008, 2009). Standard deviations of measures were less than 10% for all congeners which testified to the good reproducibility of the method. The recoveries of internal standards varied between 74% and 97% for PCB congeners, and reached 97% for BDE-139. Concentrations were not corrected for recoveries of internal standards. During analysis of the real samples, analytical blanks were systematically measured for every 10 samples. The blank concentrations were always less than the concentrations of the