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Marine Pollution Bulletin
May 2012, Volume 64, Issue 5, Pages 974–983
http://dx.doi.org/10.1016/j.marpolbul.2012.02.014
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Archimer
http://archimer.ifremer.fr

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.

Highlights

► All contaminant concentrations increase with trophic level. ► Increase is exponential for Hg, power for PCBs and PBDEs, linear for ^{137}Cs. ► Biomagnification is high for Hg, medium for PCBs and PBDEs, low for Cs.

Keywords: Persistent organic pollutants ; Mercury ; ^{137}Cs ; *Merluccius merluccius* ; Mediterranean

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; Bureau 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 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). Among 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 among 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 100mg and 5g 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, 460mm x 26mm column). The extracts were further purified and fractionated on a two layer silica/alumina column (H2O 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, 15m × 248µm i.d. × 0.10µm film thickness (J&W Scientific), fitted with a 1-2m deactivated non-polar retention gap column. The ionisation voltage was about 170eV, 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 2-200pg 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 60m x 0.25mm (film thickness 0.25µm), and a HT8 (8% phenyl-polysiloxane-carborane) column of 50m x 0.25mm (film thickness 0.25µm). Hydrogen was the carrier gas at a linear velocity of 27.6cm.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-normalized 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 ten samples. The blank concentrations were always less than the concentrations of the lowest standards of all congeners. Finally, 5 replicates of a reference material, BCR-CRM349 (Cod Liver Oil) were analyzed to determine the accuracy and precision of the method. PCB recoveries varied between 74% and 125%. Furthermore, the RSD values ranged from 4% to 19%, with a mean of 10% for all PCBs. All of these results were in agreement with certified reference values. The laboratory regularly takes part in Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME) intercomparison exercises for PCBs in biota and our Z-scores are satisfactory, i.e. between −2 and +2.

Measurement of Hg_T was performed following the protocol described by Cossa et al. (2009). Measurements of Hg_T in fish tissue were performed using the automated atomic absorption spectrophotometer by Altec (Model AMA-254). The HgT determination procedure consists of the following automatic sequences: (1) an ashing (550°C) of the freeze dried sample allowing the elemental mercury volatilisation from the sample, (2) the evolved elemental mercury amalgamation on a gold trap, (3) an atomic absorption spectrophotometric measurement of the Hg collected following the

heating of the gold trap (800°C). With a 20 mg sample the detection limit and the reproducibility were 0.007 µg.g^{-1} and 7 % respectively. The accuracy of the technique was assessed every ten samples using various certified reference materials (CRM) from the National Research Council of Canada. These CRM were fish muscle tissues (DORM-1 and DORM-2) chosen according to the Hg concentration level of the samples analysed. Mercury concentration was expressed as Hg_T dry weight concentration in fish muscle or whole plankton samples (mg.kg^{-1} dw).
Quantification of ^{137}Cs concentration was determined by gamma spectrometry as described in Charmasson et al. (1999). Approximately 3 kg of hake muscle or whole fish prey were processed for ^{137}Cs quantification, dried at 60 °C to constant weight. Depending on the quantity of recovered dried material, samples were ashed at 480 °C for 12h. Ashed or dried samples were then ground, homogenised and packed into 20 cm^3 or 60 cm^3 containers prior to undergoing gamma spectrometric analysis. Gamma spectrometry was performed for 24-48 h using N-type hyper pure germanium detector with a beryllium window 0.5 mm thick. Detectors were located underground under a 3-m thick boron concrete slab, in a room shielded with 10 cm thick lead bricks with a low background activity, lined with 5 mm electrolytic thick electrolytic copper tiles neutralizing lead X-rays. Activities expressed as Bq.kg^{-1} dw were decay corrected to the date of sample collection.
To evaluate the trophic position of individuals, stable nitrogen isotope ratio (δ^{15}N) was analysed on dorsal white muscle of hake and fish prey, or on whole plankton samples following the procedures described in Ferraton et al. (2007) and Harmelin-Vivien et al. (2008). Freeze-dried samples were ground into a fine powder using a mortar and pestle and 1 mg in tin capsule was analyzed. ^{15}N/^{14}N ratios were determined by continuous-flow isotope-ratio mass spectrometry. The spectrometer was a Europa Scientific ANCA-NT 20-20 Stable Isotope Analyser with ANCA-NT Solid/Liquid Preparation Module, with an analytical precision (SD, n=5) of 0.2 ‰ estimated from standards analysed along with the samples. Internal working standards were 1 mg leucine prepared by freeze drying 50 µl of a 20 mg mL^{-1} stock solution into tin capsules, and calibrated against IAEA standards N1 and N2. Delta notation was used as following: δX (‰) = [(R_{sample} / $R_{standard}$)-1] x 10^3, where X is ^{15}N, and R the ratio ^{15}N/^{14}N. δ^{15}N was expressed as per mil (‰) compared to the atmospheric N_2 as standard reference material.

2.3. Data analysis

Quantification of contaminant concentrations in hake diet: Hake diet has been previously studied in the Gulf of Lions (Bozzano et al., 1997; Ferraton et al., 2007). Juvenile hake prey mainly on small crustaceans, while adults shift progressively to a larger proportion of fish, consuming essentially pelagic fishes (anchovy, sardine and blue whiting). Based on diet analysis, six size classes in hake were defined for the present study (Table 1). The importance in weight (% dry weight) of each prey type was determined for each size class. The contaminant concentration of the diet of each hake size class was quantified with the equation:

$$C_{diet(i)} = \sum[C_{prey(x)} \times W_{prey(x)(i)}]$$

where $C_{diet(i)}$ is the contaminant concentration in the diet of the hake size class (i), $C_{prey(x)}$ is the contaminant concentration of the prey (x), $W_{prey(x)(i)}$ is the percentage in weight of the prey (x) in the (i)th hake size class, and $\sum$ the sum of the product for all the (x) prey types.
In a similar way, the δ^{15}N of the diet of each size class was determined:

$$\delta^{15}N_{diet(i)} = \sum[\delta^{15}N_{prey(x)} \times W_{prey(x)(i)}]$$

where $\delta^{15}N_{diet(i)}$ is the $\delta^{15}N$ of the diet of the hake size class (i), $\delta^{15}N_{prey(x)}$ is the $\delta^{15}N$ of the prey (x), $W_{prey(x)(i)}$ is the percentage in weight of the prey (x) in the (i)th hake size class, and $\sum$ the sum of the product for all the (x) prey types.

Food web and biomagnification factor calculations: To compare our results with those found in the literature, two types of trophic transfer terms were calculated following Fisk et al. (2001). The first method determined the biomagnification factor (BMF) for the different size classes of hake based on the contaminant concentrations and trophic level of hake and diet in each size class, using the following equation:

$$BMF_{hake(i)} = [(C_{hake(i)}/C_{diet(i)})/(\delta^{15}N_{hake(i)}/ \delta^{15}N_{diet(i)})]$$

Where $C_{hake(i)}$ is the concentration of contaminant in the hake size-class (i), $C_{diet(i)}$ is the concentration of contaminant in the diet of the (i) size class, $\delta^{15}N_{hake(i)}$ is the trophic level of hake in the (i) size class, and $\delta^{15}N_{diet(i)}$ is the trophic level of the diet of the (i) size class. This factor is based on the assumption that contaminant concentrations in a predator depend on those of its prey, corrected for trophic level difference between predator and prey. A mean BMF factor for hake in the Gulf of Lions was calculated as the mean of the different $BMF_{hake(i)}$ values calculated for size classes.

The second method determined the food web magnification factor (FWMF) for the entire food web based on the relationships between Napierian logarithms of contaminant concentrations and trophic level of all food web components, using the following linear regression:

$$\ln_{contaminant} = a + b \times \delta^{15}N$$

The slope of the regression of $\ln_{contaminant}$ against $\delta^{15}N$ (b) is the biomagnification power of the contaminant and represents the change in concentration per unit change in $\delta^{15}N$ over the entire food chain, and (a) is a constant dependent on the background concentration (Nfon et al., 2008). The slope *b* of this equation was used to calculate FWMF for hake using the equation:

$$FWMF_{hake} = e^{b}$$

We replace trophic level (TL) used by Fisk et al. (2001) by $\delta^{15}N$ values as a more accurate estimation of organism trophic position. Thus, all biomagnification factor calculations and linear regressions were done using $\delta^{15}N$ values. Contaminants with FWMF greater than 1 were considered to biomagnify in the food chain.

Statistical analysis: Relationships between contaminant content and fish size, age and $\delta^{15}N$ were tested on ln transformed contaminant concentration values to linearise the regression and stabilise the variances. Due to the relatively low number of size classes, linear regressions of contaminant concentrations with size, age and $\delta^{15}N$ values were performed independently. Differences in slopes and elevations were tested by appropriate *t*-test. Differences in contaminant concentrations between sexes were also tested by *t*-test.

3. Results

3.1. Bioaccumulation of contaminants in hake muscle with size and sex

Concentrations of contaminants in hake muscle were determined in the six size classes (Table 1). Concentrations of Hg_T and ^{137}Cs increased from the smallest to the largest size classes. The best fits followed an exponential function for Hg_T ($y = 0.067e^{0.687x}$, $R^2 = 0.98$, $p<0.001$) and a linear function for ^{137}Cs ($y = 0.107x + 0.335$, $R^2 = 0.95$, $p<0.001$). Organic contaminants exhibited also a trend to increased concentrations with fish size (Table1). Fish larger than 25 cm presented high average concentrations of CB-153, but the high standard deviation reflected a large individual variability in these size classes (CV> 50%). In the case of BDE-47, fish larger than 50 cm had lower levels than the preceding lower class. On an average CB-153 concentrations in hake muscle were about 30 times higher than those of BDE-47. Correlations between ln contaminant concentration and mean size, mean age and mean $\delta^{15}N$ of hake were tested statistically by linear regressions (Table 2). The best fit for the relationship between contaminant concentrations and fish size was found with $\delta^{15}N$, a proxy of the mean trophic level of each size class. Concentrations increased significantly with hake $\delta^{15}N$ for all contaminants, BDE-47 excepted, for which the regression was near significant level ($p = 0.069$). Slopes (b) of linear regressions between ln concentrations and $\delta^{15}N$ significantly differed among contaminants (*t*-test, $p<0.01$), the highest slope being recorded for Hg_T ($b = 0.717$) and the lowest for radiocesium ($b = 0.159$) (Fig. 1). The slopes calculated for CB-153 ($b = 0.308$) and BDE-47 ($b = 0.258$) presented intermediate values and were not statistically different (*t*-test, $p>0.05$), albeit lower intercept was observed for BDE-47 ($a = -2.414$) than for CB-153 ($a = 0.595$) (*t*-test, $p<0.001$). These regressions indicated that bioaccumulation in hake muscle with trophic level was the highest for Hg_T, intermediate and increasing at a similar rate for CB-153 and BDE-47 but with lower values for BDE-47, and the lowest for ^{137}Cs. Mean concentrations between the lowest and the highest values recorded in hake muscle of the different size classes were multiplied by 4.0 for CB-153, 6.2 for BDE-47, 33.8 for Hg_T, and by 2.0 for ^{137}Cs, while the $\delta^{15}N$ increased only by a factor of 1.6 (Table 1). Increases between contaminant concentration and fish size were also recorded for Hg_T, ^{137}Cs and less significantly for CB-153, but not for BDE-47. For all contaminants, concentrations in muscle were generally higher in males than females in each size class, whereas differences were rarely significant due to the high variance of data (Fig. 2). The male-female difference was more conspicuous for ^{137}Cs, and to a lesser extent for Hg_T, compared to CB-153 and BDE-47 for which differences were obscured by high concentration variability.

3.2. Biomagnification factors in hake food web

The analysis of biomagnification in hake food web was made on contaminant concentrations in hake muscle, both sexes combined, to performed comparisons on a standard basis. First, biomagnification factor (BMF) in hake with size was calculated from the difference in contaminant concentration between each hake size class and its diet which varied with size. Small crustaceans dominated in weight in the smallest size class (0-6 cm) (Table 3). Then, hake diet was mainly composed of fish with a high proportion of benthic (gobiids) and demersal (hake, red bandfish, poor cod) species in 7-14 cm sized individuals and the dominance (71-93 %) of pelagic species (anchovy, sardine and blue whiting) in hake larger than 14 cm (Table 3). Concentrations of CB-153, BDE-47, Hg_T and ^{137}Cs in the main hake prey along with their $\delta^{15}N$ values were

indicated in Table 4. Two size classes were analysed for some fish prey, small (<12 cm) and large (>12 cm) individuals, as hake selected its prey by size when growing. Diet trophic level increased as hake $\delta^{15}N$ increased. Concentrations of CB-153 in diet increased with size as for BDE-47 in diet till 25 cm fish size and slightly decreased in diet of larger hake. In contrast, Hg_T concentration in diet did not change whatever the size-dependent hake regime and ^{137}Cs presented low values in the diet of the smallest size class that increased abruptly and remained constant in the larger size classes. The patterns of BMF values according to hake size differed among contaminants (Table 5). BMF of Hg_T increased exponentially in hake with increasing size ($R^2 = 0.99$, $p<0.001$), while BMFs did not vary significantly with hake size for CB-153 ($R^2 = 0.02$, $p>0.05$), BDE-47 ($R^2 = 0.08$, $p>0.05$) and ^{137}Cs ($R^2 = 0.02$, $p>0.05$). These results implied that bioaccumulation processes in hake largely differed depending on contaminants.

Biomagnification factors in hake food web (FWMF) were estimated from the slope of the regression between ln concentration of contaminants in the different components of hake food web and their trophic level estimated by $\delta^{15}N$. The linear regression ln concentration contaminant vs $\delta^{15}N$ were all positive and significant: ln CB-153 = 0. 289* $\delta^{15}N$ + 0.978 ($R^2 = 0.74$, $p<0.001$), ln BDE-47 = 0.200*$\delta^{15}N$ - 1.638 ($R^2 = 0.30$, $p<0.05$), ln Hg_T = 0.516* $\delta^{15}N$ - 5.646 ($R^2 = 0.74$, $p<0.001$), ln 137Cs = 0.192* $\delta^{15}N$ - 2.459 ($R^2 = 0.53$, $p = 0.001$). The slope of the regression was significantly higher for Hg_T than for the other contaminants ($p<0.01$). The slope was significantly higher for CB-153 than for BDE-47 and ^{137}Cs ($p<0.05$), but did not differ between these two last contaminants ($p>0.05$). These differences were reflected on FWMF values, calculated from the slope of the regressions. FWMFs were higher for Hg (1.7) than for CB-153 (1.3), BDE-47 (1.2) and 137Cs (1.2) (Table 6). FWMFs were compared to mean BMFs calculated from hake diet concentrations of contaminants (Table 6). Discrepancies appeared between the two ways of estimation of biomagnification factors. The contrast between contaminants was much higher with BMFs for which a difference of 5.7 was observed between the highest and the lowest values, than FWMFs for which a difference of 0.46 only was observed. BMF values were lower than FWMF values for CB-153 and BDE-47, while they were higher than FWMF values for Hg_T and ^{137}Cs. The most striking difference was observed for Hg_T for which BMF was 3.8 times higher than FWMF. Both BMF and FWMF indicated a higher biomagnification in hake for Hg compared to the other contaminants. Along the hake food web, increase in CB-153 concentration with trophic level followed a power function, Hg_T an exponential function and ^{137}Cs a linear one, whereas increase in BDE-47, while following also a power function, was not significant (Fig. 3).

4. Discussion

With a few exception (Gerstenberger and Dellinger, 2002; Hisamichi et al., 2010), most studies on contaminants in marine or freshwater organisms were performed on a single contaminant compound. In contrast, this study focussed on the comparison of bioaccumulation of four types of contaminants, two organic contaminants (CB-153 and BDE-47), a trace metal (Hg) and a radioactive trace metal (^{137}Cs) in one fish species, the European hake *Merluccius merluccius*.

4.1. Variation of contaminant bioaccumulation in hake

For all contaminants, a significant increase in concentration in muscle with increasing fish trophic level was evidenced that was also age and size-dependent for Hg_T, ^{137}Cs

and CB 153, but not for BDE-47. A significant positive relationship between CB-153 concentration and fish size in hake has been observed previously in the Gulf of Lions (Bodiguel et al., 2009). A positive relationship between size and/or $\delta^{15}N$ and contaminant concentrations is also observed for PCBs and PBDEs in other fish species (Rasmussen et al., 1990; Kidd et al., 1998; Paterson et al., 2006), as for Hg_T (Cabana and Rasmussen, 1994; Magalhães et al., 2007; Senn et al., 2010) and ^{137}Cs (Kasamatsu and Ishikawa, 1997; Iibuchi et al., 2002; Heldal et al., 2003). Burreau et al. (2006) explain the increase in contaminant content with size by a slower clearance in larger fish. Growth is effectively decreasing in larger fish compared to small ones, but larger fish consume generally larger prey than smaller fish, leading to higher contaminant content in their diet. Thus, both phenomena, decrease in growth with age as observed by Mellon-Duval et al. (2009) for hake and increase in contaminant uptake by diet in larger fish (this study), induced an increase in contaminant accumulation with size in the European hake. As diet constitutes the main route for most contaminant uptake (Zao et al., 2001; Amlund et al., 2007; Elliot et al., 2009), contaminant concentration in preys is an essential parameter in understanding bioaccumulation patterns in predators.

Concentrations of the four contaminants studied in hake were generally higher in males than in females of similar size, even if the difference was not always significant. Such a difference is likely linked to the slower growth rate of males that are older than females at the same size (Mellon-Duval et al., 2009), and thus subjected a longer time to contaminants. As no difference in diet and $\delta^{15}N$ between males and females of similar size is observed (Mellon-Duval, unpublished data), difference in contaminant concentration was likely due to differences in age, growth rate and more generally metabolism between sex, and not to difference in contaminant uptake by diet. Bodiguel et al. (2009) observe also a higher concentration of PCBs in males than in females in the European hake, but no difference in PCB congener distribution, and attribute also this difference to the slower growth of hake males and to the depuration of females during spawning, as observed in other fish species (Loizeau et al., 2001). Similar results are found by Burreau et al. (2004) who observe higher PCB and PBDE contents in males than in females in different freshwater fish species in the Baltic Sea. PCBs are known to increase with organism lipid content (Rasmussen et al., 1990; Fisk et al., 2003) and some authors find that PCBs difference in fish with site is related to difference in lipid content and not to difference in bioaccumulation rate (Phillips, 1995). In hake, lipid concentration in muscle decreases with increasing size of the individuals whereas energy is mainly stored in liver, and juveniles present higher lipid content in their muscle than adults (Dominguez-Petit et al., 2010). Thus, the increase in PCBs and PBDEs contents observed in hake muscle with increasing size in the Gulf of Lions could not be related to a difference in fish lipid content, but rather to a higher mechanism of sequestration in larger fish. PCBs are associated mainly with nonpolar-lipids stored as reserves (Antunes et al., 2008). PCBs are then mobilised when reserves are used for an increase in energy demand (reproduction, activity, stress). Bodiguel et al. (2009) demonstrate that a significant part of lipids used in female gonad maturation originate from muscle and not from liver, which explains why PCBs concentration in hake muscle in females decreases after reproduction. On the reverse Hg is linked to polypeptides and proteins (Harris et al., 2003) and bioaccumulates essentially in muscle through increasing complexion with thiol groups (Bloom, 1992; Senn et al., 2010). Bioaccumulation of Hg_T is then particularly high since proteins are also less mobilised than lipids in case of short term increases in energy demand (Black and Love, 1986).

4.2. Biomagnification in hake food web

Comparison of biomagnification factors obtained for the European hake in the Gulf of Lions with values found in the literature is a difficult task. These factors vary with the type, structure and length of the food webs studied (Rasmussen et al., 1990), the methods used in determining contaminant concentrations, and the calculation procedures utilised (Fisk et al., 2001; Kelly et al., 2008). BMF factor is calculated for one species from contaminant concentration of its diet, while FWMF is calculated for a define food web composed of organisms at different trophic levels (Fisk et al., 2001). The slope of the regression of $\delta^{15}N$ against contaminant concentration in the food web, used to calculate FWMF, is also called "biomagnification power" (Bureau et al., 2006; Nfon et al., 2008; Mizukawa et al., 2009). Thus, FWMF and biomagnification power are linked together. The length of the food web studied influences greatly biomagnification factor values. The longest the food web, the highest the biomagnification factor obtained. Fisk et al. (2001) find a higher biomagnification factor (FWMF = 9.7) for CB-153 in a food web including marine mammals and birds in the Arctic than Kidd et al. (1998) who analyse a food web in the same region including only zooplankton and fish (FWMF = 4.4). The location of studies influences also the results, as the bioconcentration of contaminants in the phytoplankton at the base of the food web is linked to both contaminant loads and primary production of waters. A high primary production may induce a biomass dilution phenomenon leading to lower concentrations in organisms in spite of high contaminant concentration in water (Joiris et al., 1995; Harmelin-Vivien et al., 2009); inversely oligotrophy induces higher uptake by phytoplankton (Heimbürger et al., 2010).

For PCBs and PBDE, biomagnification greatly differs between congeners. The choice of analysing CB-153 and BDE-47 in the present study was motivated by their high biomagnification capacity (Kelly et al., 2008; Matsuo et al., 2009). In an Arctic marine food web, Kelly et al. (2008) observe a high degree of biomagnification in most PCB congeners, whereas in PBDEs a slight biomagnification is recorded only for BDE-47. Studying a lower-trophic-level food web in Tokyo Bay, Mizukawa et al. (2009) also find a higher biomagnification in PCBs than PBDEs. However, they observe the biomagnification of four other PBDE congeners in addition to BDE-47. They conclude that differential biotransformation among PBDE and PCB congeners must apply to explain the difference of biomagnification observed among them. In a previous field study Stapleton and Baker (2003) observe similar bioaccumulation of BDE-47 and PCB-153 among zooplankton, alewife, and lake trout, suggesting that these two types of compounds possess similar bioaccumulation potentials in food webs. However, it now seems clear that some species, specifically the common carp, differ in their capacity for assimilating these two types of contaminants (Stapleton et al., 2004). The low net assimilation efficiencies of BDE-28 and BDE-153 (20 and 4%, respectively) and high depuration rates suggest that they have higher biotransformation capacities and/or lower assimilation potential relative to PCBs of similar *K*ows. We observed a biomagnification in BDE-47 along the hake food web (FWMF = 1.2), but lower than for Hg_T (FWMF = 1.7) and CB-153 (FWMF = 1.3). When the biomagnification factor (BMF) was calculated from diet concentrations, BDE-47 did not show any biomagnification as the BMF value was lower than 1 (BMF = 0.7). High biomagnification factors along food webs are recorded for Hg_T and generally linked to the trophic position of organisms (Kainz and Mazumder, 2005; Magalhães et al., 2007). Similar slope (0.2) of the regression $\log_{10}$ Hg vs $\delta^{15}N$ in fish food webs is recorded in the Gulf of Lions (this study) than in other regions (Atwell et al., 1998; Swanson and Kidd, 2010). Whereas low ^{137}Cs concentrations were found in organisms in the Gulf of Lions, there was a marked biomagnification of ^{137}Cs in the hake food web with concentrations being 4.8 times higher in large hake compared to small crustaceans. A similar increase (3.7) was

observed by Heldal et al. (2003) between amphipods and cod in the Norwegian and Barents Seas.

Differences between the two biomagnification factors (BMF and FWMF) were evidenced for the European hake in the Gulf of Lions, but they depended on contaminants. BMF was lower than FWMF for CB-153 and BDE-47 and higher for Hg_T and ^{137}Cs. A discrepancy between the results of these two types of factors is also observed by Fisk et al. (2001). They find also a lower BMF than FWMF value for CB-153 for the Arctic cod (1.2 and 6.7 respectively), but higher BMF than FWMF values for birds and mammals located at higher trophic levels. The FWMF for CB-153 in our pelagic food chain was similar to those obtained for the pelagic marine food chains from the Baltic Sea and greater than those obtained in the benthic marine food chain from the same area (Nfon et al., 2008). Since BMF takes only into account the last trophic level of the food web analysed, while FWMF integrate the entire food web, this means that each type of contaminant has its own incorporation capacity depending on the type of organisms and their trophic position.

4.3. General patterns and specificities in hake contamination

Uptake and bioaccumulation of contaminants in fish is a complex process that may vary according to various biological factors (assimilation efficiency, growth rate, metabolic costs, sex and age), ecological factors (quality and quantity of food, habitat) and environmental factors (inputs loads, concentration in water, primary productivity) that explains the variety of results obtained on different species (Trudel and Rasmussen, 2006; Schwindt et al., 2008). In the present study, some general patterns of contamination in the European hake were evidenced for the four contaminants studied: (1) an increase in concentrations in hake muscle with $\delta^{15}N$ increase, and (2) generally higher concentrations in males than females, whereas the difference was not always significant. Two main factors explained these general patterns (trophic position for the first point and growth for the second one) that are recognised in numerous studies to positively influenced bioaccumulation processes (e.g. Rasmussen et al., 1990; Jarman et al., 1996; Rowan et al., 1998; Trudel and Rasmussen, 2006). However, obvious differences between contaminants were underlined, as different rates of bioaccumulation in hake were observed. The highest rate was recorded for Hg_T, intermediate and similar rates for CB-153 and BDE-47, and the lowest one for ^{137}Cs. Thus, in a same fish species the bioaccumulation of contaminants occurred at different rates according to their physico-chemical properties, the mechanisms of contaminant transfer, and their metabolisation and elimination (Phillips, 1995). Along the hake food web, CB-153 and BDE-47 increased with a power function, Hg_T an exponential function and radiocesium a linear function. In many studies, linear relationships between log PCB *vs* trophic level is given, but not the equation of the non-linearised data that may indicate the real increasing function (Jarman et al., 1996; Kidd et al., 1998; Fisk et al., 2001; Elliot et al., 2009). An exponential increase of Hg_T with $\delta^{15}N$ is also observed by Monteiro et al. (1996) in a marine food web in the Azorean waters, while Magalhães et al. (2007) record exponential model for long-lived but not short-lived fish species. In a tropical marine fish, Zhao et al. (2001) record also a linear pattern of radiocesium uptake over time and Kasamatsu and Ishikawa (1997) find a BMF factor of about 2.0 (1.8-2.2) for top marine fish, which is close to the BMF value of 1.7 found for hake. The exponential and power curves observed for Hg_T and CB-153 concentrations with trophic level respectively suggest that the organisms at the base of the food web, like phyto- and zooplankton, may mediate the transport and cycling of these contaminants in water food webs.

The results obtained on hake food web contamination in the Gulf of Lions pointed out that contaminants behave fundamentally differently from one type to the other in spite of general common patterns of increase with trophic level. These differences are mainly linked to their physico-chemical properties and their bioacumulation and elimination processes, but are modulated by the biology (growth, reproduction, diet) and ecology of the fish species. In a general context of contaminant load increase in coastal waters, understanding the processes of contaminant transfer along food webs according to the different proprieties of contaminants stays a challenging problem, particularly in the Mediterranean Sea where oligotrophy may favour contaminant accumulation at the base of the food chain.

Acknowledgements

Thanks are expressed to the crews of the R.V. 'Europe" and "Téthys" for their collaboration at sea, to Sylvette Crochet, Franck Ferraton, Catherine Munschy, François Roupsard and Hervé Thébault for assistance in sampling and analyses, and to Charlie Scrimgeour (Scottish Crop Research Institute) for stable isotope analyses. This study was financially supported by the French research programmes PNEC-MEDOC, MEDICIS and ECCO-PNBC. This work complies with the current laws of the country (France), in which it was performed. We thank M. Paul for improvement of the English and an anonymous reviewer for helpful comments regarding the manuscript.

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Figures

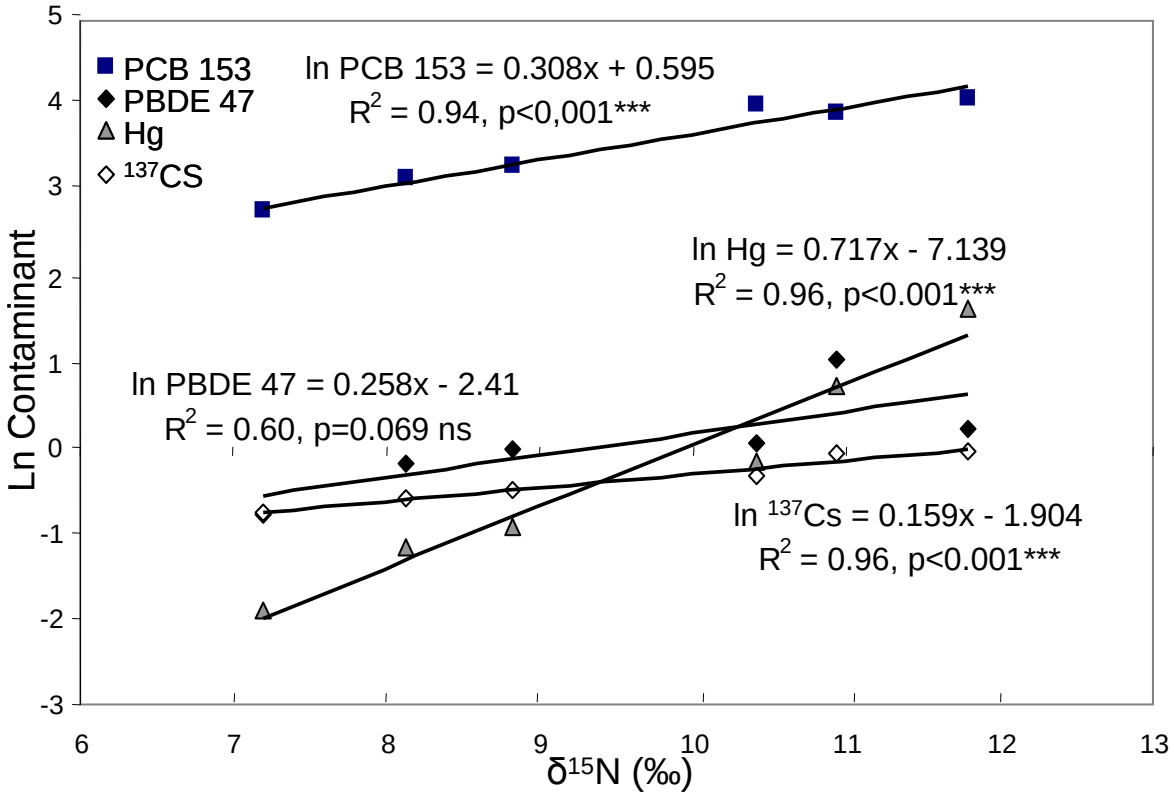

Fig.1. Linear relationships between ln contaminant concentration (dry weight) and $\delta^{15}N$ in hake muscle in the Gulf of Lions for the four types of contaminants analysed. Concentration units: CB-153, µg kg^{-1} dw; BDE-47, µg kg^{-1} dw; Hg, mg kg^{-1} dw; ^{137}Cs, Bq kg^{-1} dw

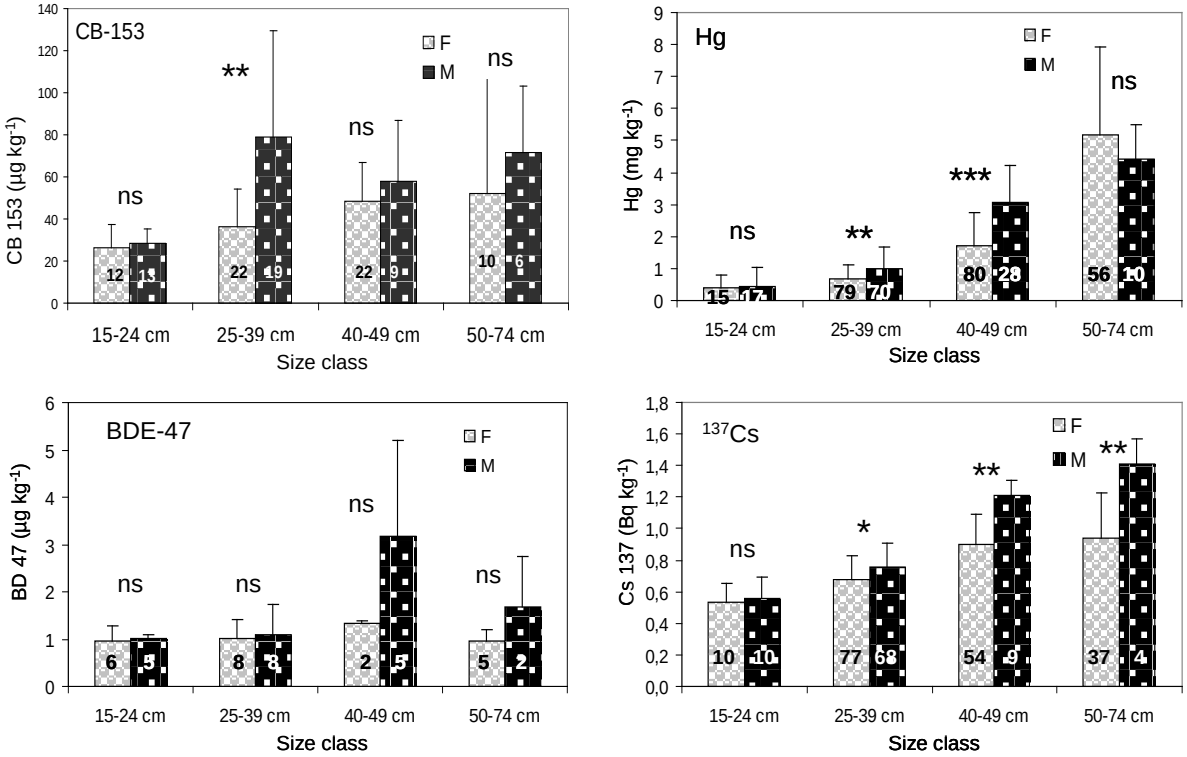

Fig. 2. Mean concentrations of contaminants (dry weight) analysed in females and males of the European hake in the Gulf of Lions. Numbers in bars indicated the number of individuals analysed for each sex and size class. Bars represent standard deviations; significance of the male-female difference: ns = not significant, * = $p < 0.05$, ** = $p < 0.01$

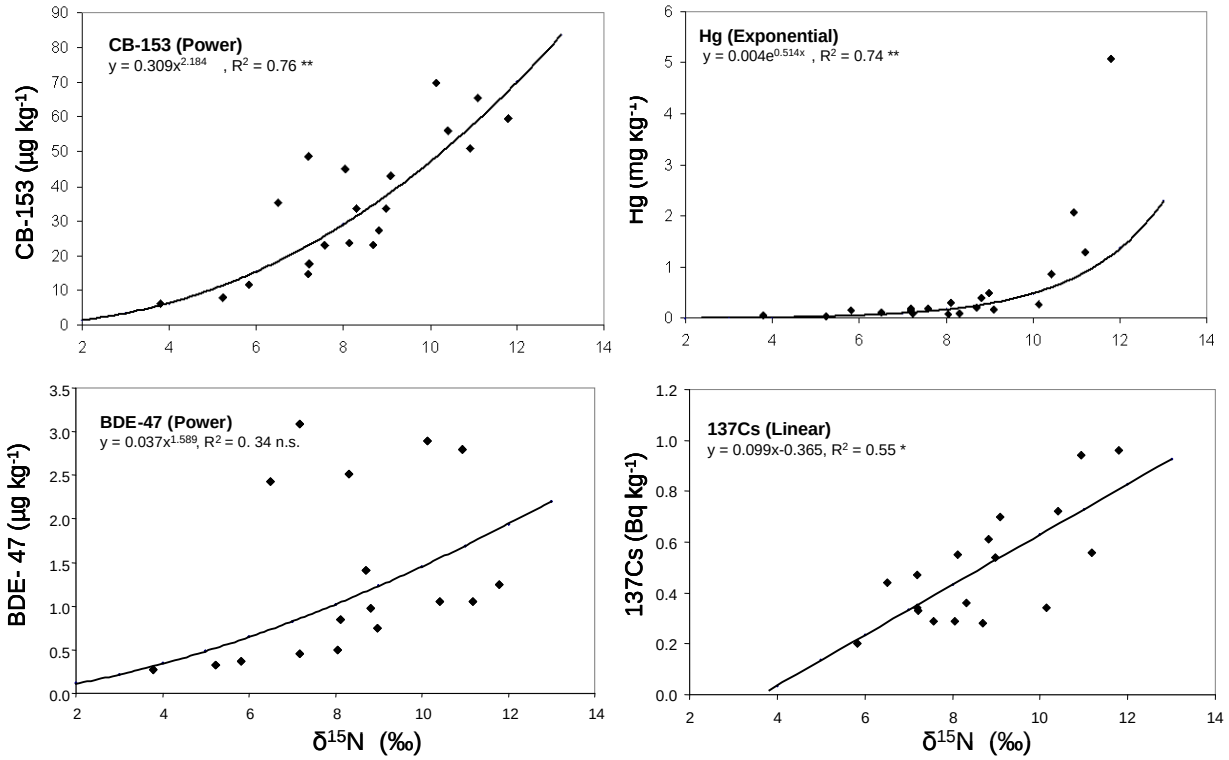

Fig. 3. Regression curves between contaminant concentration (dry weight) and $\delta^{15}N$ for CB-153, Hg and ^{137}Cs in the food web of the European hake in the Gulf of Lions evidencing the shape of contaminant increases. Equations, coefficients of determination and significance of regressions are indicated. For the representation on a common scale, concentrations of Hg were multiplied by 50 and 40 for ^{137}Cs

Table 1

Mean (± sd) trophic level ($\delta^{15}N$) and concentrations in muscle of the four classes of contaminants analysed according to size class in the European hake in the Gulf of Lions. (n) = number of individuals analysed.

Size-class	$\delta^{15}N$		CB-153		BDE-47		Hg		^{137}Cs	
(cm)	(‰)	(n)	(µg kg^{-1} dw)	(n)	(µg kg^{-1} dw)	(n)	(mg kg^{-1} dw)	(n)	(Bq kg^{-1} dw)	(n)
0 – 6	7.19 ± 0.30	(8)	14.9 ± 1.8	(5)	0.45 ± 0.00	(3)	0.15 ± 0.03	(5)	0.47 ± 0.01	(3)
7 – 14	8.13 ± 0.19	(55)	23.7 ± 5.8	(13)	0.84 ± 0.19	(3)	0.31 ± 0.17	(28)	0.55 ± 0.11	(12)
15 – 24	8.82 ± 0.11	(80)	27.4 ± 9.6	(25)	0.98 ± 0.23	(11)	0.40 ± 0.17	(32)	0.61 ± 0.09	(20)
25 – 39	10.41 ± 0.05	(176)	56.1 ± 42.1	(41)	1.05 ± 0.51	(16)	0.86 ± 0.61	(149)	0.72 ± 0.15	(145)
40 – 49	10.93 ± 0.07	(57)	51.1 ± 21.4	(31)	2.80 ± 0.51	(7)	2.07 ± 1.19	(108)	0.94 ± 0.21	(63)
50 – 74	11.79 ± 0.12	(14)	59.5 ± 47.9	(16)	1.25 ± 0.69	(7)	5.07 ± 2.57	(66)	0.96 ± 0.30	(41)

Table 2

Significance of the relationships ln contaminants in hake muscle with mean size, age and $\delta^{15}N$ for the four classes of contaminants analysed. R2 = coefficient of determination, ns = not significant, * = significant at $p < 0.05$, ** = significant at $p < 0.01$, *** = significant at $p < 0.001$.

Contaminant	ln contaminant/size	ln contaminant/age	ln contaminant/$\delta^{15}N$
CB-153	$R^2 = 0.82$, $p = 0.013$ *	$R^2 = 0.73$, $p = 0.030$ *	$R^2 = 0.94$, $p = 0.001$ **
BDE-47	$R^2 = 0.52$, $p = 0.105$ ns	$R^2 = 0.44$, $p = 0.149$ ns	$R^2 = 0.60$, $p = 0.069$ ns
Hg	$R^2 = 0.99$, $p < 0.001$ ***	$R^2 = 0.97$, $p < 0.001$ ***	$R^2 = 0.96$, $p < 0.001$ ***
^{137}Cs	$R^2 = 0.94$, $p = 0.001$ **	$R^2 = 0.89$, $p = 0.04$ **	$R^2 = 0.96$, $p < 0.001$ ***

Table 3

Relative importance (dry weight %) of the different prey types in hake diet according to size class. (n) = number of individuals analysed. Hake = *Merluccius merluccius*, Red bandfish = *Cepola rubens*, Poor cod = *Trisopterus minutus*, Anchovy = *Engraulis encrasicolus*, Sardine = *Sardina pilchardus,* Blue whiting = *Micromesistius poutassou.*

Size class	(n)	Crustaceans	Gobiids	Hake	Red bandfish	Poor cod	Anchovy	Sardine	Blue whiting
0 – 6	(75)	95	5	0	0	0	0	0	0
7 – 14	(655)	17	15	6	0	13	16	31	2
15 – 24	(631)	1	2	1	1	2	40	50	3
25 – 39	(449)	1	1	1	1	2	9	80	5
40 – 49	(160)	1	7	1	2	10	4	42	33
50 - 74	(31)	1	6	4	13	5	6	15	50

Table 4

Mean (± sd) trophic level ($\delta^{15}N$) and contaminant concentrations of the various prey types in the hake food web of the Gulf of Lions. (n) = number of samples analysed, S = small individuals (<12 cm), L = large individuals (>12 cm).

Prey types	$\delta^{15}N$		CB-153		BDE-47		Hg		^{137}Cs	
	(‰)	(n)	(µg kg^{-1} dw)	(n)	(µg kg^{-1} dw)	(n)	(mg kg^{-1} dw)	(n)	(Bq kg^{-1} dw)	(n)
Phytoplankton	3.80 ± 0.08	(24)	6.33 ± 3.43	(21)	0.27 ± 0.34	(5)	0.06 ± 0.02	(28)		(0)
Zooplankton	5.23 ± 0.90	(6)	8.09 ± 4.10	(21)	0.33 ± 0.23	(4)	0.04 ± 0.03	(19)		(0)
Suprabenthos	5.83 ± 0.90	(9)	11.62 ± 7.1	(18)	0.37 ± 0.08	(4)	0.15 ± 0.15	(24)	0.20 ± 0.09	(2)
Engraulis encrasicolus-S	7.57 ± 0.22	(39)	23.10 ±	(5)		(0)	0.18 ± 0.02	(5)	0.29 ± 0.09	(8)
Engraulis encrasicolus-L	8.70 ± 0.32	(10)	17.98	(4)	1.41 ± 0.08	(3)	0.21 ± 0.06	(4)	0.28 ± 0.08	(7)
Sardina pilchardus-S	8.32 ± 0.28	(19)	23.00 ±	(8)	2.51 ± 0.10	(3)	0.10 ± 0.02	(4)	0.36 ± 0.09	(4)
Sardina pilchardus-L	7.19 ± 0.36	(28)	17.82	(5)	3.09 ± 0.40	(3)	0.18 ± 0.04	(3)	0.34 ± 0.09	(17)
Cepola macrophthalma	8.05 ± 0.15	(15)	33.63 ±	(3)	0.50 ± 0.39	(3)	0.08 ± 0.02	(8)	0.29 ± 0.07	(5)
Micromesistius poutassou-	7.22 ± 0.05	(28)	25.58	(6)		(0)	0.09 ± 0.01	(3)	0.33 ± 0.09	(3)
S	10.14 ±	(19)	48.64 ±	(6)	2.89 ± 1.59	(3)	0.27 ± 0.31	(3)	0.34 ± 0.05	(3)
Micromesistius poutassou-	0.20	(11)	24.38	(7)	0.75 ± 0.10	(3)	0.49 ± 0.50	(7)	0.54 ± 0.10	(12)

L	8.98	±	(40)	45.04	±	(6)	1.05 ± 0.21	(3)	1.28 ± 1.00	(6)	0.56 ± 0.11	(22)
Trisopterus minutus-S	0.14		(41)	23.41		(3)	2.43 ± 0.06	(3)	0.11 ± 0.04	(3)	0.44 ± 0.09	(17)
Trisopterus minutus-L	11.19	±	(16)	17.67	±	(5)		(0)	0.17 ± 0.07	(10)	0.70 ± 0.35	(5)
Trachurus trachurus	0.25			11.29								
Gobius niger	6.51 ± 0.39			69.69	±							
	9.10 ± 0.66			30.06								
				33.62	±							
				28.00								
				65.51	±							
				49.66								
				35.40 ± 0.00								
				43.05	±							
				29.20								

Table 5

Mean trophic level ($\delta^{15}N$) and mean concentrations of contaminants in the diet of the European hake according to size class, and biomagnification factor (BMF) calculated from hake to its diet

Size Class (cm)	$\delta^{15}N$ - Diet (‰)	CB-153 - Diet ($\mu g\ kg^{-1}$ dw)	BMF CB-153	BDE-47 - Diet ($\mu g\ kg^{-1}$ dw)	BMF BDE-47	Hg - Diet ($mg\ kg^{-1}$ dw)	BMF Hg	^{137}Cs - Diet ($Bq\ kg^{-1}$ dw)	BMF ^{137}Cs
0 – 6	7.13	11.9	1.24	0.38	1.19	0.15	0.99	0.23	2.07
7 – 14	7.64	24.3	0.91	1.43	0.55	0.21	1.37	0.40	1.28
15 – 24	7.82	28.3	0.86	2.08	0.42	0.17	2.05	0.34	1.61
25 – 39	8.07	31.4	1.39	2.52	0.32	0.15	4.30	0.35	1.59
40 – 49	8.34	32.3	1.15	2.13	1.01	0.19	8.46	0.39	1.85
50 – 74	8.39	37.6	1.08	1.83	0.49	0.17	20.97	0.37	1.84

Table 6

Mean biomagnification factors calculated from hake and its diet (BMF) and for the entire food web (FWMF) for the different contaminants analysed

Biomagnification factor	CB-153	BDE-47	Hg	^{137}Cs
BMF	1.105	0.662	6.356	1.707
FWMF	1.335	1.221	1.675	1.212