Pyrethroid bioaccumulation in Mediterranean dolphins

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1. Introduction

Pyrethroids are organic pollutants with high hydrophobicity used as insecticides. Thus, they tend to rapidly bind to suspended particulate matter or sediments and low concentration is generally present in water. Applied to land or for domestic purposes as vector control, they can enter the aquatic environment through processes such as atmospheric deposition, river runoff and municipal treatment discharges. Once associated with sediments, benthic organism exposure of pyrethroids can be by ingestion or contact of sediment particles or from interstitial water. In fish, exposure to pyrethroids can be through diet or gill absorption due to their lipophilicity.

Concern has existed about aquatic organisms' exposure to pyrethroids because of their high toxicity: carcinogenic, neurotoxic, immunosuppressive and reproductive potential toxicity of pyrethroids in mammals [1]. Despite the assumption that they are hydrolysed to non-toxic metabolites in mammals, evidence of a possible bioaccumulation has recently been found in marine mammals from Brazil [2]. Marine mammals are at the top of the food web, which results in high exposure to a number of toxic compounds. The present study investigates the occurrence of ten pyrethroid compounds in liver samples from striped dolphins (*Stenella coeruleoalba*) and common dolphins (*Delphinus delphis)* from southern Spain. This is the first attempt to determine the occurrence and bioaccumulation of pyrethroid insecticides in marine mammal tissues from the Mediterranean Sea. Distribution of pyrethroids in different tissues and the isomeric proportion of pyrethroids are also assessed.

2. Materials and methods

Samples of dolphin liver (37 samples corresponding to 27 males and 10 females of different ages) were collected from striped dolphin from the Mediterranean coast of Andalusia (Alboran Sea, Spain). From these samples, 7 belong to dolphins found stranded between 2003 and 2005 and the remaining 30 were found stranded between 2008 and 2010. On the other hand, different tissues—blubber, muscle, liver, brain and kidneys—from 11 stranded common dolphins were collected between 2004 and 2009 in the same area.

The analytical method was selected to monitor 10 different pyrethroids. Sample preparation was carried out according to Feo et al. [3]. Lyophilized sample was spiked with internal standards, extracted by sonication and underwent a clean-up with alumina and C18 SPE cartridges. Extracts were analysed by GC-NCI-MS/MS [4]. Method recoveries ranged from 53 to 116 % and method limits of detection and limits of quantification are 0.02-0.46 ng/g in lipid weight (lw) and 0.08-1.54 ng/g lw, respectively.

3. Results and discussion

Pyrethroids were detected in 87 % of the striped dolphins and 100 % of the common dolphin livers, with total concentrations of nd-5,210 ng/g lw and 69-2,036 ng/g lw, respectively. These levels were higher than those reported in the first and unique investigation of pyrethroid bioaccumulation in dolphins from the Brazilian coast (7.0-68 ng/g lw) [2]. Permethrin and tetramethrin were the main contributors to the pyrethroid profiles for all tissues. Fluvalinate and resmethrin were never detected and cyflutrhin was found in just one liver sample.

The samples of striped dolphins where used to assess whether bioaccumulation of pyrethroids was similar to that of persistent organic pollutants (POPs) as there were enough samples of all age groups. Previous studies showed that an increase of POP levels with the length of the specimen (which is directly related to age) is an indication of bioaccumulation. Pyrethroids did not follow that pattern.

Figure 1a shows the box plot comparing concentration levels for calves, juveniles and adults. There are no significant differences between maturity stages. It seems, nevertheless, that concentration levels slightly increase from calves to juveniles, whereas juveniles present similar levels to adults. Metabolization of pyrethroids after achieving sexual maturity might account for this pattern, as seen for other species.

Samples of striped dolphin collected in 2003-05 were compared with those collected 5 years later, in 2008-2010 (Figure 1b). No significant differences were observed between both sampling periods. Studies of temporal trends are typically carried out with a minimum difference of 10 years. Therefore, it would be advisable to do this type of study within five years from now in order to detect any clear trend.

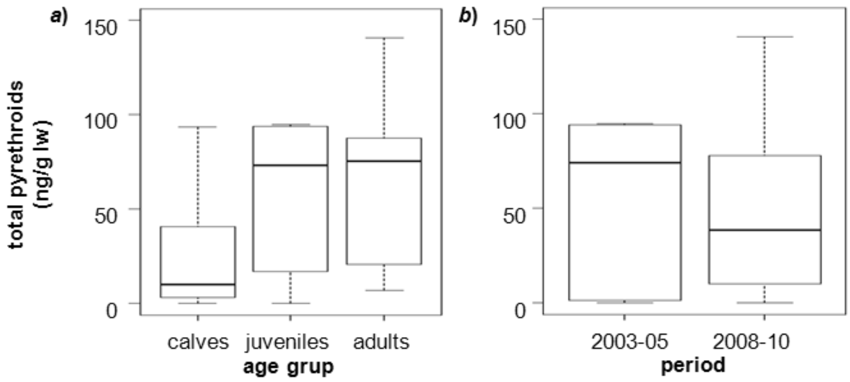

Figure 1: Box plots for pyrethroid concentrations (ng/g lw) according to (a) age group and (b) collection period.

Regarding distribution of pyrethroids in different tissues, as expected because of their lipophilic behaviour, blubber was the most contaminated tissue with a mean value of 65.3 ng/g ww. Liver, kidney and muscle presented very similar levels with means of 23.6, 17.6 and 18.6 ng/g ww, respectively. The lowest levels were found in brain with a mean concentration of 10.1 ng/g ww.

When concentration of pyrethroids was normalized to the lipid content, the highest value corresponded to muscle by far (Figure 2). This suggests a preference for accumulation in that tissue. Were there no preference, normalized concentration would be similar in all tissues. Brain tissue and blubber, which are very fatty, showed lower levels of pyrethroids per fat unit than leaner tissues, like muscle. Further studies are necessary to understand this behaviour.

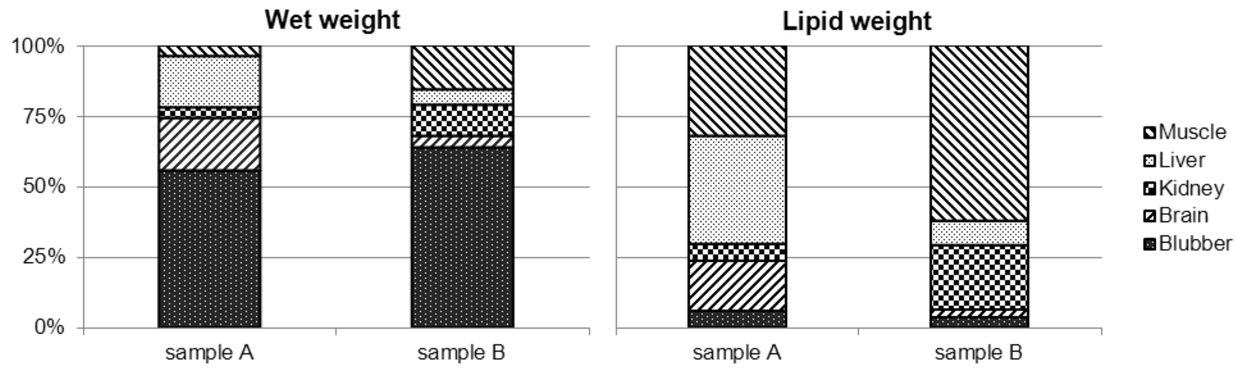

Figure 2: Distribution of pyrethroids in different tissues according to data on wet weight and on lipid weight.

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