PYRETHROIDS IN THE ENVIRONMENT: ANOTHER FAMILY OF *pseudo*-POPS?

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Introduction

Pyrethrins are natural insecticides produced by certain species of chrysanthemum (for example *Chrysanthemum cinerariaefolium* and *C. coronarium*). In order to increase their stability in the environment, some different derivatives have been synthesized. These semi-synthetic compounds are named pyrethroids. They contain 2-3 chiral centers depending on their structure, so each pyrethroid could contain 2 or 4 enantiomer pairs and different diastereoisomers.

These insecticides were the alternative to other biocides, e.g. organochlorines and organophosphates, because of their lower toxicity in mammals, their selective insecticide activity and their lower environmental persistence. Thus, in last decades the usage of pyrethroids has increased widely indoors as household insecticides, insect-control products, pet shampoos and lice treatments, and outdoors as agrarian and aquaculture pesticides and for pest control.

Nevertheless, even when it is known that pyrethroid environmental persistence is usually lower than 90 days, they are found in environmental samples, such as water and sediments[1,2], as well as in food[3]. Moreover, and despite the assumption that pyrethroids are converted to non-toxic metabolites by hydrolysis in mammals, they have been also detected in marine mammals[4] and even in human samples[5,6].

Regarding pyrethroid toxicology, they are supposed to be low toxic for non-target organisms. However, it is known their high toxicity to aquatic environments. Moreover, nowadays they are been studied because of their potential capacity to decrease fertility in mice and some authors even have described pyrethroids as carcinogenic and endocrine disruptors[7]. Furthermore, they have been related with some other diseases at sub-lethal levels[8]. In addition, their enantiomeric properties might make important to take into account the potential differences in enantiotoxicology.

In this work, we summarized the state of the art with the most relevant information about pyrethroid occurrence in the environment, and concretely, in biota samples, including aquatic (marine and fresh water) and terrestrial ecosystems. Finally, we focused on human accumulation as an important issue to take into account. Our goal is to have a general vision of pyrethroid pollution and elucidate if the behavior of this family of contaminants is related to the typical *pseudo*-POP characteristics.

Materials and methods

There are several different methodologies for pyrethroid determination in food samples. However, for environmental analysis, most of the reported methods are concerning water and sediment matrices[9]. For biota and human samples, Feo et al.[10] developed an analytical methodology based on an exhaustive extraction and clean up. Briefly, the sample treatment consisted in an extraction with an organic solvent followed by a clean-up with solid phase extraction in tandem with basic alumina and C18 cartridges. The authors demonstrated the need of the use of tandem MS/MS because of the sensitivity improvement of almost 400 times respect the analysis with single MS. The analysis was by GC-MS/MS in negative chemical ionization mode, using ammonia as reagent gas. The chromatographic column chose was a DB5-MS[4].

Some works remark the importance of enantiomer differentiation. We developed a GC-MS/MS methodology for the enantio-selective analysis of six common pyrethroids. For the first time we separate the enantiomers of bifentrhrin, cyhalothrin, cyfluthrin, cypermethrin, permethrin and tetramethrin, in a single analysis of less than 75 minutes and with resolutions upper than 0.58 in all cases. The chromatographic column selected was a DGB-172[11].

Results and discussion

Aquatic biota

A study of pyrethroid occurrence in 42 fishes collected from 4 different Iberian river basins was carried out[12]. For the first time, this work described pyrethroid bioaccumulation in edible river fish samples. Levels of concentration ranged from 12 to 4938 ng/g lipid weight (lw). Moreover, isomeric characterization remarked a general preference of *cis* isomers in bioaccumulation. Also, the enantiomeric evaluation showed that there was an enantioselective bioaccumulation of some pyrethroids, depending on the studied species.

It is important to note that all fish samples presented pyrethroid contamination. Their concentration levels were compared with other known pollutants such as flame retardants, hormones, pharmaceuticals and personal care products (Figure 1). As can be seen, only organophosphorous flame retardant levels were comparable to pyrethroid ones even when the greater concentration was 6 times higher for pyrethroid than for organophosphorous flame retardants.

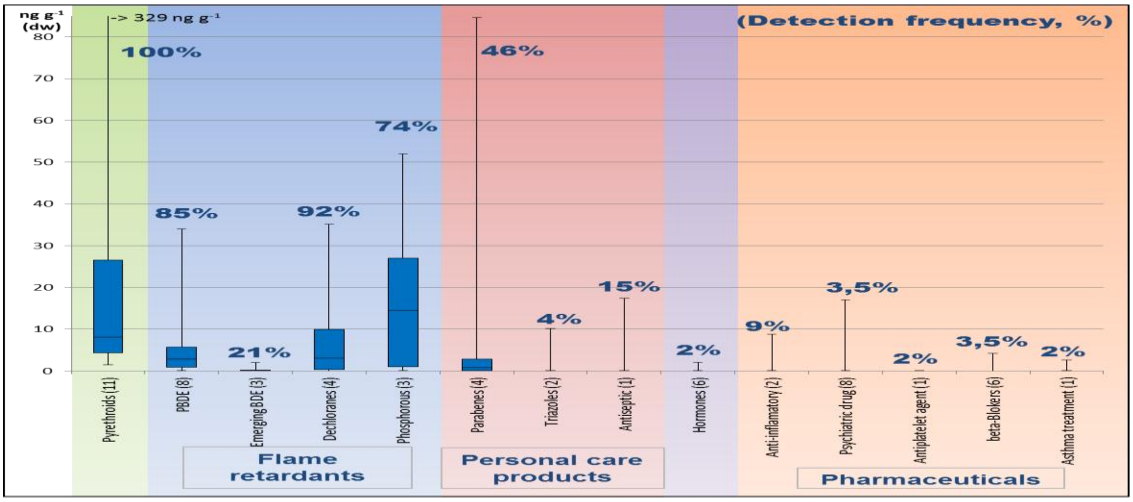

Figure 1: Medium levels of pollutants in river fishes and detection frequencies (adapted from Corcellas *et al.* 2014b).

There is another published work that constitutes the first investigation to demonstrate pyrethroid bioaccumulation in marine mammals[4]. Twelve pyrethroids were determined in liver samples from 23 male franciscana dolphins from Brazil. The median concentration values for total pyrethroids were 7.04 and 68.4 ng/g lw in adults and calves, respectively. Results showed a distinct metabolic balance of pyrethroids through dolphin life, with a remarkable difference with the typical POP behavior (Figure 2). High loads are received at the beginning of their lives and, when they reach sexual maturity, these mammals seem to degrade/metabolize pyrethroids. Maternal transfer of these compounds was also evaluated through the analysis of breast milk and placenta samples. Pyrethroids were detected in both matrices, with values between 2.53–4.77 ng/g lw and 331–1812 ng/g lw, respectively. Therefore, for the first time, a study shows mother-to-calf transfer of pyrethroids by both gestational and lactation pathways in dolphins.

Terrestrial biota

There is only one work dealing with the occurrence of pyrethroid insecticides on terrestrial biota[13]. The occurrence of pyrethroids in 138 bird eggs that had failed to hatch was studied. Samples included eggs from 15 different bird species collected from Doñana Natural Space and surrounding areas (South-western Spain). Doñana Natural Space is considered a sanctuary for more than 300 bird species. Due to its important location, between 2 continents and close to the Atlantic Ocean and Mediterranean Sea, this area represents a strategic point where numerous birds breed, winter or stage during their migration.

In this case the frequency of detection was upper than 90%. Most contaminated samples corresponded to black-headed gulls followed by far by white storks and black kites (118, 47 and 39 ng/g lw, respectively). Correlations among levels of pyrethroids and trophic level (by analysis of stable isotopes of nitrogen) were not conclusive. However, it should be pointed out that the selected species have different feeding and migratory behavior, and changes in diet along their habitats could explain this diversion. Thus, additional studies must be carried out in order to determine the potential biomagnification of pyrethroids.

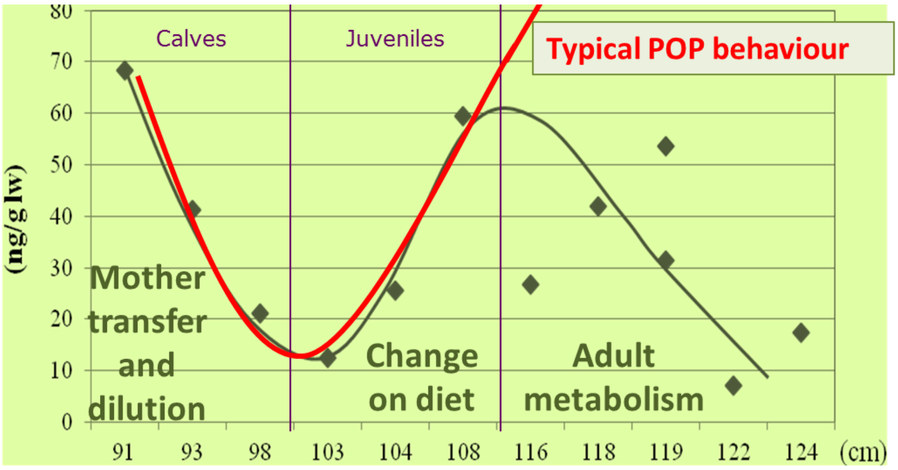

Figure 2: Trend of the levels of pyrethroid *vs.* length (adapted from Alonso *et al.* 2012). Theoretical behavior of a POP in red.

Human samples

There are few works of pyrethroids in human samples. In plasma some authors found levels below 100 pg/mL[6]. In spite of that, our international study with human breast milk from Brazil, Colombia and Spain described levels of different pyrethroids up to 24.2 ng/g lw in non-overexposed population. All the samples were positive to pyrethroids. The composition of pyrethroid mixture depended on the country of origin of the samples, bifenthrin being the most abundant in Brazilian samples, λ-cyhalothrin in Colombian and permethrin in Spanish ones. Moreover, a trend between levels of pyrethroids in breast milk and parity was observed (Figure 3)[5]. Finally, with these data of breast milk, a simple calculation of human risk for nursing babies was done. Taking into account the Admissible Daily Intake values stipulated by the authorities, no risk was observed. However, in some cases of overexposure, estimated values were very close to the maximum tolerated ones. Moreover, it is remarkable that these tabulated doses are calculated for adults. But infants are more sensitive population and it would be considered as a potentially risk group.

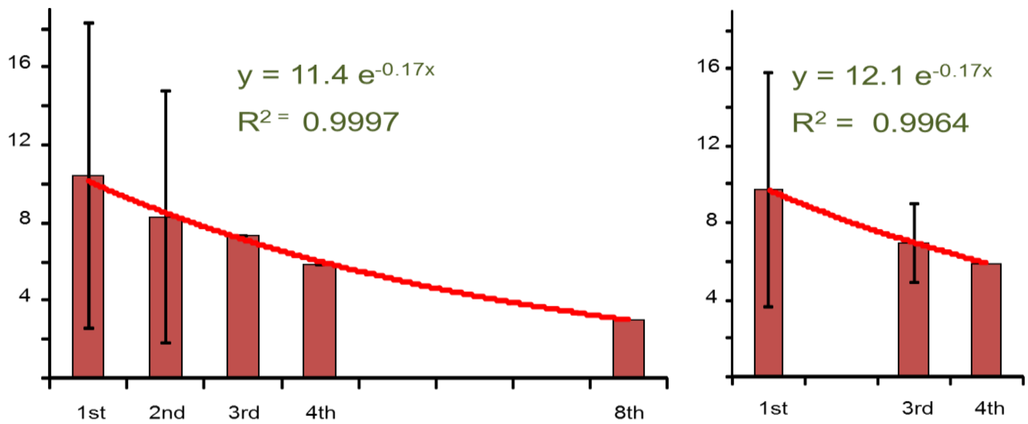

Figure 3: Trends of the levels of pyrethroid *vs.* parity (adapted from Corcellas et al 2012).

Conclusion

All these studies showed that pyrethroids are present in the environment. They have low environmental persistent (≤ 90 days), but their continuous use imply their ubiquity in the environment. Moreover, in biota samples the detection frequency was upper than 90%, demonstrating the bioaccumulation in both aquatic and terrestrial ecosystems. This could point out their potential for bioaccumulation, contradicting the assumption that all pyrethroids are metabolized by hydrolysis in mammals. It is important to note that, in addition to the high detection frequency, concentration levels of pyrethroids in biota are higher than those found for other contaminants such as flame retardants, hormones, pharmaceuticals and personal care products. It is necessary to conduct more studies assessing the potential impact on biota due to the presence of pyrethroids in biological tissues.

Thus, pyrethroids accomplish some characteristics of *pseudo*-POPs such as the environmental persistence due to the continuous dumping, the bioaccumulation in biota and human tissues, and their adverse effects on living organisms, even when this last point must be further studied. On the other hand, available data about their biomagnification is not conclusive and require more studies. Finally, there is no information about the potentially long transport of pyrethroids.

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