Environment International 75 (2015) 110–116

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

First report of pyrethroid bioaccumulation in wild river fish: A case study in Iberian river basins (Spain)

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ARTICLE INFO

Article history:
Received 2 August 2014
Accepted 11 November 2014
Available online 20 November 2014

Keywords:
Bioaccumulation
Cypermethrin
Enantioselectivity
Pyrethroids
River fish

ABSTRACT

For the first time, this work described pyrethroid bioaccumulation in edible river fish samples. We analyzed 42 whole fish samples collected in 4 different Iberian rivers. All samples were positive to these insecticides. Levels of concentration ranged from 12 to 4938 ng g^{-1} lipid weight (lw). Moreover, isomeric characterization was carried out. Our results remarked a general preference of *cis* isomers in bioaccumulation. Finally, the enantiomeric evaluation showed that there was an enantioselective bioaccumulation of some pyrethroids, depending on the studied species. Pyrethroid concentrations were compared with levels obtained for other common pollutants, such as flame retardants, personal care products, hormones and pharmaceuticals. The highest values corresponded to pyrethroid insecticides, even though, pyrethroid levels are safe for human consumption taken into account the current regulations.

1. Introduction

Pyrethroids are synthetic insecticides derived from the natural pyrethrins. Structurally they have 2 or 3 chiral centers. This means that they have 2 or 4 diastereomers and 4 or 8 enantiomers. The use of pyrethroids is extensive around the world. They are common in agronomics both on crops and directly over grain to store, in veterinary on cattle and pets, as domestic insecticides and even for health purposes against scabies, lice or vectors of some diseases such as malaria or typhus (Barr et al., 2010).

These insecticides were the alternative to other biocides, e.g. organochlorines and organophosphates, because of their low persistence and toxicity. However, even when it is known that pyrethroid environmental persistence is usually lower than 90 days (UH, 2011), it is also true that they are found in environmental samples, such as water and sediments (Feo et al., 2010b; Weston et al., 2013; Xue et al., 2005), food (Esteve-Turrillas et al., 2005; Garcia-Rodriguez et al., 2012), mammals (Alonso et al., 2012) and even human samples (Bouwman et al., 2006; Corcellas et al., 2012; Channa et al., 2012). The explanation to these findings may be the continuous, and sometimes excessive, use of these compounds.

The origin of these pyrethroids in the environment is very diverse. Agronomics should be an importance source. Despite this, some works pointed out that pyrethroid presence in river water and sediments because of the agronomic workings is punctual and it depends on how long the pesticides were applied (Feo et al., 2010b). Besides, a lot of countries have already banned some of these insecticides in agronomics (EC, 1991; EPA, 1991). However, the usage of these biocides is also very common in non-agricultural sectors such as industry, government, and home and garden. For example, the last Pesticide Industry Sales and Usage Report (EPA, 2011) estimated that in 2007, over 1500 t of pyrethroids was used only in the U.S. Home and Garden market sector. Therefore, domestic and urban uses might be other focal points of their environmental presence (Kuivila et al., 2012; Lu et al., 2013; Weston and Lydy, 2010).

Moreover, pyrethroid toxic effects in water ecosystems are not negligible. For instance, LC_{50} of bifenthrin in *Daphnia* and trout are 0.11 and 150 μg/L respectively (UH, 2011). Some authors had studied LC_{50} of some other pyrethroids in fishes. Their values ranged from 0.06 μg/L (tefluthrin on trouts) to 19 μg/L (allethrin on trouts) (UH, 2011). Even when in literature there were no studies of pyrethroid bioaccumulation in wild fish tissues, some authors had studied the bioaccumulation in exposed fishes. The main objective of most of these studies was to calculate the Bioconcentration Factor (BCF) in fishes for concrete pyrethroids. These studies demonstrated high bioaccumulation but, as well, the possibility of depuration in appropriate conditions (Devillers et al., 1996; Jackson et al., 2009; Muir et al., 1994; Schimmel et al., 1983).

Lately, pyrethroid toxicology and exposition in mammals are being further investigated (Goulding et al., 2013; Jin et al., 2012; Xu et al., 2010; Zhang et al., 2008; Zhao et al., 2010). These works included new data about isomer-toxicology, even some of them were focused on enantioselective toxicology. For instance, *cis*-isomer of permethrin

Abbreviations: dw, dry weight; LC_{50}, Lethal Concentration at 50%; lw, lipid weight; LOD, limit of detection; LOQ, limit of quantification; MRL, Maximal Residue Level; MS, mass spectrometry.

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http://dx.doi.org/10.1016/j.envint.2014.11.007
0160-4120/

seems to be less metabolized and, consequently, more toxic than *trans*-permethrin in mice (Zhang et al., 2008). Besides, one of the *cis*-enantiomers presented more toxicity than the other (Jin et al., 2012). Moreover, human exposure to pyrethroids has been widely studied by urine analysis of their metabolites and related with some diseases, such as leukemia (Ding et al., 2012). However, these analyzed metabolites are nonspecific, so it was not possible to know the contribution of each pyrethroid (Barr, 2008; Barr et al., 2010; Ding et al., 2012; Koureas et al., 2012; Olsson et al., 2004) or their isomers.

With this background, we studied for the first time the potential bioaccumulation of pyrethroids in wild river fish. We analyzed 42 pooled edible fish samples from four Iberian river basins. In these samples we determined 12 different pyrethroids: *cis*-bifenthrin, cyfluthrin, cypermethrin, cyhalothrin, deltamethrin, fenvalerate, fluvalinate, permethrin, phenothrin, resmethrin, tetramethrin, and tralomethrin. In addition, given the relevance of isomerism on toxicology, we reanalyzed these samples with an enantiomeric-selective methodology.

2. Materials and methods

2.1. Standards and reagents

All analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). As surrogate standards d_6-*trans*-permethrin and d_6-*trans*-cypermethrin were chosen and purchased from the same commercial firm. Organic solvents were obtained from J.T. Baker "for use in HPLC" quality (Deventer, The Netherlands). Standard solutions were prepared in ethyl acetate ("for gas chromatography" quality from Merck, Darmstadt, Germany). Calibration curves were prepared at different concentrations ranging between 0.4 and 150 ng mL^{-1}. Solid phase extraction (SPE) cartridges were obtained from Isolute Biotage (Uppsala, Sweden) (C18, 2 g 15 mL^{-1}) and from Interchim (Montluçon, France) (Basic alumina, 5 g 25 mL^{-1}).

2.2. Sampling

In the frame of the project SCARCE-Consolider-Ingenio, four Iberian river basins were sampled in 2010. Fig. 1 showed the distribution of these four basins in the Iberian territory as well as the sampling points. Only one of this sample points corresponded to a reservoir. For each river, two fish species were selected for monitoring along the river. These species used to be one carp and one barbel species, when it was possible. Other species were also sampled, e.g. trouts, gudgeons and catfishes. Fish samples were collected, homogenized for species by a meat grinder, freeze-dried and stored at −20 °C until analyses. More details of this procedure were specified in previous works (Jakimska et al., 2013; Santin et al., 2013). Table A summarizes sample details such as species, sampling point and pool composition. With some species, for example barbels, juvenile and adult samples were differentiated by fork length; in this particular case, barbels with length lower than 30 cm were considered as juvenile.

2.3. Analytical methods

Sample treatment was adapted from Feo et al. (2012). Briefly, 0.3 g of freeze-dried sample was spiked overnight with 10 μL of a solution of 0.025 ng L^{-1} and 0.0125 ng L^{-1} of d_6-*trans*-permethrin and d_6-*trans*-cypermethrin, respectively. Extraction procedure was carried out with 20 mL of hexane:dichloromethane 2:1 and assisted by ultrasound for 15 min. This extraction was repeated twice and all solvent dried by a N_2 stream. A following tandem SPE (basic alumina and C18 cartridges, 30 mL acetonitrile as eluent) cleaned up. The eluent was evaporated under N_2 and the sample reconstituted 100 μL of ethyl acetate.

Analyses were performed on an Agilent Technologies 7890A coupled to a 7000A GC–MS Triple Quad. The columns chosen were a DB5-ms (Agilent Technologies, Santa Clara, CA, USA) (15 m × 0.25 mm × 0.1 μm) for the quantitative analysis and a BGB-172 (BGB Analytik, Switzerland) (30 m × 0.25 mm × 0.25 μm) for the enantiomeric determination. Details of chromatographic conditions to both achiral and chiral analyses are found in Corcellas et al. (in press). The selected mass spectrometry (MS) mode was negative chemical ionization with ammonium as reagent gas. All MS parameters are found in Feo et al. (2011).

In parallel, 1 g of sample was extracted with an equivalent extraction procedure in order to determine the lipid content gravimetrically.

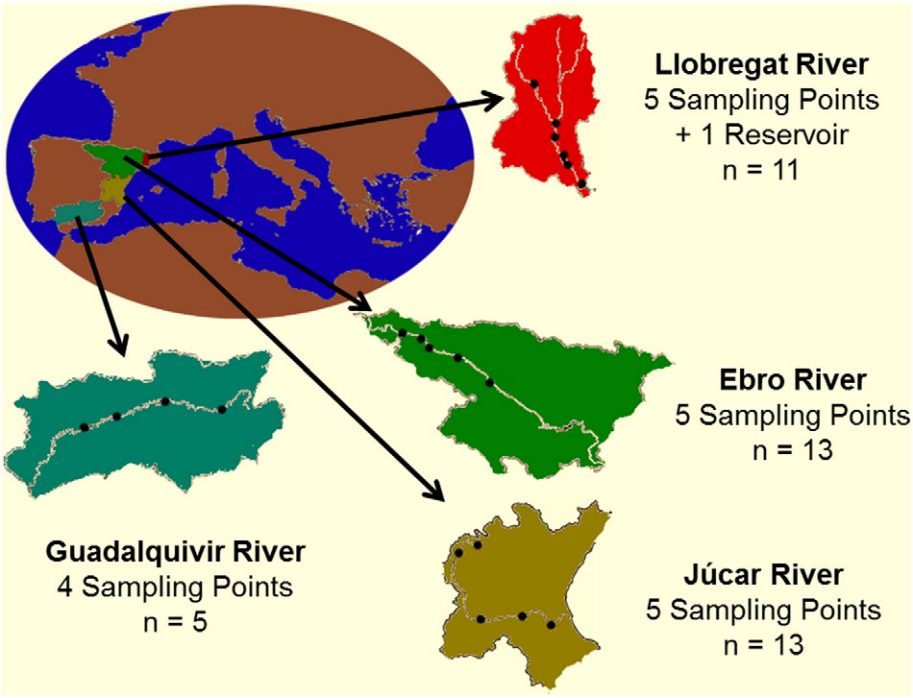

Fig. 1. Map of the four Iberian river basins, and sampling stations selected for each one (n = number of samples).