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Pyrethroids in chicken eggs from commercial farms and home production in Rio de Janeiro: Estimated daily intake and diastereomeric selectivity

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HIGHLIGHTS

- Cypermethrin was the predominant compound, with higher occurrence and concentrations.
- Estimated daily intake did not present a risk to human consumption.
- One-third of the samples had concentrations above the Maximum Residue Limits.
- Cypermethrin and phenothrin exceeded the Maximum Residue Limit, 66 and 11 times, respectively.
- We found a stereoisomeric selectivity pattern of *cis*-diastereomers.

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ABSTRACT

In this study, pyrethroids were determined in chicken eggs from commercial farm (n = 60) and home egg production (n = 30). These pyrethroids were investigated: bifenthrin, phenothrin, permethrin, cyfluthrin, cypermethrin and fenvalerate, including most diastereomers. Quantification was done using GC-MS in a negative chemical ionization mode. Pyrethroids residues were found in 79% of the analyzed samples. Cypermethrin presented the highest occurrence, being quantified in 62 samples (69%) in concentrations (lipid weight – l w.) varying between 0.29 and 6408 ng g^{-1}, followed by phenothrin (24%), 21–3910 ng g^{-1}, permethrin (14%), 2.96–328 ng g^{-1}, and bifenthrin (11%), 3.77–16.7 ng g^{-1}. Cyfluthrin and fenvalerate were not detected. Home-produced eggs had a higher occurrence of pyrethroids (97%), with a greater predominance of phenothrin. In commercial production, 70% of the samples presented pyrethroid residues (predominantly cypermethrin). This is the first report about the presence of pyrethroids in home-produced eggs and the first description of a selectivity pattern with the predominance of *cis* diastereomers in chicken eggs. In general, estimated daily intake does not present a risk to human consumption, according to Brazilian and international standards (FAO/WHO). However, one third of the samples (30 eggs) had concentrations above the maximum residue limits (MRLs). The maximum cypermethrin concentration was 66 times the MRL, while the maximum phenothrin concentration was 11 times the limit. Further studies about transfer dynamics, bioaccumulation and metabolic degradation of stereoisomers are required, as well as determining if this selectivity pattern in food can increase consumer's health risk.

1. Introduction

Poultry industry has great relevance in global food production. According to recent estimates — between 1993 and 2013 — world egg production expanded from 38 to 68 million tons, accumulating an increase of almost 80% (IEC, 2015). Consumption increasing reflects a trend in diet diversification at a global level and a growing

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demand for animal proteins with low economic cost, mainly by developing countries (Miranda et al., 2015; OECD/FAO, 2015). In Brazil, egg production is mainly destined to domestic market. However, the country is the seventh largest producer in the world, with a current consumption expansion (FAO, 2015; Rezende et al., 2013). Between 2010 and 2015, there was about 30% consumption growth, reaching an annual mean *per capita* of 191 eggs in 2015 (ABPA, 2016). Therefore, poultry farming expansion may significantly increase the risk of ectoparasites and other diseases affecting production (Manning et al., 2007; Rezende et al., 2013). In this context, an increase of veterinary drugs (e.g. antibiotics, acaricides and insecticides) applied in poultry farming is expected. Intensive or even inappropriate use of these products and the lack of safety interval monitoring after their application may expose consumers to substances potentially harmful to health (Carneiro et al., 2015; Goetting et al., 2011). There is also the possibility of indirect contamination through soybeans and maize consumption, since these crops, where pesticides are most used in Brazil, are the main protein sources for chickens (Carneiro et al., 2015; Souza et al., 2013). Pesticides presents relevant role in Brazilian agricultural development model (Jardim and Caldas, 2012; Schröder et al., 2016). In 2012, 823,000 tons of agrochemicals were commercialized in Brazil (Carneiro et al., 2015). Among the vast group of pesticides, pyrethroids can be highlighted. Over recent decades, there has been a worldwide trend towards a gradual increase in pyrethroids use as a substitute for more toxic and environmentally persistent compounds such as organochlorines, organophosphates, and carbamates (Feo et al., 2010; Li et al., 2013). Since then, it has been the most widely used class of pesticides, applied in agriculture and livestock production, in control of urban vectors and in residential use — as household insecticides, in treatment of lice and scabies, and in pet stuffs (Corcellas et al., 2015; Feo et al., 2012; Li et al., 2016a). Pyrethroids are esters derived from pyrethrins, natural insecticides, but environmentally unstable. The inclusion of nitrogen atoms and halogens to the natural compounds allowed a greater stability to their synthetic derivatives (Montanha and Pimpão, 2012). The group is divided into Type I and Type II, differing only by the presence of an α-cyano radical in Type II compounds, in addition to being considered more toxic (Rehman et al., 2014). In general, pyrethroids act by prolonging the opening of sodium channels in cell membranes, delaying repolarization in the central and peripheral nervous systems. In Type II compounds, the effect's duration at specific sites is longer, which may explain the differences in toxicity between the two types (ATSDR, 2003). A recent study indicates that pyrethroid occupational exposure may cause gene mutations, immunological disturbances and oxidative stress (Okda et al., 2017). However, there is evidence that nonoccupational exposure may be associated with heart disease, sperm DNA damage and low semen quality (Han et al., 2017; Ji et al., 2011). In addition, an epidemiological study through monitoring pyrethroid metabolites, highlight possible risk of delaying sexual maturity in girls (Ye et al., 2017).

Pyrethroids compounds consist in a complex mix of *cis* and *trans* diastereomers, with a wide variation in reported toxicities, although *cis* diastereomers show higher toxicity in mammalian assays (ATSDR, 2003). Authors also mention diastereomeric selectivity in biological matrices, such as human breast milk, dolphins' liver tissue, and in freshwater fish tissues (Alonso et al., 2012; Corcellas et al., 2015, 2012). In poultry farms, pyrethroids are widely used in ectoparasitic prevention and control, and in poultry houses treatment (Chernaki-Leffer et al., 2013; Rezende et al., 2013; Souza et al., 2013). However, when topically applied in chickens, pyrethroids can be absorbed and mobilized to eggs (Goetting et al., 2011). Many organic contaminants are lipophilic, so foods with a high lipid content, such as eggs, may contain high levels of pesticides, as well as other hydrophobic environmental contaminants (Domingo, 2014; Zheng et al., 2012). Although pyrethroids are widely used, there is little information about contamination in eggs. Only Souza et al. (2013) and Dell'Oro et al. (2014) reported residues of pyrethroids in marketed eggs in Brazil and Italy, respectively. Besides that, there is no information about this class of compounds in home-produced eggs. Due to their absorption by gastrointestinal tract and lipophilicity, pyrethroids are potentially mobilized to specific sites of action as central and peripheral nervous system tissues (ATSDR, 2003; Quijano et al., 2016). Therefore, it should be considered as target compounds for toxicity assessments through food consumption. In this case, Acceptable Daily Intake (ADI) values and Maximum Residue Limits (MRLs) in food are strategic toxicological tools for a better evaluation of the chronic risk in exposed populations. MRLs are applied, e.g. to good agricultural practices, respecting different safety intervals after the use of agrochemicals. Both parameters are established by national and international bodies (CAC/MRL, 2015). The study area is the largest poultry center in Rio de Janeiro state, located in an upland region, which has great economic importance due to its intense agricultural activity. The objective was to determine pyrethroid residues, including most of their diastereomers, in eggs produced on commercial farms and home productions. From the results, it was possible to estimate the daily intake, comparing it with the established ADIs. This is the first study to include home-produced eggs in pyrethroids monitoring and it is also the first report to describe a diastereomeric selectivity in eggs produced for human consumption.

2. Material and methods

2.1. Study area and sampling

The study area is the municipality of São José do Vale do Rio Preto (SJVRP), situated in an upland region (mean elevation 615 m.a.s.l.) of Rio de Janeiro state, in southeastern Brazil (Fig. 1). It consists of an area of 220 km^2 and is interspersed with important fragments of Brazilian Atlantic rainforest, a tropical forest biome protected by parks dedicated to its conservation. The region's main economic activity is family farming, especially poultry production. There are a hundred commercial poultry meat farms and six commercial egg farms, but there is no estimate of the number of home egg producers. The poultry and egg production sites are surrounded by intense truck farming of great relevance for supplying fresh produce to the metropolitan Rio de Janeiro region. In 2016, samples were collected from all commercial farms (F 1 to F 6) and three home egg productions (HP 1 to HP 3) from the study area (Fig. 1). Ten eggs were purchased from each of the nine sample sites, for a total of 90 samples. Among the commercial eggs, white eggs were chosen because they are the ones most consumed in Brazil (Windhorst et al., 2013).

2.2. Sample preparation

Each whole egg (white and yolk) was considered as a sample. Samples were homogenized, frozen at −80 °C, lyophilized, homogenized again, stored in a dry and dark environment, and analyzed within one week. The mass was weighed before and after lyophilization to calculate concentration in wet weight and the mass of each compound per egg. The lipid content was determined gravimetrically according to Muñoz-Arnanz et al. (2011).

2.3. Standards and reagents

Pyrethroids standard was the Pesticide Mix-114 Dr. Ehrenstorfer