

# Insecticide Contamination of Pyrethroids Group in the Poultry Farming Activities-A Review

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**Abstract-** Insects infestations in poultry farm activities are common and need to be controlled in order to keep chicken breeding quality. Poultry farming international regulations have established their control by insecticides application mainly from the Pyrethroids Groups (especially cypermethrin-CPM), both in the sheds and aviary beds. That procedure in the aviary environment and its repetitions during several cycles/batches may vary, which leads to different contamination levels, either at the breeding environment and the raised chicken (present as meat residues). This review gathers information on insecticides from Pyrethroids Group (including CPM) applications, characteristics, toxicity, international regulations and residues in the meat and environment.

**Keywords-** *Pyrethroids, Poultry, Farming, Pesticides, Residues, Chicken, Cypermethrin*

## I. POULTRY FARMING VERSUS INSECTS

Poultry farming nowadays is considered an agricultural activity of global importance, both for domestic and international trade (protein from: fresh and processed meat). The world chicken production reached 88.010 million tons in 2015 (USDA / ABPA, 2016). A major problem facing the poultry farming is the presence of insects such as beetles (*Alphitobius diaperinus* Panzer), flies (*Musca domestica* L.) and booklice (*Liposcelis sp.*), including also mites (*Dermanyssus gallinae* L.) infestation (allergies) (Nayak et al., 2014; Feo et al., 2012; Soares et al., 2017). Their presence is a problem safety wise, as they can affect chicken health and well-being (Lambkin et al., 2007; Chernaki-Leffer et al., 2001; Banjo et al., 2005). Once infestations get established in the poultry environment, they are almost impossible to eradicate. Those living organisms find in the poultry shed facilities, the proper nutrients that serve as substrates for their development and accommodation (Soares et al., 2018). Insects and mites presence means chicken health problems, performance alterations and serious financial losses (Lorini, 2015; Singh et al., 2010; Oviedo-Rondon, 2008). Their control depends mainly upon pesticide

applications of the Pyrethroid Group (Macan et al., 2005; Marangi et al., 2012).

## II. INSECTICIDES APPLICATIONS DURING POULTRY PRODUCTION

Therefore, the poultry production sectors, have adopted insects' control procedures by applying mainly insecticides from the Pyrethroids Group (Figure 1; Table 1) That application includes both, the poultry sheds' environment (roofs, floor, screens and/or curtains) and the aviary beds' (each 45 days of whole chicken growth cycle, or intermittent) to control undesirable insects mainly *A. diaperinus* Panzer (Hays and Laws, 1991; Benabdeljelil and Ayachi, 1996; Kirb, 2013). Those pyrethroids are known and currently in used to control the vectors of diseases (fungi, viruses, bacteria) in tropical and temperate climates (Neal et al., 2010; Hilbert et al., 2012; Wales, et al., 2010).

It is important that the pesticide application techniques are really effective. Otherwise, they can lead either to resistance or just do not kill part of them. An example is a spraying technique in the poultry farm that can reach only the shed's /aviary bed surfaces. It can be ineffective, as some insects (their larvae/eggs) keep ridden (mainly in day time) in the soil first layers. In addition, their incorrect application either concentration and/or repetition can favor development of resistant population infestations. The aviary bed alkalinity can also play a role on insecticide ineffectiveness as it leads to the product active ingredient destabilization (Geden et al., 2008; Chernaki-Leffer, 2004; Soares, 2018; Soares et al., 2018).

Regarding the poultry farming environment and the worker's well-being, the insecticides applied systematically in this environment can contaminate, apart from the animals themselves, also the workers. Indeed, the use of pyrethroids without control may increase the risk of both, their presence in the food (meat) and in the environment, including the wildlife (birds, insects, and mammals) (Parente et al., 2017; Montanha and Pimpão, 2012).

We gathered here information regarding the insecticide from the Pyrethroid Group characteristics, their toxicity, international regulation, exposure and residue in meat & environment reported in the literature to date, with emphasis on cypermethrin (CPM – Figure 2).

### III. PYRETHROIDS GROUP INSECTICIDES

Pyrethroid's name is derived from the pyrethrum, extracted from the flowers of *Chrysanthemum cinerariaefolium* (Figure 1a). It has been utilized since 1800 in Persia and the former Yugoslavia. It began to be processed commercially for insect control in 1828. Figure 1b shows pyrethrin (the active substance contained in the pyrethrum extracts), isolated as esters from the *Chrysanthemum* species and Figure 1c the chrysanthemic acid. Pyrethrum became the main source of domestic insecticides with the mosquito coils (1895) and sprays in the USA (1919), also as oil-based preparations (1924) in Japan.

At a later time, the insecticide ingredients changed from pyrethrins to synthetic pyrethroids (Katsuda, 2011).

Some pyrethroids, such as CPM is utilized in several agricultural commodities, more specifically in crops such as corn, soybean, rice and tobacco (MAPA, 2010; FAO, 2018; USDA, 2017). All those cultures have been present in the diets of chicken, and also are often part of the activities within the agricultural property as a source of income (Chernaki-Leffer et al., 2013). Depending on the poultry environment infestation, CPM application may be *short* (isolated - only once), *intermittent* (with intervals - between batches applications) or *frequent* (every single 45 days – whole chicken growth cycle) (Soares, 2018; Soares et al., 2018). There is currently no other insecticide reported in the literature that has contributed so successfully for the control of several different pests as pyrethroids (Abbas et al., 2015; Jardim & Caldas 2012; Rezende et al. 2013; Del Rio et al. (2014).

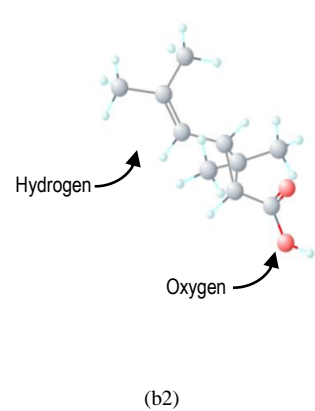
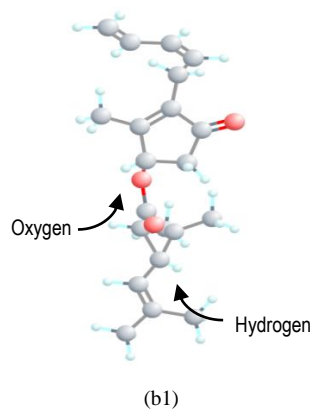


Figure 1. PYRETHROIDS (a) origin – flowers of *Chrysanthemum cinerariaefolium* and (b) chemical structures of (b.1) pyrethrin; (b.2) chrysanthemic acid (Shawkat et al., 2011; Pubchem, 2018)

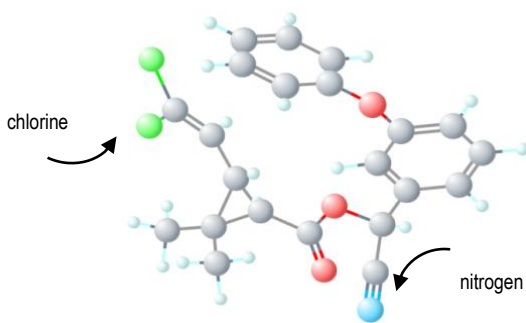


Figure 2. Chemical structure of the pyrethroid group insecticide - CYPERMETHRIN (Worjhing, 1987)

#### A. Active ingredients and physicochemical characteristics

Pyrethroids are classified according to their physical properties (also toxicological effects) in *Type I* (allethrin, benfethrin, pyrethrin, permethrin, tetramethrin) and *Type II* (CPM, cifluthrin, deltamethrin, fenprothrin, fenvalerate) (Todd, 2001; FDA, 2017). Table 1 presents the chemical structures of Types *I* & *II* pyrethroids and their applications (agricultural and domestic).

They are highly stable light crystals of different colors (from yellowish to brown), odorless, acid hydrolysis resistant, low water solubility, viscous and are semi-solid at room temperature. They are identified by application as for: (a) *domestic use* (internal and external) and (b) *external use*

(agricultural and sanitary pests control) focusing on their photo-stability (Crawford et al.,1981; Katsuda, 2011; Biondi et al., 2015). CPM, is one of the pyrethroid pesticides, acknowledged by the World Health Organization (WHO, 2018), even if presenting moderate acute public health toxicity (Figure 2). It is applied in agricultural and also in domestic environments for pest control (Hebeish, 2010). It is a

synthetic pyrethroid insecticide, utilized to control flies and beetles which can transmit bacterial, viral and fungal diseases to chickens. It is used also for control of mites that can eat the birds' blood and casually bite mammals, including humans, transmitting pruritic dermatitis to poultry farmers (Chauve 1998; McAllister et al., 1995; Hald et al 2004; Khan et al., 2017).

TABLE I. PYRETHROIDS TYPES I AND II CHEMICAL STRUCTURES, THEIR APPLICATION AND TOXICOLOGICAL CLASSES

Active ingredient	Chemical esturture	Application	Toxicological Class*
Type I			
Alethrin		Domestic	III
Byfenthrin		Agricultural Domestic	II
Pyrethrin		Domestic	III
Permethrin		Agricultural Domestic	III
Tetramethrin		Domestic	III
Type II			
Cypermethrin		Agricultural Domestic	II
Cyfluthrin		Agricultural Domestic	II
Deltamethrin		Agricultural Domestic	III
Fenpropathrin		Agricultural Domestic	II
Fenvalerate		Domestic	II

Class II and III: very hazardous and dangerous, respectively (FAO/WHO, 2004, IBAMA, 2009)

### B. Toxicity for animal and humans

As insects and humans are organisms that have nervous systems, the pyrethroids with high insecticidal potency, can be also highly toxic for humans (Júnior, 2003; Mori, 2012). The main pyrethroids are classified according to their effect intensity as *Class II* (bifenthrin, CPM, cyfluthrin, fenpropathrin and fenvalerate) and *Class III* (allethrin,

pyrethrin, permethrin, tetramethrin, deltamethrin and cyhalothrin,) (FAO, 2016; ANVISA, 2018). That means *Class II*: very hazardous and *III*: dangerous (FAO, 2003).

In mammals, pyrethroids of (*a*) *Type 1* - act on the sodium channels of the nerve filaments, shortening the depolarization phase (ion permeability). The opening stage of the channels is prolonged causing the cell to positively polarize (by

suppressing the refractive period), promoting repetitive neural-firing in a single stimulus. The pyrethroid intoxication causes the T-syndrome (tremor) by altering the behavior and sensitivity to external stimuli causing tremor and can lead to death (Romanini, 2011). On the other hand, pyrethroids (*b*) *Type II* - diminishes the action power amplitude by prolonging the opening of the sodium channels. Depending on the doses there is a total block of neural activity due to membrane depolarization, being responsible for the symptomatology of intoxication - the CS syndrome. It causes choreoathetosis and profuse salivation. It is characterized by the behavior of

digging, burrowing, hyper salivation, tremors and motor incoordination (Ray, 1979; Righi, 2003; Clark and Smington, 2012).

It is noteworthy that both, small and large animals have similar symptoms for both pyrethroids *Types I and II*: salivation, vomiting, weakness, convulsions, dyspnea, tremors, prostration and death (de Souza, 2010). Despite that, poultry seems to be somewhat resistant (via oral), different of fish and bees. Tables 2 show the animals CPM lethal doses (LD<sub>50</sub>) for oral & dermal exposure, respectively.

TABLE II. CYPERMETHRIN LETHAL DOSES FOR POULTRY AND OTHER ANIMALS

Animals	LD <sub>50</sub> (µg.g <sup>-1</sup> )	
	Oral	Dermal
Poultry		
Chicken	2000	NI
Duck ( <i>Mallard</i> )	10,000	NI
Others		
Honey bee	0.023-0.56 µg/bee	NI
Rainbow trout	0.00082/trout	NI
Rabbit	NI	2,460
Rat (male/female)	247/ 309	NI

NI: not informed (Delabie et al.,1985; Jones, 1995; EPA, 2006, 2009)

By *ingestion* and/or *inhalation*: pyrethroids can cause in mammals and birds intoxications at different degrees (acute, subacute and chronic). Depending on the exposure time and insecticide concentration, the symptoms include dyspnoea, motor incoordination, hyperexcitability, hypersalivation, sore throat, paresthesia, tremors, uncomfortable eye sensations, nausea, and shortness of breath at the time or days after exposure and to death in some animals (Lessenger, 1992; Righi and Palermo-Neto, 2003; de Souza, 2010; Spinosa, 2010).

Regarding *absorption* (cypermethrin), most pyrethroids are lipophilic substances of rapid absorption by *dermal*, *oral* and *respiratory*. Their biotransformation happens rapidly in the gastro intestinal tract. The main adverse effect by dermal exposure by pyrethroids is paresthesia (burning and numbness) due to hyperactivity of the sensory nerve fibers of the skin. There are cases of facial paraesthesia in workers who have been exposed to CPM associated with erythema (vasodilation of cutaneous capillaries) related to scratches and frictions due to symptoms (Spinosa, 2010; Perkins et al., 2016).

The neuroexcitatory symptoms of acute pyrethroid poisoning are related to the ability of these insecticides to alter electrical activity at various sites of the nervous system. Quasi-lethal doses of pyrethroids cause axonal lesions, however, in surviving animals, this damage is reversed. Occupational exposure often leads to paraesthesia and respiratory irritation, which is probably due to repetitive firing of sensory nerve

endings (Vijverberg and VandenBercken, 1990; Siegfried, 1993; Wilks, 2000; Lee et al. 2015).

*In vivo* and *in vitro* tests indicate that *Types I and II* pyrethroids are able to induce chromosomal damage. In addition, they affect the cell cycle in humans (*in vitro*) by reducing proliferative rate index (Puig et al., 1989).

### C. Ecotoxicity and bioaccumulation

Regarding the effects on ecosystem, pyrethroids are highly toxic to birds, bees and the aquatic life. Despite that, the levels of toxicity vary quite widely among them. Table 2 shows the variation of CPM lethal doses for different animals, including wild ducks, honey bees, rainbow trout, rats and rabbits. For mallard ducks the oral LD<sub>50</sub> is as high as 10,000 µg.g<sup>-1</sup>, the opposite is for chicken/birds with only 2000 µg.g<sup>-1</sup>. Regarding rainbow trouts, they are quite sensitive (0.00082 µg/trout) (Delabie et al, 1985; Jones, 1995, EPA, 2006, 2009).

Pyrethroids cause serious environmental damages, as they are very persistent, accumulative and easily dispersed (Rafiq and Tariq 2015; Corcellas et al., 2017). Several research studies have reported the presence of CPM in the environment (rivers, rainwater and groundwater), thus reaching food of animal origin (milk, meat, honey) and vegetables (leaves, fruits, tubers) for human consumption inclusive reaching high levels. Indeed, *in vitro* studies corroborate their bioaccumulation in different animal tissues. In a study by Saleh et al. (1986) using doses (10 µg.g<sup>-1</sup>) of pyrethroid

insecticides (CPM and fenvalerate) in laying hens, their presence was observed more in the brain than in other tissues (skin, egg, fat, kidneys and heart). An *in vitro* study with laying hens, after continuous beta-CPM exposure authors registered accumulation in the eggs (also in the blood and droppings) (Liu et al., 2017). In aquatic mammals (dolphins) at different ages (adults and pups), Alonso et al. registered pyrethroids concentrations in their liver, milk and placenta. Authors

observed that CPM was transferred also to fetus via the gestational route (Alonso et al., 2012). Neelima et al., reported an increase in the activity of transaminase enzymes, a stress indicator in fish (*Cirrhinus rigala*) raised in the laboratory under pyrethroids exposure (Neelima et al., 2015). Tables 3 and 4 show the maximum limits and residues detected in the environment, including food matrices.



Figure 3. INSECTS infestation on the: (a) poultry farming structures - wooden pillar & floor (*Alphitobius diaperinus* - adult beetles); (b) feeders – *A. diaperinus* (beetles - adult & larvae); and (c) animals – carcass & affected chick (*Musca domestica* L. - flies) (Soares et al., 2018).

#### IV. EXPOSURE TO PYRETHROIDS

Exposure to pyrethroids can occur *directly* - during product handling (atomizer, spray or haul) at occupational activities / incorrect used (overdoses) and *indirectly* - by contact (dermal, eyes), ingestion (foods contamination - residues) and /or through inhalation (environment) (Spinosa, 2010). Inclusive it can occur by drinking contaminated water, as their have been detected in water's surface worldwide and in rainwater (Laabs et al., 2002).

##### A. Exposure effects

Regarding *animals* CPM acts in a harmful manner in exposed broiler chicks (*Gallus domesticus*), giving rise to malformations and preventing the complete development of the birds, compromising the eyes, feet, wings and feathers (Anwar, 2003). By spraying a compound containing CPM and chlorpyrifos, Ong et al. (2016) demonstrated a half-time of 3.75 days for the degradation of CPM and recommended a 7 days interval. In rabbits treated with CPM authors have reported injuries in the liver and kidneys with symptoms such as muscle tremors, reducing food intake, depression and licking (of different body parts). In addition, reduction of the progesterone hormone in females submitted to reproduction (Hasan et al 2016 ; Sallam et al 2015). According to Elbetieha et al., the exposure by ingestion of CPM for a certain period reduced the number of viable fetuses in rats. Body weight gain, sperm production, and testosterone production in adult males were also reduced (Elbetieha et al., 2001). Studies have indicated that when administered to pregnant and lactating rats, CPM can lead to genotoxicity and also neurotoxicity by delaying functional development in the brain in pups (Suman, et al., 2006).

As far as *humans* exposure is concerned, the absence of personal protective equipment, erroneous dilutions and overdose exposure, lead to occupational and/or accidental intoxication humans (de Araújo et al. 2007). The use of synthetic pyrethroid pesticides can lead workers, applicators and ecosystems to their toxic effects exposure (Polat et al., 2002; El-Sayed , Saad, 2007; Osti et al., 2007; Velisek et al., 2007). *In vitro* experiments on human lymphocytes indicated that the CPM cytotoxic effects are doses dependent (Corsini et al., 2013). Cell viability was reduced by increasing the pesticide concentration. Hanke et al. (2003) observed that the exposure to pyrethroids during pregnancy is associated with low birth weight and several authors reported synaptic disorders in the sodium, calcium and chloride channels in the membranes (Narahashi, 1996; Soderlund et al., 2003; Lee et al., 2015). The Environmental Protection Agency (EPA) published a comprehensive paper on the *developmental neurotoxicity* (DNTs) effects of pyrethroids from the public health information (EPA, 2010).

##### B. Occupational hazard

Reports worldwide (Brazil, China, Colombia, Egypt, Italy, Spain, Philippines, USA, among others) have registered

pyrethroids occupational hazard effects on different workers (Chen et al,1991; IBAMA, 2009; Rebelo et al., 2011; Costa et al., 2013; Singleton et al., 2014).

In *China*, a survey conducted by Chen et al, authors highlighted acute pyrethroid intoxication of cotton growers. Out of 3,113 workers (2230 males - 71.6% and 883 females - 28.4%), 26.8% showed abnormal sensations in the face, dizziness, headache, fatigue, nausea and loss of appetite. Ten of them, who developed significant systemic symptoms of apathy or muscle contraction, were diagnosed as pyrethroids acute occupational poisoning. The compounds concentrations in the air, skin and urine showed that skin contamination was the main pyrethroids route of exposure (Chen et al., 1991). Also, a study carried out in *Egypt* through consecutive CPM applications in cotton fields, authors characterized CPM occupational exposure in the agricultural workers either before, during and after that insecticide application. The results showed higher levels of CPM metabolites in urine of those workers compared to other workers such as technicians and engineers (Singleton et al., 2014).

In *Italy* 30 workers in greenhouses occupational activities which were exposed to a CPM, had their pro-inflammatory cytokine levels significantly affected. The cytokine plays important role against cancer and infections. The results showed that the immune system was sensitive to that pesticide (Costa et al., 2013; Corsini et al., 2013). In addition, *Philippines* farmers and the agricultural workers were reported with health problems such as: tiredness, vomiting, weakness, rash, dizziness, nausea, burning sensations in the throat, breathing after applying CPM in their eggplant crops (Del Prado Lu, 2014; Lu and Cosca, 2010).

Regarding also occupational CPM hazard, in a study carried out in *USA*, 5 poisoning cases were reported when the pesticide was improperly introduced into the air-conditioning ducts leading patients to inhale it. The exposed patients had nausea, shortness of breath, headaches, and irritability (Lessenger, 1992). In *Brazil*, studies around the country show the problems caused by exposure of pyrethroid pesticides. In Nova Friburgo (Rio de Janeiro state), 102 farmers who applied pyrethroids in different crops, complained of related symptoms (sweating, hypersalivation, tearing, headache, coryza, nausea, spasms and abdominal cramps), including insomnia, anxiety and irritability (Araújo et al., 2007). Other studies carried out in Mato Grosso do Sul state and Brasilia (country's capital) also reported pyrethroids (CPM or deltamethrin) being responsible for 60% of intoxications (in domestic and rural areas) (Rebelo et al., 2011; Pires, 2005). In a study by Corcellas et al. carried in countries from south America (*Brazil, Colombia*) and Europe (*Spain*) from urban, rural and industrial areas, authors reported CPM bioaccumulation in human milk, contradicting studies reporting that all pyrethroids are metabolized by hydrolysis in mammals (Corcellas et al., 2012).

## V. REGULATION FOR PYRETHOIDS RESIDUES IN CHICKEN MEAT

Several countries such as Brazil, China, European Union, Japan, United States, among others, have established residue limits for pesticides including pyrethroids use in food and feed. They are represented as the pesticide maximum residue level (MRL) i.e., the maximum amount of contaminant accepted after adequate application (production to consumption), expressed as contaminant per million parts of food/feed (ppm or mg.kg<sup>-1</sup>) (MAPA, 2002; FAO, 2018). The MRL is established to inform that not all chemical compounds leave residues that can be harmful to the animals and human health. When they exceed the concentration limit, they become harmful according to FAO (2018). Table 3 presents the MRL of pyrethroid insecticides Type II established by different countries (Brazil, Japan, European Union - EU, United States of America – USA) and FAO for chicken meat. Some of them established similar MRLs for different pyrethroids compounds.

The EU set pyrethroids MRLs for a wide variety of products from vegetables and animal origin intended for

human consumption, including chicken meat through the EC396/2005 (EFSA, 2011). It established residue levels of 0.02, 0.05, 0.02 and 0.02 µg.g<sup>-1</sup> for cyfluthrin, CPM, deltamethrin, and fenvalerate, respectively for chicken meat (Table 3).

Regarding USA, the US Department of Agriculture which plays a key role in food security, set for CPM and deltamethrin MRLs of 0.05 and 0.02 µg.g<sup>-1</sup>, respectively. Fenvalerate (0.1 µg.g<sup>-1</sup>) has the lowest MRL in chicken meat according to the Japan Food Chemical Research Foundation (JFCRF, 2018). CPM (0.05 µg.g<sup>-1</sup>) has similar values to other countries mentioned in Table 3. In Brazil, a high chicken meat producing country, monitoring programs for meat residues has been set since 2008 by the Ministry of Agriculture (MAPA, 2008). However, specifically for CPM, it was introduced much later in 2015 (MAPA, 2015). In the same year, the Ministry of Health set similar MRLs for CPM and deltamethrin 0.05 and 0.01 µg.g<sup>-1</sup> for chicken meat tissue (ANVISA, 2018).

TABLE III. MAXIMUM RESIDUE LEVELS OF PYRETHROID INSECTICIDES TYPE II ESTABLISHED BY DIFFERENT COUNTRIES FOR CHICKEN MEAT

Country	Pyrethroids Type II MRL (µg.g <sup>-1</sup> )			
	Cyfluthrin	Cypermethrin	Deltamethrin	Fenvalerate
Brazil	0.02	0.05	0.01	0.02
European Union	0.02	0.05	0.02	0.02
Japan	0.02	0.05	0.04	0.10
United States	0.01	0.05	0.02	NT*
FAO/WHO	0.01	0.10	0.10	NI**

\* no tolerance \*\* not informed (FAO/WHO 2018; EC, 2018; JFCRF, 2018; ANVISA, 2018)

## VI. RESIDUES IN CHICKEN MEAT, MILK AND OTHERS

### A. Contaminant residues in food

Contamination during broiler rearing and further residues may occur either from the (a) environment in which animals are grown or by the (b) chicken themselves (ingestion/absorption) to the final product (meat / edible viscera). That contamination may come from the growth control program for living organisms (insects, fungi) that may develop in the environment (facilities), or by the insecticides application (before and during the period of use of the aviary bed for different rearing plots of chickens) - pest prevention and control (Spinosa, 2010; Soares et al., 2018).

As far as pyrethroids residues in food proteins are concerned, ca. 100% of samples (milk, liver, fish) reported worldwide (Brazil, China, Egypt, Italy, Pakistan, Vietinan) contamination by CPM (Table 4). Despite that, some studies reported a rather low (3/4, 4/4, 10/10, respectively) total numbers of samples analyzed (Sassine et al., 2004; Rezende et al., 2013; Hoai et al., 2011). Regarding chicken meat and their

viscera (liver/kidney) pyrethroids (CPM and permethrin - PRM) residues levels detected, varied among them from as low as 0.006 to 3.9 µg.g<sup>-1</sup> (Saleh et al., 1986; Silva et al., 2007; Marangi et al 2012). Important to emphasize that, in a study carried out by Silva et al, CPM levels were detected below the recommended maximum limit (0.05 µg.g<sup>-1</sup>) in the meat of broilers which was considered safe and also that the degradation took place in due time (Silva et al., 2007). Regarding PRM residues, they were also found in other tissues (fat and liver) of laying hens (0.006-0.012). Those residues were derived from acaricides applications during the egg production cycle (Marangi, et al.2012).

Regarding dairy products, they may also contain CPM residues, due to its use for control of external parasites in animals and farms. In a study carried out by Sassine et al. detected from 0.074 to 0.16 µg.ml<sup>-1</sup> in milk (Sassine et al., 2004). Evaluating the persistence of alpha-CPM (α-CPM) residues in lactating donkey milk, the authors found that after α-CPM application, residues of that compound were found in the milk even after a few hours later (Chirollo et al.2014).

## B. Contaminant residues in the environment

As far as the environment (water, soil) is concerned, when the pesticide is applied, only 1% reaches the target (insects), while 99% is dispersed around them (Pimentel and Teixeira, 2012). Regarding water (rain e well), Moreira et al. evaluated CPM and PRM residues and reported positives 5.8%(5) samples out of 104 total species of birds with diets based on anthropogenic foods are susceptible to pesticide contamination of the Pyrethroid Group. A study by Lu and Cosca (2011) reported the presence of CPM residues in 2.7/73 of soil samples (3.8%) with levels ranging from 0.005-0.002  $\mu\text{g}\cdot\text{g}^{-1}$ . 3.8% from agricultural areas in Benguet province, Philippines Corcellas et al. (2017) reported CPM in 77% of wild birds egg samples (0.149-0.162  $\mu\text{g}\cdot\text{g}^{-1}$ ).

## VII. METHODOLOGY FOR PYRETHROIDS DETERMINATION

Several chromatographic techniques and detection have been used for the determination and quantification of pyrethroid residues in different food matrices (Table 4). They are mainly by gas chromatography (GC) (Sassine et al., 2004; Pitella., 2009; Hoai et al., 2011; Rezende et al., 2013; Yuan et al., 2014; Corcellas et al., 2017). However, some studies have reported pyrethroids analysis by liquid chromatography (LC) and also ultra high (UH) LC (Marangi et al., 2012; Chirollo et al., 2014; Jabeen et al., 2015; Ong et al., 2016). Both GC and LC utilize different detectors such as electron capture and mass (MS).

Despite the chromatographic techniques, the detector most recommended nowadays is the MS in the series detector (Tandem MS/MS), as it offers increased sensitivity and provides additional information (Alonso et al., 2012). They can be very sensitive, reaching limit of detection down to 0.00005  $\mu\text{g}\cdot\text{g}^{-1}$  (Scussel et al., 2014; Tonon et al., 2017). Some more sophisticated chromatography techniques (UHPLC-MS/MS) are being used mainly for multi-pesticide analysis. Table 4 presents also details of limit detection and quantification as well as the concentration levels in different biological matrices.

Several food matrices can be used either for food (meat, milk, honey, among others) and environment (water, manure, wild animals) in order to detect and quantify pyrethroid. They can be applied also in studies involving insecticides degradation in poultry manure spread in the poultry farms areas (Ong et al., 2016). Authors demonstrated through UHPLC-MS analysis the CPM lifetime of 3.75 days in the poultry feces/manure. This helps to design a sustainable control of pesticides in the poultry environment (Zhang et al. 2010; Chirollo et al. 2014; Ong et al., 2015; Tette et al., 2016).

Extraction techniques, such as centrifugation, liquid-liquid partitioning, gel permeation, solid phase dispersion, solid phase extraction and microextraction are the sample preparation applied for pesticides residues (Zang et al., 2008; Santos et al., 2008; Gullick et al., 2016; Scussel et al., 2014; Tonon et al 2017).

## VIII. PYRETHROIDS DEGRADATION

### A. By environment conditions and time

Several authors have reported the pyrethroids residues in different crops and their food products (Queiroz, 2001). However, with the allowed insecticides application (at recommended levels) occurs, residues are not expected to be present/detected as they suffer degradation (Santos et al., 2008). Their degradation depends upon several factors such as the ultraviolet light exposure, high temperature (solar radiation), humidity (hydrolysis), air/oxygen (oxidation), which can lead to their total destruction (Laskowski, 2002). Physical, biological and chemical processes of soil biota and environment factors should be taken into account to regarding biodegradation (Sharma et al., 2016; Akbar et al., 2016). Pesticides degradation often involves the formulation where essential oils with repellent and insecticidal action are inserted (Soonwera et al., 2015; Testa et al., 2018).

### B. By oxidative agents

The application of ozone gas has been utilized in the human and veterinary medicine to inactivate bacteria, viruses, fungi, stimulate oxygen metabolism and treatment of injuries (Sharma et al., 2004; Skov et al., 2004). It also removes contaminants present in ground- and surface-waters (Lu and Cosca, 2011; Moreira et al., 2012). Industries use as an effective tool for the controlled living organisms including insects (*Tribolium* and *Oryzaephilus*) and fungi (*Aspergillus*, *Fusarium*, and *Penicillium*) as well as toxins and pesticide (Chen et al., Saenz et al., 1994; Beber et al., 2016; Christ et al., 2017). Regarding pyrethroids degradation by ozone, Savi et al. (2014) highlighted its effectiveness on pyrethroids, more specifically deltamethrin, and bifenthrin. Authors reported the need for more studies regarding ozone large installations application (Christ et al., 2016; 2017).

## IX. CONCLUSION

Pyrethroids have been allowed worldwide as insecticides in the poultry farming activities, especially when animals are raised in the intensive-systems. Those pesticides in the poultry production chain became another route to food (chicken/meat) contamination apart from those applied to the crops during vegetable development.

As pyrethroids are classified by of toxicological properties as *Class II* and *III* (very hazardous and dangerous, respectively), care should be taken into account regarding their toxic effects to animals and humans.

Among the pyrethroids compounds, CMP followed by PRM are the main products applied with from toxic effect of includes nausea, paresthesia, tremors. Despite that, only a few studies have investigated CPM residues in poultry meat.

Workers poultry farming activities workers are increasingly exposed to pyrethroids and they must protect themselves by using EPIs. Effective safety equipment are expensive, leading to inaccessibility to them. In addition, the equipment is often



impregnated with the toxic substances exposing them (by contact) even more to the pesticide.

Regarding aviary beds, regions with high concentration of poultry farming activities generate a huge volume of aviary beds discard. When their destination is to be re-used as fertilizer, they may contaminate the soil and crops due to the pyrethroids pesticides residues used during poultry breeding.

They can get back to farms by the aviary bed when re-used, exposing workers, vegetables, and further food consumers. The presence of pesticide residues of the Pyrethroid Group in animal tissues during pregnancy exposes a serious public health problem. Considering that the control using chemical insecticides can lead to residues in poultry meat, it shows the need to search for *green* alternatives to control these insects.

TABLE IV. RESIDUES OF INSECTICIDES FROM THE PYRETHROIDS GROUP REPORTED IN FOOD AND THE ENVIRONMENT FROM DIFFERENT COUNTRIES.

Sample			Pyrethroid	Contaminated samples			Methodology of analysis			Reference
Origin Country	Year	Type		Positive/total	(%)	Concentration ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Detection	LOD <sup>a</sup> ( $\mu\text{g}\cdot\text{g}^{-1}$ )	LOQ <sup>b</sup> ( $\mu\text{g}\cdot\text{g}^{-1}$ )	
FOOD										
Brazil	2004	Milk	CPM <sup>c</sup>	3/4	100	0.074 - 0.168*	GC <sup>e</sup> /MS	33	NI <sup>d</sup>	Sassine et al., 2004
	2006	Meat (chicken)	CPM	NA <sup>f</sup>	NA	NA	GC/MS <sup>g</sup>	NI	0.05	Silva et al., 2007
	2008	Liver (cattle)	CPM	4/4	100	0.010 - 0.025	GCMS	0.005	0.432.9 – 0.126.7	Resende et al., 2013
	2009	Honey	CPM	8/46	17	NI	GC/MS	0.0004 - 0.0013	0.014 - 0.0608	Pitella, 2009
China	2013	Vegetables	CPM	7/17	41.17	0.01-1.83	GC/MS	NI	NI	Yuan et al., 2014
Italy	2012	Meat (chicken)	PRM	4/225	1.7	0.006-0.012	LC/MS <sup>j</sup>	NI	NI	Marangiet al., 2012
Pakistan	2014	Fish	CPM & DLT <sup>l</sup>	3/9	33	0.141-0.197	LC/MS	NI	NI	Jabeenet al., 2015
Vietnam	2011	Fish	CPM	10/10	100	0.109-0.802	GC/MS	NI	NI	Hoaiet al., 2011
	2013	Milk (donkey's)	CPM	5/7	71	ND-0.0055	UHPLC/MS	NI	NI	Chirollo et al., 2014
Egypt	1986	Tissue <sup>**</sup> (chicken)	CPM & FEN <sup>m</sup>	NI	NI	0.03-3.9	GC/ECD <sup>n</sup>	NI	NI	Saleh et al., 1986
Environment										
Brazil	2012	Liver (dolphins)	CPM & PRM <sup>i</sup>	23/23	100	0.011-0.605	GC/MS/MS <sup>h</sup>	0.11	0.037	Alonso et al., 2012
	2012	Water (rain e well)	CPM & PRM	5/104	4.8	0.00002-0.00005*	GC/MS	NI	NI	Moreira et al., 2012
Espanha	2017	Eggs (wild bird)	CPM	270/360	77	0.149-0.162	GC/MS	0.030-0.046	0.01-0.0145	Corcellas et al., 2017
malaysia	2016	Poultry (manure)	CPM	5/5	100	0.01- 0.02	UHPLC <sup>k</sup> /MS	NI	NI	Ong et al., 2016
Philippines	2011	Soil	CPM	2.7/73	3.8	0.005-0.002	NI	0.002	NI	Lu and Cosca, 2010

a) detection limit b) Limit of quantification c) cypermethrin d) not informed e) gas chromatography f) not applicable g) mass spectrometry h) mass<sup>b</sup> spectrometry i) permethrin j) liquid chromatography/mass spectrometry k) ultra-performance liquid chromatography l) deltamethrin m) fenvalerate n) electron capture detector \*  $\mu\text{g}\cdot\text{ml}^{-1}$  \*\* fat/liver/kidney/heart/egg

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