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Evaluation of pesticide residues in honey from different geographic regions of Colombia

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ABSTRACT

To assess potential exposure of bees to chemicals contaminants, pesticides and other management practices of local beekeepers and farmers, four Colombian regions were surveyed and residue concentrations were determined on some pesticides used and others banned for honey. A total of 61 honey samples were collected and analyzed during 2011. Residual levels of selected insecticides, fungicides and acaricides were determined by a multiresidue method, using gas chromatography with nitrogen phosphorous detector/micro electron capture detector for the analysis and gas chromatography coupled to mass spectrometry detector to confirmation. In this study, pesticide residues were identified in 32 samples (52.4% incidence), where organochlorine and organophosphorus pesticides were frequently found. The main detected compounds were chlorpyrifos (36.1% incidence), followed by profenofos (16.4% incidence), DDT (6.6% incidence), HCB, γ-HCH (4.9% incidence) and fenitrothion (1.6% incidence).

However, the found concentrations found were low and just 4.9% of the samples exceeded the MRL concentration established in Regulation (EC) No 396/2005 by European Parliament. According to the survey results, it is highly probable that the honey contamination produced in Colombia beekeeping regions under study, is caused by agricultural practices developed around of the hives installed.

1. Introduction

Honey is a natural product of bees and is recognized as a food with nutritional properties and is known like a food with valuable therapeutic applications. Most of the honey is produced by domesticated bees (*Apis mellifera* L.) from the nectar of flowers or from the sugar secretions from the leaves of arboreal essence. Honey is composed primarily of carbohydrates, proteins, minerals, vitamins and other substances, but its composition mainly depends on the floral origin of the nectar (Ball, 2007).

However, bee products can also be a source of toxic substances, such as antibiotics, pesticides and heavy metals due to environmental pollution and misuse of beekeeping practices. Honey bees collect pollen and nectar from the surrounding flowers (over very large areas) and then they may return to hives collecting significant amounts of toxic contaminants, therefore their hives and products can result contaminated with many different kinds of pollutants (Bogdanov, Imdorf, Charrière, Fluri, & Kilchenmann, 2003; Morgano et al., 2010; vanEngelsdorp & Meixner, 2010). At environmental level, honey bees pick contaminants through a wide range of pathways: (i) by consumption of pollen and contaminated nectar, (ii) by contact with plants and soil from crops in which farmers apply pesticides (iii) by inhalation during flight and recollection, (iv) by ingestion of polluted surface water and also (v) by direct overspray or flying through spray drift, among others (Bogdanov, 2006; Colin et al., 2004). Thus, some studies related to the presence of contaminants in samples from the bees' products, provide information about the environmental compartments near to the hives and can serve to indicate anomalies in the environment in time and space (Conti & Botrè, 2001). In addition the honeybees are also exposed to pesticides and antibiotics administered by beekeepers as part of the hive to control some infestations such as *Varroa destructor*, *Acarapis woodi* and *Paenibacillus larvae* (Fell & Cobb, 2009; Genersch, Evans, & Fries, 2010); unfortunately the

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Table 1
Pesticide residues reported most frequently in honey.

Pesticides	Concentration μg/kg	Country of origin of honey
Organohalogens	0.1–4310	Brazil, Turkey, Spain, Portugal and India.
Organophosphates	2.4–243	Brazil, China, France, India, Portugal, Spain and Turkey.
Organonitrogen	0.05–116	Brazil, Belgium and France.
Pyrethroids	1–92	Brazil, China, India and Poland.
Carbamates	1–645	China, Portugal and Spain.

conventional commercial beekeepers frequently apply agrochemicals whether there are healthy or sick bees (Blacquière, Smagghe, Gestel, & Mommaerts, 2012; Kevan, 1999), therefore, the presence of pesticides and antibiotics in bees' products has become commonplace. Due to this situation, the European Union has established maximum residue limits (MRLs) for a large number of pesticides used in agricultural and beekeeping practices, through the Regulation (EC) No 396/2005.

Pesticides in both bees and in bees' products have been the subject of many studies, in recent years the presence of pesticide residues in honey were determined in some countries such as Belgium (Pirarda et al., 2007), Brazil (Rissato, Galhiane, de Almeida, Gerenutti, & Apon, 2007), China (Jin et al., 2006), France (Wiest et al., 2011), India (Choudhary & Sharma, 2008), Poland (Bargańska, Ślebioda, & Namieśnik, 2013), Portugal and Spain (Blasco et al., 2003), and Turkey (Erdogrul, 2007). Table 1 shows the commonly reported pesticide residues in honey produced in these countries.

It is noteworthy that in most of these studies the pesticide detected/quantified do not present a risk to human health but in many cases whether they pose a risk to bees. Finally in Colombia there is only one published study about the development of a method for pesticide residues determination in bees products, specifically in bee pollen (Rodriguez, Díaz, Zamudio, & Ahumada, 2012).

The lack of information about pesticide residues in honey in Colombia implies the necessity to determinate the pollution of those bees' products in the country. In that way, the aims of this study were to (1) identify currently used pesticides and common pesticide management practices through interviews for beekeepers, (2) validate a multiresidue analysis method based on a liquid–liquid extraction followed by clean up with a classic chromatographic column, and (3) assess the presence of residues of selected currently applied pesticides and some widely used and/or persistent in the nearly areas at four honey productive areas in Colombia.

2. Materials and methods

2.1. Study locations

During 2011, a total of 61 samples of multifloral honey were collected from individual beekeepers in four regions of Colombia: Cundinamarca, Boyacá, Santander and Magdalena states; the geographical position of the regions is shown in Fig. 1. These states represent about 50% of honey production in the country and 35% of the population of beekeepers identified by the Ministry of Agriculture and Rural Development of Colombia (Martínez, 2006).

Upon collection, all honey samples were placed into clean glass bottles, labeled, placed in an ice-chest kept at 4 °C, transferred to the laboratory and kept at −20 °C until analysis. The sample size was at least 500 g and the minimum weight was 250 g.

2.2. Identification of pesticides

The beekeepers and farmers (around the hives of interest.) were selected by the Instituto de Ciencia y Tecnología de Alimentos (ICTA), Universidad Nacional de Colombia to represent the beekeeping and/or agricultural practices in each area. They were interviewed individually using a questionnaire on pesticide management prepared by the Laboratorio de Análisis de Residuos de Plaguicidas (LARP), Universidad Nacional de Colombia. The questions were directed to know the bee type, diseases in apiaries, type of crops planted around the hives, environmental conditions, and the pesticides or drugs applied to control specific pests and/or diseases on the hives or crops. A total of 110 beekeepers and farmers were visited as follow: 20 in Boyacá, 30 in Cundinamarca, 30 in Magdalena and 30 in Santander.

2.3. Pesticide residues analysis

2.3.1. Reference materials, reagents and solutions

Pesticide reference standards, all >95% purity, were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Chemservice (West Chester, USA). Stocks solutions were prepared in a

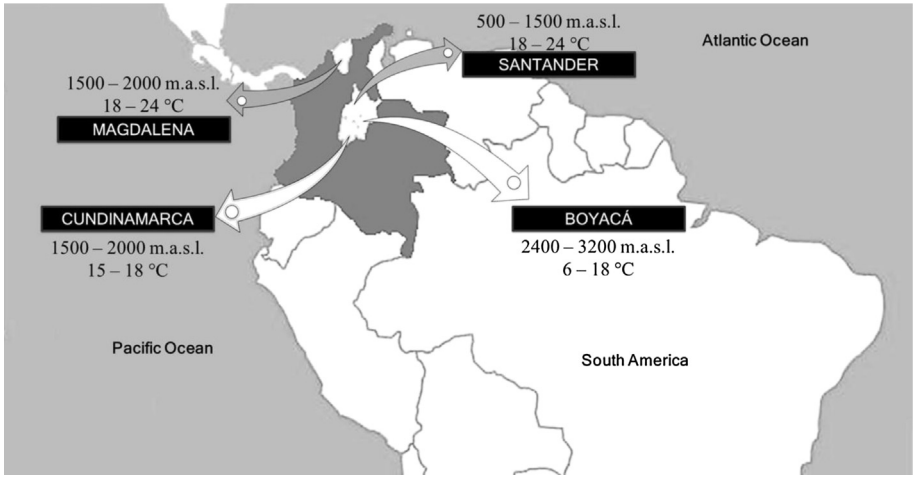

Fig. 1. Map showing sampling locations of honeybee analyzed in this study.