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Determination of Pesticide Residues in Honey Samples from East Shewa and West Arsi Zones of Oromia, Ethiopia

Taye Beyene*, Desta Abi, Mekonen Woldatsadik

Oromia Agricultural Research Institute (IQQO), Adami Tulu Agricultural Research Centre, Adami Tulu, Ethiopia

Email address:
tayebeye@yahoo.co.uk (Taye Beyene)
*Corresponding author

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Abstract: Honeybees (*Apis mellifera L.*) play an important ecological and economic role in the pollination service of crops. Pesticide residues in honey can happen when bees in search nectar and pollen, visit crops that have been treated with various agrochemicals for different reasons. The presence of pollutants in honey can influence honeybee colony performance and devalue its use for human consumption. The aims of this study were to determine pesticide residue levels in honey samples from East Shewa and West Arsi zone and to identify type of pesticides present in honey samples. A total of 24 honey samples were collected from apiaries different localities just after harvesting. Honey samples were analyzed using gas chromatography mass spectrometry. Among different pesticides analyzed in honey samples, Chlorpyrifos was the most frequently detected (16.7%) followed by Endosulfan sulphate (12.5%) and Profenofos (8.3%). The average recoveries of pesticides ranged between 72% and 102.4%, with relative standard deviation less than 20%. All the pesticide residues detected were very low and below their respective maximum residue limits set by the European Union. Hence, pesticide residues in honey samples analyzed do not pose any health risk to consumers. Although the study results showed none significant pesticide residue in the analyzed honey samples, a special precaution should be taken regarding to production of pesticides, their sale, and application in the future.

Keywords: Honey, Honeybees, Pesticides Residues, Organophosphorus

1. Introduction

Pesticides have played a vital role in protecting crops from pests and disease invasion thereby boosting crop productivity that is much needed to meet the world food demands [1, 14]. However, indiscriminate and incorrect use can be devastating for human health and the environment all over the world. Several studies have confirmed that exposure to pesticides groups such as organophosphates and Organochlorine can cause risk of cancers [9], interruption of circulating hormones, reproductive problems [15] and neurological disorders [11].

Honeybees (*Apis mellifera L.*) play an important role to boost yields and other quality parameters of different crops [10]. However, currently global decreasing honeybees have reported due to several factors such as misuse and practice of pesticides. Farmers apply pesticides during flowering plants, and this is a time which honeybee colonies actively move to collect nectar and pollen; thus, it affects the honeybees. The use of pesticides was affecting the bees either through poisoning or destroying the honeybees' forage.

Honey is a complex food substance produced by bees from the nectar of flowers or honeydew. Honey has different nutritional composition such as carbohydrates, vitamins, proteins, minerals, waters and polyphenolic compounds, but its composition is determined by floral origin [2]. Honey is widely used for both nutritional and medicinal purposes and it is known to have therapeutic actions against infections, wounds, and cancers. It has been used to treat cough and sore throat, ulcer, earache, measles, and eye diseases. However, the cumulative levels and presence of pesticides in hive products over time can pose health problems for both honeybees and humans. These toxic contaminants come to hive products with pollen and nectar when honeybees collected pollen and nectar from the surrounding frowners and then they may return to hives [5, 16, 18]. At environmental level, honeybees pick contaminants through different pathways including consumption of pollen and contaminated nectar, via contact with plants and soil from crops in which farmers apply pesticides, inhalation during flight and recollection, ingestion of polluted surface water and by direct over spay or flying through spray drift, among others [6, 7]. Some studies related to the occurrence of toxic substance in bees products, demonstrated the environmental section near to the hives and can provide to the presence of contaminant in time and space [7]. The honeybees are also affected by pesticides and antibiotics when beekeepers apply agrochemicals to control some infections such as varroa destructor, Acarapis wood and Paenibacillus larvae [12, 13]. In many cases, pollution of honey is caused by pesticide application in the surrounding area or by environment contamination and not by the beekeepers practices resulting in the unavoidable presence of toxic substances [3]. Therefore, the presence of pesticides and antibiotics in bees' products has become common place.

Currently the steady growth of vegetable production under irrigation has created a greater demand for pesticides in the central rift valley of Oromia, Ethiopia. Many shops involved in selling of pesticides and farmers have easy access to get these chemicals. However, level of pesticide residues in honey is unknown in central rift valley of Oromia, Ethiopia. Therefore, this study was conducted to determine pesticide residues in honey samples from East Shewa and West Arsi zones of Ethiopia and to identify type of pesticides present in honey samples.

2. Materials and Methods

2.1. Honey Collection

Honey samples were collected from three districts purposively from the areas intensively utilizing pesticides namely Dugda, Negele Arsi and Shashemene districts just after harvesting. A total of 24 honey samples of each weighing 0.5 kg were collected randomly from beekeepers after harvesting. The collected honey samples were labeled and stored at room temperature until extraction and analysis. Then samples were transferred to Addis Ababa University Chemistry Laboratory for conducting pesticide residuals analysis.

2.2. Reagents

All pesticide standards were of high purity and obtained from Addis Ababa University, Chemistry Department. All reagents analytical grade such as Chloroform, Acetone, and Methanol were purchased from different suppliers and distributors.

2.3. Sample Preparation

10 grams of honey was weighed from each sample and dissolved with 10 ml ultrapure water and hand-shaken for 5 minutes. The extract wasfiltered using whatman 42 filter paper; the resulting solution was spiked with surrogate standards at 5 ng/g honey and mixed thoroughly. Thereafter, 450 µL acetone and 100 µL chloroform were prepared and added to the sample to obtain an emulsion. The tube was hand shaken for 5 second and subsequently centrifuged at 3500 rpm for 5 minutes and a two-phase solution was obtained. The chloroform phase at the bottom of the conical vial 21 was collected with a microlitre syringe, and 2 µL were injected on GC/Ms column.

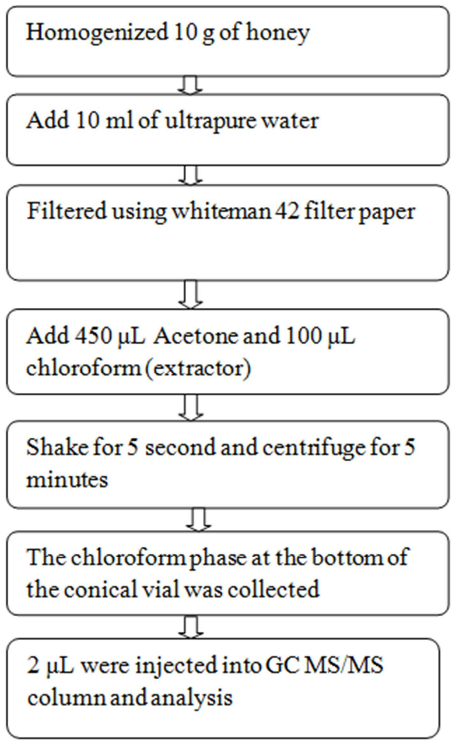

Figure 1. *Flow chart of pesticides analysis.*

2.4. Validation of the Analytical Procedure

The validation procedure was performed following some parameters of SANCO guidance "Method Validation and Quality Control Procedures for Pesticides Residues Analysis in Food and Feed" [17]. Limit of detection (LOD) and limit of quantification (LOQ), were calculated by running at least five samples of known concentration for each pesticide. The results were recorded on control charts. The recovery mean values ranged between 70-120%, with Relative Standard Deviations less than 20%.

2.5. Instrumentation

Analysis was performed on a GC MS/MS Triple quadrupole System (Shimadzu TQ 8037). The injector temperature was 280 degree C. The samples were injected in the split mode, and the splitless was opened after 2 minutes. Injection volume was 2 µL. A capillary column HP-5MS (5%- phenyl, 95%-dimethylpolysiloxane), 30 m x 0.25 mm x 0.25µm, was used. Gas career was He with constant flow of 1.90 mL/min. The oven temperature was as follows: initial temperature of 60°C, held for 2 min, increased to 25°C/min up to 150°C, at 3°C /min up to 200°C held for 1 min, and then increased to 290°C at 8°C/ and held for 43 min.

3. Results and Discussion

3.1. Recoveries and Validation Information

The average recoveries of pesticides ranged between 72% and 102.4%, with relative standard deviation less than 20%. The limits of detection (LOD) and limits of quantification (LOQ) in pesticides detected between 0.001-0.124 mg/kg and 0.002-0.162mg/kg. The average recoveries ranged between 70% and 120%, with RSDs in general below <20% (European Commission, 2010).

Table 1. *Percentage recoveries and validation information of the studied pesticides.*

Pesticides	Recovery (%)	RSD (%)	Limit of detection (mg/kg)	Limit of quantification (mg/kg)
Diazinon	90.8±0.77	4.0	0.001	0.030
Endosulfan	76.5±1.06	5.7	0.015	0.162
Chlorpyrifos	102.4±0.65	6.4	0.005	0.013
Profenofos	72.0±0.81	9.6	0.124	0.002
p, p-DDT	96.7±0.72	11.2	0.008	0.021
Malathion	88.0±1.30	7.5	0.003	0.012

3.2. Pesticide Levels in Honey Samples

This study was conducted to investigate the presence of pesticide residues in honey samples from various areas of central rift valley of Oromia, Ethiopia. From the total of 24 honey samples analyzed, only twelve samples contaminated with six active compounds including Diazinon, Malathion, Profenofos, Chlorpyrifos, Endosulfan sulphate and p, p-DDT pesticide were detected (Table 2). The results indicated that, the total contamination with pesticides residues was 50%, mainly with organophosphorus (66.7%) and Organochlorine (33.3%) pesticides. The most abundant pollutant was Chlorpyrifos (16.7%) followed by Endosulfan sulphate (12.5%) and Profenofos (8.3%). The highest contamination of pesticides residues was found in Dugda district (41.7%) followed by Negele Arsi district (33.3%) and Shashemene district (25%). All the pesticide residues detected were very low and below their respective maximum residue limits set by the European Union. Comparisons of average mean concentration of detected pesticide residues with MRLs established by the European Union (EU) was indicated in Table 2.

Table 2. *Showing range and mean concentration of pesticides detected in honey samples.*

Location of honey sample	Total no. of samples	Pesticides found	Frequency	Range (mg/kg)	Mean concentration (mg/kg)	EU MRLs (mg/kg)
Dugda	8	Diazinon	1	0.0001-0.0027	0.001	0.01
		Endosulfan sulphate	2	0.0002-0.1062	0.005	0.05
		Chlorpyrifos	2	0.0001-0.1147	0.002	0.05
Shashemene	8	Profenofos	2	0.0004-0.0028	0.007	0.05
		p, p-DDT	1	0.0000-0.0164	0.003	0.01
Negele Arsi	8	Malathion	1	0.0004-0.0250	0.005	0.02
		Chlorpyrifos	2	0.0021-0.0510	0.002	0.05
		Endosulfan sulphate	1	0.0040-0.0031	0.006	0.05

The prevalence of pesticide contamination of vegetables in our study is comparable with pesticide residue prevalence reported in honey elsewhere. The result of our findings was in agreement with those found by the study which investigated 15 organophosphorus insecticides in 275 honey samples in 33 different cities of Turkey, using gas chromatography with electron capture detector [8]. No insecticide residue was detected in the samples analyzed. The study also detected Organochlorine, organophosphates and Carbamate insecticides residues in honey from Portugal and Spain, with residues ranging 0.03-4.31 mg/kg [4].

4. Conclusion and Recommendations

Pesticides play a very important role for ensuring food security and economic growth but their improper can cause harmful effects to human health and to the environment. Honeybees (*Apis mellifera L.*) play an important ecological and economic role in the pollination service of crops. But recent global declining on pollinators, including honeybees' has reported owing to several factors includes improper use and practice of pesticides. Honey can present pesticide residues due to the contamination of bees during the collection of pollen and nectar. All the pesticide residues detected had concentration lower than the recommended EU maximum residue limits. Hence, pesticide residues in honey samples analyzed do not pose any health risk to consumers. The fact that no pesticides were detected does not necessarily mean that farmers are not using pesticides because some time honeybees can make biological transformation/detoxification of toxic substances and extract through their feces to sustain their life. Although the results show a negligible risk associated with exposure via honey consumption, a special precaution should be taken with the possible total exposure to these chemicals in the future. Tighter regulation in the production of pesticides, their sale, and application are needed as well as implementation of integrated pest management methods. Additionally, further monitoring studies must be performed to improve food safety and protect consumers' health.

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