RISK ASSESMENT OF SOME PESTICIDES ON INFANT FOOD

Submitted By

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Master of Environmental Science, Institute of Environmental Studies & Research
Ain Shams University, 2012

A thesis submitted in Partial Fulfillment

Of

The Requirement for the Doctor of Philosophy Degree

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APPROVAL SHEET

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ABSTRACT

A simple and rapid multiresidue method for the determination of different pesticide residues, PCBs and M1 in baby food and powdered milk-based infant formulae (PMIF). The method involves an extraction procedure based on buffered QuEChERS (quick, easy, cheap, effective, rugged and safe) methodology, without any further clean-up step, followed by liquid-high performance chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) for pesticides and PCBs using (GC-MS/MS) but for M1 using HPLC. Results of baby food samples for age day to year divided into two stages from one day-6 months and 6-12 months. In our study 164 samples were analyzed for detection of pesticide residues, pcbs and M1 with 49 canned baby food and 73 fresh samples then calculate health risk assessment and 42 samples of milk were analysed for detection of for pcbs and M1, the results showed that 39% canned food were contaminated, but73 % of fresh samples contaminated and 27% of fresh samples were completely free from any pesticides as Potato, Sweet Potato, and Banana. The most pesticides appeared in canned food samples were Chloropyrifos, Carbendazim, malathion and acetamiprid but for fresh samples food were chloropyrifos, Malathion and profenofos. Almost violated pesticides exposures through foodstuffs consumption were far below the acceptable daily intake (ADI) as established by FAO/WHO. The most critical pesticides were Dimethoate, Omethoate and Diazinon to the hazard index (HI).In the results of milk were free from PCBs from age one day-6 and also age 6-12 year but M1 were free except two samples were contaminated with 0.522,0.173µg/kg respectively and both of them for baby in age less than 6 months and both of them exceed the allowable limits 0.025µg/kg.

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ADI	Accepted Daily Intake
ALARA	An acronym reasonably achievable
ASE-GC/MS	Accelerated Solvent Extraction- gas chromatography/ mass
CAC	Codex Alimentarius Commission
DDE	Dichloro-Diphenyl Dichloroethene
ECD	Electron Capture Detector.
EDI	Estimated dialy intake
EFSA	Egyptian Financial Supervisory Authority
EU	European United
FAO	Food and agriculture organization
G. beans	Green beans
GC	Gas Chromatography
HCB	Hexachloro benzene
HCHs	Hexachlorocyclohexane
HI	Hazard index
HRGC/HRMS	High Resolution Gas Chromatography/High Resolution Mass Spectrometry
IARC	International agency for research on cancer
JECFA	Joint FAO/WHO Expert Committee on Food Additives
JMPR	Joint Meeting on Pesticide Residues
LOD	limit of Detection
LOQ	Limit of Quantitation
MRL	Maximum Residue Limit
MRM	Multiple Reaction Monitoring
nd	Not detected
PCBs	Poly chlorinated biphenyl
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
PHI	pre-harvest interval
SPE	Solid phase extraction
UNEP	internationally recognized persistent organic pollutants
USEPA	United state environmental protection agency
WHO	World health organization

3-INTRODUCTION

Pesticides are defined as substances or mixtures of substances intended for controlling, preventing, destroying, repelling, or attracting any biological **organism** deemed to be a pest. **Insecticide**s, **herbicide**s, **defoliants**, **desiccants**, **fungicide**s, **nematicides**, **avicides**, and rodenticides are some of the many kinds of pesticides (**Dogheim *et al.,* 2001**). Pesticides are grouped or classified according to the pests they control, their chemical structure, how/when they work, or their mode of action (site of action). One traditional classification of pesticides places them in one of two groups: **organic** and **inorganic**. **Organic pesticides** are based on chemicals having carbon as the basis of their molecular structure (**Gebara *et al.,* 2005).** The chemicals in organic pesticides are more complex than those of **inorganic pesticides**, and usually do not dissolve easily in water. Inorganic pesticides are simpler compounds. They have a crystalline, salt-like appearance, are environmentally stable, and usually dissolve readily in water. The earliest chemical pesticides were inorganic, and included substance such as sulfur and lime. (**Gonzalez *et al.,* 2008a&b**).

Pesticide residues in food and crops with mass spectrometric detection are a direct result of application of pesticides to crops growing in the field, and to a lesser extent from pesticide residues remaining in the soil (**Businelli *et al.,* 1992**). However, many pesticides are toxic substances and persistent in character. There is a growing social desire to reduce the use of pesticides in agriculture and horticulture (**Freidberg, 2003**). Supermarkets are under increasing pressure to adapt to a changing consumer preference that perceives pesticides as an undesirable component of food production. When seeking to rationalize pesticide use, both government (**Council Directive, 1990**) and supermarkets have tended to make the implicit assumption that any rationalization is primarily an issue of decreasing the quantity of pesticides used, coupled with the banning of specific, highly toxic substances (**Freidberg, 2003; Gallivan *et al*., 2001 ; Levitan, 2000**). Thus, pesticides with high toxicity to humans are targeted for rationalization, irrespective of the quantity used. Such actions may not reflect the actual risk to humans or the full hazard profile of the pesticide. For these reasons, decisions as to which pesticides to target for reduction can be problematic unless they are

made with full knowledge of their relative toxicological properties, environmental fate and mobility (**Kovach *et al*., 1992; Levitan, 2000**).

To protect consumer's health, many countries have established legal directives to control levels of pesticides in food, through maximum residue levels, MRLs (**FAO/WHO, 2004; Council Directive, 2003**). The levels of pesticide residues in foodstuffs are generally legislated so as to minimize the exposure of the consumer to harmful or unnecessary intakes of pesticides, to ensure the proper use of pesticides in terms of granted authorization and registration (application rates and pre-harvested intervals) and to permit the free circulation of pesticide-treated products, as long as they comply with the fixed MRLs (**Mansour et *al*., 2009**).

Monitoring of pesticide residues in vegetables for an extensive evaluation of vegetable quality is a priority objective of pesticide research to avoid possible risks to human health. Highly sensitive and selective analytical procedures to determine residues of these compounds in a variety of food matrices have been developed (**Paulino *et al*., 2010**). **Different chromatographic method such as** gas chromatographic methods with mass spectrometric detection (GC– MSMS) and High liquid chromatography with mass spectrometric detection (LC-MS/MS) have been used successfully for the analysis of many pesticides.

The level of several pesticide residues such as organophosphorus, organochlorine and organo-nitrogen in vegetable and infant food have been determinedGC/ MSMS and LC/ MSMS (**Andersson and Palsheden, 1991; Specht *et al.,* 1995; Stan, 2000; Pugliese *et al.,* 2004; Rial-Otero *et al*.,2005; Pose-Juan *et al*., 2006, 2009; Balinova *et al*., 2007; Berrada *et al*., 2010**).

The risk assessment of pesticide residues in food is based on toxicological evaluation of the single compound and no internationally accepted procedure exists for evaluation of cumulative exposure to multiple residues of pesticides in crops, except for a few groups of pesticides sharing a group ADI (**Reffstrup *et al*., 2010).**

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) are three of the 12 United Nations Environment Program (UNEP) internationally recognized persistent organic pollutants (POP) included in the

Stockholm Convention. PCBs have been used widely in heat exchangers and dielectric fluids; as stabilizers in paints, polymers, adhesives; and as lubricants in various industrial processes (**Safe, 1994**).

Aflatoxin M1 (AFM1) appears in milk and milk products as the direct result of the intake of aflatoxin B1 (AFB1) contaminated feed by dairy cows. Exposure of children, including infants, to AFM1 is worri-some, because they are considered more susceptible to its adverse effects, and their capacity for biotransformation of carcinogens is generally slower than in adults. Aflatoxins may be produced by three species of Aspergillus A. flavus, A. parasiticus, and rare A. nomius-that contaminate plants and its products. A. flavusproduces only B aflatoxins, while the others produce both B and G aflatoxins. Aflatoxins M1 and M2 are the hydroxilated metabolites of aflatoxin B1 and B2 and may be found in milk products obtained from livestock that have ingested contaminated feed (**Alborzi *et al.*, 2006)**.

The higher the ADI, the "safer" a compound is for regular ingestion. The ADI concept can be understood as a measure to indicate the toxicity from long-term exposure to repeated ingestion of chemical compounds in foods (present and/or added), as opposed to acute toxicity (**WHO, 1997)** and also help in deciding pesticides strategy in the country.

No data are available on the levels of pesticide residues in vegetables and, infant foods in local markets of Egypt. Therefore, the present study was undertaken to monitor pesticide residues in the collected vegetables and infant food from different local markets .Sensitive, and selective chromatographic methods (GC- MSMS and LC- MSMS) were used in the present study.

4-REVIEW OF LITERATURES

4. Pesticides:

4.1-Pesticides

Pesticides are essential for agricultural and horticultural crops production. Pesticides are commonly classified as **insecticide, fungicide, herbicide, rodenticide**, etc. (**Lopez *et al.,* 2012**). These pesticides act against insects, rodents, weeds which are harmful in agricultural or horticultural planting. Normally, farmers use the pesticides following the instruction written in the package. In most cases, the pesticides are mixed with water and sprayed over the plants. Basically, after spraying fruits or vegetables with pesticide, a period of 10 to 14 days is required to allow the chemical to degrade. However, the full degradation of pesticide is not always achieved (**Lopez *et al.,* 2007**). In recent years, some farmers ignored to use the pesticide correctly and rationally. In order to chase a better insecticidal effect and the economic interests, the phenomenon of using pesticide excessively, or selling the fruits or vegetables just after spraying the pesticide in few days are not difficult to see. Moreover, the pesticides overdosing also have the potential to contaminate the soil, air, and river. (**Schenck *et al*., 2008**).

4.2-Effects of Pesticides on Human Health

Pesticide formulations contain both "active" and "inert" ingredients. Active ingredients are what kill the pest, and inert ingredients help the active ingredients to work more effectively. These "inert" ingredients may not be tested as thoroughly as active ingredients and are seldom disclosed on product labels. Solvents, which are inert ingredients in many pesticide formulations, may be toxic if inhaled or absorbed by the skin (**Keikotlhaile**,***et al*., 2010**).

Pesticides are designed to kill and because their mode of action is not specific to one species, they often kill or harm organisms other than pests, including humans. The World Health Organization estimates that there are 3 million cases of pesticide poisoning each year and up to 220,000 deaths, primarily in developing countries. The application of pesticides is often not very precise, and unintended exposures occur to other organisms in the general area where