DETECTION OF CARBAMATE RESIDUES INDIFFERENT BIOINDICATORS OF PESTICIDE POISONING

Submitted By

Adel Mostafa El Metwally Awad

B.Sc. of Science (Chemistry), Faculty of Science, Cairo University, 1996

A thesis submitted in Partial Fulfillment
Of
The Requirement for the Master Degree
In
Environmental Science

Department of Environmental Basic Sciences
Institute of Environmental Studies and Research
Ain Shams University

2015

APPROVAL SHEET

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Ministry of Justice

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Abstract

Introduction Pesticides constitute a very important group of chemical compounds that have to be controlled due to their high toxicity and their wide spread use in agricultural practice for field and post harvest production. The presence of pesticide residues in food is a direct result of pesticide use on over 1000 compounds may be applied to agricultural crops in order to control undesirable moulds, insects and weeds . Thiobencarb is a thiocarbamate herbicide widely used for weed control in Egyptian paddy fields. Beside the use of thiobencarb by direct application for weed control; it may enter to aquatic ecosystem through off site movement from treated fields, by surface run off or adsorbed to suspended particles

Objective

The objective of this work is to perform a study on thiobencarb chemically and its behavior analytically and moreover study its pass through tissue organs of rats administered thiobencarb intramuscular and determine its highest levels in different tissue organs.

Subject and method:

- Employ the different toxicological analytical procedures (spot tests), TLC, UV spectrophotometry and GC to reveal which of these methods or all together more suitable for the identification and differentiation of the studied carbamate pesticide, thiobencarb.

Results

Paladus chloride reagents produced orange colors with Thiobencarb which is a distinctive color. As it works on sulpher containing compounds.

It is of much interest to notice that iodoplatinate and fast blue B salt reagents may be considered as specific one to identify and differentiate the studied pesticide, since it produced a characteristic and specific color (yellow with Thiobencarb).

- The present study demonstrated that Thiobencarb did not need eluting solvents of higher polarity. Different eluting solvents of moderate polarity were used in the present work with a considerable RF values. These are cyclohexane : diethylether 4:1 (RF=0.58), cyclohexane (RF=0.49), acetone: ammonia 80:15 (RF=0.89) for Thiobencarb
- The present finding that the studied thiocarbamate has its own spectrum λ= 225 nm for Thiobencarb.

Mass spectrum of thiobencarb shows [M+] at m/z =[257].+, and base peak at 100.

Conclusion

- Femoral muscle, brain and spleen showed the higher of thiobencarb concentration than hair, heart muscle, kidney, blood and liver with no dose dependency.

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Introduction

Pesticides constitute a very important group of chemical compounds that have to be controlled due to their high toxicity and their wide spread use in agricultural practice for field and post harvest production. The presence of pesticide residues in food is a direct result of pesticide use on over 1000 compounds may be applied to agricultural crops in order to control undesirable moulds, insects and weeds (Ortelli and Corvi, 2006).

According to Food Agriculture Organization (FAO) it has defined the term of pesticide as :- Any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feed stuffs or substances which may be administrated to animals for control of insects arachnids or other pests in or on their bodies. The term includes substance intended for use as a plant growth regulator, defoliant, desiccant or agent for tinny fruit or preventing the premature fall of fruit.

Numerous investigations have been made about the effects of pesticides on non-target organisms over the years (Parr, 1974; Rogers *et al.*,

1994; Johnsen *et al.,* 2001; Park *et al.,* 2005 and Christen *et al.,* 2006). However, for some pesticides despite their extensive use in agriculture and well documented persistence in the soil (Quayle *et al.,* 2005 and Castro *et al.*, 2005). There is a crucial lack of information on their impact on soil and organisms.

It is well known that the use of large quantities of pesticides in agricultural activities is one of the main causes of pollution of surface and ground water. Consequently, very strict programs to control and monitor the levels of these contaminants in water sources have long been instituted in countries such as the USA and members of the European Community. These programs are based on the use of thoroughly validated analytical methods which allow determination of contaminants at trace levels. In Egypt, these programs must be implemented.

Rice is a main cereal crop all over the world, it is considered as most important food for about the half of the world population, it is a principle food of the majority of the Egyptians. Rice mainly replaced cotton and maize areas, becoming as major summer crop on agricultural map. FAOSTAT2, stated that the Egyptian total consumption, production and export of rice where 3.28,3.74 and 1.07 million tons, respectively.

carbamate group is one of Pesticides, which are commonly used in Egypt, have been found in the environment, especially in aquatic habitats where many of this group of pesticides has a high potential of contamination.

Thiobencarb is a thiocarbamate herbicide widely used for weed control in Egyptian paddy fields. Beside the use of thiobencarb by direct application for weed control; it may enter to aquatic ecosystem through off site movement from treated fields, by surface run off or adsorbed to suspended particles (Corbett *et al.,* 1984 and Tomlin, 2003).

Thiobencarb is used as pre-emergence herbicide in rice culture in California, between early May and the end of June each year, about 9000000kg of this material is applied in California alone. Thiobencarb imports an off taste to the drinking water that can be tasted by some people at very low concentrations. Because of these problems, the California Department of Food and Agriculture (CDFA), the local water quality control board and manufactures of these thiocarbamates has a program to monitor drainage canals and river water for this compound.

Moreover, because of different contaminations in tap water, most people prefer using bottled mineral waters; pesticides (e.g

organophosphorous, carbamates ect.) are among most dangerous chemicals that may be found in drinking water which can cause long term-short term complications. Rezaee *et al.*(2012), determined the concentration of three pesticides (aldicarb, thiobencarb and parathion) in 13 tap water samples collected from 13 different urban areas and 10 samples of bottled mineral water in mashhad, a major city in northeast Iran. Samples were analysed using GC/FID detector after solid phase extraction. Results showed that 2 of 13 tap water samples and 2 of 10 bottled mineral water trade marks were contaminated either by parathion or by thiobencarb or both, with concentrations ranging between 0.6 and 0.8 ppb.

According to the defined guideline values, determined concentrations are below the permissible WHO level for these toxic agents. But, it has to be mentioned that because exposure to pesticides also occurs through other media (e.g food), the attribution of the exposure through drinking water to overall risk need to be known. On the other hand many pesticides are persistent and may therefore bioaccumulate in the environment. In addition to acute effects, there is evidence that links long-term exposure to some pesticides with chronic diseases including cancer (Younes and Gala-gorchev, 2000), it is much better to perform strict supervision on the use of these chemical agents.

Therefore, monitoring the residual levels of pesticides from various matrices is very important for human health and environmental control.

Thiobencarb is the common name for S-{(4-chlorophenyl) methyl}diethyl carbamothioate, it was developed by Kumiaichem.ind.co.ultd and introduced in market in 1970 (Ishkawa *et al.*,1976). It was first registered for use on rice in 1982.

In 1991, it was issued regional tolerances for the use on celery, endives and lettuce in the state of Florida. Currently, there are five products containing thiobencarb registered under section 3 of the federal insecticides, fungicides and rodinticide Act. They consist of one technical (manufacturing use) product containing 97.4% active ingredient, two emulsifiable concentrate end- use products each containing 84.0% active ingredient, and two granular end – use products each containing 10% active ingredient (Regestration Eligibilty Decision List case 2665) .

Thiobencarb is a preemergent and early postemergent systemic herbicide used to control many broad leaves. Weeds, grasses, and sedge in food crops such as rice, lettuce, celery and endive (U.S.EPA Red facts, 1997, Meister, 1998). The primary target weed is barnyard grass, Echinochloa crus- galli, the most serious pest in rice crop.

Thiobencarb is not currently regulated under the safe drinking water act (SDWA). I was ranked by the U.S.EPA reference dose (RFD)/Pear Review committee as a group D chemical that is not classifiable as to human carcinogenicity.

On the other hand, the European Food Safety Authority (2011) published that, a decision not to include thiobencarb in Annex I to Directive 91/414/EEC entered into force on 31 December 2008. EFSA is therefore required to provide a reasoned opinion on the review of the existing MRLs for that active substance in compliance with Article 12(1) of Regulation (EC) No 396/2005. Considering that the use of thiobencarb is no longer authorised within the European Union and that no import tolerances were notified by the designated reporter Member State Spain, EFSA based its assessment mainly on the conclusions derived by Spain in the framework of Directive 91/414/EEC. On 22 March 2011 EFSA issued a draft reasoned opinion that was circulated to Member State experts for consultation. Comments received by 27 May 2011 were considered for finalization of this reasoned opinion.

The following conclusions are derived.The toxicological profile of thiobencarb was evaluated by Spain in the framework of Directive

91/414/EEC. Based on available information, Spain proposed an ADI of 0.01 mg/kg bw/d and an ARfD of 0.25 mg/kg bw. EFSA emphasizes that these toxicological reference values have never been peer reviewed, neither by Member States, nor by EFSA.

Considering that the use of thiobencarb is no longer authorised within the EU, that no CXLs are available for this active substance and that no uses authorised in third countries were notified to the RMS, residues of thiobencarb are not expected to occur in any plant commodity. Nevertheless, primary crop metabolism of thiobencarb was investigated for rice. A number of metabolites were formed but metabolite 4-chlorobenzyl methyl sulfone is the most relevant residue in rice grain. Consequently, 4-chlorobenzyl methyl sulfone is considered to be the only relevant residue for enforcement of a potential illegal use. There are indications that this residue may be enforced with a LOQ of 0.005 mg/kg in cereal grains. Residues of thiobencarb are also not expected to occur in livestock. Moreover, studies on the metabolism of thiobencarb in lactating cow and laying hens demonstrated that 4-chlorobenzyl methyl sulfone is the most relevant indicator for enforcement of a potential illegal use. No validated analytical methods for enforcement of this residue definition in product of animal origin are available.