

## **Decontamination of pesticide packing using ionizing radiation**

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### **ABSTRACT**

The Brazilian agriculture activities have consumed about 288,000 tons of pesticides per year conditioned in about 107,000,000 packing with weight of approximately 23,000 tons. The discharge of empty plastic packing of pesticides can be an environmental concern causing problems to human health, animals and plants if done without inspection and monitoring. The objective of this work is to study the ionizing radiation effect in the main pesticides used in Brazil for plastic packing decontamination. Among the commercial pesticides, Chlorpyrifos has significant importance because of its wide distribution and extensive use and persistence. The radiation-induced degradation of Chlorpyrifos in liquid samples and in polyethylene pack was studied by gamma-radiolysis. Packing of high density polyethylene three layer coextruded, named COEX, contaminated with chlorpyrifos, were irradiated using both, a multipurpose Co-60 gamma irradiator and a gamma source with 5,000 Ci total activity, Gamma cell type. The chemical analysis of the Chlorpyrifos was made using a Gas Chromatography associated to the Mass Spectrometry - GCMS from Shimadzu Model QP 5000. Gamma radiation was efficient for removing chlorpyrifos from the plastic packing, in all studied cases.

### **KEYWORDS**

Gamma radiation, Chlorpyrifos, Packing Decontamination, pesticides

## INTRODUCTION

Pesticides are substances, or mixture of substances, intended for repelling, destroying or controlling any pests, including vectors of human or animal disease, nuisance pests, unwanted species of plants or animals causing harm. A single active ingredient may be comprised of one or more chemical or biological entities, which may differ in relative activity. A formulation may contain one or more active ingredients (Hajslová et al., 1999).

As a consequence, the human population is constantly exposed to numerous chemical species present in the environment. The Brazilian agriculture activities have consumed about 288,000 tons of pesticides per year conditioned in about 107,000,000 packing with weight of approximately 23,000 tons. The discharge of empty plastic packing of pesticides can be an environmental concern, causing problems to the human health, to animals and plants if done without inspection and monitoring. (INPEV, 2005).

The disposal responsibility of the pesticide plastic packing is by Brazilian Federal law attributed to the industry. This fact led the segment to mobilize and create the National Institute of Processing of Empty Packing – inpEV, with the objective of coordinating this operation (INPEV, 2005).

Silage wrap, bags and sheets, heavily contaminated with organic material, are notoriously difficult to reprocess into any form of commercial commodity. Since is no longer allowed the uncontrolled burying and burning of the waste, only two options remain, to dispose, or to recycle, in ways that protect the environment and human health. Cleaning the pesticide containers is the crucial on-farm activity. Triple rinsing has proved to be effective, but not without its problems.

Chlorpyrifos, o, o- Diethyl - o- (3,5,6 – trichloro – 2 - pyridyl) phosphorothioate, has significant importance because of its wide distribution, extensive use and persistence. The most commonly used formulations include the emulsified concentrate, granule, wet powder and dispersible granule (Serrano et al., 1997; Kulkarni et al., 2000).

The generated OH radicals “in situ” by the interaction of ionizing radiation with water was successfully applied for organic pollutants removal in environmental samples and industrial effluents (Duarte, et al., 2004, Duarte et al., 2006, Getoff et al., 1988). The other main radicals formed by ionizing radiation are the reducing radical solvated electron (e-aq), and H. atoms. These reactive species react with organic compounds inducing their decomposition. Various research groups in the world have studied the degradation of pesticides in different matrices. (Bachman et al., 1982, Luchini et al., 1999, Kubesh et al., 2005).

The main objective of the present paper is to study the efficiency of ionizing radiation on the chlorpyrifos removal from commercial plastic packing of high-density polyethylene type COEX, used in agriculture. The byproducts study of chlorpyrifos gamma radiolysis were evaluated elsewhere by the same group (Mori et al, 2006). The major products of initial degradation have been identified as the desulphuration product, Chlorpyrifos-oxon and the hydrolysis product, 3,5,6-trichloro-2-pyridinol (TCP). It is interesting to note that gamma radiolysis follows the same pathway as chlorpyrifos environmental degradation, involving chemical and microbiological processes. Others studies have found both Chlorpyrifos-oxon and the hydrolysis product 3,5,6-trichloro-2-pyridinol (TCP), in urine of contaminated animals and in environmental samples.

## EXPERIMENTAL

**Sampling:** Packing with one liter volume contaminated with two types of chlorpyrifos commercial formulation called as “A” and “B”, were used (Table 1). For the first experiment, 11 packing contaminated with pesticide “A” type, were used; from these, five packing were triple rinsed using 250 mL of distilled water and six packing were used without triple rinse.

For the second experiment, two packing contaminated with pesticide “A” and “B” were used. These packing, without triple rinsing, were cut in small pieces (1.5 cm x

5.0 cm) and placed in bottles with 22 mL of water, in triplicate. The purpose was to maintain the proportion of water volume per packing area of the first experiment.

**Radiation Processing:** The packing samples of pesticide “A”, as described in the Table 2, were irradiated with 17.0 kGy and 26.0 kGy absorbed doses. The irradiation was carried out at room temperature using a Cobalt-60 gamma irradiator, semi industrial type, with 92,000 Ci at dose rate 4.5 kGy/h, in a batch system and “Perspex” dosimeter was employed to determine the absorbed dose of the system.

The packing in pieces of pesticide “A” and “B” was irradiated with 15 kGy, 30 kGy, 50 kGy and 100 kGy absorbed doses at Cobalt-60 gamma irradiator, Gammacell-type, at dose rate 3.4 kGy/h, and Fricke dosimeter was employed to determine the absorbed dose rate of the system.

**Chemical Analysis:** The chemical analysis of the Chlorpyrifos and other organic compounds were performed using gas chromatography with FID detector Shimadzu, model GC-FID 17-A, and gas chromatography associated to mass spectrometry using Shimadzu, model GC-MS QP-5000 in the following conditions:

- DB5 fused capillary columns with low polar bonded phase,
- Mass detector operation in electron impact mode (EI), using 1.50 kV of ionizing voltage and temperature 250°C,
- Interface temperature 240°C and continuous operation mode (SCAN).

## RESULTS AND DISCUSSION

**Chemical Analysis:** Due to the higher Chlorpyrifos concentrations used in this study, it was necessary to evaluate various solvents to avoid the precipitation of Chlorpyrifos. Acetonitrile showed to be more adequate because of the total dissolution of Chlorpyrifos and low volatility. Acetonitrile is a polar, non-hydroxylic solvent with relatively low reactivity to hydroxyl radical.

The calibration curve of Chlorpyrifos dissolved in acetonitrile, using GC-MS and GC-FID was compared; in the case of Chlorpyrifos, the FID detector showed more

sensibility and reproducibility. The detection limit, LMD, using GC-FID was 1.7  $\mu\text{M}$ , while using the MS-GC was 5.7  $\mu\text{M}$ , and the obtained experimental variability (N=10), expressed as standard deviation, was 4 % and 10 %, respectively.

The commercial chlorpyrifos showed to contain other toxic organic compounds used as solvent and stabilizer. These organic compounds were identified by mass spectrometry; in the pesticide "A" the main compounds were hexylenoglicol, trimethylbenzene, 1,2- dimethylindane, naphthalene, 1-methylnaphtalene, 1,4-dimethylnaphtalene and in the pesticide "B" were methylethylbenzene, trimethylbenzene, propenylbenzene and very small quantities of naphthalene (Fig. 1).

The main differences between the two commercial formulations of the pesticides is the high concentration of naphthalene and its methyl derivatives in the pesticide "A" and the very high concentration of trimethylbenzene in the pesticide "B".

**Whole packing decontamination:** The obtained results after packing processing by radiation in different conditions and absorbed doses (E1 to E7) plus respective control (E0A to E0D) are showed in Table 2. In all conditions the packing presented a contamination reduction, but the triple rinsing before irradiation showed to be fundamental to the contamination reduction. Only triple rinsing reduced the Chlorpyrifos concentration from 140.352,0  $\mu\text{M/L}$  (E0A) to 484,9  $\mu\text{M/L}$  (E0C).

Comparing the removal rate in the packing E4 (55.5%) and E5 (72.3%) against E6 (93.2 %) and E7 (99%) all triple rinsed, it was observed higher chlorpyrifos removal rate in the packing E6 and E7, where water was present. The presence of water showed to be more efficient than the applied absorbed dose. In this preliminary experiment, the total removal (99%) of chlorpyrifos was reached in the packing E7, triple rinsed, in presence of water and with 26 kGy of absorbed dose.

The removal of chlorpyrifos in those packing was followed by the reduction of the other organic contaminants (Fig.2). Trimethylbenzene, used as a solvent in the commercial formulation of pesticide A, showed more resistance to ionizing radiation than chlorpyrifos and it was detected even in the packing E7.

The removal behavior of other organic compounds followed the same way than chlorpyrifos. The removal rate of the solvents for 15 kGy and 26 kGy was less than 50% for the packing without triple rinsing, when the packing was triple rinsed and irradiated with water the removal rate reached 98%.

**Packing in piece decontamination:** The pesticide “B” presented lower proportion of solvent/chlorpyrifos than pesticide “A”. The results of organic compound removal average, in various absorbed doses, are presented in Figure 3; the obtained experimental variability, expressed as standard deviation was about 10%.

A removal of about 70% of solvents was reached with 20 kGy absorbed dose, while with the same dose, the chlorpyrifos removal was 40% in the pesticide B. With 70 kGy it was not detected solvents but the remaining fraction of chlorpyrifos was 20% (Fig. 3). The detected solvents are from 20 to 60 times more soluble in water than chlorpyrifos; this fact may be the responsible for its lower removal rate.

The whole packing without triple rinsing (E0A) presented a lower removal rate (25%) than the packing in pieces (>90%) for the same absorbed dose (Fig.3). The irradiation of packing in pieces showed better yield than the whole packing, due to in that case the interaction of the radiation with the pesticide is facilitate, because the sample volume decrease and the water contact and consequent production of free radicals increase. While in wet samples only the direct interaction of the radiation with the pesticide molecule is responsible by the degradation.

The formulation showed affect the degradation yield of chlorpyrifos. Chlorpyrifos in pesticide “B” was removed less than 40% with 15 kGy while in the pesticide “A”, presented a removal >80% for the same absorbed dose. The viscosity and solubility in the solvents could be the responsible for the different behavior, interfering in the hydroxyl radicals reaction.

## CONCLUSION

Gamma radiation was efficient in the removal of chlorpyrifos and other solvents from the plastic packing, but the presence of water showed to be fundamental. Total removal of chlorpyrifos was reached in the packing triple rinsed, in presence of water, and with 25 kGy of absorbed dose.

When a new technology is proposed for commercial use, some factors such as applicability and practicality have to be considered. Although the presence of water showed to be fundamental, it is not economically feasible, and more studies have to be made taking into account this fact. The initial idea was to irradiate the packing without destruction, but it may be necessary to cut or to mill the packing before irradiation to optimize the process, because in this case a conveyor can be used. The radiation of the packing can be advantageous considering that the contaminated pesticide packing are destroyed by incineration that is a very expensive process that obstruct the recycle of the high density polyethylene (HDPE).

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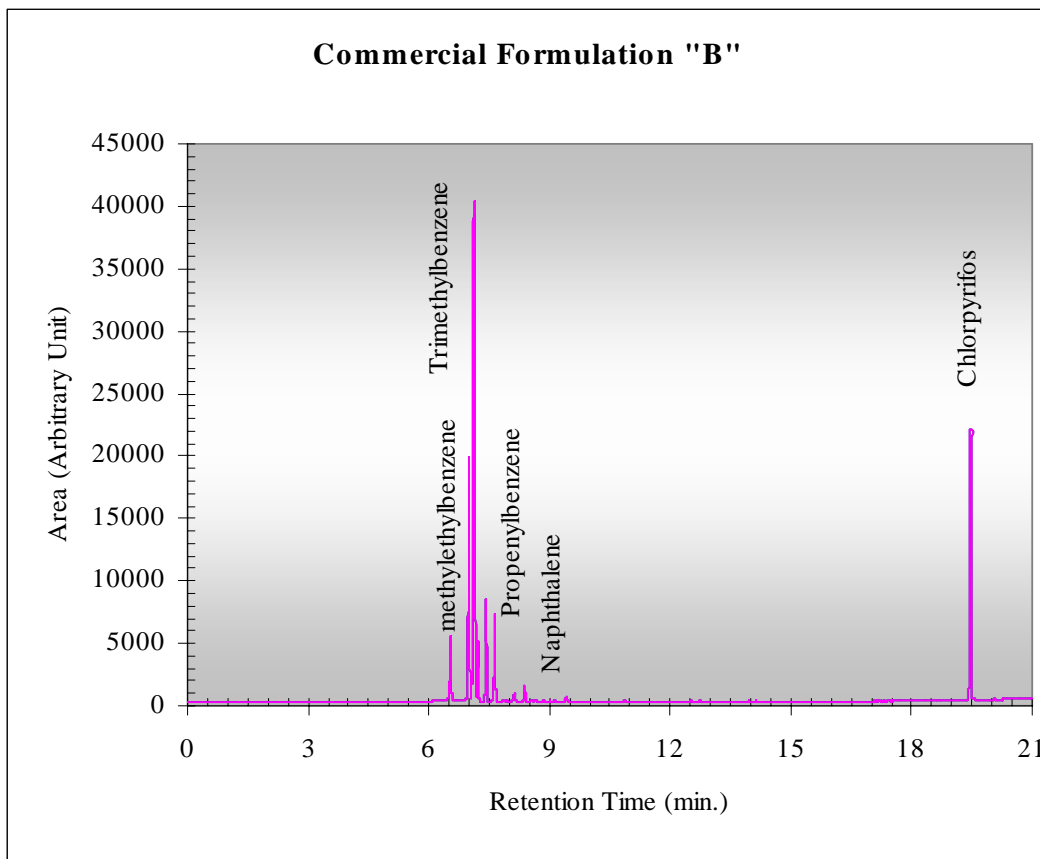
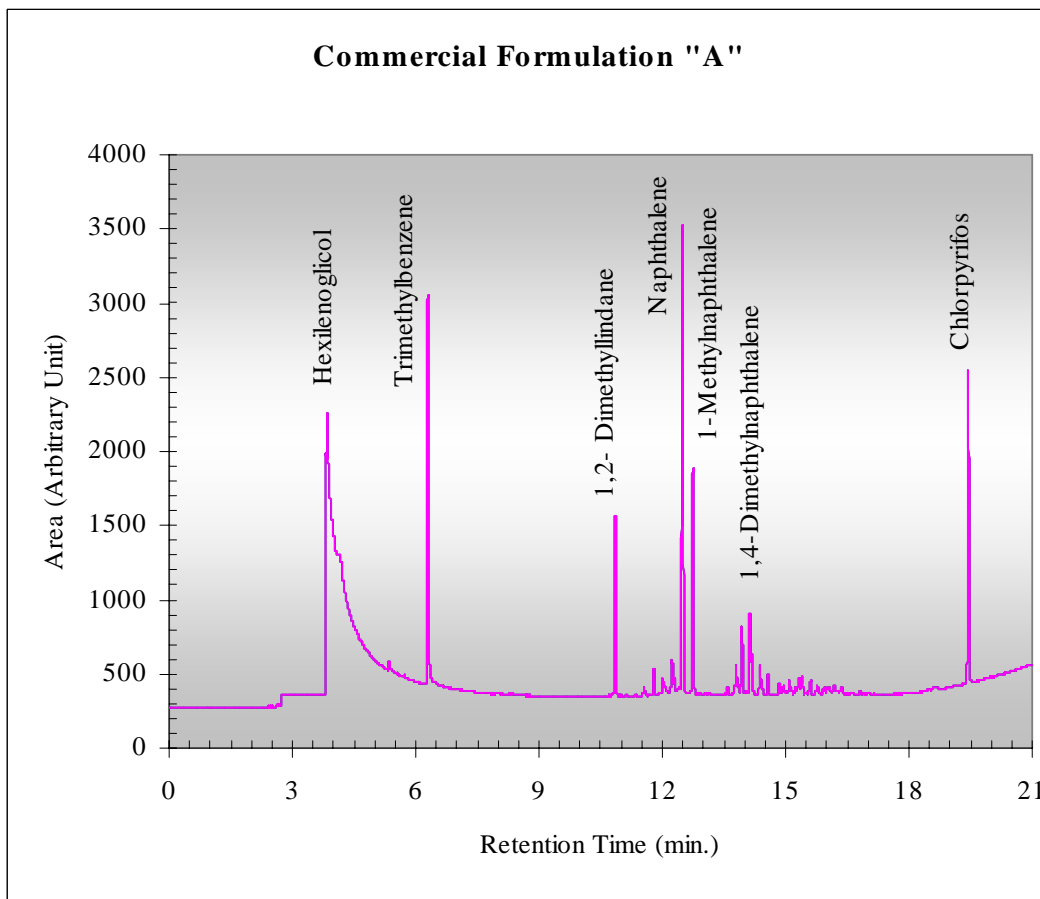
**TABLE 1.** Characteristics of commercial pesticides used in the present study

<b>Commercial Formulation</b>	<b>Class</b>	<b>Chemical Characteristic</b>	<b>Concentration (g/L)</b>	<b>Viscosity (cP a 20<sup>0</sup>C)</b>
Emulsionable Concentrate (B)	insecticide	Organofosphorate	480	10,1
Concentrate emulsion (A)	insecticide	Organofosphorate	450	364

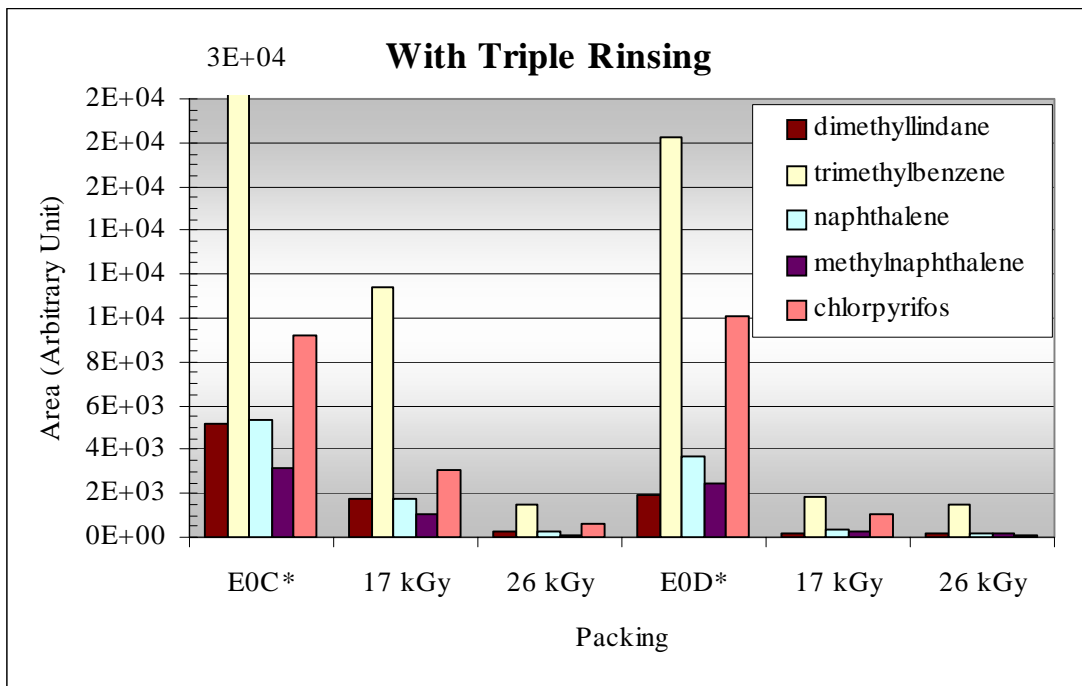
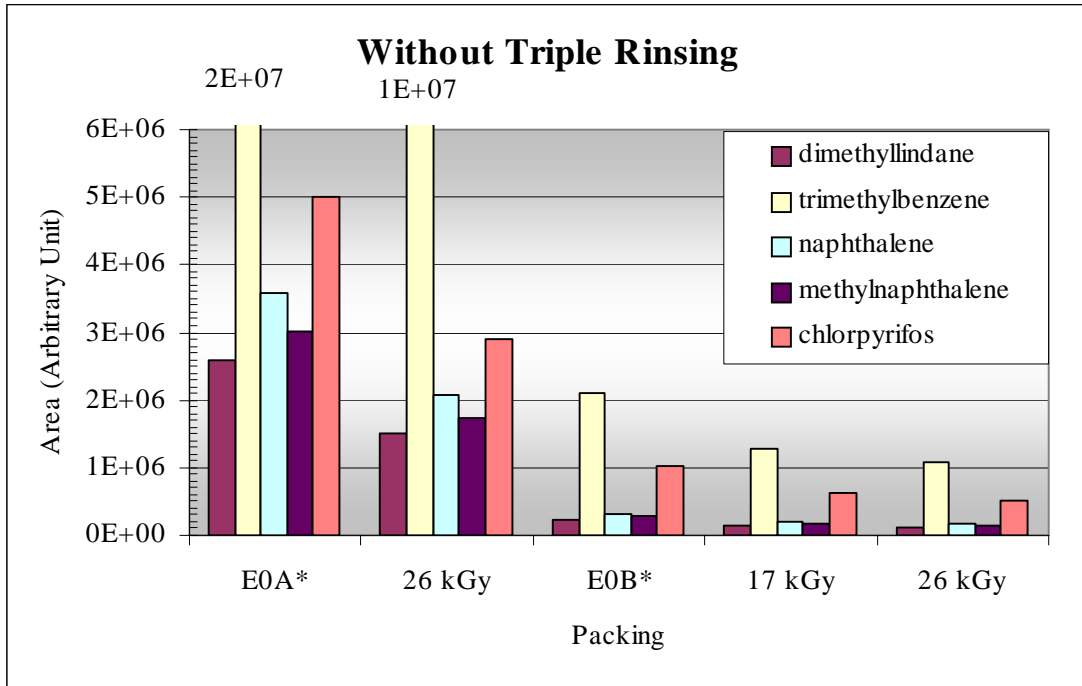
**TABLE 2.** Concentration and removal of chlorpyrifos from packing “A”, in the packing after radiation processing and extraction with acetonitrile for 30 minutes and 24 hours, in different conditions.

<b>PACKING</b>	<b>ABSORVED DOSE (kGy)</b>	<b>TRIPLE RINSING</b>	<b>FILLING</b>	<b>CHLORPYRIFOS (μM/L)</b>	
				<b>Σ extraction in acetonitrile</b>	<b>Removal rate (%)</b>
<b>E0A*</b>	<b>00</b>	<b>no</b>	<b>Empty</b>	<b>146,943.0</b>	
E1	26	no	Empty	110,282.0	<b>25.0</b>
<b>E0B*</b>	<b>00</b>	<b>no</b>	<b>Distilled water</b>	<b>38,919.9</b>	
E2	17	no	Distilled water	24,291.9	<b>37.6</b>
E3	26	no	Distilled water	22,725.7	<b>41.6</b>
<b>E0C*</b>	<b>00</b>	<b>yes</b>	<b>Empty</b>	<b>570.5</b>	
E4	17	yes	Empty	254.2	<b>55.5</b>
E5	26	yes	Empty	158.3	<b>72.3</b>

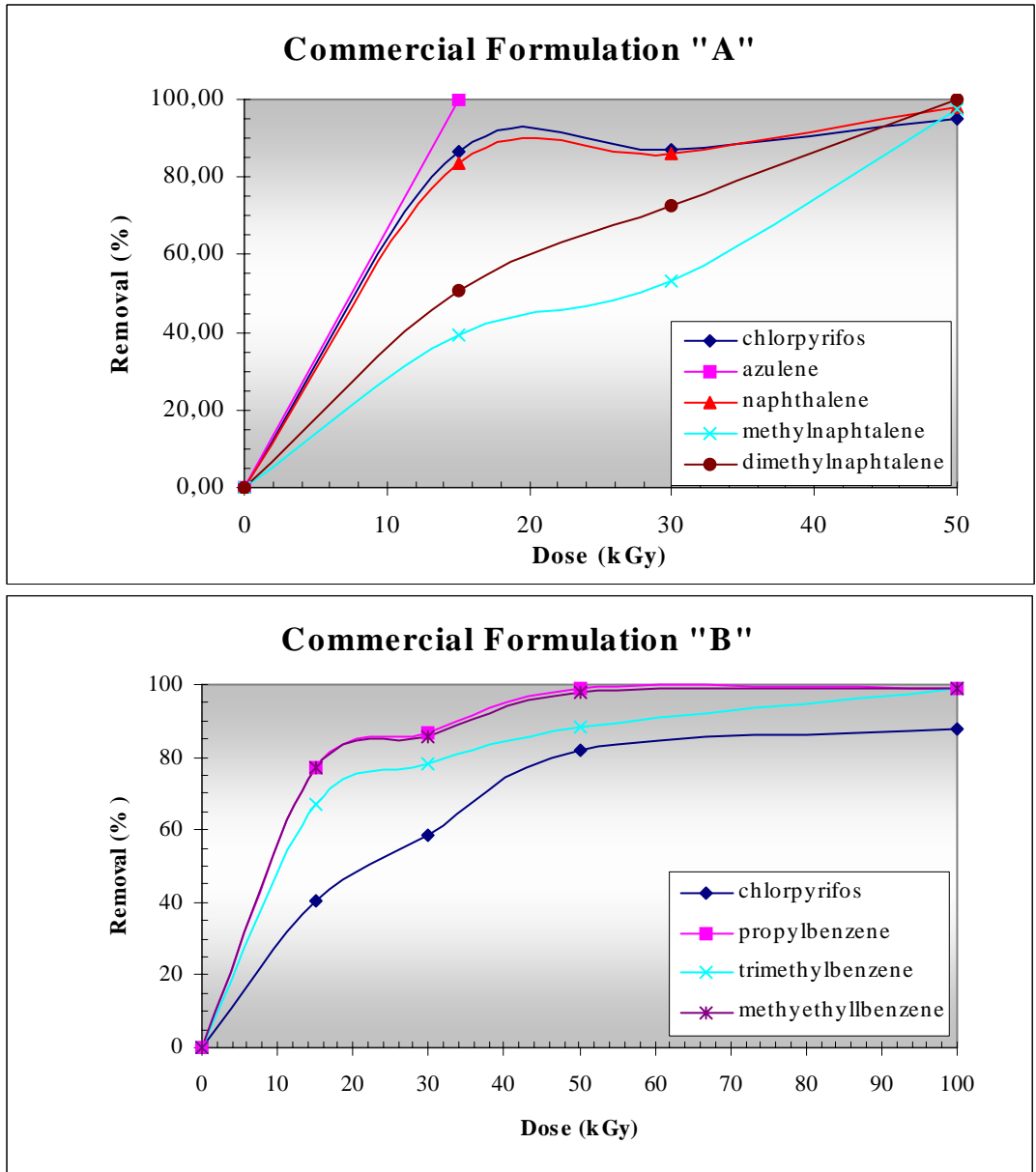
E0D*	00	yes	Distilled water	115.6	
E6	17	yes	Distilled water	7.8	<b>93.2</b>
E7	25	yes	Distilled water	<LMD	<b>99.0</b>



**Figure 1**



**Figure 2**



**Figure 3**

## LIST OF FIGURE CAPTIONS

- Figure 1.** Chromatogram with the main organic compound present in commercial formulation of chlorpyrifos called “A” and “B”
- Figure 2.** Organic compounds removal after radiation processing of pesticide “A” packing , without and with triple rinsing in different absorbed doses.
- Figure 3.** Organic compounds removal after radiation processing of pesticide “A” and “B” packing, in pieces, without triple rinsing, in different absorbed doses.