Degradation of chlorinated organic and pyrethroid pesticides induced by gamma irradiation in cultural heritage

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1.Background and goal of the present work

To protect collections from pests, museums have historically used hazardous chemicals (Fig. 1). However, residues from these substances persist in artifacts, posing risks to both preservation and health. Previous studies reported pesticide concentrations in museum collections ranging from 0.01 ppm to 21,000 ppm (Uden et al., 2014; Salmo et al, 2017).

Fig. 1. Contaminated object with a label indicating pesticide treatment from the Museu de Arqueologia e Etnologia (MAE-USP) collection.

Mitigation is essential, and ionizing radiation presents a promising approach for cultural heritage decontamination. This study explores the application of gamma radiation to degrade DDT, lindane, hexachlorobenzene, and permethrin, pesticides that have been historically used on cultural heritage objects.

2. Materials and methods

2.1. Chemicals and reagents

The following pesticide reference materials were purchased from Dr. Ehrenstorfer (Augsburg,Germany): DDT (97.8% chemical purity), hexachlorobenzene (99.9% chemical purity), lindane (γ-HCH) (99.7% chemical purity). The reference of permethrin of isomers cis (30,3%) and trans (61,5%) was purchased from Sigma-Aldrich (St. Louis, USA). In order to prepare the diluted solutions, organic solvents (residue analysis grade) as acetone and methanol were used from Labsynth (São Paulo, Brazil).

2.2. Samples preparation

A 1,000 ppm stock solution was prepared for each pesticide. DDT and lindane were diluted in methanol, while hexachlorobenzene and permethrin were diluted in acetone. The same solvents as the reference standards were used, except for permethrin, which was in solid form. Working solutions were prepared at concentrations of 0.1, 0.2, 0.5, 1, 5, and 10 ppm.

2.3 Radiation processing

A Cobalt-60 gamma-ray source was used for all irradiation experiments. The processing was conducted at the Multipurpose Cobalt-60 Irradiator facility at the Radiation Technology Center (CTER) of the Nuclear and Energy Research Institute, IPEN-CNEN/SP (Fig. 2).

Fig. 2. Multipurpose Cobalt-60 Irradiator - IPEN–CNEN/SP.

In this experiment, standard pesticide solution samples at concentrations of 1, 5, and 10 ppm were irradiated with doses of 0 (control), 1, 3, 6, 10, 25, 50, and 100 kGy. Irradiation of the samples was conducted at a dose rate of 5-6 $kGy.h^{-1}$.

2.4 Chromatographic conditions

A Shimadzu GC-MS 2020 (Shimadzu Corporation, Kyoto, Japan) gas chromatograph (GC 2010) with quadrupole mass analyzer and the analytical capillary column DB-5 (5%phenylsilicone, 95% methylsilicone; 30m, 0.25mm I.D., 0.25 mm film thickness) (Agilent Technologies, Santa Clara, California, USA, J&W Serial Number USN108762H) were used.

The program of GC was set as follows: the initial temperature of the oven was 60°C and held for 1 min, and then the temperature increased at a rate of 10°C/min up to 250°C and held for 15 min. Injection was performed in split ratio mode (5.0) with an injection volume of 3 µL. Helium (99.999% chemical purity) was used as the carrier gas with a column flow rate of 1.63 ml/min.

3. Results and Discussion

The effects of gamma radiation on the degradation of pesticide solutions at concentrations of 1, 5, and 10 ppm are shown in Figure 3. In general, higher absorbed doses correlate with lower pesticide concentrations, with the reduction extent varying by pesticide type and initial concentration.

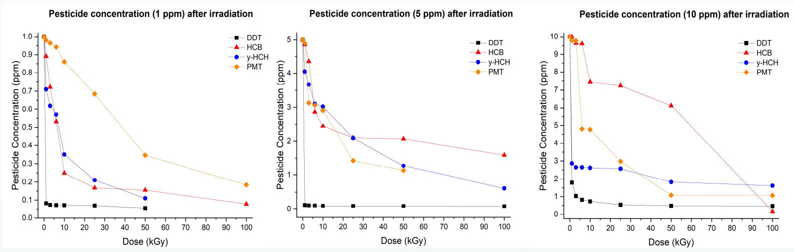

Fig. 3. Degradation of pesticide standard solutions at 1, 5 and 10 ppm under different irradiation doses.

G-values are key indicators of radiolytic reactions, reflecting the efficiency of pesticide removal in relation to radiation chemical yield. The results suggest that G-values decrease with increasing absorbed dose due to analyte degradation and competition between degraded pesticide molecules and reactive radicals. As the dose rises, intermediate concentrations increase while pesticide levels drop, leading to a higher likelihood of radicals reacting with intermediates rather than the original compound, resulting in lower G-values (Ghaffar et al., 2023).

This indicates that pesticide degradation is dose-dependent, with higher doses leading to greater analyte reduction, though G-values tend to decline from 25 kGy onwards (Figure 4).

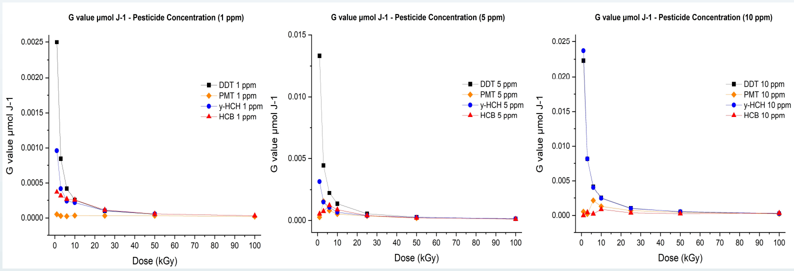

Fig. 4. G-value for 1, 5 and 10 ppm standard pesticide irradiated solutions.

The degradation products formed after irradiation are potentially less toxic than the original compounds (Table 1). This suggests that the technique effectively degrades pesticides, yielding products with reduced toxicity.

Pesticide	Mammals - Acute oral LD_{50} (mg kg^{-1})	Possible degradation product	Mammals - Acute oral LD_{50} (mg kg^{-1})
DDT	87	DDD	3400
Hexachlorobenzene	10	Pentachlorobenzene	1125
Lindane	76	Pentachlorocyclohexene	3500
Permethrin	430 – 4000	Unable to identify	---

Table 1. Comparison of the toxicity of irradiated pesticides and their potential degradation products.

4. Conclusion and Ongoing Studies

The results confirm that gamma radiation effectively reduces pesticide concentrations and shows promise for decontaminating cultural heritage items. Higher absorbed doses led to greater pesticide degradation, with G-values decreasing and stabilizing from 25 kGy onwards.

Ongoing studies are assessing whether degradation efficiency is maintained in mockup museum materials and how different substrates may influence the results. The use of ionizing radiation on cultural heritage must be carefully controlled to prevent undesirable side effects. Therefore, current investigations aim to determine whether doses effective for pesticide degradation in solutions are safe for cultural heritage materials.

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