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Degradation of profenofos in aqueous solution and in vegetable sample by electron beam radiation

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ABSTRACT

In this study, the role of accelerated electron irradiation on the removal of profenofos in aqueous solution and in peas was investigated. The samples were irradiated with a Rhodotron E-beam accelerator with 10 MeV energy at doses of 0 (control), 4.6, 12 and 32 kGy. Irradiated vegetable samples were extracted using a QuEChERS protocol (quick, easy, cheap, effective, rugged, and safe), allowing analysis of pesticide traces. Quantification of profenofos in aqueous solution was performed by using GC-MS in SIM mode and GC-MS/MS in MRM mode in vegetable sample. Degradation of profenofos increased with the E-beam dose and was much more important in aqueous solution than in vegetable. In irradiated aqueous solution, one degradation product was detected.

1. Introduction

Pesticides belong to a class of chemical compounds intended for preventing, destroying, repelling or mitigating any pest or used to control organisms that are considered a potential to damage crops. Organophosphate insecticides have been widely used by farmers to control fungal diseases and insect pests of vegetables, fruits, ornamental plants, turf, and other agricultural crops. An example of this pesticide class is profenofos.

Profenofos (O-(4-bromo-2-chlorophenyl phosphorothioate) O-ethyl S-propyl) is a pesticide that remains in the environment and is widely used in Brazil, unlike in Europe where it is banned (EU pesticides database). According to the World Health Organization (WHO), profenofos has been classified as a moderately hazardous pesticide. In Brazil this pesticide is used for the cultivation of onions, corn, soybeans, coffee, tomato, cotton, beans, potatoes, peas and others. In peas, the maximum residue level (MRL) is 0.1 μg/g, established by the Ministry of Agriculture, Livestock and Food Supply (MAPA).

Several methods can be used for removing pollutants from contaminated environmental components (Basfar et al., 2012). In the field of chemical water treatment, several oxidative degradation processes, called advanced oxidation processes (AOPs), have been developed (Picó and Kozmutza, 2007). These include UV photolysis, photocatalysis (hydrogen peroxide and ozone), Fenton reagent and water radiolysis (Angthararuk et al., 2017; Burrows et al., 2002; Zamy et al., 2004). Radiation is one of the most powerful AOPs, where the use of accelerated electrons or gamma radiation decomposes pollutants such as pesticide residues (Basfar et al., 2012; Hossain et al., 2013; Mohamed et al., 2009). Radiation is a process also used in the food industry. This consists of exposing food to ionizing radiation, such as high energy ($E < 10$ MeV) electrons, X-rays produced by electron accelerators ($E < 5$ MeV) or gamma rays (1.17 and 1.33 MeV) emitted from the radioisotope ^{60}Co. Depending on the absorbed dose, various effects can be achieved resulting in reduced storage losses, extended shelf life, and/or improved microbiological and parasitological safety of foods (Farkas, 2006). The World Health Organization (WHO) has approved the irradiation of a variety of foods with doses greater than the level of 10.0 kGy recommended by the Codex Alimentarius Commission.

Most research studies working on the decomposition of pesticides by irradiation have used gamma rays (Trojanowicz et al., 2018). This choice could be explained by the fact that this technique is easier to use than other techniques such as electron beam radiation. Indeed, due to the high penetrative power of gamma rays, this technique does not require attention to the geometry of the sample to be irradiated. However, a major disadvantage is that it is much more polluting because it requires a radioactive source. Another technique, which is the most widely used for technical applications, is electron beam irradiation (Trojanowicz et al., 2018). One essential disadvantage is the

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limited penetration depth of the e-beam in the irradiated samples, which therefore requires a higher level of technical competency to use. Nevertheless, its main advantage is a much higher dose rate and instant on/off operation (Trojanowicz et al., 2018). Thus, in this study, the effect of accelerated electron beam radiation on the removal of pesticides was evaluated, and more particularly the degradation of profenofos in aqueous solution and in food samples (peas) was quantified. In addition, degradation products of profenofos formed in aqueous solution were also studied and detected by gas chromatography coupled with mass spectrometry (GC-MS).

2. Experimental procedure

2.1. Chemicals

Profenofos ($C_{11}H_{15}BrClO_3PS$, 96.9%), atrazine ($C_8H_{14}ClN_5$, 98.8%), anhydrous magnesium sulfate ($MgSO_4$, ≥97%), acetonitrile (for pesticide residue analysis), ethyl acetate (for pesticide residue analysis), toluene (for pesticide residue analysis), carbon/NH_2 dual layer SPE tube, QuEChERS salt kit containing 6 g of magnesium sulfate ($MgSO_4$) and 1.5 g of sodium acetate (CH_3COONa) and ethanol absolute (≥99.8%) were purchased from Sigma-Aldrich (Steinheim, Germany). The chemical structure of profenofos is as follows in Fig. 1.

The experiments were performed with water purified with a Synergy Milli-Q System (Millipore, Molsheim, France).

Pea samples were collected at random from a local supermarket in Strasbourg (France) and stored in refrigeration (4 °C).

2.2. Sample preparation

Standard stock solutions of 1 mg/mL profenofos were prepared in acetonitrile.

2.2.1. Aqueous solution

The aqueous solution of profenofos was prepared as follows: 84 µL of a 1.0 mg/mL solution of profenofos were diluted in 3 mL of purified water to a final concentration of 28 µg/mL (corresponding to its limit of solubility). All samples were placed in 20 mL glass vials previously heated in an oven at 400 °C for 8 h, closed by teflon-based caps protected with aluminum foil. Each sample was assayed in triplicate.

2.2.2. Vegetable sample: pea

For the pea, a total of 10 µL of solution of 100 µg/mL of profenofos in ethanol were added to 10 g of pea. All samples were weighed, packed in polyamide/polyethylene plastic sachets, sealed and identified with their respective radiation doses. Each sample was assayed in triplicate.

2.3. Irradiation source

Profenofos aqueous solutions and peas were irradiated with a Rhodotron E-beam accelerator (IBA, Louvain la Neuve, Belgique) facility installed at BGS GmbH & Co. KG, located in Bruchsal, Germany. The energy of the electron beam was 10 MeV with a 15 mA current and 160 cm scan width. Irradiation treatments were conducted at room temperature (25 °C) and atmospheric pressure (1 atm). For the aqueous solution of profenofos, the electron beam passed through the diameter of the tube (1 mm of glass, 1 cm of water and 1 mm of glass).

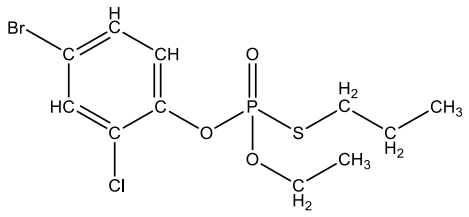

Fig. 1. Molecular formula of profenofos.

The applied doses were 0 (control), 4.6, 11.7 and 31.6 kGy for the aqueous solution, and 0 (control), 4.5, 12.2 and 30.4 kGy for the peas. In both experiments, absorbed doses were monitored with FWT 60.00 radiachromic dosimeters (Far West Technology, Goleta, CA), previously calibrated with an alanine dosimeter (Aérial, Illkirch, France) (Kuntz et al., 1996). Dosimetric readings confirmed that dose uniformity was about 10% within the sample.

For the peas, the irradiated and control samples were frozen after electron-beam irradiation.

2.4. Extraction procedure

2.4.1. For aqueous solution of profenofos

After irradiation, the aqueous sample (3mL) was transferred to a test tube to carry out the profenofos extraction process. In each tube, 84 µL of atrazine solution (1 mg/mL in acetonitrile) was added as an internal standard before extraction. Profenofos was then extracted with ethyl acetate (3 × 3 mL). To analyse the radiolytic breakdown of profenofos products, five irradiated test tubes were pooled into one and submitted to the same extraction procedure (3 × 3 mL) with ethyl acetate. The combined three organic extracts were evaporated to dryness under a gentle nitrogen flow.

To each dry extract 1 mL of ethyl acetate was added and carefully transferred using a pipette to a 2 mL injector vial and 1 µL of each sample was injected into the GC-MS.

2.4.2. Vegetable sample: pea

After irradiation, 20 µL of internal standard solution (atrazine at 100 µg/mL in ethanol) was added to the pea samples. 10 g of peas were added to the 50 mL polycarbonate crushing vials with a stainless steel impinge. The pea samples were finely mixed in liquid nitrogen (Air Liquide, Paris, France) for 9 min with a cryogenic ground (6870 Freezer/Mill, Spex CertiPrep, Stanmore, UK) at a rate of 20 impacts/sec.

The QuEChERS procedure was employed in respect of each sample. Fig. 2 illustrates the scheme of the entire analytical protocol used during the present study.

2.5. GC-MS analysis

GC-MS analysis was performed on a Varian STAR 3400 chromatographic system with an on-column SPI injector hyphenated with a Varian SATURN 2000 mass sensitive detector (Varian, France). The instrumental control, data acquisition and processing were performed using Varian Saturn WS software 5.11.

Samples were separated with a VF-5ms capillary column (60 m, 0.25 mm internal diameter, Varian, France). The column temperature gradient was programmed from 80 °C (held for 2 min) to 280 °C at 5 °C/min (held for 1 min). The SPI injector operating conditions were as follows: injection volume 1 µL; initial injector temperature of 105 °C was increased to 280 °C at 100 °C/min held for 40 min. The carrier gas (helium, purity 99.9995%) flow was 1 mL/min.

Electronic impact (EI) ionization mode mass spectra were obtained at 70 eV. Quantitative data analysis was carried out using Selected Ion Monitoring (SIM) analysis of profenofos aqueous sample and using Multiple Reaction Monitoring (MRM) for profenofos contaminated pea samples.

Peak areas were normalized using atrazine as an internal standard. The analytes were quantified as follows (Equation (1)):

$$n_C = (n_{is}.\ A_c)/(RRF_c.\ A_{is}) \quad (1)$$

Where: A_c and A_{is} are the areas of the chromatographic peak of profenofos and of atrazine, respectively; RRF_c is the response factor of profenofos. The response factor of atrazine, by definition, is equal to 1. The

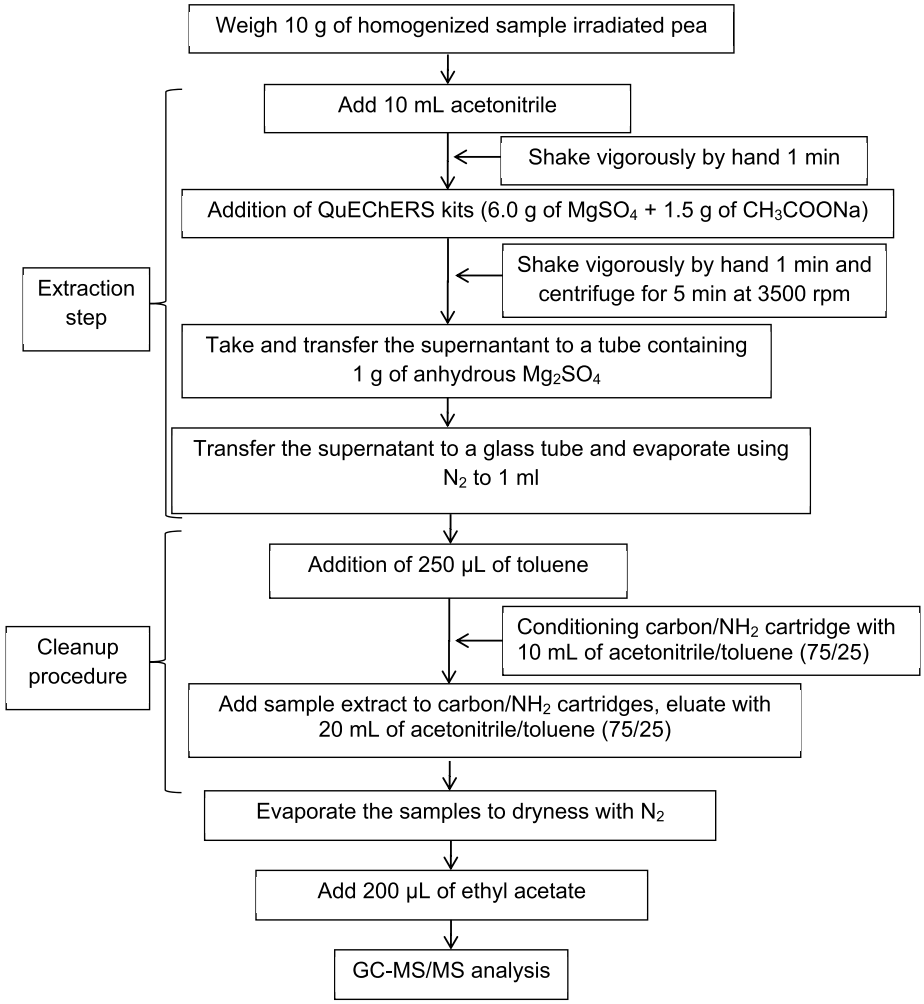

Fig. 2. Schematic description of QuEChERS and cleanup procedures for irradiated peas.

RRF_c was calculated using equation (2):

$$RRF_C = (n_{is}.\ A_c)/(n_c.\ A_{is}) \quad (2)$$

Where: n_c and n_{is} are the moles of profenofos and of atrazine, respectively present in the mixture injected in the GC-MS. Relative Response Factor (RRF) is an analytical parameter used in chromatographic procedures as a measure of the relative response of the detector to profenofos as compared to atrazine (internal standard). The RRF_c was calculated within different concentrations of atrazine and profenofos.

Peak areas were detected by MS operating in SIM mode for the aqueous solution and by MS-MS operating in MRM mode for the pea sample. The experiments were performed in triplicate.

2.6. Linearity and limit of detection

Limit of detection (LoD) was defined as the lowest analyte mass yielding a signal-to-noise (S/N) ratio of 3. The limit of quantification (LoQ) was defined as the lowest analyte mass yielding a signal-to-noise (S/N) ratio of 10. LoD and LoQ were obtained by successively injecting each pure compound solution in ethyl acetate with decreasing concentrations of analyte. Linearity was tested by triplicate analyses of profenofos at different concentrations ranging from 0.5 to 90 µg/mL in SIM mode and 0.002–0.5 µg/mL in MRM mode.

Linear regression analyses of the standard solutions were performed at four different concentrations levels, in triplicate. Linear plots of peak areas versus concentration were calculated.

2.7. Profenofos G-value

Radiation chemical yield of pesticide degradation (defined by the number of molecules formed or destroyed in solution absorbing 100 eV of radiation energy) was calculated at each absorbed dose using Equation (3) given by Kurucz et al. (1991):

$$G = ([R].\ Na)/(D.\ (6.\ 24x10^{16})) \quad (3)$$

Where: [R] is the change in profenofos concentration in $mol.L^{-1}$; D is the dose absorbed in Gy; N_A is Avogadro's number (6.02×10^{23}); 6.24×10^{16} is the conversion factor from Gy to 100 $eV.L^{-1}$. To calculate the G-value in the SI unit (µmol/J), the value is multiplied by 0.1036.

2.8. Dose constant (K)

The dose constant, **K**, was obtained by plotting the logarithm (ln) of the profenofos concentration versus the absorbed dose (Gy). The absorbed dose required for degradation of 50% ($\mathbf{D}_{0.5}$) and 90% ($\mathbf{D}_{0.9}$) were calculated by using the following formulas (Eq. (4) and (5)):

$$D_{0.5} = \ln 2/K \quad D_{0.9} = \ln 10/K \quad (4,5)$$

3. Results and discussion

3.1. Quantification of profenofos

Chromatographic separation of atrazine, profenofos and its degradation product in different samples were well achieved on a VF-5ms capillary column and identified by their MS data. In the case of an aqueous solution of profenofos, quantification was performed using SIM mode. For the sample of contaminated peas, the use of selected tandem mass spectrometry (MS/MS) was used due to the very low amount of profenofos. Quantification of profenofos was done by using an internal standard, not isotope-labeled IS but another pesticide for economic purpose.

Mass spectra of profenofos gives characteristic isotopic clusters due to chlorine and bromine atoms with ^{35}Cl, ^{37}Cl and ^{79}Br, ^{81}Br significant natural isotopes and several characteristic ions produced due to the presence of the phosphorothioate group containing chlorine and bromine substituted on benzene ring. Most of the ions containing the aromatic ring have a significant intensity due to the stability of the aromatic system (Hong et al., 2000). All data, retention time, RRF, the selected ions chosen for identification and quantitation along with their relative abundances are summarized in Table 1. In this table the linearity and limit of detection and quantification for profenofos in the analytical conditions (SIM mode and in MRM mode) described in the present study are also summarized.

The calibration of peak areas versus concentrations generated a linear function ($R^2 = 0.998$ in SIM mode, $R^2 = 0.9958$ in MRM mode).The LoD and LoQ were estimated to be 0.2 μg/mL and 0.5 μg/mL respectively in SIM mode and 0.02 μg/mL and 0.05 μg/mL in MRM mode. In this last case, the LoQ was lower than the maximum residue limit (MRL) for profenofos in peas established by the MAPA.

3.2. Degradation of profenofos in aqueous solution

Electron beam irradiation is a process which involves accelerated electrons in a continuous exposure mode being able to penetrate different products to just beyond a few centimetres, depending on the thickness of the product, the energy of the e-beam and the electronic density of the processed material.

Degradation efficiency of profenofos is presented in Table 2, and Fig. 3 indicates the relationship between the absorbed dose and profenofos concentration. The results indicate that degradation of profenofos fits with an exponential first order law. Removal percentages of 72.6%, 96% and 99.8% can be achieved with absorbed doses of 4.6, 11.7 and 31.6 kGy respectively when irradiation is performed on aqueous solutions.

Results show that the degradation by E-beam of organophosphate compounds, like profenofos, in aqueous solution is possible. In fact, exposure of aqueous solutions to ionizing radiation causes radiolysis of water and as a result, the formation of primary radiolytic products (equation (6)). These radical and molecular products are homogeneously distributed throughout the solution. The simplified reaction scheme of water radiolysis could be summarized by (Le Caër, 2011):

$$H_2O \rightsquigarrow HO^{\bullet}, e^-_{aq}, H^{\bullet}, H_3O^+, H_2O_2, H_2, HO^- \quad (6)$$

During this step, the radiolysis products can react with each other or with the molecules of solutes present in the solution. In this study, these species were leading to complete degradation of the investigated molecule.

The radiation chemical yield (G-value) and the dose constant (K) are two parameters used to quantitatively evaluate the elimination efficiency of profenofos after irradiation. From this value, $D_{0.5}$ and $D_{0.9}$ values were also calculated (Table 2). The result showed that the G-value decreased with the augmentation of the dose. The radiation chemical yield trends reported here are similar to those reported for gamma ray irradiation of organophosphate and organochlored

Table 1
Chromatographic data used for the identification and the quantification of profenofos using SIM mode and MRM mode.

	Rt (min)	RRF		[a]Linearity: Equation, R^2		LoD/LoQ(μg/mL)		Ions		
		SIM mode	MRM mode	SIM mode	MRM mode	SIM mode	MRM mode	SIM mode (Relative abundance, %)		MRM mode
								identification	quantification	transitions
Profenofos	31.39	0.64 ± 0.05	0.50 ± 0.05	y = 2.1124 x – 0.0292 R^2 = 0.998	y = 2.0749x-0.0001 R^2 = 0.9958	0.2 /0.5	0.02/0.05	339 (100), 337(92), 269 (30), 267 (28),297(25),295 (24)	**337 + 339**	337 → 309 (quantification) 339 → 309 (identification)
Atrazine	23.06	1.0	1.0	–	–	–	–	200 (100),215 (68), 216 (65), 202 (35), 173 (30), 217 (25)	**215**	215 → 200 (quantification) 215 → 173 (identification)

[a] Calibration curves were obtained by peak areas (y) vs. concentration (x).

Table 2
Degradation efficiencies and dose constants of profenofos in aqueous solution.

Absorbed doses (kGy)	Degradation (%)	G-value (μmol.J^{-1})	Parameter		
			K	$D_{0.5}$	$D_{0.9}$
4.6	72.6	1.1×10^{-2}	0.19	3.57	11.86
11.7	96.0	5.4×10^{-3}			
31.6	99.8	2.1×10^{-3}			

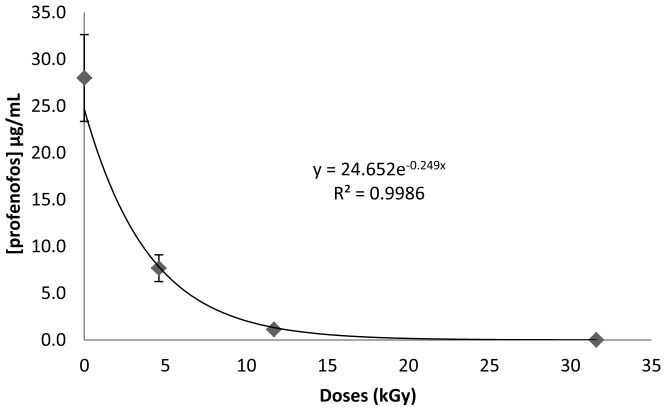

Fig. 3. Degradation of profenofos aqueous solution as a function of absorbed dose.

pesticides (Mohamed et al., 2009; Ismail et al., 2013). The decrease of G-value could be explained by the formation of by-products and their competition with different reactive species (Ismail et al., 2013). The $D_{0.5}$ and $D_{0.9}$ calculated values were equal to 3.57 kGy and 11.86 kGy respectively, showing the influence of the absorbed dose on the degradation rate of profenofos. These values were notably higher than those observed in the degradation of an aqueous solution of organophosphate pesticides such as diazinon (Basfar et al., 2007) or malathion (Mohamed et al., 2009) after gamma ray treatment, but remain below those observed for an aqueous solution of an organochloride pesticide such as lindane (Mohamed et al., 2009) which reflects the role of pesticide chemical structure in degradation.

The profenofos standards were not soluble in water and necessitated the use of ACN as a cosolvent. As the quantity of ACN and profenofos were the same, it can be theorised that ACN may act as a scavenger of the radialoytic compounds generated in water during radiation processing. The results presented in this work should be considered together with this scavenging capacity of ACN, decreasing the radiosensitivity of profenofos. Nevertheless, ACN is mandatory as profenofos is poorly soluble in water.

A radiolytic breakdown product was detected during this study. For this purpose, five irradiated samples in test tubes were pooled into one test tube, extracted, concentrated to dryness and finally dissolved in 1 mL of ethyl acetate. These steps were undertaken in order to increase the detection sensitivity of very low concentrations of profenofos radiolytic breakdown products, and then to facilitate their spectral identification. Fig. 4 illustrates the chromatographic profiles obtained during the analysis of an 11.7 kGy irradiated solution of profenofos. One compound was detected and clearly separated from the peak of profenofos and atrazine (IS), indicating that at least one radiolytic breakdown product is formed. This product was detected only at absorbed doses of 4.6 and 11.7 kGy. This compound could not be identified by the NIST or other online libraries. Based mass spectrum a molecular mass of m/z = 259 amu (Fig. 4) was attributed to it, whose precursor is profenofos (374 amu) that has lost a bromide and a chloride $[M\text{-}Br\text{-}Cl]^+$, the empirical formula of which can be presumed to be $C_{11}H_{15}O_3PS$. This compound is formed after the cleavage of carbon-bromine and carbon-chlorine bonds on the benzene ring. The

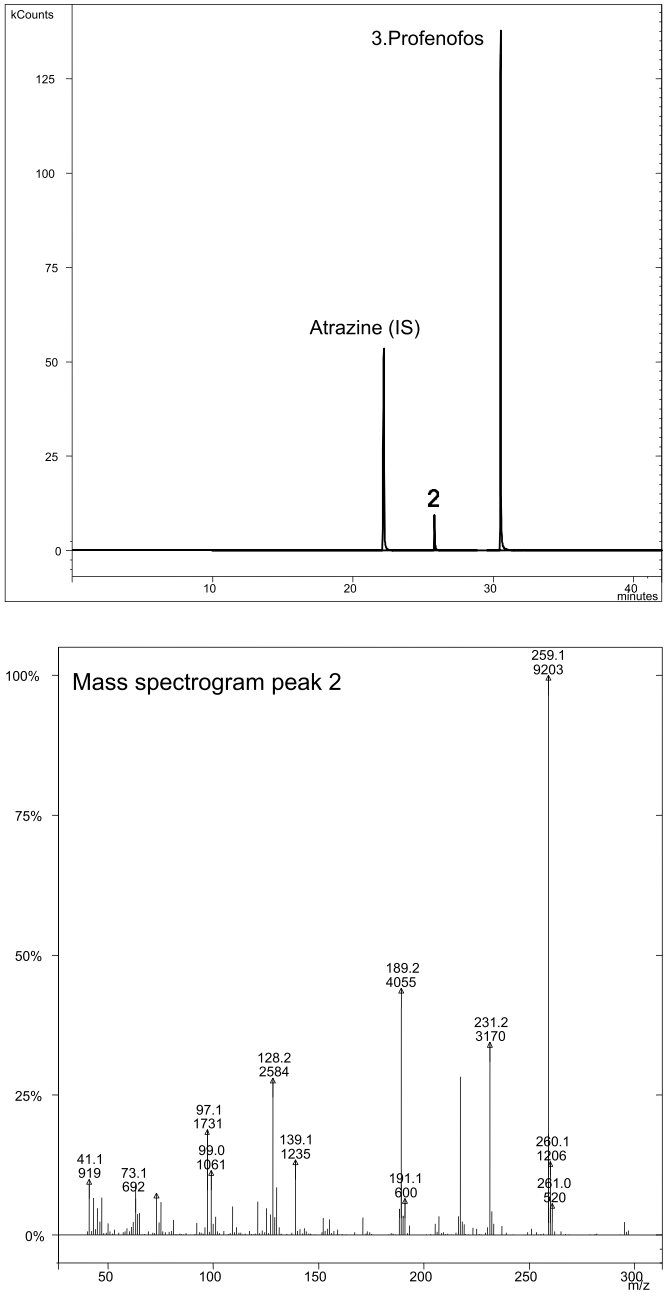

Fig. 4. GC-MS Chromatogram of profenofos solution irradiated at 11.7 kGy atrazine (peak 1), breakdown product (peak 2), profenofos (peak 3) and the mass spectrum of to the profenofos breakdown product (m/z 259.1).

absence of characteristic peaks of bromine and chlorine atoms in the mass spectrum confirms the loss of these elements. To elucidate the structure of this compound, an analysis by RMN will be necessary. But due the low sensitivity of this technique it will be difficult to have the amount necessary knowing that it is formed in very few quantities. In fact to detect this compound by GC-MS, it was necessary to pool 5 tubes of irradiated aqueous solution of profenofos.

This breakdown compound could not be quantified due to the lack of a standard, so the ratio of the peak area of this product to the peak area of the internal standard (atrazine) was used in order to evaluate the formation of this molecule (Fig. 5). This ratio is higher in the irradiated sample at 4.6 kGy, and the compound seems to be degraded by the electron beam, since its quantity decreases with higher doses. Some studies have investigated the photochemical transformation of

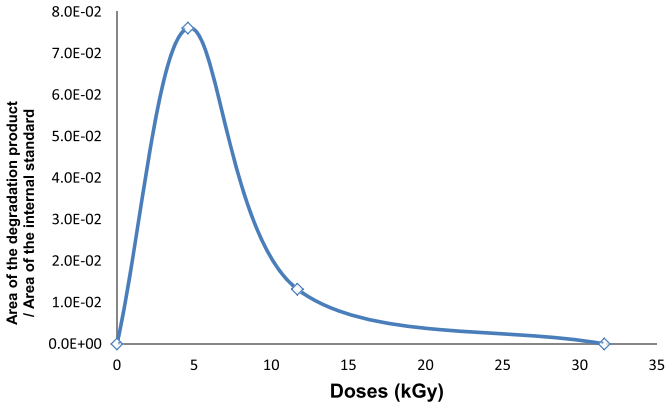

Fig. 5. Degradation breakdown products formed as a function of absorbed doses.

Table 3
Removal efficiency (%) of profenofos presents in peas and in aqueous solution after irradiation by E-beans at different doses.

Estimated dose (kGy)	0	4.5	12	31
Removal (%) in vegetable	0	38.2	41.8	47.9
Removal (%) in aqueous solution	0	72.6	96.0	99.8

profenofos in water using monochromatic light (Angthararuk et al., 2016; Zamy et al., 2004). Several products were identified, but not the product of this study.

3.3. Degradation of profenofos in pea sample

3.3.1. QuEChERS method

The role of ionizing radiation in removal of pesticide residue in contaminated vegetables (in this study in peas) was investigated. Since the concentration of pesticides present in vegetable is extremely low, the extraction step, concentration and reduction or elimination of interference is a critical procedure.

Different techniques of sample preparation for pesticide analysis can be used, such as molecular imprinting technology (Sanagi et al., 2013), solid-phase extraction/microwave extraction (Fang et al., 2012), supercritical fluid extraction (Rissato et al., 2005) and many others. However, these methods are often time consuming and labour intensive. Compared to these techniques, QuEChERS is an alternative extraction method which enables covering a very wide analyte scope, including highly polar pesticides as well as highly acidic and basic ones, uses fewer organic solvents, produces lower detection limits and presents a simple operation protocol. Therefore, this technique was used in this study.

The QuEChERS procedure involves an initial extraction with acetonitrile used for sample cleanup. The addition of a sorbent (CH_3COONa + $MgSO_4$) improves the purification step, removes the water content in the extract of pea and consequently enhances the partition of the above-mentioned matrix interfering compounds. Pea sample extracts were percolated in an SPE tube to offer superior cleanup when conducting multi-residue pesticide analysis. According to information from the manufacturer, the carbon/NH_2 cartridges have spherical, non-friable particles that improve flow characteristics and reduce susceptibility to the formation of interference. The particles with a carbon layer have the capacity to remove pigments and sterols, commonly present in many foods, and those with aminopropyl (NH_2) layer removed organic acids, polar pigments and sugars.

3.3.2. Chromatographic determination using GC-MS/MS

Quantitation of profenofos degraded by e-beam in pea was calculated using equation (1). Removal efficiency of profenofos is illustrated in Table 3, showing the influence of absorbed dose on the rate of degradation of profenofos in peas compared to the aqueous solution of profenofos.

It was observed that profenofos samples were influenced by E-beam, and the highest degradation efficiency was achieved at 30.4 kGy absorbed dose with a removal percentage of around 47.9%. However, compared to irradiated aqueous solution of profenofos, the percentage of removal in vegetable was much lower. In fact, for the same absorbed dose, the degradation of profenofos was twice as high when the pesticide is in water was when it was in the pea. This could be explained by the difference in concentration. Indeed, the concentration of profenofos in the experiment in aqueous solution was 28 μg/mL, whereas in the pea it was 1 μg/mL (corresponding to the MRL (0.1 μg/g) of profenofos in peas established at the MAPA in Brazil). Nevertheless, this difference can also be explained by the fact that plants are of more complex composition, in which a large number of organic substances can compete with pesticide residues for the various reactions produced with reactive species generated in peas after radiation. These same observations were also noted in the study of Basfar et al. (2012), in which decontamination of pesticide residues in an aqueous solution was more efficient than in contaminated fruits and vegetables after irradiation with gamma radiation.

4. Conclusions

This study has demonstrated that profenofos contained in aqueous solution or in vegetable could be effectively degraded and removed by E-beam irradiation. Increasing absorbed doses promoted a decrease in profenofos concentration. The removal of pesticide from an aqueous solution compared with vegetable was greater in irradiated aqueous solution than in vegetable.

Based on GC–MS analysis, one degradation product of profenofos in aqueous solution was detected but not quantified because of the lack of an authentic chromatographic reference. The QuEChERS method provided a fast and simple approach for extracting and analysing profenofos in pea samples. The GC-MS/MS analysis allowed the analysis of trace of profenofos contained in vegetable.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.radphyschem.2019.108441.

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