

Analysis of Pesticides in Water Samples and Removal of Monocrotophos by γ -Irradiation

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Abstract

The analysis of 20 organochlorine pesticides has been carried out in surface water samples collected from Peshawar, KPK, Pakistan, using SPME-GC-ECD method. This method showed good linear response with R^2 values in the range of 0.9933 to 0.9999 for all pesticides. Percent recoveries at $1 \mu\text{g L}^{-1}$ for all the pesticides ranged from 89.9 to 106.1%. A total of 59 surface water samples were tested for 20 organochlorine pesticides residues, of which, 37 samples were found contaminated with γ -BHC, 12 samples with β -BHC, 25 samples with heptachlor and 25 samples with aldrin with a maximum concentration of 0.092, 0.053, 0.089 and $0.036 \mu\text{g L}^{-1}$, respectively. However other pesticides were found in lesser no. of water samples. The Gamma irradiation decomposition of monocrotophos aqueous solution at various concentrations (60 - 150 mg L^{-1}) was carried out and their removal efficiency was investigated. Gamma irradiation showed 100% degradation for a 60 mg L^{-1} solution at an absorbed dose of 1200 Gy. The dose constants investigated in this study ranged from 1.4×10^{-3} to $3.0 \times 10^{-3} \text{ Gy}^{-1}$. The effect of saturated solutions of N_2 and N_2O , and radical scavengers such as *tert*-butanol and *iso*-propanol, on the degradation of monocrotophos were also studied. The results showed that degradation of monocrotophos mainly proceeded through oxidative $\cdot\text{OH}$ radical. The inorganic by-products NO_3^- , NH_4^+ and PO_4^{3-} were quantitatively determined by ion chromatography.

Keywords: Organochlorine pesticides; Monocrotophos; SPME-GC-ECD; IC

Introduction

Pesticides are chemical or biological products which are used in direct form, in aqueous solutions or as mixtures for preventing, fighting and killing a variety of pests, such as weeds, insects, rodents, and fungi [1]. The widespread occurrence of pesticides in natural waters is due to their widespread application in agriculture throughout the world [2]. Human being is constantly exposed to a large number of pesticides present in the environment.

Surface and ground water contamination due to extensive use of pesticide for agricultural purposes is a serious threat to the environment. Most important among them is pollution due to OCPs, because of their high toxic effect and persistence for a long time in the environment. Pollution by some common pesticides, such as organophosphorous pesticides (OPPs) due to mistreatment, direct run off, empty containers careless discarding, leaching, and utensils and apparatus washings, etc. is also important [3]. Chlorinated pesticides have fatal toxic effects for aquatic life forms such as fish. These pesticides are counted hazardous for the environment and human beings as well, due to bioaccumulation and biomagnifying effects in the food chain and because they may produce reproductive and carcinogenic effects in animals and human beings [4]. The Guideline values recommended by WHO for various pesticide residues in drinking water are $2 \mu\text{g L}^{-1}$ (Lindane), $0.03 \mu\text{g L}^{-1}$ for (Aldrin/dieldrin), $2 \mu\text{g L}^{-1}$ (DDT), $0.2 \mu\text{g L}^{-1}$ (Chlordane), $0.03 \mu\text{g L}^{-1}$ (Heptachlor + epoxide) and $20 \mu\text{g L}^{-1}$ (Methoxychlor) [5]. Monocrotophos ($\text{C}_7\text{H}_{14}\text{NO}_5\text{P}$) is an organophosphorus compound and used as a systemic insecticide and acaricide. It prevents pests on a variety of crops, such as sugarcane, cotton, rice and fruits and vegetables etc. Monocrotophos is commonly used for agriculture purposes in Pakistan to control boring, chewing and sucking insects (such as aphids, Helicoverpa spp, caterpillars, moths, mites, jassids, budworm, scale and stem borer, as well as locusts) for a large range

of crops. Unfortunately, the extensive use and easy approach of monocrotophos has resulted in enhanced utilization for homicidal and suicidal poisoning cases.

Monocrotophos is highly toxic compound and inhibits cholinesterase. It is very dangerous by all routes of exposure. Monocrotophos can be absorbed following ingestion, inhalation and skin contact. Monocrotophos can cause various diseases such as the damage of respiratory system, trigger runny nose, tears, pain, chest discomfort, coughing, localized sweating and involuntary muscle contractions, blurred vision and pupil constriction [6]. It is very toxic to bees, birds, mammals and aquatic invertebrates. The acute oral lethal dose (LD_{50}) of monocrotophos is 21 mg kg^{-1} for rats [7]. According to World Health Organization, the ingestion of monocrotophos (120 mg) may be fatal to humans [6]. Monocrotophos is classified a highly hazardous pesticide (Class Ib) according to World Health Organization 2004 edition of the recommended classification of pesticides by hazard [8]. OPPs are a large group of pesticides, which replaced organochlorine pesticides due to their higher acute toxicity, lower accumulation in the environment and relatively higher decomposition rate. They are widely used since 1970s for pest control in agriculture and in households.

The widespread occurrence of pesticides in natural waters is due

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to their widespread application in agriculture throughout the world [9]. Several studies have showed that organophosphorus pesticides have endocrine-disrupting effects [10], mutagenicity [11], cytotoxicity [12] and immunosuppressive effects [13]. In addition, it is necessary to mention that the joined consequences of different pesticides may cause more toxic effects on human health [14]. Therefore, more concentration should be necessary for the removal of organophosphorus pesticides from the drinking water.

AOPs are very effective in destroying organic pollutants and overcome issues of air pollution in aeration stripping or regenerating the sorbent(s) used in conventional processes. AOPs are used in addition to the conventional processes, as advanced processing of treated wastewater also. Irradiation of aqueous solutions by ionizing radiation produces three primary transient species: e_{aq}^- , $\bullet OH$ and $\bullet H$ that can oxidize or reduce contaminants. When using ionizing radiation as an AOP, pollutants can be oxidized or reduced in most cases to less toxic and in some cases to more biodegradable compounds that do not pose adverse environmental consequences [1]. Several studies have been reported using AOPs for degradation of various contaminants including pesticides and organic pollutants [15-20]. Organic pollutants are ultimately converted to carbon dioxide and water by AOPs [21]; however, the economic feasibility of this approach is often not acceptable. To evaluate the application of AOPs it is necessary to obtain fundamental data on degradation and formation of reaction by-products.

Among sources of environmental pollution, pesticides contamination is wide spread and is source of concern all over the world. Therefore, in this research work efforts has been made to determine the concentration levels of selected chlorinated pesticides contamination in water samples of selected areas of Khyber Pukhtoon Khwa, to provide useful information for the growing public awareness about chlorinated pesticides exposure, diseases and adverse effects caused due to pesticides contamination.

The present study focused on to degrade monocrotophos using gamma radiations as an AOP. The main objectives of present research work can be summarized as follow: (1) to study decomposition of monocrotophos solution in aqueous media by gamma radiation; (2) to determine the monocrotophos decomposition kinetics and effect of initial concentration on decomposition process; (3) to investigate the effects of different radical promoters and scavengers on the degradation of monocrotophos by gamma irradiation; (4) to determine pesticides contamination levels in water samples of selected areas.

Experimental

Extraction of pesticides from water

Normally, pesticides contamination in water is very low. Therefore, for the analysis of pesticides requires first good extraction and concentration. The solid-phase micro-extraction (SPME) is a fresh extraction method from liquid samples. This method needs no solvent and no need of complicated equipment. It includes the immersion of a fused silica rod coated with a stationary phase. Pesticides are adsorbed on the fiber first and then desorbed to the GC injector (for gas chromatography) or by liquid removing (for HPLC) [22].

Standards and reagents

The chlorinated pesticide mixture and monocrotophos (standards) were obtained from Supelco (Bellefonte, PA, USA) with >99% purity.

The methanol and acetonitril (HPLC grade) was purchased from Merck (Darmstadt, Germany). All of the chemical reagents used (perchloric acid, sodium hydroxide, *tert*-butanol and *iso*-propanol) were high-purity analytical grade reagents purchased from Sigma-Aldrich. All aqueous solutions were prepared in deionized water. Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for deionized water. High purity nitrogen gas (99.99% purity) was used in the present study.

Solutions preparation

10 PPM stock solution containing all the 20 organochlorine pesticides was prepared in methanol from 2000 PPM standard solution (Supelco, 47426-U, Bellefonte, PA, USA) and stored at 4°C. A fresh standard working solutions of various concentrations (0.01, 0.05, 0.1, 0.3, 0.5, 1 and 2 $\mu g L^{-1}$) containing all 20 pesticides were prepared from 10 PPM stock solution in deionized water for calibration curves which were used for quantitative analysis of pesticides in water samples.

1000 ppm monocrotophos stock solution was prepared by dissolving solid monocrotophos in Milli-Q water. 60 mg L^{-1} aqueous solutions of monocrotophos were prepared from stock solution in deionized water for gamma radiolysis study. Different concentrations of various additives (*tert*-butanol and *iso*-propanol) were added into 60 mg L^{-1} monocrotophos aqueous solution to study their effects on decomposition of monocrotophos by gamma radiation. Aqueous solutions of different concentrations of monocrotophos (60-150 mg L^{-1}) were prepared to examine the effect of initial concentration on degradation efficiency of monocrotophos in the same gamma irradiation absorbed dose.

Samples collection

The Peshawar district was selected for analysis of pesticides in water samples, which is an agricultural area. A total of 59 water samples (from fields as well as canals) were collected from various locations of district Peshawar. Figure 1 indicates various water samples sites of Peshawar area. All water samples were collected in washed and clean plastic bottles. To remove particulate matter from the samples, water samples were first filtered with wattman filter paper and then with 0.45 μm filter paper. After filtration samples were stored in 20 ml dark glass vials for GC determination. A DVB-PDMS fiber was used for pesticides extraction from water samples.

Irradiation process

Cesium-137 source (J. L. Shepherd Mark I Model A68 Irradiator) was used for gamma radiolysis. It has a fixed Cesium-137 source central rod in a cavity 30 cm in diameter and 33 cm high. The Cesium-137 gamma radiation source was available in the University of California, Irvine, CA, United States.

A Cesium-137 gamma radiation source was calibrated by Fricke dosimetry. The dose rate of source was 2 kGy h^{-1} . All the aqueous monocrotophos solutions were placed in 20 mL air tight glass vials for desired series of gamma radiation doses. All experiments were performed at room temperatures.

Analytical instrumentation

A DVB-PDMS fiber was used for pesticides extraction from water samples obtained from Supelco (Bellefonte). Chromatographic analysis was performed on an Agilent gas chromatograph (6890 N series, Agilent Technologies, Palo, CA, USA) equipped with (ECD)

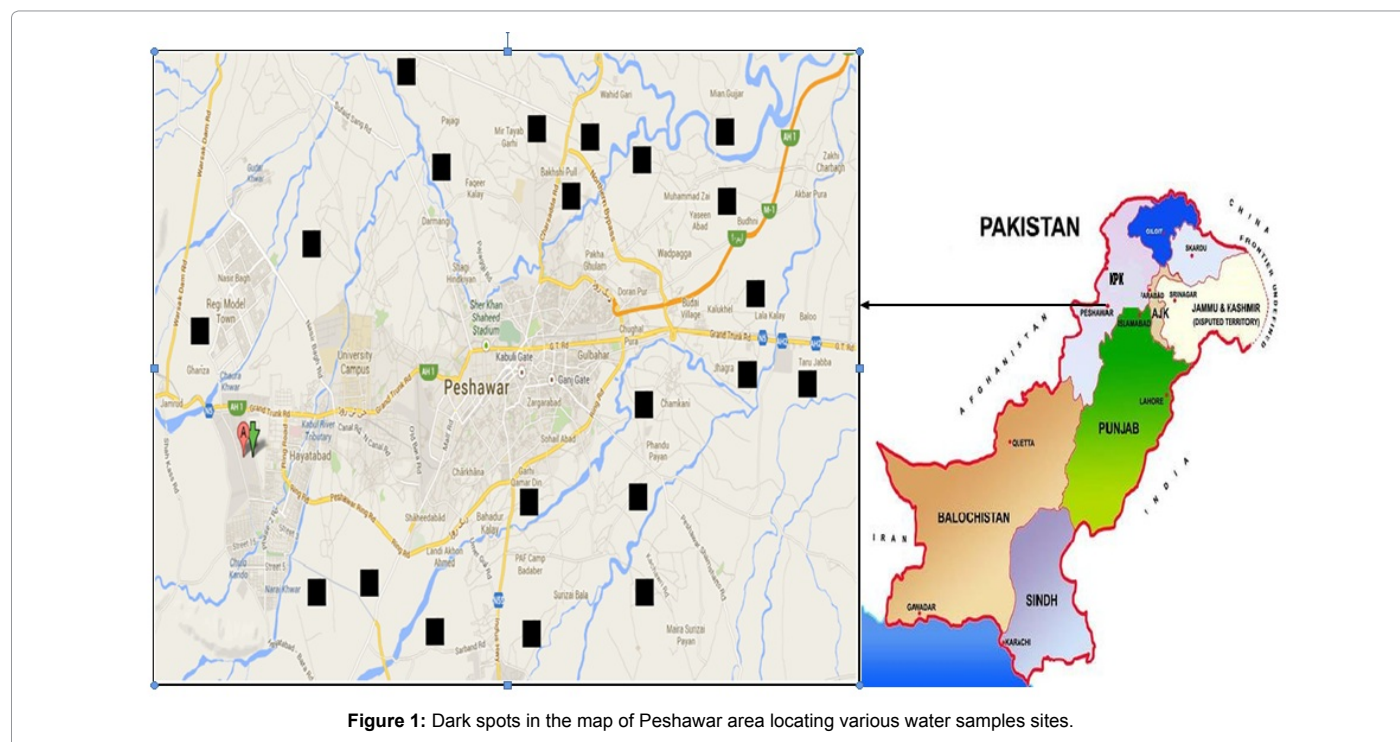


Figure 1: Dark spots in the map of Peshawar area locating various water samples sites.

electron capture detector (^{63}Ni) and split/splitless injector. Column used was Hp-5 fused-silica capillary column, 30 m \times 0.32 mm i.d. and 0.25 μm film thicknesses from Agilent. The operating conditions for GC were as follows: starting oven temperature was 80 $^{\circ}\text{C}$ for 4 m, then it is increased at 15 $^{\circ}\text{C min}^{-1}$ to 215 $^{\circ}\text{C}$ and remains constant for 30 s. Then it is increased again at 2 $^{\circ}\text{C min}^{-1}$ to 230 $^{\circ}\text{C}$ and remains constant for 3 m at this temperature. After this it is increased at 10 $^{\circ}\text{C min}^{-1}$ and reached to 260 $^{\circ}\text{C}$. The detector temperature was 300 $^{\circ}\text{C}$ and injector temperature was 250 $^{\circ}\text{C}$. A single GC run was completed in 28 min. N_2 gas (99.999% purity) was used as a make-up and carrier gas at a flow rate of 45 ml min^{-1} and 1 ml min^{-1} , respectively. The extraction time for fiber was (45 min), desorption time (2 min), and agitator speed (250 rpm) were selected.

The monocrotophos solutions were analyzed by HPLC (Agilent Technologies) equipped with a Phenomenex Gemini C_{18} column (4.6 \times 250 mm). The mobile phase used was the mixtures of acetonitrile and water (20:80%) at a flow rate of 1.2 ml min^{-1} . UV detector at λ_{max} of 210 nm was used. The HPLC/MS system equipped with an 1100 HPLC Pump (Agilent) and a Waters LCT Classic Mass Spectrometer. The Mass Spectrometer equipped with an electrospray ionization source. The by-product formed during gamma irradiation of monocrotophos was analyzed by Ion Chromatography. Metrohm Ion- Chromatograph (IC) equipped with electro chemical anion self-regenerating suppressor, conductivity detector, analytical column Metrosep Assup-7 was used for analysis of by-product.

Results and Discussions

Pesticide residues in water samples of Peshawar

The chromatogram using solid-phase micro-extraction (SPME) of the 20 organochlorine pesticides standard is shown in Figure 2. All the organochlorines are eluted within a very reasonable time, about 28 min and well resolved under the optimized GC conditions. The extractions

of pesticides from water were performed in 20 mL dark glass vials at room temperature with the SPME fiber immersed in the solution. To investigate an SPME procedure for the analysis of organochlorine pesticides, optimization of several variables related to the extraction and desorption steps are required to achieve maximum efficiency. The parameters used were extraction time (45 m), desorption time (90 s), pH of solution (6.2), agitation and stirring speed (250 rpm). After extraction of pesticides by SPME fiber, the analytes were desorbed into the hot injector of the GC by thermal desorption. All studies were carried out in triplicate and average values were calculated.

The analytical parameters evaluated to validate the method were linearity, selectivity, accuracy, precision and detection limits. The method used to quantify the analytes of interest was using calibration curves obtained by plotting peak area versus pesticide concentration. The linearity was evaluated by linear regression analysis, which was calculated by the least square regression method and linearity was observed at different concentrations. The calibration curves of 20 organochlorine compounds at various concentrations (0.01, 0.05, 0.1, 0.3, 0.5, 1 and 2 $\mu\text{g L}^{-1}$) were obtained by plotting peak areas verses concentration. A good linear correlation between the chlorinated pesticides concentrations and peak areas were found with R^2 values in the range of 0.9933 to 0.9999 (Table 1). Lower limits of detection were calculated based on a signal-to-noise ratio (S/N) 3:1. The R^2 values and lower limits of detection are shown in Table 1. The lower limits of detection for all 20 organochlorine pesticides were found very less than their maximum contamination level.

As the solid-phase micro-extraction (SPME) technique is a non-exhaustive extraction procedure, the relative recovery, which is defined as the ratio of GC peak areas of spiked ground water sample extracts to spiked Milli-Q water extracts, was employed. Relative recovery tests were carried out spiking the real sample with standards (1 and 2 $\mu\text{g L}^{-1}$) and values are shown in Table 2. The Percent recovery found at 1 μg

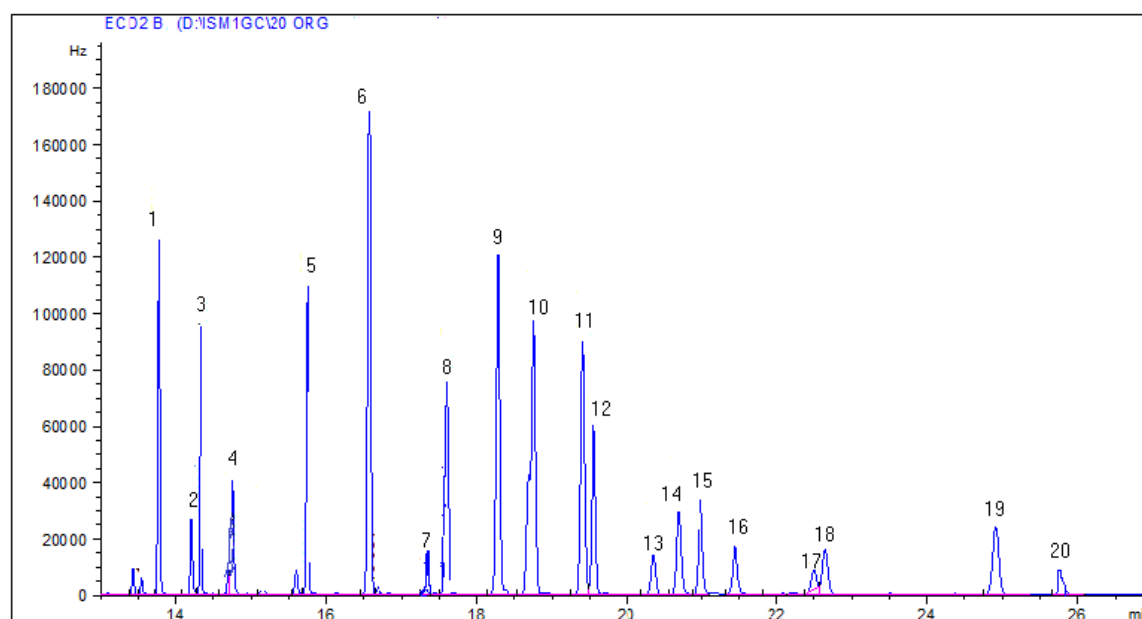


Figure 2: Chromatogram peaks identification of standard solution using solid-phase micro-extraction (SPME) technique: (1) α -BHC; (2) β -BHC; (3) γ -BHC; (4) δ -BHC; (5) heptachlor; (6) aldrin; (7) heptachlor epoxide; (8) γ -Chlordane; (9) α -Chlordane (10) endosulfan I; (11) 4,4'-DDE; (12) dieldrin; (13) endrin; (14) endosulfan II; (15) 4,4'-DDD; (16) endrin aldehyde; (17) endrin ketone; (18) 4,4'-DDT; (19) endosulfan sulfate; (20) methoxychlor.

No	Compound	Linear range ($\mu\text{g L}^{-1}$)	R^2	LOD ($\mu\text{g L}^{-1}$)	Guideline value ($\mu\text{g L}^{-1}$)
1	α -BHC	0.01-1	0.9995	0.003	-
2	β -BHC	0.05-1	0.9996	0.006	-
3	γ -BHC	0.01-1	0.9998	0.002	2, 0.2 ^b
4	δ -BHC	0.01-1	0.9995	0.003	-
5	Heptachlor	0.01-1	0.9996	0.004	0.03, 0.4 ^b
6	Aldrin	0.01-1	0.9999	0.002	0.03
7	Heptachlor epoxide	0.05-2	0.9980	0.02	0.03, 0.2 ^b
8	γ -Chlordane	0.01-1	0.9997	0.003	0.2, 2 ^b
9	α -Chlordane	0.01-1	0.9995	0.002	0.2, 2 ^b
10	Endosulfan I	0.01-1	0.9998	0.002	0.05 ^a
11	4,4'-DDE	0.01-1	0.9997	0.004	-
12	Dieldrin	0.01-1	0.9998	0.002	0.03
13	Endrin	0.01-1	0.9944	0.004	2 ^b
14	Endosulfan II	0.01-1	0.9998	0.003	0.05 ^a
15	4,4'-DDD	0.01-1	0.9957	0.005	-
16	Endrin aldehyde	0.01-1	0.9976	0.004	-
17	Endrin ketone	0.05-1	0.9968	0.003	-
18	4,4'-DDT	0.05-1	0.9955	0.009	2
19	Endosulfan sulfate	0.01-1	0.9999	0.002	-
20	Methoxychlor	0.05-2	0.9933	0.03	20

WHO guideline value, a: Australia guideline value, b: U.S. EPA maximum permissible level
LOD: Lower limits of detection

Table 1: The Linear range, R^2 values and lower limits of detection for selected pesticides.

L^{-1} and at $2 \mu\text{g L}^{-1}$ concentration of pesticides ranged from 89.87 ± 3.9 to 106.05 ± 2.3 and 88.50 ± 2.6 to 109.22 ± 2.9 , respectively. All These results show that SPME-GC-ECD technique is an excellent and valid method for the analysis of chlorinated pesticides in real water samples.

The results of determination of pesticides in the surface water samples collected from Peshawar area are summarized in Table 3. A total of 59 surface water samples were tasted for 20 organochlorin pesticides residues, of which most of the samples were found

contaminated with various pesticides. Among the various pesticides analyzed, β -BHC, γ -BHC, heptachlor, aldrin, α -chlordane, endosulfan I, 4,4'-DDE and dieldrin were detected in most of the water samples. The representative chromatograms of 20 organochlorine pesticides and some pesticides contamination in surface water samples from Peshawar area are given in Figures 2 and 3. The identification of each chlorinated pesticide present in the water samples were confirmed by comparing their retention times with the standards of chlorinated pesticides.

In 59 surface water samples of Peshawar, 37 samples were found contaminated with γ -BHC, 12 samples with β -BHC, 25 samples with heptachlor and 25 samples with aldrin with a maximum concentration of 0.092, 0.053, 0.089 and 0.036 $\mu\text{g L}^{-1}$, respectively. γ -BHC (Lindane) has been used to treat food crops, seed treatment, soil treatment, forestry products and to treat livestock and pets. It was used widely in cultivating cocoa, cotton, sugar cane, coffee and others crops. BHC isomers can undergo long-range transport and be deposited into aquatic systems, where it can bioaccumulate in the food chain. Heptachlor has been used to kill soil insects and termites, to control grasshoppers, cotton insects and some crop pests, particularly infecting

corn.6 samples of α -chlordane, 8 samples of endosulfan I, 12 samples of 4,4'-DDE and 17 samples of dieldrin were found contaminated with a maximum concentration of 0.013, 0.014, 0.036 and 0.011 $\mu\text{g L}^{-1}$, respectively. The endosulfan I was predominant than the other endosulfans. The 4,4'-DDE is the byproduct of DDT degradation and is more stable in the environment. In surface water samples of Peshawar, the pesticides heptachlor epoxide, γ -chlordane, endrin, 4,4'-DDD, endrin ketone, 4,4'-DDT and methoxychlor were not detected in any samples in the present study. However, α -BHC, δ -BHC, endosulfan II, endrin aldehyde and endosulfan sulfate were found only in 2, 5, 5, 2 and 1 surface water samples of Peshawar, respectively.

No	Compound	Retention times	1 $\mu\text{g L}^{-1}$	2 $\mu\text{g L}^{-1}$
1	α -BHC	13.78	96.19 \pm 0.9	97.39 \pm 97.39
2	β -BHC	14.18	106.05 \pm 2.3	109.22 \pm 2.9
3	γ -BHC	14.34	98.21 \pm 1.7	102.89 \pm 2.4
4	δ -BHC	14.78	97.32 \pm 3.5	98.08 \pm 1.8
5	Heptachlor	15.74	90.56 \pm 4.3	89.36 \pm 3.4
6	Aldrin	16.57	98.14 \pm 2.8	96.79 \pm 1.9
7	Heptachlor epoxide	17.33	89.87 \pm 3.9	91.81 \pm 2.7
8	γ -Chlordane	17.60	95.36 \pm 1.2	96.02 \pm 3.1
9	α -Chlordane	18.30	92.78 \pm 2.5	88.50 \pm 2.6
10	Endosulfan I	18.77	93.52 \pm 2.8	95.10 \pm 4.1
11	4,4'-DDE	19.43	91.35 \pm 4.6	90.25 \pm 3.8
12	Dieldrin	19.57	96.89 \pm 1.8	98.39 \pm 2.9
13	Endrin	20.35	101.08 \pm 2.2	97.04 \pm 1.7
14	Endosulfan II	20.72	103.78 \pm 0.8	107.90 \pm 3.2
15	4,4'-DDD	21.02	94.81 \pm 2.4	95.70 \pm 2.8
16	Endrin aldehyde	21.45	98.18 \pm 0.6	99.53 \pm 0.7
17	Endrin ketone	22.53	103.72 \pm 1.9	105.95 \pm 2.3
18	4,4'-DDT	22.64	87.51 \pm 3.7	90.15 \pm 4.1
19	Endosulfan sulfate	24.91	97.98 \pm 1.2	96.75 \pm 3.3
20	Methoxychlor	25.81	96.89 \pm 1.5	95.02 \pm 3.9

Table 2: Percent recovery of selected pesticides at two concentration levels by using SPME-GC-ECD technique.

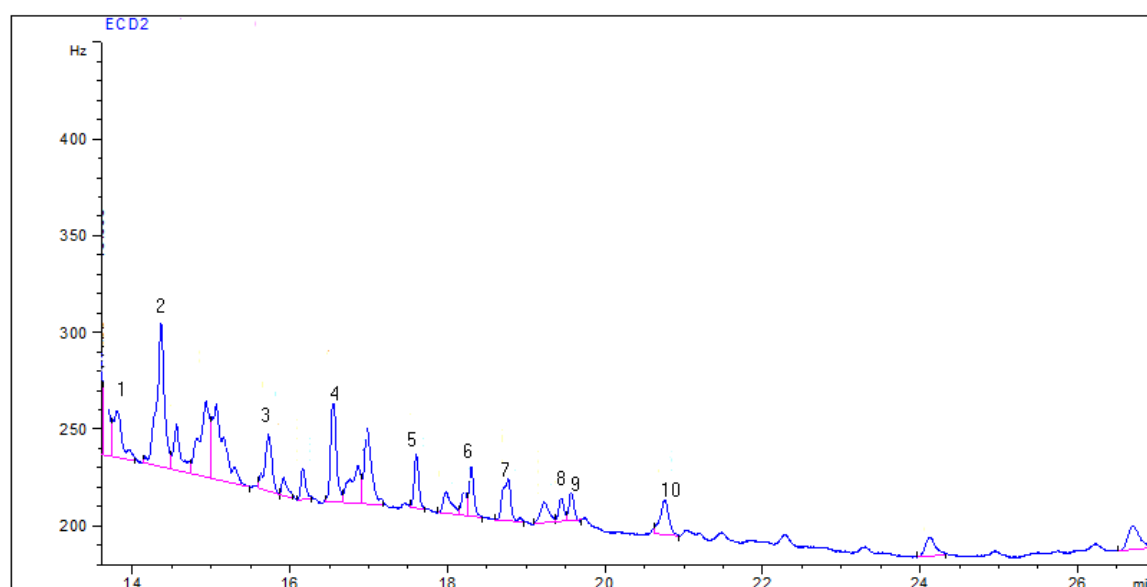


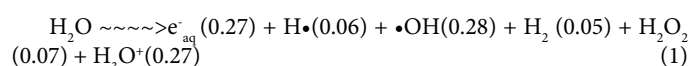
Figure 3: Chromatogram peaks identification of pesticides present in surface water sample: (1) α -BHC; (2) γ -BHC; (3) heptachlor; (4) aldrin; (5) γ -Chlordane ; (6) α -Chlordane (7) endosulfan I; (8) 4,4'-DDE; (9) dieldrin; (10) endosulfan II.

No	Compound	Total samples tested	Contaminated samples	Range ($\mu\text{g L}^{-1}$)
1	α -BHC	59	2	Nd - 0.022
2	β -BHC	59	12	Nd - 0.053
3	γ -BHC	59	37	Nd - 0.092
4	δ -BHC	59	5	Nd - 0.087
5	Heptachlor	59	25	Nd - 0.089
6	Aldrin	59	15	Nd - 0.036
7	Heptachlor epoxide	59	0	-
8	γ -Chlordane	59	0	-
9	α -Chlordane	59	6	Nd - 0.013
10	Endosulfan I	59	8	Nd - 0.014
11	4,4'-DDE	59	12	Nd - 0.036
12	Dieldrin	59	17	Nd - 0.011
13	Endrin	59	0	-
14	Endosulfan II	59	5	Nd - 0.028
15	4,4'-DDD	59	0	-
16	Endrin aldehyde	59	2	Nd - 0.026
17	Endrin ketone	59	0	-
18	4,4'-DDT	59	0	-
19	Endosulfan sulfate	59	1	Nd - 0.007
20	Methoxychlor	59	0	-

Table 3: Brief description of selected pesticides contamination in surface water samples of Peshawar area.

Decomposition of monocrotophos aqueous solution by gamma radiation

In the present study gamma irradiation of aqueous solutions of monocrotophos was investigated as a surrogate for the application of advanced oxidation processes, such as the electron beam process [23]. The structure of monocrotophos is given in Figure 4. Gamma irradiation of aqueous media results in the formation of three reactive species, the hydrated electrons e_{aq}^- , hydroxyl radicals $\cdot\text{OH}$, hydrogen radicals $\cdot\text{H}$, and less reactive species, which are given by the following equation [24];



where, the numbers in parentheses are radiation yield (G value) of each species in $\mu\text{mol J}^{-1}$ absorbed energy. The three reactive species can react with each other or with other solutes present in the solution [25].

A decay curve of monocrotophos by gamma radiation is shown in Figure 5, where the solute was almost completely degraded at 1200 Gy. The degradation of monocrotophos follows first order kinetics with respect to dose.

Calculation of percent degradation efficiency (η)

Percent degradation efficiency (η) was calculated by the following formula [1]:

$$\eta = [(C_0 - C_D) / C_0] \times 100 \quad (2)$$

where, C_0 is the initial concentration of monocrotophos at zero dose and C_D is the concentration at a specified dose.

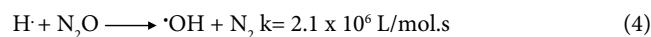
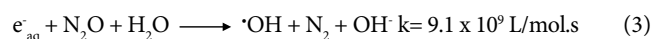
Different concentrations of monocrotophos (60-150 mg L^{-1}) were prepared in deionized water and irradiated up to 1500 Gy. All aqueous solutions were saturated with N_2 prior to gamma irradiation and η was calculated. Figure 6 shows the % degradation efficiency of monocrotophos solutions at different concentrations at various doses of gamma radiation. The data shows that η increased with increased radiation dose. At a given dose, the η decreased as the concentration

of monocrotophos increased, presumably due to competition for the reactive species by the reaction by-products produced.

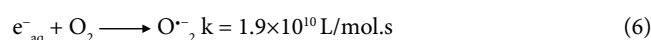
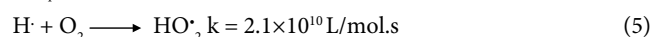
Effect of N_2 -saturated N_2O -saturated and dissolved oxygen gases on monocrotophos degradation

Experiments were performed to study effect of various gases on the decomposition of monocrotophos solution by gamma radiation. Aqueous solutions of 60 mg L^{-1} monocrotophos saturated with N_2 , N_2O and dissolved oxygen were irradiated with doses of 0, 125, 250, 500, 750 and 1125 Gy in 20 ml glass vials by gamma radiation. Figure 7 shows the effect of dissolved oxygen, N_2 -saturated and N_2O -saturated gases on monocrotophos degradation by gamma irradiation. Figure 7 indicates that monocrotophos was degraded in all the three cases and with the higher absorbed dose, η were increased. However the η in the N_2O saturated solution was higher than that in the N_2 saturated solution. The η in the N_2 saturated solution was higher than that in aerated solution.

In solutions of monocrotophos saturated with N_2O , the e_{aq}^- and $\text{H}\cdot$ atoms are converted to $\cdot\text{OH}$ making the concentration of $\cdot\text{OH}$ radicals more than double as shown below [25];



In nitrous oxide saturated condition, the $\cdot\text{OH}$ is the major radical that attack on the monocrotophos. Whereas in nitrogen saturated solution of monocrotophos, all the three radicals i.e. e_{aq}^- , $\cdot\text{OH}$ and $\cdot\text{H}$ may attack on monocrotophos. In aerated solution, oxygen can react with e_{aq}^- and $\cdot\text{H}$, and forming $\text{O}_2^{\cdot-}$ and $\text{HO}_2\cdot$ by following equation;



Due to this reason some decrease occurs in the degradation efficiency of monocrotophos. It shows that $\cdot\text{OH}$ is the major radical that play the significant role in the degradation process of monocrotophos. The other radical species ($\cdot\text{H}$ and e_{aq}^-) play role in the degradation process of monocrotophos but have lesser contribution.

Determination of radiation chemical yield (G-value)

Radiation chemical yield (G-value) is defined as the number of species of products formed or of the reactants destroyed with the absorption of 100 eV of radiation energy. It can be calculated using the following equation [26];

$$G = \frac{R (6.02 \times 10^{23})}{D (6.24 \times 10^{16})} \quad (7)$$

Where R is the change in the concentration of pollutant [M]. D is the absorbed dose (Gy), 6.02×10^{23} is the Avogadro's number and 6.24×10^{16} is the conversion factor from Gy to 100 eV/L.

Table 4 shows the G-values of monocrotophos solution saturated with N_2 gas, N_2O gas and aerated solution at various gamma radiation doses. The results indicate that the G-values of monocrotophos solution ranged from 2.305-6.432, 2.305-5.716, and 2.301-4.824 molecules/100 eV for N_2O saturated, N_2 saturated and aerated solution, respectively, at various doses of gamma radiation. At all condition a decrease in G-values with increasing irradiation doses were observed. It is probably owing to the presence of intermediate reaction by products and their possible competition for different reactive species with parent compound. However, G-values were found somewhat higher for N_2O saturated, followed by N_2 saturated and lastly for aerated solution at the same given dose. It is due to higher degradation rate of monocrotophos in N_2O saturated solution than that in the N_2 saturated solution and in aerated solution.

Determination of dose constant and kinetic study

The dose constant, k, was obtained by plotting the natural logarithm (ln) of the monocrotophos concentration [M] versus dose (Gy). Figure 8 shows gamma radiation degradation of monocrotophos solution saturated with N_2 gas at four different concentrations i.e. 60, 90, 120 and 150 $mg L^{-1}$. At 1200 Gy dose of gamma irradiation, 60 $\mu g L^{-1}$ aqueous solution of monocrotophos was completely degraded. It is clear from the Figure 8 that concentration of monocrotophos decreases exponentially with γ -irradiation absorbed doses, which can be represented by equation [27].

$$C_d = C_0 e^{-kD} \quad (8)$$

Where C_d is the concentration of monocrotophos after radiation dose, C_0 is the initial concentration of monocrotophos, k is the dose constant and D is the absorbed dose. This equation is similar to pseudo-first-order reaction. The above equation can also be modified as;

$$-\ln(C_d/C_0) = kD \quad (9)$$

Experiments were carried out to investigate the effect of initial concentration on the decomposition of monocrotophos using γ -irradiation. The aqueous monocrotophos solutions saturated with N_2 gas were irradiated to various doses. Figure 9 shows the decomposition kinetics of monocrotophos by γ -irradiation as a function of adsorbed dose, for initial concentrations of 60, 90, 120 and 150 $mg L^{-1}$ (268.8×10^{-6} , 403.2×10^{-6} , 537.6×10^{-6} and 672.0×10^{-6} M, respectively) at a dose rate of 2 $kGy h^{-1}$. The kinetic experiments were performed in triplicate for each radiation dose. It is clear that decomposition was more efficient at lower concentrations than at higher concentration suggesting that the formation of reaction by-products competed with the initial degradation of monocrotophos.

The dose constant decreased with the higher initial concentration of monocrotophos and increased with the lower initial concentration

Absorbed dose (Gy)	G-values (molecules /100 eV)		
	Aerated	N_2 saturated	N_2O saturated
0	-	-	-
125	4.824	5.716	6.432
250	4.364	5.322	5.827
500	3.746	4.035	4.436
750	3.227	3.312	3.422
1125	2.301	2.305	2.305

Table 4: G-values of monocrotophos solution saturated with N_2 gas, N_2O gas and aerated solution at various gamma radiation doses.

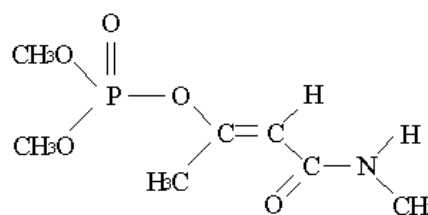


Figure 4: Structure of monocrotophos.

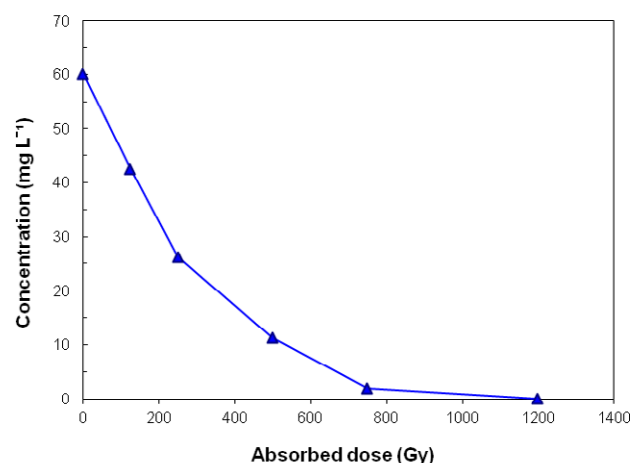


Figure 5: Degradation of monocrotophos by gamma irradiation.

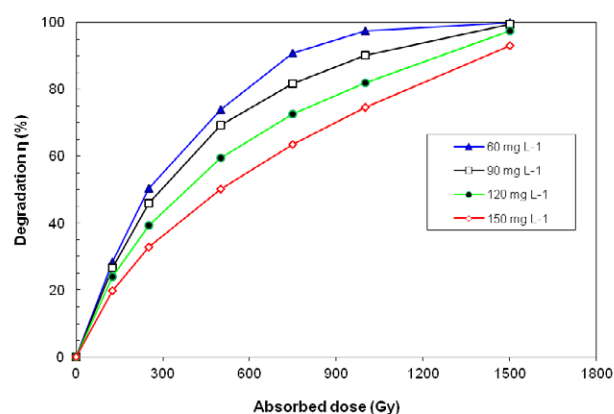


Figure 6: Percent degradation efficiency of monocrotophos solutions at different concentrations by gamma irradiation.

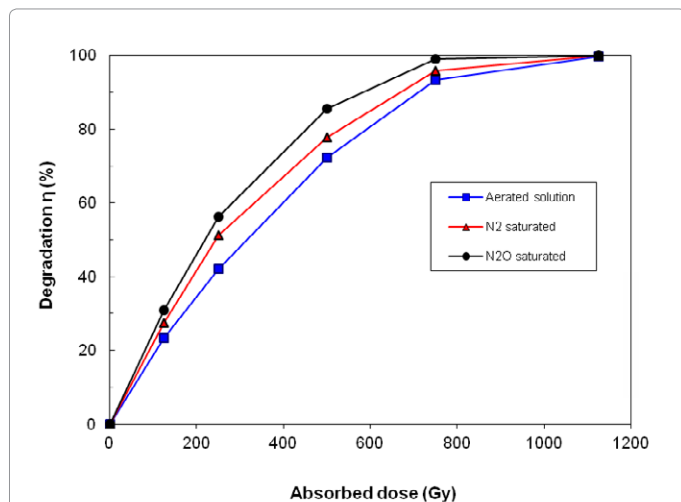


Figure 7: Percent degradation efficiency of monocrotophos solution saturated with N_2 gas, N_2O gas and aerated solution at various gamma radiation doses.

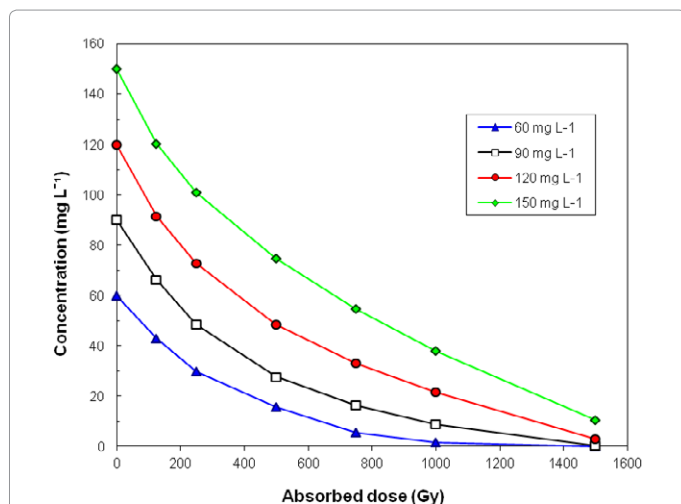


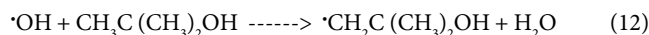
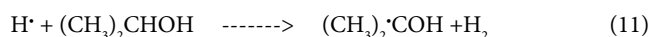
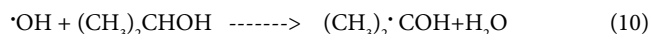
Figure 8: Degradation of monocrotophos solutions at different concentration saturated with N_2 gas by gamma radiation.

of monocrotophos as shown in Figure 9. It is clear that dose constant markedly decreased with higher initial monocrotophos concentration, from $3.0 \times 10^{-3} \text{ Gy}^{-1}$ for a concentration of $268.82 \times 10^{-6} \text{ M}$ to $1.4 \times 10^{-3} \text{ Gy}^{-1}$ for a concentration of $672.04 \times 10^{-6} \text{ M}$. This reveals that monocrotophos can be degraded at higher rate at smaller concentrations as compared to larger concentration. It can also be explained that higher radiation dose will be required with the increasing concentration of monocrotophos. These results are comparable with the earlier reported results in literature [1,27,28].

Effect of *iso*-propanol and *tert*-butanol additives on degradation of monocrotophos

iso-propanol and *tert*-butanol were used as radical scavengers to investigate that which species play the main role in the gamma radiation degradation of monocrotophos. Figure 10 shows the effect of *iso*-propanol and *tert*-butanol on the irradiation degradation process of monocrotophos solution saturated with nitrogen gas. *iso*-propanol has very high rate constant with $\cdot\text{OH}$ and $\cdot\text{H}$ radical ($1.9 \times 10^{10} \text{ L/mol.s}$

and $7.4 \times 10^7 \text{ L/mol.s}$, respectively). It can scavenge $\cdot\text{OH}$ and $\cdot\text{H}$ and less amount of these radicals will be available for target compound in the present of this scavenger [25]. Whereas *tert*-butanol also reacts very fast with $\cdot\text{OH}$ ($6.0 \times 10^8 \text{ L/mol.s}$) and scavenging $\cdot\text{OH}$ as shown below;



In the presence of *iso*-propanol, e_{aq}^- plays the key role while in the presence of *tert*-butanol, $\text{H}\cdot$ and e_{aq}^- play the predominant role. Figure 10 shows that *iso*-propanol and *tert*-butanol greatly inhibits the irradiation degradation process of monocrotophos, as both additives scavenging $\cdot\text{OH}$ radical, however, the degradation rate is somewhat lower in *iso*-propanol solution as compared to the *tert*-butanol solution because *iso*-propanol has high rate constant with $\cdot\text{OH}$ and $\text{H}\cdot$ as compared to the *tert*-butanol. So it is clear from the Figure 10 that $\cdot\text{OH}$ plays significant role while $\text{H}\cdot$ and e_{aq}^- also take part in the degradation

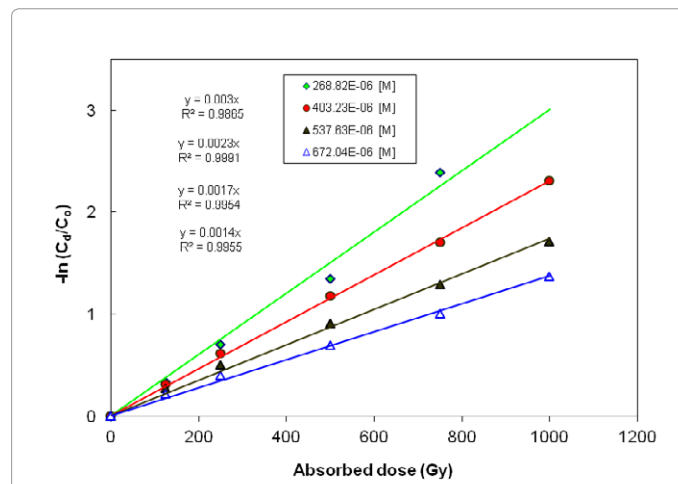


Figure 9: Determination of dose constant for the radiolytic decomposition of monocrotophos at different initial concentrations saturated with N_2 gas at various gamma radiation doses.

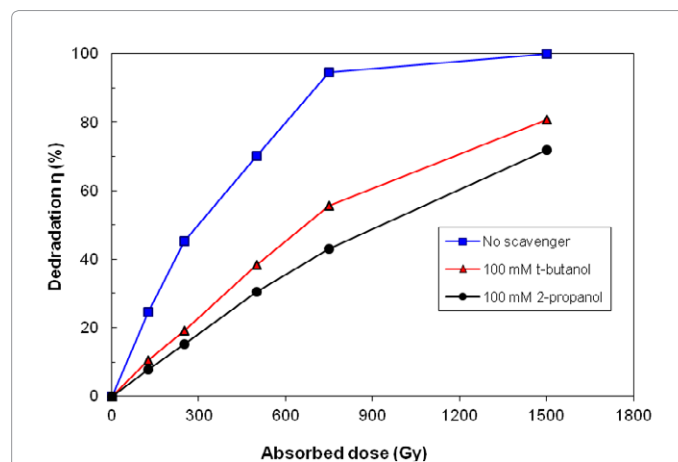


Figure 10: Effect of radical scavengers (*tert*-butanol and *iso*-propanol) on percent degradation efficiency of monocrotophos solution saturated with N_2 gas at various gamma radiation doses.

process but play a minor role in the gamma degradation process of monocrotophos.

By-product analysis

Monocrotophos solution can be effectively degraded by gamma irradiation. The by-product formed during gamma irradiation of monocrotophos were analysed by Ion Chromatography. Metrohm Ion-Chromatograph (850 Professional IC, 872 Extension Module with 858 Professional sample Processor) equipped with electro chemical anion self-regenerating suppressor, conductivity detector and analytical column Metrosep Assup-7 (250/4.0 mm) was used for analysis of by-product. The eluent used was 0.36 M sodium carbonate and suppressor reagent solution 0.1 M H_2SO_4 was used with a flow rate of 0.8 ml/min.

The inorganic reaction by-products of monocrotophos degradation, Nitrate and phosphate anions were determined at various irradiation doses. Some low molecular weight organic acids i.e., formic acid and acetic acid were also determined as reaction by-products of monocrotophos degradation at various irradiation doses. Figure 11 summarizes the formation of reaction by-products of monocrotophos degradation i.e. Nitrate, phosphate, formate, acetate, NH_4^+ and CH_3NH_2 . The quantitative conversion of the organic phosphorus was observed at 8 KGy. These results suggest that nearly complete degradation of monocrotophos was achieved to inorganic anions at dose of about 8 KGy.

Conclusions

The SPME-GC-ECD technique is an excellent and reliable method for the determination of various pesticides in water samples. This method showed good liner response with R^2 values in the range of 0.9933 to 0.9999 and good percent recoveries for all 20 organochlorin pesticides. The results of present study demonstrated that the gamma irradiation treatment was very effective in the degradation of aqueous monocrotophos solution. 100% degradation η of 60 mg L^{-1} monocrotophos solution saturated with N_2 gas was achieved at 1200 Gy dose of gamma radiation. The kinetic study showed that the gamma irradiation degradation of monocrotophos followed pseudo first-order reaction. The results showed that monocrotophos degradation takes place mainly due to $\cdot OH$ radicals, because the maximum % degradation

η was achieved when the production of $\cdot OH$ radicals was enhanced in the solution.

The G-value decreased with higher doses of gamma irradiation. The effect of N_2O and N_2 gases showed that decomposition rate of monocrotophos in the N_2O saturated solution was greater than those saturated with N_2 . The study of various radical scavenger experiments indicated that oxidative radical $\cdot OH$, were mainly responsible for irradiation decomposition of monocrotophos. However, e_{aq}^- and $\cdot H$, has less contribution to the decomposition of monocrotophos. In conclusion the application of radiation technology is very effective and promising to destroy and remove pesticides and organic pollutants from contaminated water.

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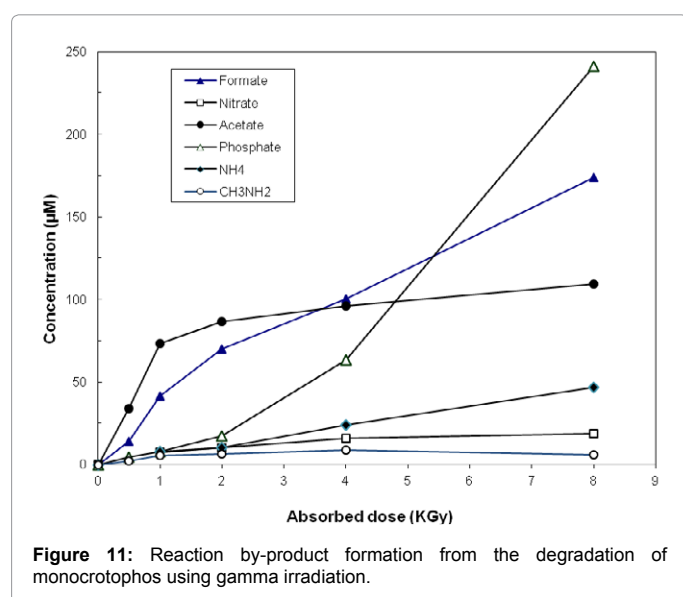


Figure 11: Reaction by-product formation from the degradation of monocrotophos using gamma irradiation.

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