



Radiolytic decomposition of organochlorine pesticides in soil

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Received: February 24, 2021; Revised: March 22, 2021; Accepted: March 25, 2021

Abstract – The Kinetics of radiolytic decomposition of organochlorine pesticides (OCPs) in soil under γ -irradiation (using ^{60}Co source) at absorbed doses 10.8 kGy and 36.0 kGy were studied. Radiation-chemical yields of radiolytic decomposition processes were calculated. It was revealed that the decomposition of pesticides at the absorbed dose of 36.0 kGy is more than 70%, radiation-chemical yields are in the range of $(2.10 - 494) \cdot 10^{-8}$ molecule/100 eV for individual pesticides.

Keywords: gamma-irradiation, ^{60}Co , OCPs, degree of decomposition, radiation-chemical yield, GC/ECD.

Технологии ликвидации источников химической опасности

Радиолитическое разложение хлорорганических пестицидов в почве

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Поступила в редакцию: 24.02.2021 г.; после доработки: 22.03.2021 г.; принята в печать: 25.03.2021 г.

Аннотация – Изучена кинетика радиолитического разложения хлорорганических пестицидов (ХОП) в почве, в поглощенных дозах 10,8 кГр и 36,0 кГр при γ -облучении (^{60}Co) и рассчитаны радиационно-химические выходы процессов радиолитического разложения. Выявлено, что степень разложения пестицидов при поглощенной дозе 36,0 кГр составляет более 70%. Радиационно-химические выходы составляют $(2,10 - 494) \cdot 10^{-8}$ молекул / 100 эВ для отдельных пестицидов.

Ключевые слова: γ -облучение, ^{60}Co , ХОП, степень разложения, радиационно-химический выход, GC / ECD.

INTRODUCTION

As a result of anthropogenic pollution of the biosphere, the components of the environment inevitably contain toxic substances that are inappropriate to control.

These may include also the widespread certain organochlorine pesticides (OCPs) contained in micro-concentrations of these substances pose a threat to human health and subject to mandatory control. The problem of the formation of secondary toxic substances after radiation processing in which OCPs trace elements are present is a particular importance [1].

Application of radiation technologies [2, 3] lead to the decomposition of residual OCPs [4, 5] and necessitate the study of their radio-chemical transformations. The decomposition of primary toxicants after radiation treatment can create the illusion of the absence of toxic substances in the controlled object, if the control is carried out only on the presence of the primary toxicant. Currently, considerable experience has been accumulated in the field of radiation chemistry and detailed results have been obtained on the effect of high-energy ionizing radiation on solutions of various high-concentration chemicals. Therefore, it is difficult to predict the degree of conversion of OCPs, the composition of the decomposition products and the toxicity of the resulting new substances.

From a review of scientific publications, it was found that the study of chemical transformations of OCPs under the influence of γ -radiation was carried out unsystematically. The effect of gamma radiation loads and initials the state of the irradiation medium of the initial concentration of the pesticide, the presence of oxygen and homogeneous molecules of organochlorine hydrocarbons capable of competing in radiation-chemical reactions. The conclusions regarding the radiation stability of OCPs in different polarity media are also ambiguous. In addition, the composition and properties of radiation metabolites of OCPs have been little studied.

Their exceptional stability results in the contamination of the natural environment for long years, and yet they are still used in certain regions of the world. There is an apparent need for both monitoring of their residues and development of methods for their removal or decomposition [6]. Although the pioneering works on the application of radiation technologies for the environmental protection concerned the chemical treatment and disinfection of waters and wastes [7, 8], in the case of pesticide residues the first attempts dealt with both their removal from waters and foods and decomposition in organic solvents [9–14], in soils [15–17].

The radiation treatment was also examined for the remediation of artificially contaminated soil. Azerbaijan, which regained its independence after the collapse of the Soviet Union, has also joined several global programs to address domestic environmental problems, one of which has tightened controls on banned chemicals. Pesticide storage areas have been dismantled and regular monitoring has begun. One such area is a former pesticide base in Dayikand, Salyan region of Azerbaijan. Thirty years later, traces of the OCPs still remain in the soil samples taken from this area.

The aim of this work was to study the radiation-chemical transformations of OCPs under the influence of gamma irradiation in soil.

MATERIALS AND METHODS

For this study 16 OCPs were investigated: α -, β -, γ - and δ - (HCH), p,p'-DDE, p,p'-DDD, p,p'-DDT, aldrin, dieldrin, endrin, α -, β - endosulfan, endosulfan sulfate, endrin aldehyde, heptachlor and heptachlor epoxide-B. Pesticide standards (including

2,4,5,6-Tetrachlor-M-Xylene and decachlorobiphenyl) (purity > 97.0%) and other reagents, were purchased from LGC and Sigma-Aldrich. The mixed stock solution for calibration of the GC/ECD, containing all OCPs, was prepared in n-hexane.

Solvents used in the extraction and cleanup procedures including methylene chloride and acetone exchanged to n-hexane prior to analysis. All solvents were in gas chromatographic quality grade and each solvent was free of phthalates. EPA Method 8081B [18] used as base method for the determinations of OCPs. For extraction process EPA Method 3550C [19] (ultrasonic extraction), for clean-up EPA Methods: 3660 (sulfur cleanup) [20] and 3630 (Silicagel cleanup) [21] was used for preparation of samples.

For irradiation of soil samples ^{60}Co was used as a source; rate of absorbed dose is about 0.2 Gy/sec. Samples irradiated in static conditions in room temperature. The stability of the compound when exposed to γ -radiation can be evaluated using indicator values such as degree of decomposition (P) and the radiation-chemical yield (G).

The degree of decomposition (P, %) of organochlorine pesticide was determined using the change in the concentration of the pesticide and measured peak areas on the chromatograms of the studied samples containing pesticides, before and after their irradiation [22, 23]. The G value refers to the number of molecules consumed or produced per 100 eV of energy absorbed. Radiation-chemical yield (G) is the ratio of the concentration of the irradiated product per unit of absorbed dose.

The concentration of OCPs before and after γ -irradiation in the samples was determined using capillary gas chromatography and chromatography-mass spectrometry systems. Measurement procedure was carried out in following conditions:

1. Gas chromatograph (GC) Varian 3800 (Varian, Inc. (USA)), detector - ECD (^{63}Ni), on a column 30 m x 0.250 mm x 0.25 μm , phase DB-5MS, temperature programming was used. The oven temperature was programmed starting at 80°C and held for 0.5 min, followed by increases of 26°C/min to 175°C, then 6.5°C/min to 235°C, and then 15°C/min to 300°C and held 6 min. The injection port was at 250°C splitless mode, and the detection was carried out at 340°C. Nitrogen (purity $\geq 99.999\%$) was used as carrier gas at constant flow rate of 3.0 mL/min, whereas nitrogen (purity $\geq 99.999\%$) was employed as makeup gas at flow of 27 mL/min. The system was operated by GC Solution Star Workstation software [24, 25].
2. In addition, the real samples with positive results by GC/ECD were analyzed using GC/MS (Thermo-Electron Ultra Trace DSQ, Quadrupole (Finnigan, (USA))). Thermo Trace-Ultra gas chromatograph coupled to a quadrupole mass detector Thermo DSQ, operated in the electron impact ionization (EI) at 70 eV. The ion source temperature was 250°C and the MS transfer temperature, 250°C. The system was operated by Xcalibur 1.3 version software. Confirmation of residues was carried out by GC-MS/SIM using a Agilent column fitted with an DB-5MS (30 m 0.25 mm, 0.25 μm film thickness) column operating in the splitless mode; helium was used as carrier gas at a constant flow rate of 1.3 mL/min. The injector was maintained at 240°C. The oven temperature was programmed starting at 40°C and held for 2 min, followed by increases of 30°C/min to 220°C, held for 5 min,

then 10°C/ min to 270°C, and held for 1 min. For the identification of pesticides, the retention time, and three ions, the NIST and Wiley pesticide libraries were used. The SIM conditions were fixed for each compound, trying to select as precursor ion the one with the highest m/z ratio and abundance.

Soil samples were taken from five different points from depths of 30 ÷ 45 cm, from heavy clay soil. Samples from five points were dried at room temperature for 12 hours and a homogeneous mixture was prepared by mixing. After sieving to a maximum particle size of <2 mm, the soil kept in plastic bag at 4°C for 14 days before use.

Physical and chemical properties of the soil are identified by methods (EPA Method 9045D; EPA Method 9050A [26, 27].

For irradiation of soil samples by γ -irradiation (^{60}Co) used glass ampoules. The ampoules were prepared in a special cylindrical shape. After adding the dried and homogenized soil to the ampoules, they were sealed by forging to ensure complete isolation from the air.

RESULTS AND DISCUSSION

The influence of gamma irradiation on OCPs in the soil

The results of the pesticide degradation in soil samples under gamma irradiation are shown in table 1. Analyzes were repeated three times for each irradiation dose and mean values of results were presented in the table.

As seen, the concentration of all identified pesticides decreases with an increase in the absorbed dose. Results show that absorbed dose has a significant effect on the decomposition of pesticides.

Table 1. Dependence of the concentration of the OCPs on absorbed doses

Compounds	CAS Number	Concentration, $\mu\text{g/kgdw}$		
		0 kGy	10.8 kGy	36..0 kGy
Alpha-BHC	319-84-6	1.83	0.81	0.27
Beta-BHC	319-85-7	12.9	3.63	3.88
Gamma-BHC	58-89-9	3.66	1.67	1.27
Delta-BHC	319-86-8	2.13	0.39	0.26
4, 4' - DDT	50-29-3	104	6.6	6.72
4, 4' - DDE	72-55-9	70.2	17.5	13.5
4, 4' - DDD	72-54-8	191	13.9	13.9
Aldrin	309-00-2	0.84	0	0
Dieldrin	60-57-1	8.99	1.38	1.29
Heptachlor	76-44-8	26.1	6.74	7.36
Heptachlor Epoxide Isomer B	1024-57-3	2.84	0.88	1.34
Endosulfan I (Alpha)	959-98-8	4.73	0.3	0.24
Endosulfan II (Beta)	33213-65-9	7.53	0.68	0.82
Endosulfan Sulfate	1031-07-8	10.1	0.26	0.46
Endrin Aldehyde	7421-93-4	1.66	0.08	0.16
Total OCPs		449	54.8	51.5

Degree of decomposition of OCPs at various absorbed doses of gamma irradiation for soil samples were calculated and given in Figure 1. Concentration of investigated pesticides in soils decreases more than 70% when they are irradiated with an absorbed dose of up to 36.0 kGy.

As can be seen from table 1, irradiation leads to a strong degradation of pesticides, where the average degradation degree rate is about 70%. Such a strong influence of the absorbed dose on the degree of decomposition is associated with the heterogeneity of the irradiated system. Metal oxides – main component of soils (SiO_2 , Al_2O_3 , MgO , etc.), absorbing the energy of ionizing radiation, transfers part of the energy to the adsorbed molecules. Since the efficiency of the interaction of gamma radiation is much higher than the efficiency of the absorbed gas or liquid phase, therefore, for the same irradiation time, the amount of energy absorbed by metal oxides is much higher than the energy of the absorbed liquid or gas phase. In other words, the observed high decomposition yields are apparently related to the heterogeneity of the irradiated system.

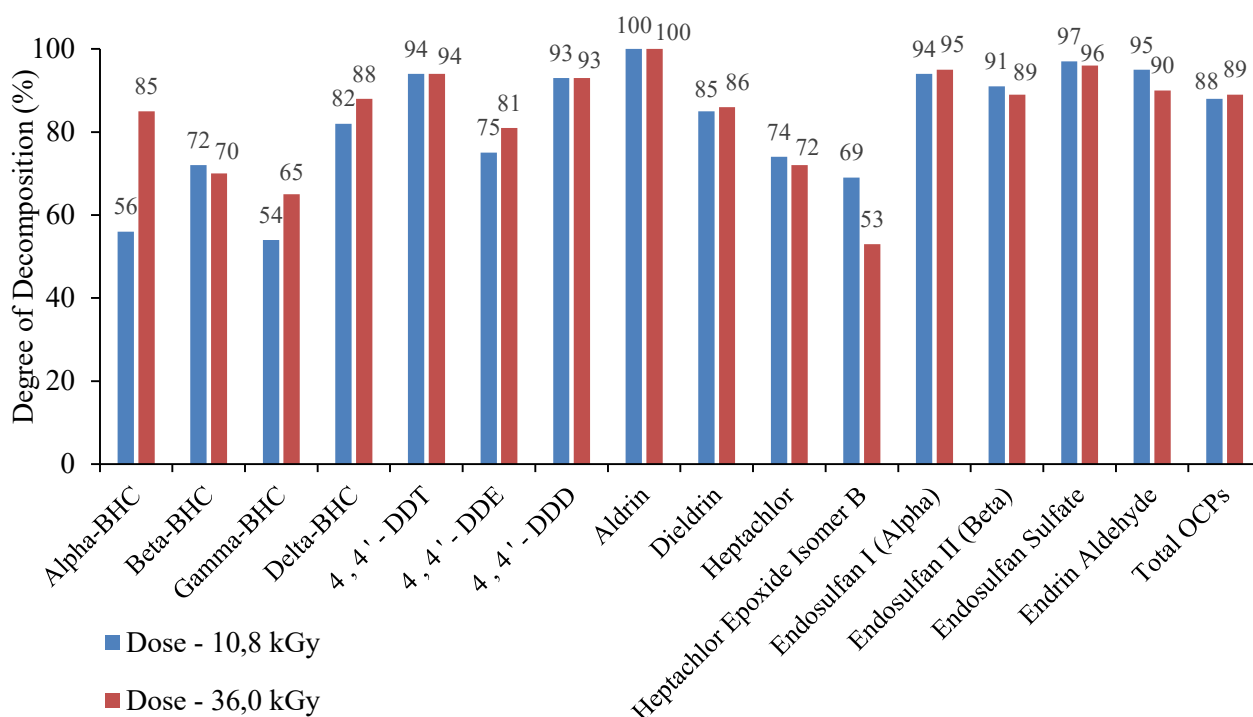


Fig. 1. Dependence of the decomposition degree of OCPs with absorbed dose.

The nature of the dependence of the degree of decomposition on the absorbed dose remains unchanged for various OCPs when the concentration of the initial substance changes.

As it can be seen from table 2 radiation-chemical yield values of decomposition processes of pesticides are in the range of $(2.10 \div 494) \times 10^{-8}$ molecule/100eV.

Table 2. Radiation-chemical yields of OCPs

OCPs	Radiation-Chemical Yield, $\cdot 10^{-8} \cdot (\text{molecule}/100\text{eV})$
Alpha-BHC	3.10
Beta-BHC	28.7
Gamma-BHC	6.10
Delta-BHC	5.40
Heptachlor	46.4
Aldrin	2.10
Heptachlor Epoxide Isomer B	4.50
Endosulfan I (Alpha)	9.70
4,4' - DDE	148
Dieldrin	17.8
Endosulfan II (Beta)	15.0
4,4' - DDD	494
Endrin Aldehyde	3.70
Endosulfan Sulfate	20.8
4,4' - DDT	245

Possible mechanisms of radiation-chemical transformations of OCPs in the soil

In this study, main component of irradiated system is soil. Detailed physical and chemical parameters of investigated soil samples are given in table 3 [28].

Table 3. General characteristics of the investigated soil

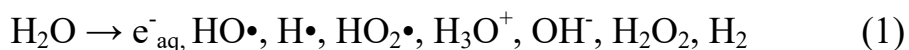
Parameter	Value*
Value pH (in water) (1:5)	7.83
Moisture content, (w/w) (%)	5
Cation exchange capacity (CEC), (cmol /kg)	15.2
Water holding capacity (WHC), (%)	10
Total Organic Carbons (TOC), (%)	0.85
Total Nitrogen (N _{tot.}), (%)	0.5
Microbial biomass (mg/ kgdw)	564
Conductivity (uS/cm)	7.13
Total Dissolved Solids (g/L)	4.12
Salinity (%)	0.36
Content of chemical elements	
Fe, mg/kg	36107
Na, mg/kg	1446
Ca, mg/kg	30652
Cu, mg/kg	50.8
Ni, mg/kg	83.6
Zn, mg/kg	82.7
As, mg/kg	10.4
Pb, mg/kg	5.77
V, mg/kg	97.8
Cr, mg/kg	72.1
Cd, mg/kg	0.176
Mg, mg/kg	15844
K, mg/kg	4726
Mn, mg/kg	765
Co, mg/kg	16.4

*The values are the means of three replicates.

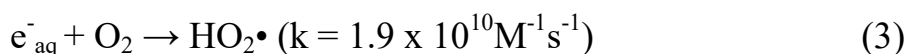
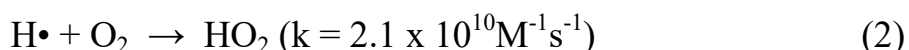
Soil is a variable mixture of minerals, organic matter, and water, capable of supporting plant life on the earth's surface [29]. The solid fraction of a typical productive soil is approximately 5% organic matter, originating from plant debris in various stages of decay, and 95% inorganic matter. Soil usually contains air spaces and generally has a loose texture. The majority of inorganic components (>90%) are crystalline and noncrystalline amorphous minerals including primary and secondary minerals; the former includes quartz and micas and the latter phyllosilicates (clay minerals), allophones, and metal oxides. Quartz and micas are simple SiO_2 minerals whereas clay minerals are basically aluminosilicates. There are three types of hydroxyl groups existing on silica gel with a different acidity: geminal silanol ($\text{Si}(\text{OH})_2$), nongeminal (SiOH), and hydrated silanol ($\text{SiOH}\cdots\text{OH}_2$), as demonstrated by ^{19}Si - and H-NMR and fluorescence analysis [30]. Clay minerals possess layered structures consisting of silica tetrahedral and alumina octahedral sheets with a ratio of 1:1 or 2:1 [31]. Kaolinite is the typical clay in the former type and pyrophyllite, smectite, and vermiculite groups constitute the latter. The isomorphous substitution of central atoms in tetrahedral and octahedral structures with another of a lower valency resulted in a net negative charge for clay sheets and electrostatic force via counteractions, making them loosely bound to each other [32]. The presence of interlayer space thus gives a sterically constrained reaction environment for pesticide molecules when intercalated. Iron is one of the most abundant transition metals in soil and is considered to play a large role in photo induced redox reactions generating active oxygen species such as $\text{OH}\cdot$. [33] It was demonstrated by Mössbauer spectroscopy that most Fe^{3+} and Fe^{2+} ions were found to occupy the octahedral sites and that some ions might occur as an interlayer species such as a Fe^{3+} -aquo complex in the 2:1 clay minerals. Instead of the Fe^{3+} -aquo complex, $\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4$ would condense to form ferric hydroxyl polymers.

Humic substances account for 60% - 70% of soil organic matter, consisting of a series of highly acidic, yellow to black, high molecular weight polyelectrolytes and characterized by their high content of oxygen-containing functional groups such as COOH , phenolic, aliphatic, and enolic OH and C=O , together with amino, heterocyclic amino, imino, and sulfhydryl groups [34, 35]. The higher total acidity of fulvic acid (FA, $\sim 10 \text{ mEqg}^{-1}$) than humic acid (HA, $\sim 7 \text{ mEqg}^{-1}$) can be accounted for by the higher content of a COOH group in FA. The typical content of each functional group was reported to be 3,6-8,2 mEqg^{-1} (COOH), 3,0-3,9 mEqg^{-1} (phenolic OH), 2,6-6,1 mEqg^{-1} (alcoholic OH), 2,7-2,9 mEqg^{-1} (quinoid and ketonic C=O), and 0,6-0,8 mEqg^{-1} (OCH_2) [36]. Similar results have been confirmed [37] by using several soil humic substances and Suwannee River soil. The clay surface is usually covered with these humic substances, probably via formation of clay-metal-organic complexes. Through adsorption study of atrazine, the contribution of clay surface on adsorption was proposed to be important when organic matter content was less than $\sim 6\%$ [34]. Proposed mechanisms of interactions are ionic bonding via cation exchange, hydrogen bonding charge-transfer interaction with a quinoid moiety embedded in a humic structure, cation-bridged ligand exchanged with humic carboxyl moiety, covalent binding, hydrophobic adsorption, and partitioning via dipole-dipole and/or van der Waals interaction [34, 38, 39].

Another unique feature characteristic of soil humic substances is the presence of stable radical species detected by ESR. [40] Have reported the ESR signal at $g = 2.0032-2.0050$ without a hyperfine splitting for FA whose intensity increased with either chemical reduction under more acidic conditions. They proposed semiquinones or its ions as the most likely partial structure of stable radical species. Further investigation on various soil HAs and FAs has shown the presence of two types of ESR signals originating from a quinhydrone-type structure and a phenoxide ion [41]. These stable radicals would be involved in photoinduced transformation of pesticides as well as formation of active oxygen species, especially when a transition metal or its oxide coexists [35]. Radiolysis of soil samples leads to direct absorption of ionizing energy by main components of soil and formation of various active particles which react with organic and water molecules. In the case of reactions with water molecules the formation of free radicals $\text{HO}\cdot$, $\text{H}\cdot$ and $\text{HO}_2\cdot$ and hydrated electrons e_{aq}^- takes place [42].



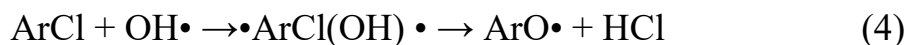
From the practical point of view, it is essential whether radiolytic processes are carried out in deaerated or aerated solutions. In the solutions containing oxygen, both reducing reactants are scavenged by molecular oxygen, according to the reactions (2) and (3) (Buxton et al., 1988) [43].



As far as the reactions of the two main products of water radiolysis are concerned, the hydrated electron behaves as a nucleophile in the reactions with organic compounds. Then, hydroxyl radical can take part in the electron transfer reactions, hydrogen atom abstraction or in the addition to aromatic rings or such bonds as $\text{C}=\text{C}$, et al..

The hydroxyl radical ($\text{OH}\cdot$) is a powerful oxidizing species that reacts with OCPs via addition to the benzene rings. The $\text{OH}\cdot$ radicals likely add to all of the carbons though a slight selectivity toward a ring that does not contain chlorine atoms may be expected due to steric and electronic effects. When addition occurs at a chlorine-laden carbon, rapid dechlorination is achieved.

Various isomeric OCPs adduct radicals are intermediate species that undergo rapid elimination of HCl to form phenoxyl-type radicals:



If the treated matrix contains additional organic compounds such as solvents, hydrocarbons, humic material, or inorganic ions such as metal and chloride ions, the $\text{OH}\cdot$ radicals will preferentially react with these materials and the degradation of OCPs by $\text{OH}\cdot$ radicals is not very efficient. This is particularly the case when OCPs are present at much lower concentrations relative to other organic compounds.

In contrast, the hydrated electron (e_{aq}^-) is a strong reducing agent whose reactivity depends on the availability of a suitable vacant orbital and its reactivity is

enhanced by electron withdrawing atoms, such as chlorine. Hence, it is preferentially captured by OCPs molecules and as a result the carbon-chlorine bond breaks very rapidly:



The reductive process (Eq. 5) tends to be the dominant pathway for OCPs dechlorination via radiation treatment due to the more selective nature of e_{aq}^- . Hydrated electrons also react very rapidly with oxygen ($e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^{\cdot-}$) and with the H_3O^+ formed in the radiolysis ($e_{\text{aq}}^- + \text{H}_3\text{O}^+ \rightarrow \text{H}\cdot + \text{OH}$). These reactions compete with the dechlorination process.

Examination of gas chromatograms from an electron capture detector of an irradiated sediment also revealed the degradation of 4,4'-DDE [44]. As an added benefit, it is likely that transition metal ions, including lead and mercury, were likely reduced to lower oxidation states that led to insoluble metals [45, 46]. The complexity of sediments makes it difficult to elucidate the mechanisms and kinetics associated with the dechlorination processes in the same detail as that for water [46–48] and oil [49–51]. The soil system is a non-homogeneous system. A portion of the OCPs will be associated with soil particles (such as SiO_2) and a portion will be in the aqueous phase. Upon irradiation, aqueous electrons from the radiolysis of water are produced as well as Compton electrons from irradiated solid particles. Each type of electron may react with OCPs.

The values of the reaction rate-constants for the DDT and Lindane with $\text{OH}\cdot$ radicals presented in Table 5.

Table 5. Rate constants for reactions of DDT and Lindane with hydroxyl radicals water

Compound	Rate-constants, $\text{M}^{-1}\text{s}^{-1}$	Solvent system	Dose required for a given yield (%) of decomposition, kGy
Dichlorodiphenyltrichloroethane (DDT)	$(6\div 170) \cdot 10^8$ [52]	7.1 g/L in 2-propanol	2.1 (75%) [10]
		0.1 g/L in 2-propanol	10 (99.2%) [4]
		0.1 g/L in ethanol	10 (78%) [53]
Lindane (Gamma-BHC)	$(5,2\div 11) \cdot 10^8$ [38]	0.2 mg/L in water	30 (100%) [54]
		0.25 g/L in ethanol	50 (88%) [53]

The rate-constant values reported by different authors for the reaction with OH^* radicals may differ by more than one order of magnitude [38]. It can also be noted that in some cases these values are similar to the rate-constants reported for the reactions of $\text{OH}\cdot$ or e_{aq}^- with inorganic anions commonly present in the environmental samples [43]. This means that these anions may act as scavengers of the reactive products of water radiolysis, significantly lowering the efficiency of the

radiation treatment, although it essentially depends on the initial concentration level of target pollutant and the potential scavengers. Although it is not very often encountered situation, the presence of certain components of natural matrices of irradiated samples may enhance the formation of especially active free radicals or hydrated electrons, which results in the increase of the yield of radiolytic decomposition of target pollutants. Based on the assumption about the possibility of the existence of several mechanisms of the effect of γ -irradiation on OCPs, the obtained dependence of the radiation-chemical yield on the concentration G is explained by the fact that with an increase in the concentration of OCPs, the processes of recombination and neutralization of their parts are enhanced, which ultimately leads to a decrease in the radiation-chemical yield of these pesticides [6].

CONCLUSION

The influence of gamma irradiation on OCPs in the soil was studied. The regularities of the radiation-chemical decomposition of microimpurities of various OCPs in the soil were determined, depending on the dosimetric characteristics of gamma irradiation and the composition of complex impurities. Possible mechanisms of radiation-chemical transformations of OCPs were experimentally studied. The kinetics of radiolytic decomposition of 15 organochlorine pesticides (OCPs) in soil with absorbed doses of 10.8 kGy and 36.0 kGy was studied and the radiation-chemical yields of radiolytic processes under the influence of gamma irradiation of the Co^{60} were calculated. It was revealed that the decomposition of pesticides at the absorbed dose of 36.0 kGy is more than 70%, radiation-chemical yields are $(2,10 - 494) \cdot 10^{-8}$ molecule / 100 eV.

ACKNOWLEDGMENTS:

Thank you to all staff at Laboratory of "Physics and Chemistry of harmful factors effecting the environment" Institute of Radiation Problems of the Azerbaijan National Academy of Sciences for support throughout this paper.

CONFLICT OF INTERESTS:

The authors declare no conflict of interests.

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