

**THE REMOVAL OF CHLORINATED ORGANIC
PESTICIDES IN GROUND AND SURFACE WATERS BY
GAMMA-IRRADIATION**

**YERALTı VE YÜZEY SULARINDAKİ KLORLU ORGANİK
PESTİSİTLERİN GAMA-IŞINLARI İLE GİDERİLMESİ**

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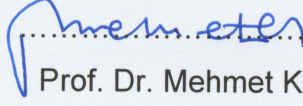
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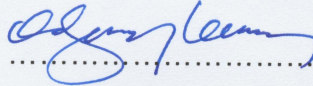
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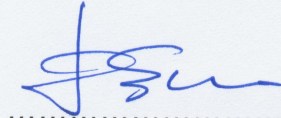

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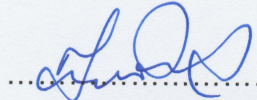

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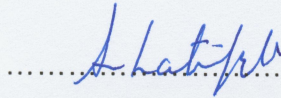
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YERALTI VE YÜZEY SULARINDAKİ KLORLU ORGANİK PESTİSİTLERİN GAMA-IŞINLARI İLE GİDERİLMESİ

Murat Torun

ÖZ

Bu çalışmada, 2-4-diklorofenoksiasetik asit (2,4-D) ve 2-4-diklorofenoksipropiyonik asit (2,4-DP) herbisitlerinin sulu çözeltilerindeki bozunması iyonlaştırıcı radyasyona maruz bırakılarak incelenmiştir. (2,4-D) ve (2,4-DP) herbisitlerin sulu çözeltide ışınlama-etkili bozunması çeşitli koşullarda ışınlama dozunun fonksiyonu olarak hidrojen peroksit ve ozon varlığında ve yokluğunda incelenmiştir. e^-_{aq} , $H^\cdot$, $OH^\cdot$ ve HO_2/O_2^- türlerinin spesifik aktiviteleri hakkında bilgi edinmek için çözeltiler H_2O_2 ve O_3 varlığında ve yokluğunda hazırlandı. 2,4-D ve 2,4-DP sulu çözeltileri, suyun γ ışınlarıyla radyolizi sonucu oluşan kısmi aktif radikal türlerin baskın olduğu değişik koşullarda ışınladı. Elde edilen verilere göre yükseltgenmenin hidroksil radikalleriyle sağlandığı durumda yükseltgenme işlemi/iyonlaştırıcı radyasyonla radyolitik bozunmanın en verimli olduğu saptandı.

İyonlaştırıcı radyasyonun 2,4-D ve 2,4-DP herbisitlerinin bozunması için uygun bir yöntem olduğu kanıtlanmıştır. 50 ppm 2,4-D ve 2,4-DP herbisitlerin tamamıyla bozunması için gereken doz hidrojen peroksit ve ozon varlığında daha azdır. Oluşan ara ürünlerin, 2,4-diklorofenol (2,4-DCP) ve 4-klorofenol (4-CP) olduğu gözlenmiştir. Hidrojen peroksin ışınlamadan önce kullanılması durumunda, 2.0 ve 3.0 kGy civarında bu ara ürünlerde bozunmuştur. Asetik asit, formik asit ve okzalik asit gibi alifatik asitlerin oluşması ile de reaksiyon mekanizması önerilmiştir. Hidrojen peroksit ve ozon derişimi etkin olarak bozunmayı ve mineralleşmeyi sağlamaktadır.

2,4-diklorofenoksiasetik asit, 2,4-diklorofenoksipropiyonik asit ve radyolitik bozunma sonucu oluşan ara ürünler için kimyasal analizler Kütle-Kütle Spektrometresi bağlı

İyon Tuzağı (ITD) Dedektörlü Gaz kromatografisi (GC-MS-MS) ve İyon Kromatografisiyle yapılmıştır. GC-MS-MS yöntemi ile, başlangıç radyoliz verimleri (G_i) değerleri substratın bozunmasının yanında radyolitik ürünlerin miktarı da saptanmıştır. Klorofenollerin oluşmasının yanında serbest klor, formaldehit ve karboksilik asitler absorplanan dozun fonksiyonu olarak incelenmiştir. Deneysel veriler baz alınarak, 2,4-D ve 2,4-DP'nin γ -ışınları ile bozunması için olası reaksiyon mekanizmaları önerilmiş ve saptanan ürünlerin oluşumu değişik koşullar için belirtilmiştir. Hidrojen peroksit ve ozon varlığında ve yokluğunda bozunmanın değişik yollardan ilerlediği saptanmış ve iki ayrı bozunma mekanizması önerilmiştir.

Pestisit bozunması 5 ana ara basamak içermektedir: (a) hidroksillenmiş ürünler ve türevleri eğer gruba halojen bağlı ise genellikle halojen kopması (b) eğer mevcut ise yan zincirin yükseltgenme ürünleri (c) aromatik pestisitler için halka açılması ürünleri (d) dekarboksilasyon ürünleri ve (e) izomerleşme ve halkalaşma ürünleri. Arıtılan suda düşük derişimlerde bile olsa yüksek toksititeye sahip bileşiklerin oluşma olasılığının değerlendirilmesi olmazsa olmaz koşuldur. Türkiye'de hidrojen peroksit ve ozon varlığında ve yokluğunda ışınlanan herbisit çözeltileri için toksitite testi yaptırılma imkanı olmamıştır.

Anahtar kelimeler: fenoksiasit herbisitler, gama-ışınlama, 2,4-diklorofenoksiasetik asit ve 2,4-diklorofenoksipropiyonik asit bozunması, fenoksiasit herbisitlerin ozonlanması, hidrojen peroksit ve ozon etkisi, yer altı ve yüzey suları.

Danışman: Prof. Dr. Dilek Şolpan Özbay, Hacettepe Üniversitesi, Kimya Bölümü, Fizikokimya Anabilim Dalı.

THE REMOVAL OF CHLORINATED ORGANIC PESTICIDES IN GROUND AND SURFACE WATERS BY GAMMA-IRRADIATION

Murat Torun

ABSTRACT

In this study, the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) herbicides in aqueous solutions was performed by exposition to ionizing radiation. The radiation-induced degradation of (2,4-D) and (2,4-DP) herbicides in aqueous solution was studied under various conditions as a function of irradiation dose in the absence and presence of hydrogen peroxide and ozone. In order to get information about the specific action of e^-_{aq} , $H^\cdot$, $OH^\cdot$ and $HO_2^\cdot/O_2^{\cdot-}$, the solutions were prepared in the absence and presence of H_2O_2 and O_3 . The aqueous solutions of 2,4-D and 2,4-DP were γ -irradiated in different conditions, where particular active radical species from water radiolysis predominate. The obtained data confirmed that largest yield of radiolytic degradation is obtained in oxidation processes/ionizing radiation, where oxidation is carried out with hydroxyl radicals.

Ionizing radiation has been proved as a promising method for the degradation of the herbicides 2,4-D and 2,4-DP. For complete degradation of 50 ppm 2,4-D and 2,4-DP, a required doses were lower in the presence of hydrogen peroxide and ozone. The formed intermediates were 2,4-dichlorophenol (2,4-DCP) and 4-chlorophenol (4-CP). Using hydrogen peroxide before irradiation, they were degraded again with a approximately dose of 2.0 and 3.0 kGy. For the formation of the aliphatic acids such as acetic, formic and oxalic acid a reaction mechanism was discussed. Hydrogen peroxide and ozone concentration enhanced strongly fragmentation and mineralization.

The chemical analysis of the 2,4-dichlorophenoxyacetic acid, 2,4-dichlorophenoxypropionic acid and the intermediates resulted from the radiolytic degradation were made using a Gas Chromatography associated to Mass-Mass Spectrometry (GC-MS-MS) and gas chromatography with Ion Trap Dedector (ITD) and Ion Chromatography (IC). Using GC-MS-MS-method, the initial G_i -values of the substrate degradation as well as of a number of radiolytic products were determined. The formation of chlorophenols in addition to chloride, formaldehyde and carboxylic acids was studied as a function of absorbed dose. Based on the experimental data, probable reaction mechanisms for the degradation of 2,4-D and 2,4-DP by γ -rays and the formation of the identified products were presented at various conditions. It was found that the degradation proceeded differently in the presence and absence of hydrogen peroxide and ozone and consequently two degradation pathways were proposed.

The main intermediates of pesticide degradation are of five types: (a) hydroxylated products and derivatives usually after dehalogenation of the parent pesticide, if halogen substituents are present (b) products of oxidation of the side chain, if present (c) ring opening products for aromatic pesticides (d) decarboxylation products and (e) isomerization and cyclization products. The identification of possible formation of highly toxic compounds even at low concentrations is essential for the assessment of treated water. Therefore, toxicity tests for the irradiated samples are also important to be conducted in combination with the identification of the intermediates. We couldn't perform toxicity tests for the irradiated herbicide solutions in the absence and presence of hydrogen peroxide and ozone in Turkey.

Keywords: phenoxyacid herbicides, gamma-irradiation, degradation of 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenoxypropionic acid, ozonation of phenoxyacid herbicides, effect of hydrogen peroxide and ozone, groundwater, surfacewater.

Supervisor: Prof. Dr. Dilek Şolpan Özbay, Hacettepe University, Department of Chemistry, Physical Chemistry Section.

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CURRICULUM VITAE		

ABBREVIATIONS

AGC	Automatic Gain Control
AOP	Advanced Oxidation Process
CI	Chemical Ionization
4-CP	4-Chloro Phenol
4-CPA	4-Chlorophenoxyacetic Acid
2,4-D	2,4-Dichlorophenoxyacetic Acid
2,4-DB	2,4-Dichloro Phenoxy Butanoic Acid
2,4-DCP	2,4-Dichloro Phenol
2,4-DP	2,4-Dichloro Phenoxy Propionic Acid
DDT	Dichloro-Diphenyl Trichloroethane
EB	Electron Beam
EI	Electron Impact Ionization
EPA	Environmental Protection Agency
eV	Electron Volt
GC	Gas Chromatograph
GLC	Gas Liquid Chromatography
GC-MS	Gas Chromatography-MassSpectrometry
GC/MS-MS	Gas Chromatography-MassSpectrometry- MassSpectrometry
GSC	Gas Solid Chromatography
HCH	Hexachlorocyclohexane
HPLC	High Performance Liquid Chromatography
HS	Head Space
IC	Ion Chromatography
IS	Internal Standart
ITD	Ion Trap Detector
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
MCPA	4-Methyl Chloro Phenoxy Acetic Acid
MCPB	2-(2-Methyl-4-chloro Phenoxy) Propionic Acid
MCPP	4-(4-Chloro-2 Methyl Phenoxy) Butanoic Acid
MS	Mass Spectroscopy
MS-MS	Mass Spectroscopy- Mass Spectroscopy
MTBE	Methyl Tert Butyl Ether
MW	Molecular Weight
OCP	Organochlorinated Pesticides
SDB	Styrene-Divinyl Benzene
SFE	Supercritical Fluid Extraction
SPE	Solid Phase Extraction
SPE/GC	Solid Phase Extraction/ Gas Chromatography
SPME	Solid Phase Micro Extraction
2,4,5-T	2,4,5-Trichlorophenoxy Acetic Acid
2,3,6-TBA	2,3,6-Trichloro Benzoic Acid
2,4,6-TCP	2,4,6-Trichloro Phenol
2,4,5-TP	2,4,5-Trichlorophenoxypropionic Acid

TEA	Triethylammonium 3,5,6-trichloro-2-pyridyloxyacetate
TOF	Time of Flight
UV	Ultra Violet
VOC	Volatile Organic Compound
WHO	World Health Organization

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1. INTRODUCTION

Water is one of the most important foodstuffs for human beings and all living systems. Hence, it is of great importance to keep water resources as clean as possible. However, as a consequence of the rapid development of various industries, where halogenated hydrocarbons are used as solvents, flame retardants, dielectric fluids, propellants etc. As well as the worldwide application of fertilizer, pesticides, fungicides etc. in modern agriculture, the quality of drinking water has deteriorated in many parts of the world, due to surface and groundwater pollution. The disinfection of drinking water containing humic compounds by chlorination also leads to the formation of various halogenated hydrocarbons (Rook,1974). Hence, the environmental and toxicological effects of such compounds has essentially increased (Hutzinger et al., 1982).

Conventional water treatment plants utilize the processes of mechanical removal, filtration, activated sludge, and chlorination to clean wastewaters. Unfortunately, these processes are typically not effective in remediating industrial organic contaminants such as herbicides. In fact, the chlorination process often increases the toxicity of organic compounds through the formation of chlorinated hydrocarbons and aromatics. (Nikolaou, 2004; Golfinopoulos, 2001; Bedner, 2004). Because the breakdown of organic compounds can lead to the formation of substances equally or more toxic than the parent compounds, effective remediation processes must also address the need for transformations to nontoxic compounds or to mineralization (formation of CO₂ and inorganics substances) of the contaminants (Hwang,1998). These realizations have led to detailed research on advanced oxidation processes (AOPs) (Stock, 2000; Peller, 2003).

On the other hand advanced oxidation process (AOP) based on various techniques have been applied mostly on laboratory scale and are proposed for purification of drinking water, industrial wastewater, surface and groundwater (Getoff, 1993, 1997; Balcioglu and Getoff, 1998). Advanced oxidation processes are defined as

technologies that employ the highly reactive hydroxyl radical as the main oxidative species for the breakdown of organic contaminants such as herbicides. The hydroxyl radical can be formed by a number of methods in aqueous systems: high-frequency ultrasound waves, γ -rays or high-energy electrons, TiO_2 and UV-light, H_2O_2 and UV light, O_3 and UV light, the Fenton reaction ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), and various combinations of these processes (Peller, 2004).

Advanced methods are in demand for effective treatment of pesticide-polluted ground and surface waters. Advanced oxidation processes (AOP) are particularly attractive as a method for removing organic pollutants as pesticides from water such as ozonation or oxidation with H_2O_2 under gamma-irradiation, etc. Ideally, the end products of these processes are carbon dioxide, water and inorganic mineral salts. Advanced Oxidation Process (AOP), using ozone, hydrogen peroxide, ultraviolet and gamma-irradiation, are promising technologies for generation of OH radicals and removal of organic pollutant from the environment.

The most simple and efficient method for generating OH radicals “in situ” is the interaction of ionizing radiation with water. This method was successfully applied for liquid samples containing chlorinated aliphatic, aromatic hydrocarbons and pesticides. The reactive species formed by the water irradiation are the reducing radicals solvated electron (e^-_{aq}), H atoms and the oxidizing radical hydroxyl $\text{OH}^\cdot$. The reactive species react with organic compounds in water inducing their degradation. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical, chemical and biological methods. It degrades organic compounds, generating substances that are easily biodegraded without the necessity of adding chemical compounds.

Many of the strengths and weaknesses of these processes have been assessed, leading to a better understanding of their practical implementation potentials (Tobien, 2000). At the same time, many details of the oxidation mechanisms are still not known, and the exact mechanisms involved may depend on the advanced oxidation

process(es) used. Hence, comparative photo- and radiation induced studies in the absence and presence of ozone are undertaken for the degradation of water pollutants.

Another approach to detoxification of water is ozonation. Ozone is a powerful oxidizing agent and hence is used on a technical scale for purification of drinking water as well as wastewater (Getoff, 1997; Hoigne, 1983a; Yao, 1991; Rice, 1996). Ozone may react with solutes either by direct oxidation (O_3 attack takes place at the electron rich site of the solute) or after radiolysis or photolysis, whereby OH radicals are resulting. Although, these radicals react very rapidly with organic and inorganic solutes, they exhibit little solute selectivity.

The radiolytic degradation of organic pollutants by the use of ionizing radiation was employed in recent years for treatment of natural waters and wastes of different origin. This technology was reported for drinking water treatment (Getoff, 1989) the decoloration of humic substances in water (Andayami and Bagyo, 2002) and treatment of effluents of various origin (Taghipour and Evans, 1996; Gehringer and Fiedler, 1998; Borrelly et al., 2000; Rela et al., 2000; Basfar and Abdel Rehim, 2002; Jung et al., 2002; Pikaev, 2002; Shin et al., 2002). Residual pesticides are very serious and common environmental pollutants, which may be removed from the environment by means of various chemical oxidation processes (Chiron et al., 2000). For degradation of several pesticides, γ -irradiation has been employed by several authors. This was used, for instance, for degradation of atrazine (Leitner et al., 1999; Angelini et al., 2000), different triazine herbicide Ametryn, carbamate insecticide Applaud and chlorinated pesticides Aldrin and Chlorothalonil (Dessouki et al., 1999) and also 2,4-dichlorophenoxyacetic acid (2,4-D) (Zona et al., 2002; Zona and Solar, 2003). In none of these works was the toxicity of the irradiated solution monitored, but only changes of concentration of the target decomposed compound and several selected products of radiolysis.

Several papers published recently have been devoted to radiolysis of pesticides. Gamma radiolysis was reported for herbicide 2,4-D (Peller et al., 2004; Peller, 2005; Zona, 2003) and acetochlor (Liu et al., 2005) and also atrazine (Vel Leitner et al., 1999; Angelini et al., 2000) and lannate (Abdel Aal, 2001). The studies of Trojanowicz are on radiolytic degradation of pesticides included degradation of 2,4-D (Drzewicz et al., 2004) and dicamba (Drzewicz et al., 2005). Generally, chlorophenoxy herbicides, which have potential toxicity towards humans and animals, and are suspected mutagenes and carcinogens, are used world-wide on a large scale as plant growth regulator for agricultural and non-agricultural purposes.

In the literature on degradation or removal of phenoxyacid herbicides for environmental purposes mostly photodegradation methods have been reported. Phenol, chlorophenols and phenoxyacid herbicides are widely distributed at low concentrations in surface and groundwaters. They have detrimental effects on water quality and are toxic for aquatic life. Radiolytic degradation of phenolic compounds, and especially chlorophenols for environmental purposes has not focused so far much attention in the literature.

In general, environmental waters cannot be analyzed without sample pretreatment because they are too diluted or too complex. A simple preparation step is necessary to extract traces of pesticides from aqueous medium, bring the analytes to a suitable concentration level and remove them from interfering components in the matrix before the chromatographic analysis. Current methods of analysis for aqueous systems involve solid phase extraction (SPE) .

Chromatographic methods are most widely used for analytical separation, identification and quantitation of pesticide residues in different matrices including water. Application of selective and highly sensitive detection systems is essential in water analysis because of the very small level of admissible concentrations of pesticide residues in water.

The aim of this study is to identify the products of radiolytic degradation of two herbicides, 2,4-D and 2,4-DP, and to determine the effect of various experimental factors (such as presence of H_2O_2 and O_3) on removal and on the effectiveness of radiolytic degradation. During radiolytic degradation, transient toxic products such as chlorophenols or dihydroxybenzenes may be formed, and it is of great importance to find out how these species may affect the toxicity of the irradiated solutions at various doses of radiation.

2. GENERAL INFORMATION

2.1. Water

Nearly, 70% of the earth is water. The 97% of this water is oceans and seas which includes salts. The 1% of the other 3% of the fresh water is in polars and in glaciers. The distribution of the world's water is given in Figure 2.1 and the situation of Turkey and water sources in the world is also given in Figure 2.2. Thus, the human beings can use only 1% of the reservoirs, surface and underground waters, directly. Until an economic process developed to obtain freshwater from salty water, there may be some problems such as reaching to freshwater problem and like in the case of petroleum, the sources of freshwater may become a commercial area and to control these sources may cause critical disagreement problems.

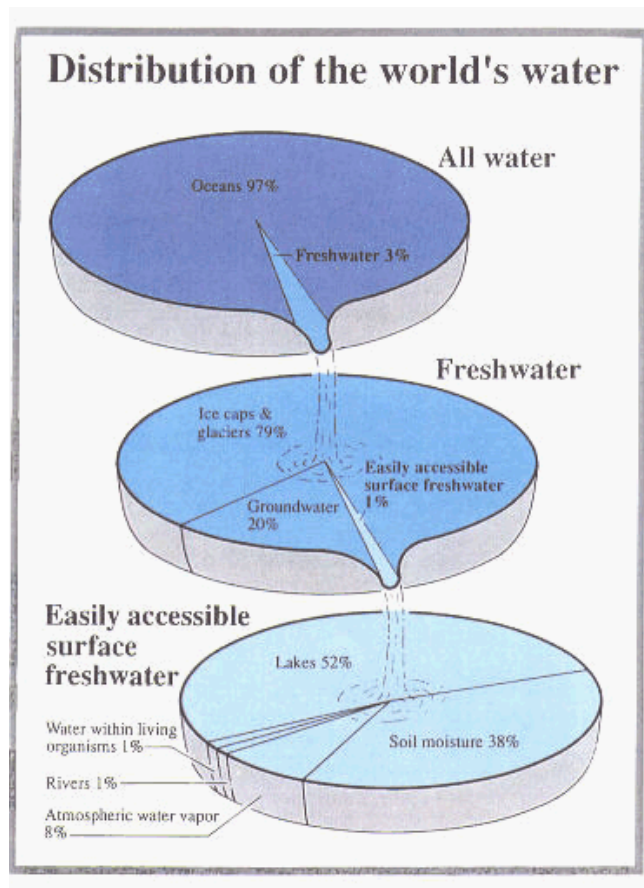


Figure 2.1. Distribution of the world's water (Delen et. al., 2005).

In the world, the consumption of the fresh water is 70% in agricultural activities. Thus, it is very important to use water in agricultural activities with a best yield and economical. For example, in developing countries, the 60% of the used water in irrigation reached to the surface or underground water sources due to vaporization or with other forms. The 22% of the fresh water is used for industrial activities and 8 percent is used for drinking or for other demands. In Europe, the 33% of the water is used for irrigation, 51 % is used for industrial activities and 16% is used for drinking and other activities. In Turkey, the 72% of the water is used for irrigation, 10 % is used for industrial activities and 18% is used for drinking and other activities. In individual person bases, the increase in the consumption of water is more than the twice of population increase. In the world, the consumption of water is nearly 800 m³ per person in a year. In developed countries, the consumption per person in a year is very high (in USA it is 380 liter, in Germany it is 129 liter), but in developing countries 20-30 liter is assumed to be enough for fundamental requirements. In Turkey, the consumption per person is 111 liters. If it is considered that the requirement for water is 150 liters per person for a modern life, it must be important for Turkey to consider the above amounts water usage.



Figure 2.2. The situation of Turkey and water sources in the world (Delen et.al.,2005).

2.1.1. Water Sources

The classification of countries according to their water sources are as following:

Water poor: the usable water is less than 1000 m^3 per person in a year.

Water insufficiency: the usable water is less than 2000 m^3 per person in a year.

Water rich: the usable water is more than $8000 - 10000 \text{ m}^3$ per person in a year.

In Turkey, the consumption of water per person in a year is 1500 m^3 , so Turkey is in the class of water insufficiency. It is not possible to live on the earth without water. From old periods to now, all central civilizations were founded close to the water basins and civilizations developed on the areas which were given life with water. In all the historical periods, the societies which have a possibility to use river water founded the developed civilizations in these periods, but societies which can not use water had to leave their areas and moved to use water easily. In the earth, first civilization which is assumed as Mesopotomia developed alphabets, first agricultural activities were accomplished and it is called as “abundant crescent” due to Dicle and Firat rivers. It is known that in B.C. 3000, Sumerians bandaged Firat and Dicle rivers to each other to use these rivers more functional. At the present time, water and irrigation has also importance, and increase in the demand of water with population increase gives a trend of water strategy. In the future, the most important parameter to use water sources and the quality will be the population. Official Institute of Statics projected that in 2030, the population of Turkey will be 100 million. In this case, the water consumption will be 1000 m^3 per person in a year (Figure 2.3). With the effects like present development and change in water consumption, it is possible to estimate the compulsion on Turkey, and, it will be necessary to transfer these water sources to 25 years later without any damage. So, water sources must be protected and used economically to transfer these sources sufficiently and clean to the future.

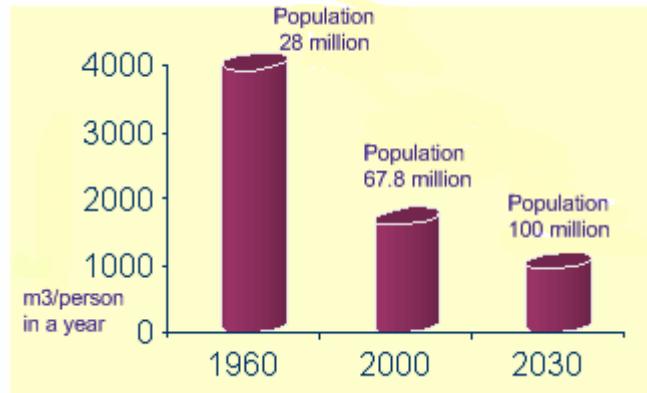


Figure 2.3. The variation of the usable amount water per person in a year with population (Delen et.al., 2005).

Water is an important resource, vital for both social and economic growth. It is thus imperative that water should be managed according to the principles of sustainable development to counteract the combination of increasing economic development and environmental degradation. The constantly increasing degree of industrialisation and urbanisation, rising standards of living, increasing population growth and agricultural activities are strongly impacting on the use of available water sources and on the quality of water that is found therein. This exhaustive use of limited resources and energy by modern society implies a need for changes in present and future urban water and wastewater treatment systems (Holtzhausen, 2002).

Since the world population is steadily increasing, there is an increasing demand for water. In many areas of the world, especially the drier ones, ground water is the main world's fresh water source (Bouwer, 2000). However, when ground water withdrawal exceeds the natural ground water recharge, aquifer water depletion occurs. Therefore, there is an urgent need for artificial storage of water by suitable facilities. Generally it has been achieved by the construction of different surface reservoirs, such as dams. However, proper sites are getting scarce and an adverse environmental impact on the area is produced. In addition, water stored in surface reservoirs is exposed to evaporation losses, especially important in areas of warm

climates (Postel et al., 1999; Bouwer, 2000; Asano and Cotruvo, 2004; Diaz-Cruz, 2008).

Several sources of water have been used for recharge purposes, including: surface water (streams, canals, and lakes), reclaimed wastewater (domestic and industrial), urban and rural storm water runoff, and treated drinking water (National Academy of Sciences, 2007). However, all those sources are exposed to permanent and sudden pollution by a wide variety of chemicals that are potentially adverse to the aquifer system (Kolpin et al., 2002). At present, the main source of water for ground water recharge is surface water, which is affected by industrial, agricultural, and domestic contamination. Urban development increases storm water runoff, meanwhile decreases natural infiltration areas. Because of that, the use of storm water runoff as a recharge water may be a promising approach (EPA, 1983).

2.1.2. Ground Water

Ninety-five percent of all fresh water on earth is ground water. Ground water is found in natural rock formations. These formations, called aquifers, are a vital natural resource with many uses. Nationally, 53% of the population relies on ground water as a source of drinking water. In rural areas this figure is even higher. Eighty one percent of community water is dependent on ground water. Although the 1992 Section 305(b) State Water Quality Reports indicate that, overall, the Nation's ground water quality is good to excellent, many local areas have experienced significant ground water contamination. Some examples are leaking underground storage tanks and municipal landfills.

2.1.3. Water Pollution

Pollution is defined as: "to make foul or unclean; dirty." Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. When it is unfit for its intended use, water is considered polluted. Two

types of water pollutants exist; point source and nonpoint source. Point sources of pollution occur when harmful substances are emitted directly into a body of water. A nonpoint source delivers pollutants indirectly through environmental changes. The technology exists for point sources of pollution to be monitored and regulated, although political factors may complicate matters. Nonpoint sources are much more difficult to control. Pollution arising from nonpoint sources accounts for a majority of the contaminants in streams and lakes.

Many causes of pollution including sewage and fertilizers contain nutrients such as nitrates and phosphates. In excess levels, nutrients over stimulate the growth of aquatic plants and algae. Excessive growth of these types of organisms clogs our waterways, use up dissolved oxygen as they decompose, and block light to deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiration ability of fish and other invertebrates that reside in water.

Pollution is also caused when silt and other suspended solids, such as soil, wash off plowed fields, construction and logging sites, urban areas, and eroded river banks when it rains. Under natural conditions, lakes, rivers, and other water bodies undergo Eutrophication, an aging process that slowly fills in the water body with sediment and organic matter. Pollution in the form of organic material enters waterways in many different forms as sewage, as leaves and grass clippings, or as runoff from livestock feedlots and pastures. When natural bacteria and protozoan in the water break down this organic material, they begin to use up the oxygen dissolved in the water.

Pathogens are another type of pollution that prove very harmful. They can cause many illnesses that range from typhoid and dysentery to minor respiratory and skin diseases. Pathogens include such organisms as bacteria, viruses, and protozoan. These pollutants enter waterways through untreated sewage, storm drains, septic tanks, runoff from farms, and particularly boats that dump sewage.

2.1.4. Additional Forms of Water Pollution

Three last forms of water pollution exist in the forms of petroleum, radioactive substances, and heat. Petroleum often pollutes waterbodies in the form of oil, resulting from oil spills. These large-scale accidental discharges of petroleum are an important cause of pollution along shore lines. Besides the supertankers, off-shore drilling operations contribute a large share of pollution. One estimate is that one ton of oil is spilled for every million tons of oil transported. This is equal to about 0.0001 percent. Radioactive substances are produced in the form of waste from nuclear power plants, and from the industrial, medical, and scientific use of radioactive materials. Specific forms of waste are uranium and thorium mining and refining. The last form of water pollution is heat. Heat is a pollutant because increased temperatures result in the deaths of many aquatic organisms. These decreases in temperatures are caused when a discharge of cooling water by factories and power plants occurs.

2.1.5. Classifying Water Pollution

The major sources of water pollution can be classified as municipal, industrial, and agricultural. Municipal water pollution consists of waste water from homes and commercial establishments. For many years, the main goal of treating municipal wastewater was simply to reduce its content of suspended solids, oxygen-demanding materials, dissolved inorganic compounds, and harmful bacteria. In recent years, however, more stress has been placed on improving means of disposal of the solid residues from the municipal treatment processes. The basic methods of treating municipal wastewater fall into three stages: primary treatment, including grit removal, screening, grinding, and sedimentation; secondary treatment, which entails oxidation of dissolved organic matter by means of using biologically active sludge, which is then filtered off; and tertiary treatment, in which advanced biological methods of nitrogen removal and chemical and physical methods such as granular filtration and activated carbon absorption are employed. The handling and disposal of solid residues can

account for 25 to 50 percent of the capital and operational costs of a treatment plant. The characteristics of industrial waste waters can differ both within and among industries. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic and organic substances. Three options are available in controlling industrial wastewater. Control can take place at the point of generation in the plant; wastewater can be pretreated for discharge to municipal treatment sources; or wastewater can be treated completely at the plant and either reused or discharged directly into receiving waters.

Agriculture, including commercial livestock and poultry farming, is the source of many organic and inorganic pollutants in surface waters and groundwater. These contaminants include both sediment from erosion cropland and compounds of phosphorus and nitrogen that partly originate in animal wastes and commercial fertilizers. Animal wastes are high in oxygen demanding material, nitrogen and phosphorus, and they often harbor pathogenic organisms. Wastes from commercial feeders are contained and disposed of on land; their main threat to natural waters, is from runoff and leaching. Control may involve settling basins for liquids, biological treatment in aerobic or anaerobic lagoons, and a variety of other methods.

2.1.6. Ground Water Contamination

Aquifers do not have an infinite or totally reliable capacity to purify the water which passes through them. Ground water as environmental compartment is substantially different from other aqueous systems. Long residence times, low temperatures, low degrees of dilution and decreased microbial population are factors favoring persistence of organic microcontaminants in ground water (Roberts and Valocchi, 1981; Prommer and Stuyfzand, 2005). Large aquifers allow long water retention times favoring contaminant removal; but when organic contaminants are introduced into an aquifer through artificial recharge, they will either move with the water or be adsorbed on the solid surfaces. Whenever retained contaminants do not break down they will

accumulate in the aquifer. This accumulation may have long-term impacts (Anders and Schroeder, 2001). An early study on the transport and fate of more than fifty volatile organic compounds (VOCs) evidenced their long persistence (>50 years) and the long distances reached (>10 km) (Barber et al., 1988).

Reclaiming an aquifer that has been contaminated is a difficult, long and expensive process; therefore, a prerequisite of artificial recharge is that it should not risk the quality of the ground water resource. Point source pollution may be controlled and prevented by accomplishing the standing legislation and directives. But even so, there are episodes of uncontrolled (fortuitous or not) chemical spills from industry causing serious water contamination. Agriculture is the main cause of diffuse pollution, which is quite difficult to face and prevent, since, pesticides, herbicides and fertilizers are spread on extensive fields. Animal farms are other important non-point source pollution since a quite wide variety of pharmaceuticals (antibiotics, hormones and other veterinary formulations) are used in the prevention and treatment of microbial infections and as growth promoters. Following medication, the treated organism excretes between 40% and 90% of the dosage applied in the feces and the urine as the parent compound or metabolites, which in some cases can be bioactive residues even more harmful than the parent compound (Jjemba, 2002). This manure is commonly used as organic fertilizer and is spread on agricultural soils from where the pharmaceutical residues excreted can contaminate ground water directly by percolation or indirectly via surface water contamination during runoff.

When an excess of drinking water is produced in water works, part of this potable water can be used for recharging the aquifer, which will improve the yield of the aquifer as well as the quality of the ground water. However, disinfection byproducts can be introduced (Diaz-Cruz, 2008).

Many ground water basins have been contaminated by a huge range of pollutants derived from industrial, municipal, and agricultural activities. When an aquifer area is polluted it is difficult and expensive to restore its availability. As a consequence,

concern about the potential impact of transported micropollutants in recharge waters on an aquifer system has arisen, especially when the recovered waters are used for further drinking water production (Postel, 2000; Asano and Cotruvo, 2004; Levine and Asano, 2004; Amy and Drewes, 2007).

Water is one of the most important foodstuffs for human beings and all living systems. Hence, it is of great importance to keep water resources as clean as possible. However, as a consequence of the rapid development of various industries, where halogenated hydrocarbons are used as solvents, flame retardants, dielectric fluids, propellants etc. As well as the worldwide application of fertilizer, pesticides, fungicides etc. in modern agriculture, the quality of drinking water has deteriorated in many parts of the world, due to ground water pollution. The same happens in some countries by pumpings industrial waste water into deep wells. The disposal of chemical waste material containing chlorinated compounds in rivers, seas and oceans has enormous environmental implications (Getoff, 1989).

The disinfection of drinking water containing humic compounds by chlorination also leads to the formation of various halogenated hydrocarbons (Rook,1974). Hence, the environmental and toxicological effects of such compounds has essentially increased (Hutzinger et al., 1982). Finally, the combustion of waste material containing chlorine organic substances results in the formation of acids in the atmosphere, which can be distributed by the wind over a larger area, but finally come to the ground as atmospheric fallout, resulting in an additional contribution to the pollution of drinking water. The metabolism of halogenated compounds in the human body has been implicated in a number of diseases (Mason and Chignell,1981).

2.2. Radiation Chemistry and The Environment

As a consequence of the growing of the world population and the strong development of various industries as well as the increasing traffic on the roads, the seas and in the air, rather heavy pollution of the global environment is occuring. A very essential contribution in this respect is the usage of fossil energy sources (coal, oil, natural gas)

and this will not change for the next 50-60 years. The search for replacement of fossil fuels by alternative energy sources (solar energy, hydrogen as energy carrier, nuclear and fusion energy etc.) are still not yet satisfactory. A survey of the negative consequences of the human activities is given in the following.

Human activity=pollution in:
Air Water Soil

-Pollutants in air: CO_2 , CO, NO_x , SO_2/SO_3 etc.,
Resulting from combustion of fossil fuels (coal, oil, natural gas)
 $\text{CO}_2 \rightarrow$ world warming (climate change)
CO $\rightarrow$ chemical&biological problems
 NO_x , $\text{SO}_2/\text{SO}_3 \rightarrow$ acid rain

-Pollutants in water: biologically resistant compounds, chlorinated substances etc. from chemical, pharmaceutical and other industries, dyestuffs from dyehouses etc.

-Pollutants in soil: various chemicals solids etc.
originating from chemical and others industries;
application of pesticides and other chemicals in agriculture, household waste etc.

The consequences of the environmental pollution are manifold:

- Health hazard for the population:** respiratory diseases, cancer, allergies etc.
- Environmental impact on a local scale:** polluted soil, drinking water, agriculture products and hence animal diseases, pollution of rivers and oceans resulting in plankton killing and reduction of fishes etc.
- Environmental impact on a global scale:** acid rain, CO_2 -greenhouse effect resulting in global warming etc.

Water usage is expected to increase as a result of continuing industrial development. A UNIDO study showed that current trends will lead to more than doubling of 1995 industrial water use by 2025 with over four-fold rise in industrial pollution unless changes are made. If more efficient water treatment technologies are used, this would cut wastage and reduce the amount of water that needs to be taken from various sources. Radiation technology helps to solve environmental problems. Its main principals and advantages are:

- No radioactivity is produced during the treatment procedure
- No waste
- Safe for operating personnel
- Environmentally safe
- Safe for general public
- Economically competitive
- Higher efficiency

In addition to this, it has to be mentioned that new "clean technologies" for the production of goods based on radiation processing are developed which cause no or very small load for the environment. High-energy radiation of any system generates highly reactive intermediates (hydrated electrons, OH radicals and H atoms in water) that interact with a wide range of pollutants. The interaction processes include redox reactions, decompositions of organic compounds and decolorization of dyes, among other chemical reactions and biological sterilization. These effects are the basis for the development of radiation methods for the purification and disinfection of gaseous, liquid and solid wastes.

The first studies on the radiation treatment of wastes, predominantly for disinfection, were carried out in the 1950s. In the 1960s these studies were extended to the purification of water and later to the purification of flue gases. There are a number of radiation chemistry methods for solving environmental problems (Dolin, 1973; Shubin, 1979). They are compiled in the following. Other methods, e.g. the utilization of CO₂ and CO as well as the degradation of biologically resistant pollutants in drinking water and industrial wastewater are more specific in respect to the given situation (origin, content of total pollutants etc.) are still under development.

Radiation chemistry methods for solving environmental problems

- Radiation treatment of natural and polluted water,
- Radiation purification of industrial liquid wastes,
- Radiation treatment of sewage sludge,
- Radiation purification of flue gases,
- Radiation purification of solid wastes: hospital and airport wastes, contaminated soil.

2.2.1. Natural and Polluted Drinking Water

Domestic drinking water is treated before use to remove microorganisms that are harmful to human health both with organic compounds that give rise to objectionable color and odor. Treatment typically involves addition of a coagulant, pH adjustment (with the addition of lime if necessary), settling, filtration, and the addition of chlorine, chlorinated lime, or ozone, to bring about disinfection. Since the standard treatment is comparatively involved and the removal of organic compounds incomplete (Brusentseva, 1983), it has been suggested that ionizing radiation can be used to decompose the organic materials. At the present time, the most common process used throughout the world in disinfection of drinking water is use of chlorine. However, chlorine is known to have some disadvantages, namely in the formation of by-products which may be carcinogenic or have other toxicological effects, what may effect the public health. Active research in many areas of the world is focused on studying alternatives to the chlorination process (Dolin, 1973; Takehisa, 1985).

2.2.2. Wastewater

Domestic and industrial wastewaters differ from polluted drinking water in the variety of pollutants present in higher concentrations (e.g. industrial wastewater often contains substances that are toxic or difficult to destroy such as salts of mercury and bismuth, cyanides, phenols. and dyes). High doses are generally required to remove organic pollutants by radiation treatment.

Because of the high absorbed dose necessary to purify wastewater by irradiation alone combined processes have been developed in which radiation treatment is used in combination with a conventional process such as chemical, biological, or thermal treatment or flotation (Takehisa, 1985 and 1982). A synergistic effect is often observed in these cases; that is the combined purification effect is better than the sum of effects obtained in the treatment processes applied separately.

In some cases chlorine is used after biological treatment process to minimize the biological “load” of the wastewater. This is widely found to be of minimal impact on the overall quality of effluent, producing halogenated by-products that may possess harmful effects.

2.2.3. Sources of Water

Groundwater is a source of drinking water in many areas of the world. A number of drinking water contaminants are known as endocrine disrupters, which are chemicals that interfere with the normal function of the endocrine system. Maximum contaminant levels have been established under the Safe Drinking Water Act by US EPA for a number of suspected endocrine disrupters: pesticides (atrazine, chlordane, DDT, endrin, lindane, methoxychlor, simazine and toxaphene), non-pesticide organics (pyrenes, phthalates, dioxin, polychlorinated biphenyls).

2.2.4. Water Radiolysis

Water and aqueous solutions have been studied extensively by radiation chemists and the basic mechanisms are reasonably well established for water itself and a range of inorganic and organic aqueous systems. Although wastewater is usually characterized by rather high solute concentrations as compared to ground or drinking water with regard to the effect of ionizing radiation wastewater has also to be classified as dilute aqueous solution. When dilute aqueous solutions are irradiated practically all the energy absorbed is deposited in water molecules and the observed chemical changes are brought about indirectly via the free radical species formed in water by so-called water radiolysis (Figure 2.4) (Swallow, 1982) and (Gehring, 2003). Direct action due to energy deposited directly in the solute is generally unimportant in dilute solutions.

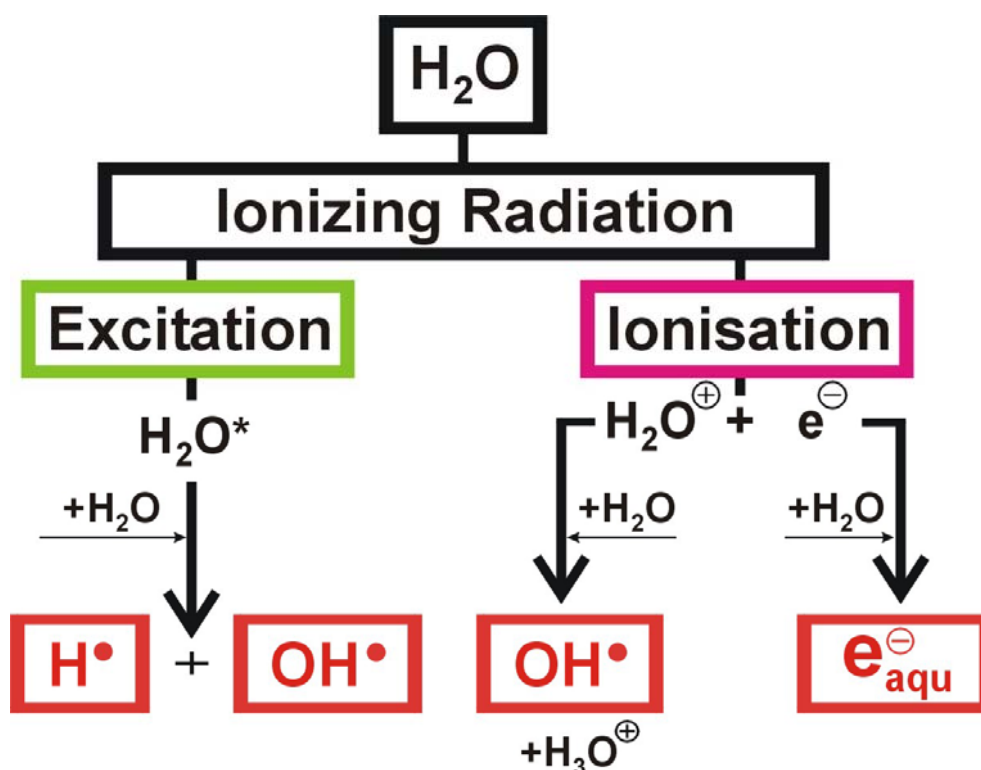


Figure 2.4. Water radiolysis: Formation of free radical species in water by means of ionizing radiation (Gehring, 2003).

Figure 2.4 illustrates the effect of ionizing radiation on water which is known to result in the formation of molecular species and free radicals, as well as some ions. For pollutant decomposition and microorganism inactivation, respectively just the free radical species are of interest. Pollutants and microorganisms are quite different targets for the attack of the free radical species. The free radicals formed during water radiolysis are highly reactive, the $\text{OH}^\bullet$ radicals are the most powerful oxidant known to occur in water, the same is valid for the hydrated electron e_{aq}^- as reductant. In consequence these radicals do not only react with target pollutant(s) but also with many other solutes contained in the water, even with some inorganic ions like e.g. bicarbonate and nitrate, respectively. In consequence a competition for the free radical species between the target pollutants and other solutes in the aqueous system occurs which determine the efficiency of the radiation process for pollutant decomposition.

Exposure of water to ionizing radiation produces ionized and excited water molecules and free electrons. In liquid water the ionized molecules react rapidly to form hydroxyl radicals:



while the electrons become hydrated:



Excited water molecules appear to play a relatively small role in liquid water and to return to the ground state with little chemical effect. During this early stage some of the transient radicals react together or with hydrogen ion (H_3O^+) to form smaller amounts of H_2 , H_2O_2 and $\text{H}\cdot$ and, to some extent, to reform H_2O . The yields when these processes are complete are often described as the radical (e_{aq}^- , $\text{H}\cdot$, and $\text{OH}\cdot$) and molecular product (H_2 , H_2O_2) yields. Values of the radicals and molecular product yields have been established by extensive experimental studies and are shown in Table 2.1 for electrons with energies in the MeV range. The values are pH dependent in strongly acid and strongly basic solution and the table includes data for pH 0.46. This is the pH of 0.4 mol/L sulfuric acid, the solvent used in the Fricke dosimeter and a number of other chemical dosimeters. At low pH hydrated electrons react rapidly with hydrogen ion (shown as H_3O^+ or H^+) forming hydrogen atoms.



The yields (G values) in Table 2.1 illustrate this and the fact that the relatively high solute (hydrogen ion) concentration scavenges some radicals that would otherwise recombine to form water so that overall yields are somewhat higher at pH 0.46.

Absorbed dose is the energy absorbed by any material exposed to a radiation field. The absorbed dose or amount of energy absorbed per unit of mass is defined as 1J/kg, equivalent to 1 Gray=100 rad = 6.24×10^{15} eV/g.

The G value is a measure of the radiation-chemical yield. It was originally defined as the number of molecules formed (consumed) per 100 eV absorbed energy. Since the eV is a non-SI unit, the G value is now given in units of mol/J. In the earlier literature the G values are always given in units of molecules/100 eV, but the new SI units will be used. (1 molecule/100 eV corresponds to 1.036×10^{-7} mol/J) (Gehring, 2003).

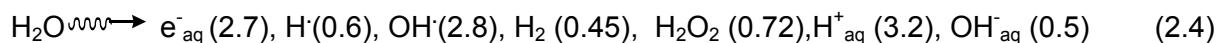
Table 2.1. Radical and molecular product yields (in mol/J) in electron-irradiated water.

pH	e^-_{aq}	H.	OH.	H ₂	H ₂ O ₂
3-11	2.7×10^{-7}	0.57×10^{-7}	2.8×10^{-7}	0.47×10^{-7}	0.7×10^{-7}
0.46	0	3.8×10^{-7}	3.0×10^{-7}	0.41×10^{-7}	0.8×10^{-7}

The radical products are highly reactive and are responsible for most of the chemical reactions observed when aqueous solutions are irradiated. Of the molecular products, hydrogen is unreactive and will almost always escape from the irradiated system unchanged while hydrogen peroxide tends to react slowly, if at all. The radiation-induced oxidation of ferrous sulfate solutions is one of the most thoroughly studied reactions in radiation chemistry, is the basis for the widely used Fricke dosimeter, and illustrates the behaviour of the radical and molecular products with a typical transition-metal compound.

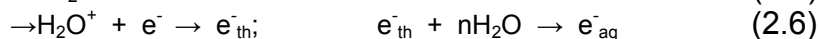
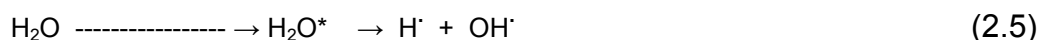
The radiation chemistry study consists of the experimental determination of the radiation-chemical products, specifying the primary products in the physical stage and following their fate in temporal sequence until observable chemical changes appear. The primary products are usually extremely unstable and initiate a sequence of events. When an aqueous mixture of compounds is irradiated by ionizing radiation, the water and mixture absorb the energy. By the irradiation of diluted aqueous solutions, the primary products of water radiolysis are attacking to the dissolved compound. Therefore, the water radiolysis is briefly mentioned. As a sequence of interaction between ionizing radiation (electrons, γ -rays) and water, electronically excited and ionized molecules are formed. This leads to the productions of several very reactive species ($OH^\cdot$, e^-_{aq} , $H^\cdot$) and molecular products (H₂, H₂O₂).

Gross reaction expresses the primary products of water radiolysis, where their yields (G values) are given in brackets for pH-range of about 6 to 8.5:

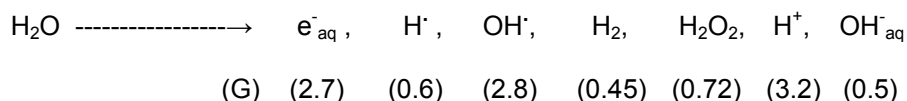


The primary reactions of water radiolysis and G-values of the primary products are given below (Spinks, 1990; Getoff, 1996).

Primary reactions:



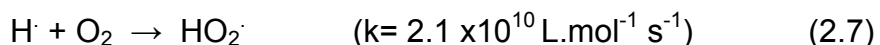
Gross reaction of water radiolysis (the G-values at pH=7 are given in brackets):



If we consider pure water, each 100 eV of energy absorbed will generate: 2.8 radicals $\text{OH}^\cdot$, 2.7 e^-_{aq} , 0.6 radicals $\text{H}^\cdot$, 0.45 H_2 molecules and 0.72 molecules H_2O_2 . It is well known that e^-_{aq} and H atoms have strong reducing properties, where as $\text{OH}^\cdot$ radicals are acting as strong oxidizing agents.

2.2.5. Effect of O_2

Oxygen is a very efficient scavenger for hydrogen atoms, combining with them to give hydroperoxyl radical, $\text{HO}_2^\cdot$



This reaction almost invariably occurs in irradiated aqueous solutions if dissolved oxygen has not been carefully removed, although solutes which react very readily with hydrogen atoms can compete with the oxygen so that only a fraction of the hydrogen atoms are converted to hydroperoxyl radicals .

The $\text{HO}_2^\cdot$ radical is not as reactive as the hydrogen atom and unlike the latter, rarely abstracts hydrogen from organic solutes. It is however a strong oxidizing agent and reacts with hydroxyl radicals (which are themselves oxidizing agents) and other $\text{HO}_2^\cdot$ radicals to give oxygen,



The yield of hydrogen peroxide in irradiated water is increased when oxygen is present because of reaction

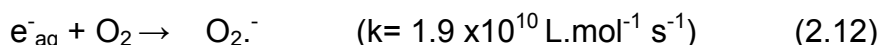


and because removal of hydrogen atoms by reaction $\text{H}^\cdot + \text{O}_2 \rightarrow \text{HO}_2^\cdot$ prevents the back reaction,



and it has been suggested that this may occur to some extent in the spurs and track zones where hydrogen peroxide is formed as a molecular product. When it is formed under these circumstances, the $\text{HO}_2^\cdot$ radical can be considered as a primary radical product.

In the presence of O_2 , also, e_{aq}^- is scavenged (Hayon, 1962).

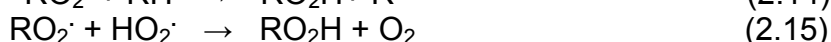


So, the overall result is that in the absence of oxygen both solvated electrons and hydrogen atoms are observed, but when oxygen is present only solvated electrons and the product formed from them, $\text{O}_2^{\cdot-}$, is observed.

Oxygen readily adds to free radicals and if present will almost invariably play a part in radiation induced reactions.



the product is a relatively stable peroxy radical. Peroxy radicals are the initial products formed by addition of oxygen to an organic radical, and they can form hydroperoxides (RO_2H) by hydrogen abstraction or by reaction with a perhydroxyl radical:



In some cases, hydroperoxides can be formed directly by addition of oxygen to an excited molecule. Combination of two peroxy radicals may give an organic peroxide,



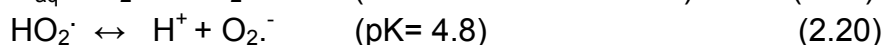
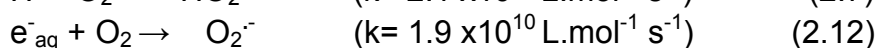
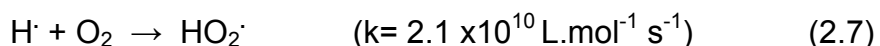
Other reactions which have been suggested by a peroxy radical is degraded to an alkoxy radical include



Alkoxy radicals are more reactive than peroxy radicals and can abstract hydrogen from most organic compounds, resembling hydroxyl radicals in this respect, (Spinks and Woods, 1962).



While a number of reactive species are formed during radiolysis hydroxyl radicals are the most important for remediation and react with organic compounds to form radicals, which in the presence of molecular oxygen undergo radical chain oxidation processes. Superoxide anion radical formed by reaction of oxygen with hydrated electrons and hydrogen atoms, can also be involved in the formation of hydrogen peroxide and radical chain processes. Radiolysis leads to the formation of hydroxyl radicals in a homogeneous environment. Under such conditions the reactions follow condensed phase reaction pathways and can be accurately predicted and modeled. In the presence of air the reducing species: “solvated electrons” e^-_{aq} and H atoms are converted into oxidizing species: hydroperoxyl radicals: ($\text{HO}_2\cdot$) and perhydroxyde radical anions ($\text{O}_2^{\cdot -}$):

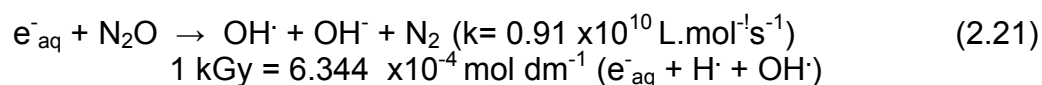


2.2.6. Effect of N_2O

$\text{O}_2^{\cdot -}$ together with $\text{OH}\cdot$ radicals can initiate degradation of water pollutants. Nitrous oxide gas can be used to convert the hydrated electrons to hydroxyl radicals, although it is generally not practical for environmental applications. Hydroxyl radical scavengers such as t-butanol can be used to consume the hydroxyl radical for selectively studying hydrated electron. Hydrated electron is a powerful reducing agent and potentially could be used for treatment of halogenated compounds, but it is

extremely reactive towards molecular oxygen requiring that the solutions be deoxygenated prior to treatment, a costly prospect.

By saturation the solution with N₂O the e_{aq}⁻ are transformed into OH[•] radicals:



Therefore, it is clear that in solutions containing oxygen (pH: 6 to 8,5) involved free radicals are: 46% OH[•] and 54% O₂^{-•}. On the other hand in solutions saturated in N₂O the acting radicals are: 90% OH[•] and 10% H[•] (Getoff, 2002).

2.2.7. Effect of H₂O₂

The hydrogen peroxide reacts with H[•] (k_(20°C) = 2.4 × 10¹⁰ M⁻¹s⁻¹) and e_{aq}⁻ (k_(20°C) = 1.5 × 10⁷ M⁻¹s⁻¹) as follows (Zona, 2003; Jankowska, 2004):



In the presence of excess hydrogen peroxide in solution, it can scavenge the hydroxyl radicals with rate constant (k_(20°C) = 3.1 × 10¹⁰ M⁻¹s⁻¹), according to reactions:



The total effect of reactions (2.13) and (2.14) is the following process:

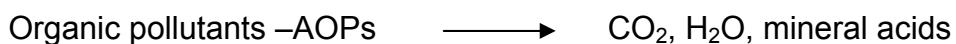


From the obtained results under corresponding experimental conditions one can estimate which type of free radicals is mostly involved in degradation of given substrate. It is interesting to point out that when the primary radiolytic species (OH[•], H[•], e_{aq}⁻, H₂, H₂O₂) are formed, a number of very fast reactions take place. When we deal with high dose rates, a very high concentration of primary species along electron traces is formed. They have less chance to diffuse away in order to react with pollutants because they are consumed within the trace by reactions among

themselves. As a consequence of this fact, the degradation yield is low. This effect is strongly pronounced in the case of low pollutant concentration and implementation of higher dose rates (Getoff, 2002; Borrely, 1998).

2.3. Advanced Oxidation Processes (AOPs) for Water Treatment

There is a critical need for the development of innovative technologies for the cleanup and purification of water for human consumption and re-use. Current adsorption and air stripping water treatment methods simply transfer pollutants from one medium to another and may require additional treatment. A number of organic pollutants are resistant to bioremediation, or the longer trains of processes known as tertiary (or advanced) treatment, however radicals generated during advanced oxidation technologies can lead to the remediation of an extensive variety of organic pollutants. Hydroxyl free radicals are the strongest oxidants known to occur in water. Processes which generate hydroxyl free radicals for the subsequent use of pollutant decomposition are generally referred to as “Advanced Oxidation Processes” (AOPs) (Peller, 2004). AOPs are characterized by the production of the highly oxidative hydroxyl radical at ambient temperatures for oxidative destruction of organic compounds, which can ultimately lead to complete mineralization with the formation of CO₂, H₂O and mineral acids.



A wide range of AOPs have been developed for the treatment of aqueous waste streams with a single treatment process or by combinations of ozonation, UV irradiation with or without catalysts such as TiO₂, ultrasonic irradiation, electron beam irradiation, γ-ray irradiation, Fenton processes and hydrogen peroxide in Figure 2.5. AOPs fundamentally rely on the production of large fluxes of hydroxyl radicals which, in the presence of complementary oxidants (e.g. ozone or H₂O₂) or upon extended treatment can bring about (in favorable cases) complete mineralization of organic matter. Hydroxyl radicals can oxidize a variety of organic materials and are central to the application of AOPs for treatment of pollutants in water.

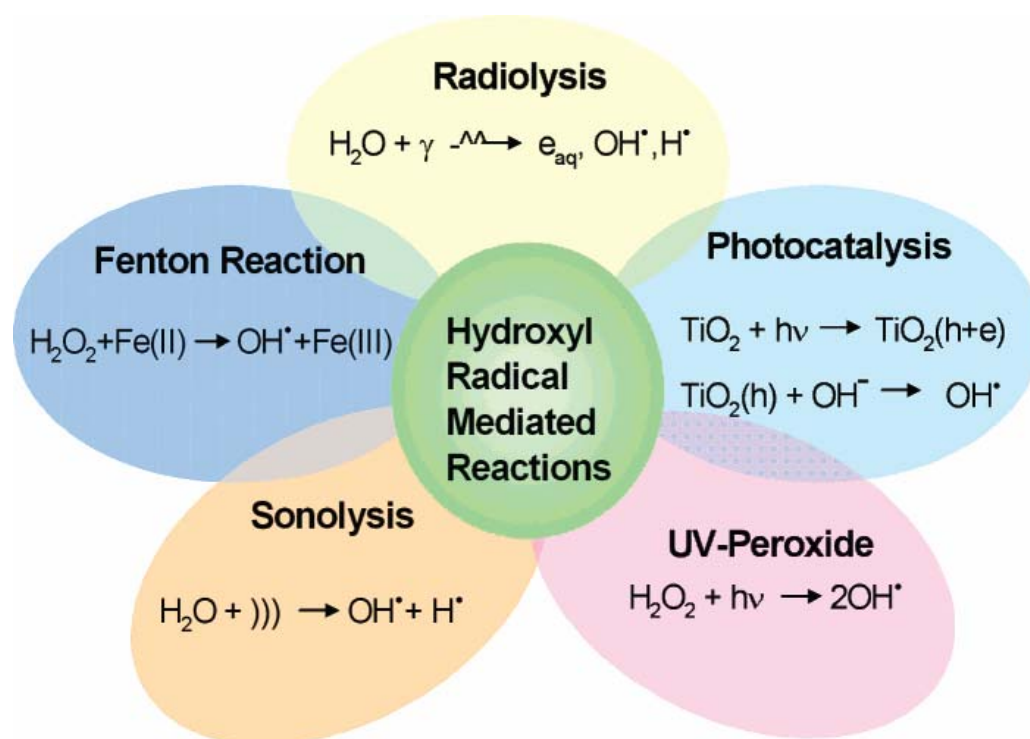


Figure 2.5. Examples of advanced oxidation processes employing hydroxyl radical (Peller, 2004).

The reactions of hydroxyl radicals with organic substrates can involve a number of competing reaction pathways, addition, electron abstraction and hydrogen abstraction being the most common, as illustrated below.

- Hydrogen Abstraction $\text{R-CH}_3 \rightarrow \text{R-CH}_2^\bullet + \text{H}_2\text{O}$
- Addition $\text{H}_2\text{C=CH}_2 + \text{HO}^\bullet \rightarrow \text{HOCH}_2\text{CH}_2^\bullet$
- Electron Abstraction $\text{Y} + \text{HO}^\bullet \rightarrow \text{Y}^\bullet + \text{HO}^-$

The bimolecular rate constants for these hydroxyl radical reactions are large typically range from 10^8 to $10^{10} \text{ sec}^{-1} \text{ M}^{-1}$. These paths usually result in the formation of free radical species react with molecular oxygen to form peroxy radicals and undergo standard chain oxidation reaction pathways. The typical products of such radical chain oxidation reactions are carbonyl compounds (aldehydes and ketones), organic acids, esters and alcohols which are often less toxic and more amenable to bioremediation.

Ozone is a commonly used oxidant for drinking water treatment. Ozone is much more selective than hydroxyl radical and may be advantageous especially in the treatment of drinking waters containing significant levels of dissolved organics which readily consume hydroxyl radical. Regardless ozone has will be effective for the treatment of a limited number of pollutants.

2.3.1. Ionizing Radiation Degradation of Organic Compounds

High-energy ionizing radiations used to initiate radiation-chemical reactions include radiation from natural and artificial radioisotopes (i.e., α , β and γ radiation), X rays, neutron beams and beams of charged particles (including both electron beams of positively charged particles). Of these, γ radiation and electron beam are used most frequently in radiation processing applications.

The global water resources became rather polluted in the last decades. The supply of drinking water in some regions of the world makes problems. This is the sequence of lack of responsibility of industrial enterprises as well as of the corresponding governmental authorities. There are a number of methods for water purification which are comprised in the following.

Methods

- Radiation-induced oxidation of pollutants using: electrons, γ -rays, x-rays; synergistic effect in the presence of O_3/O_2 , eventually H_2O_2 ; as additive.
- Biological process for biodegradable pollutants used for wastewater treatment.
- Ozone treatment: O_3 or O_3/H_2O_2
- Photoinduced oxidation by UV (185 & 254 nm) or UV/ O_3 , UV/ H_2O_2 and UV/ O_3/H_2O_2 resp. using e.g. low pressure Hg-lamp.
- Photocatalytic treatment: UV/VIS light using TiO_2 , ZnO etc. as catalyst.
- Thermal oxidation of pollutants, used for liquid industrial wastes.
- Fenton processes: H_2O_2/Fe^{2+} or $H_2O_2/O_3/Fe^{2+}$ (acid media).
- Photo-Fenton process: U V/ H_2O_2/Fe^{2+} or UV/ $H_2O_2/O_3/Fe^{2+}$ (acid media)
- Ultrasonic treatment (sonolysis of water)
- Electrochemical oxidation
- Solar energy in combination with O_3 and/or TiO_2 .

It should be stressed that the most efficient method for degradation of biologically resistant water pollutants in industrial scale is the electron beam processing of water in the presence of ozone (synergistic effect) (Getoff, 1999; Lessel, 1997; Takacs, 2002; Borrely, 1998).

2.3.2. Waste Water Treatment Processes

In general the overall pollutant concentration in a waste water is rather high but still in a range (below 1 mol/L) in which no direct action of the radiation occurs. Accordingly the pollutant decomposition is caused by free radical species only. The experiments can be performed with different types of waste water and each of them treated with

- ozone alone
- irradiation alone
- combination of ozone with irradiation
- hydrogen peroxide alone
- combination of hydrogen peroxide with irradiation

It has been found that the addition of ozone in combination with UV radiation or hydrogen peroxide can promote the decomposition of ozone and generate hydroxyl free radicals. Combining hydrogen peroxide and UV radiation alone will achieve similar results as the a forementioned ozone based processes by generating hydroxyl free radicals but with considerably lesser yield (Gehring, 1992). What all these AOPs have in common is that the hydroxyl free radicals originate from one single source only (ozone or hydrogen peroxide, respectively), i.e., the hydroxyl free radical concentration obtained is comparatively low. On the other hand groundwater very often is contaminated by rather small amounts of highly toxic compounds. To be effective in the treatment of groundwater containing trace amounts of pollutants high hydroxyl free radical concentration is necessary. Combination of ozone with EB irradiation which represents ionizing radiation — is able to produce much higher hydroxyl free radical concentrations than the AOPs mentioned before because in this combination the hydroxyl free radicals originate from two different but simultaneously

working sources: (1) directly from the water to be purified by the action of the EB irradiation (so-called water radiolysis), and (2) from ozone decomposition accelerated by the reducing species formed during water radiolysis (Gehring, 1992).

Table 2.2 shows the most important steps of all ozone based AOPs including also the combination of ozone and hydrogen peroxide. It clearly illustrates that O_3/UV and O_3/H_2O_2 processes are one and the same regarding hydroxyl free radical generation: in the former, one is merely forming hydrogen peroxide in situ, rather than adding it from the outside. From this table it comes out clearly that two completely different mechanisms for $OH^\cdot$ free radical generation occur. UV radiation is absorbed by ozone (and, if present, by other organics absorbing UV at 254 nm) while the energy of the fast electrons is totally absorbed by water and not by any solute. In other words, under the conditions given, UV irradiation represents the direct effect of radiation while EB irradiation stands for the indirect effect of radiation.

The latter produces hydroxyl free radicals directly from water and simultaneously the promoters for ozone decomposition (by formation of the solvated electrons e^-_{aq}) while the former only produces the promoter for ozone decomposition (by formation of hydrogen peroxide and its deprotonated anion, respectively). Accordingly EB irradiation must be more efficient regarding hydroxyl free radical generation than any other ozone based process. Since UV irradiation of hydrogen peroxide is less effective than ozone/UV (Gehring, 1992) it is obvious that ozone/EB irradiation is the most attractive AOP for groundwater remediation.

2.3.3. Ozone and Ozonation

Ozone was first used for drinking water treatment in 1893 in the Netherlands. While being used frequently in Europe for drinking water disinfection and oxidation, it was slow to transfer to the United States. Ozone is used in water treatment for disinfection and oxidation. Early application of ozone in the United States was primarily for non-disinfection purposes such as color removal or taste and odor control.

Ozone exists as a gas at room temperature. Ozone gas is highly corrosive and toxic. Ozone is a powerful oxidant, second only to the hydroxyl free radical, among chemicals typically used in water treatment. Therefore, it is capable of oxidizing many organic and inorganic compounds in water. These reactions with organic and inorganic compounds cause an ozone demand in the water treated, which should be satisfied during water ozonation prior to developing a measurable residual.

Ozone is sparingly soluble in water. At 20°C, the solubility of 100 percent ozone is only 570 mg/L (Kinman, 1975). While ozone is more soluble than oxygen, chlorine is 12 times more soluble than ozone. Ozone concentrations used in water treatment are typically below 14 percent, which limits the mass transfer driving force of gaseous ozone into the water. Consequently, typical concentrations of ozone found during water treatment range from <0.1 to 1mg/L, although higher concentrations can be attained under optimum conditions.

Basic chemistry research (Hoigné and Bader, 1983a and 1983b; Glaze et al., 1989a) has shown that ozone decomposes spontaneously during water treatment by a complex mechanism that involves the generation of hydroxyl free radicals. The hydroxyl free radicals are among the most reactive oxidizing agents in water, with reaction rates on the order of $10^{10} - 10^{13} \text{ M}^{-1}\text{s}^{-1}$, approaching the diffusion control rates for solutes such as aromatic hydrocarbons, unsaturated compounds, aliphatic alcohols, and formic acid (Hoigné and Bader, 1976). On the other hand, the half-life of hydroxyl free radicals is on the order of microseconds, therefore concentrations of hydroxyl free radicals can never reach levels above 10^{-12} M (Glaze and Kang, 1988). As shown in Figure 2.6 ozone can react by either or both modes in aqueous solution (Hoigné and Bader, 1977):

- Direct oxidation of compounds by molecular ozone ($\text{O}_{3(\text{aq})}$).
- Oxidation of compounds by hydroxyl free radicals produced during the decomposition of ozone.

The two oxidation pathways compete for substrate (i.e., compounds to oxidize). The direct oxidation with aqueous ozone is relatively slow (compared to hydroxyl free radical oxidation) but the concentration of aqueous ozone is relatively high. On the other hand, the hydroxyl radical reaction is fast, but the concentration of hydroxyl radicals under normal ozonation conditions is relatively small. Hoigné and Bader (1977) found that:

- Under acidic conditions, the direct oxidation with molecular ozone is of primary importance; and
- Under conditions favoring hydroxyl free radical production, such as high pH, exposure to UV, or addition of hydrogen peroxide, the hydroxyl oxidation starts to dominate.

The spontaneous decomposition of ozone occurs through a series of steps. The exact mechanism and reactions associated have not been established, but mechanistic models have been proposed (Hoigné and Bader, 1983a and 1983b; Glaze, 1989b).

2.3.3.1. Primary Uses of Ozone

Ozone is used in drinking water treatment for a variety of purposes including:

- Disinfection;
- Inorganic pollutant oxidation, including iron, manganese, and sulfide;
- Organic micropollutant oxidation, including taste and odor compounds, phenolic pollutants, and some pesticides; and
- Organic macropollutant oxidation, including color removal, increasing the biodegradability of organic compounds.

Table 2.2. Ozone based AOPs with regard to their most essential reactions for hydroxyl free radical formation in water (Gehring and Eschweiler, 2001).

Irradiation of groundwater containing dissolved ozone	
UV-irradiation	Electron beam irradiation
<i>Initiation</i>	
$O_3 \xrightarrow[254]{h\nu} O + O_2$	$H_2O \xrightarrow{e^-} H_2O^+ + e^-$
<i>Propagation</i>	
$O + H_2O \rightarrow H_2O_2$	$H_2O^+ + H_2O \rightarrow H_3O^+ + OH.$
$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	$e^- + H_2O \rightarrow e^-_{aq}$
<i>O₃ Decomposition</i>	
$O_3 + HO_2^- \rightarrow O_3^- + HO_2$	$O_2 + e^-_{aq} \rightarrow O_2^-$
$HO_2 \rightleftharpoons H^+ + HO_2^-$	$O_3 + O_2^- \rightarrow O_3^- + O_2$
$O_3 + O_2^- \rightarrow O_3^- + O_2$	$O_3 + e^-_{aq} \rightarrow O_3^-$
$\downarrow$ $O_3^- + H^+ \rightarrow HO_2$ $HO_3 \rightarrow O_2 + OH.$	
• Radiation is only absorbed by ozone • The only source for OH₂ free radical is ozone decomposition	• Radiation is only absorbed by water • There are two sources for OH₂ free radical 1. water ionization 2. Ozone decomposition

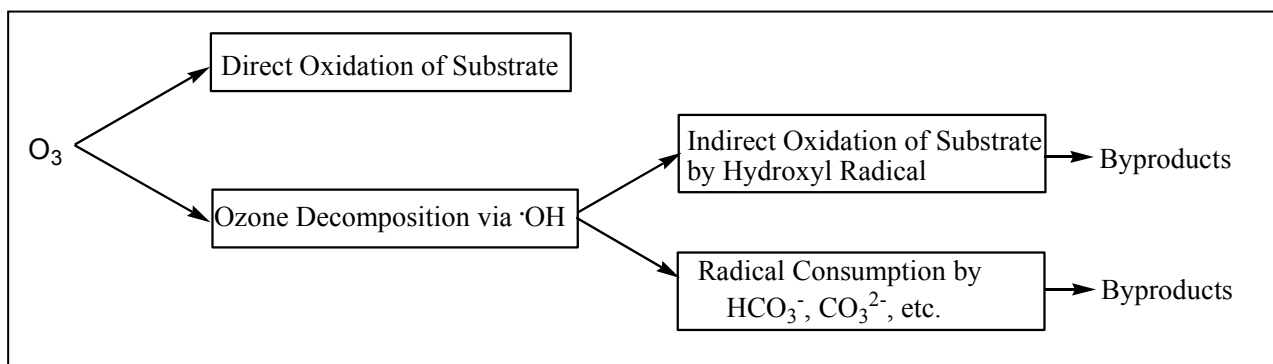


Figure 2.6. Oxidation reactions of compounds (substrate) during ozonation of water.

2.3.3.2. Ozonation Disinfection Byproducts

Byproducts such as aldehydes, ketones, acids, and others will be formed upon ozonation of water. The primary aldehydes that have been measured are: formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal (Glaze et al., 1991). Total aldehyde concentration in drinking water disinfected with ozone range from less than 5 mg/L to 300 mg/L, depending on the TOC concentration and the applied ozone to organic carbon ratio (Van Hoof et al., 1985; Yamada and Somiya, 1989; Glaze et al., 1989a; Krasner et al., 1989; Glaze et al., 1991; LeLacheur et al., 1991). Aldehydes with higher molecular weights have also been reported (Glaze et al., 1989b). Other organic byproducts of ozonation are indicated in Table 2.3.

Table 2.3. Principal known byproducts of ozonation.

Aldehydes	Aldo and Ketoacids
Formaldehyde	Pyruvic Acid
Acetaldehyde	Brominated Byproducts*
Glyoxal	Bromate ion
Methyl Glyoxal	Bromoform
Acids	Brominated Acetic Acids
Oxalic Acid	Bromopirrin
Succinic acid	Brominated acetonitriles
Formic acid	Others
Acetic acid	Hydrogen peroxide

*Brominated byproducts are produced only in waters containing bromide ion

2.4. Pesticides

There is no universal biological meaning of the word *pest*. Any living thing that successfully competes with people for food, space, or other essential needs is called a pest (Anderson, 1987). The term therefore includes different living things in various parts of the world. Food competitors include birds, rodents, insects, bacteria, mollusca, and nematodes, while weeds, bears, elk, birds, and small mammals are space competitors.

Pesticide is a general term denoting substances such as insecticides, herbicides, fungicides, fumigants, algacides, aviacides, and rodenticides used to control objectionable populations. Ecologists use the term biocide to indicate all chemicals

that destroy pests. Pesticides are substances or mixtures of substances used for preventing, controlling, or lessening the damage caused by a pest. A pesticide may be a chemical substance, biological agent (such as a virus or bacteria), antimicrobial, disinfectant or device used against any pest. Pests include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes (roundworms) and microbes that compete with humans for food, destroy property, spread or are a vector for disease or cause a nuisance (EPA, 2007).

Since before 2500 BC, humans have utilized pesticides to protect their crops. The first known pesticide was elemental sulfur dusting used in Sumeria about 4.500 years ago. By the 15th century, toxic chemicals such as arsenic, mercury and lead were being applied to crops to kill pests. In the 17th century, nicotine sulfate was extracted from tobacco leaves for use as an insecticide. The 19th century saw the introduction of two more natural pesticides, pyrethrum which is derived from chrysanthemums, and rotenone which is derived from the roots of tropical vegetables. In 1939, Paul Müller discovered that DDT was a very effective insecticide. It quickly became the most widely-used pesticide in the world (Daly et.al., 1998). Some sources consider the 1940s and 1950s to have been the start of the "pesticide era." Pesticide use has increased 50-fold since 1950 and 2.5 million tons (2.3 million metric tons) of industrial pesticides are now used each year. Seventy-five percent of all pesticides in the world are used in developed countries, but use in developing countries is increasing. In the 1960s, it was discovered that DDT was preventing many fish-eating birds from reproducing, which was a serious threat to biodiversity. Rachel Carson wrote the best-selling book *Silent Spring* about biological magnification. DDT is now banned in at least 86 countries, but it is still used in some developing nations to prevent malaria and other tropical diseases by killing mosquitoes and other disease-carrying insects (Miller, 2004).

Today, over 500 compounds are registered worldwide as pesticides, or metabolites of pesticides, (van Der Hoff et.all.,1999). Pesticides can be classified based on functional groups in their molecular structure (e.g. inorganic, organonitrogen, organohalogen or organosulfur compounds), or their specific biological activity on

target species (e.g., insecticides, fungicides, herbicides, acaricides, etc.) (van Der Hoff et. al., 1999; Hajslova, J., 1999). Herbicides are by far the most commonly used pesticides followed by insecticides, fungicides, and others. Pesticide use in agriculture has progressively increased after World War II leading to increased world food production. Nevertheless, this use and additional environmental pollution due to industrial emission during their production have resulted in the occurrence of residues of these chemicals and their metabolites in food commodities, water and soil.

2.4.1. Classification of Pesticides

Pesticides can be classified according to their use and chemical structure. According to use, pesticides are classified as follows:

Algicides: Control algae in lakes, canals, swimming pools, water tanks, and other sites.

Antifouling agents: Kill or repel organisms that attach to underwater surfaces, such as boat bottoms.

Antimicrobials: Kill microorganisms (such as bacteria and viruses).

Attractants: Attract pests (for example, to lure an insect or rodent to a trap) (However, food is not considered a pesticide when used as an attractant.)

Biopesticides: Biopesticides are certain types of pesticides derived from such natural materials as animals, plants, bacteria, and certain minerals.

Biocides: Kill microorganisms.

Disinfectants and sanitizers: Kill or inactivate disease-producing microorganisms on inanimate objects.

Fungicides: Kill fungi (including blights, mildews, molds, and rusts).

Fumigants: Produce gas or vapor intended to destroy pests in buildings or soil.

Herbicides: Kill weeds and other plants that grow where they are not wanted.

Insecticides: Kill insects and other arthropods.

Miticides (also called acaricides): Kill mites that feed on plants and animals.

Microbial pesticides: Microorganisms that kill, inhibit, or out compete pests,

including insects or other microorganisms.

Molluscicides: Kill snails and slugs.

Nematicides: Kill nematodes (microscopic, worm-like organisms that feed on plant roots).

Ovicides: Kill eggs of insects and mites.

Pheromones: Biochemicals used to disrupt the mating behavior of insects.

Repellents: Repel pests, including insects (such as mosquitoes) and birds.

Rodenticides: Control mice and other rodents.

The term pesticide also includes these substances:

Defoliants: Cause leaves or other foliage to drop from a plant, usually to facilitate harvest.

Desiccants: Promote drying of living tissues, such as unwanted plant tops.

According to their chemical structure, pesticides are classified as inorganic and organic. The inorganic pesticides now constitute only a small part of the pesticides in use. Examples of inorganic pesticides are:

- arsenical pesticides: Paris green $[\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}_3(\text{AsO}_3)_2]$
- fluoride insecticides: Cryotile (Na_2AlF_6)
- inorganic herbicides: Borax ($\text{Na}_2\text{B}_4\text{O}_7$)
- inorganic fungicides: Bordeaux mixture ($3\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4 \cdot \text{CaSO}_4$)

Among the organic pesticides, the following main groups are found:

organochlorine pesticides (chlorinated hydrocarbons), organophosphorus pesticides, carbamates, derivatives of phenoxyacetic acid, urea pesticides, derivatives of triazines. Example of main groups are:

- Organochlorine Pesticides: Hexachlorocyclohexane, DDT, dieldrin, aldrin, endrin, chlordane, endosulphan, mirex, heptachlor, isobenzene, methoxychlor, pentachlorophenol.
- Organophosphorus Pesticides: Dimethoate, parathion, malathion, dichlorvos, fenthion, chlorpyrifos, chlorfenvinphos, glyphosate.
- Carbamate Pesticides: Aminocarb, propoxur, carbaryl, aldicarb, dioxacarb, maneb.
- Phenoxyacetic acid Herbicides: 2,4-D (2,4-dichlorophenoxyacetic Acid), dicamba, 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), silvex, 2,3,6-TBA.
- Triazine Herbicides: Simazine, atrazine, propazine.
- Urea Pesticides: Monuron, linon, fenuron, isoproturan, chlorotoluran.
- Pyridinium Herbicides: Diquat, paraquat.

Several hundred pesticides of different chemical nature are currently used for agricultural purposes all over the world. Because of their widespread use, they are detected in various environmental matrices, such as soil, water and air. Pesticides are divided into many classes of which the most important are organochlorine and organophosphorus compounds (Sankararamakrishnan et al., 2005).

2.4.2. Organochlorinated Pesticides

Organochlorinated pesticides (OCPs) have been used for agricultural purposes for decades and they are distributed control algae in lakes, canals, across the globe, even in pristine regions, such as Antarctica. Their chemical properties such as high lipophilicity, bioaccumulation potential, long half-life in the environment, and potential to long-range transport are the main reasons for their persistence in the environment. They are among the most prevalent contaminants and can be found in water (Abbassy et al., 1999; Caldas et al., 1999), soil (Pilidis et al., 1996; Muraya et al., 1997), or food (Newsome et al., 1998; Schade, 1998) even decades after being banned.

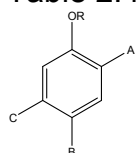
These compounds are primarily applied to the foliage of crops and weeds and their metabolism in plants has been extensively studied. The persistence and degradation of the phenoxyalkanoic acids in the soil environment has also been the subject of detailed study since these compounds reach the soil both during application and by transfer from plants to the soil by rainwater (Hill and Wright, 1978).

2.4.3. Phenoxy Herbicides

Phenoxy herbicides have been commercially available and are the most widely used family of herbicides worldwide. 2,4-dichlorophenoxyacetic acid (2,4-D), the most common of the phenoxy herbicides, is one of the best studied agricultural chemicals (Table 2.4). Several phenoxy acids have been used as herbicides, including 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4-(2,4-dichlorophenoxy) butyric acid (2,4-DB), 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP), 2-(2-methyl-4-chlorophenoxy)-propionic acid (MCP), 2-methyl-4-chlorophenoxyacetic acid (MCPA) and 2-(2,4,5-trichloro phenoxy)propionic acid (2,4,5-TP), with the most commonly and widely used herbicide being 2,4-D. 2,4,5-T and 2,4,5-TP are no longer manufactured or sold (Doull et. al., 2001).

For over 50 years, 2,4-D has been the most commonly and widely used herbicide throughout the world. When applied to plants, 2,4-D is absorbed through the roots and leaves within 4 to 6 hours and is distributed in the plant via the phloem (WHO, 1984). In addition, 2,4-D affects plant metabolism, which leads to interference with food transport . 2,4-D is primarily used as a herbicide in agriculture, forestry and lawn care practices, with the majority (>60%) of the total usage in the United States being reported for use as weed control in agriculture (EPA, 2007). To a lesser extent, 2,4-D is used as a growth regulator on various crops ranging from potatoes to citrus fruits (WHO, 1975).

Table 2.4. Structures of most commonly used phenoxy alkanoate herbicides.



(General Structure)

<u>Substituents</u>		<u>Chemical Name</u>	<u>Common Name</u>
R= -CH ₂ CO ₂ H	A = CH ₃ B = Cl, C = H	2-methyl-4-chloro phenoxy acetate	MCPA
R= -CH ₂ CO ₂ H	A = Cl B = Cl, C = H	2,4-dichloro phenoxy acetate	2,4-D
R= -CH ₂ CO ₂ H	A = Cl B = Cl, C = Cl	2,4,5-trichloro phenoxy acetate	2,4,5-T
R= -CHCO ₂ H CH ₃	A = CH ₃ B = Cl, C = H	2-(2-methyl-4-chlorophenoxy)-propionate	MCPP
R= -CHCO ₂ H CH ₃	A = Cl B = Cl, C = H	2-(2,4-dichlorophenoxy)-propionate	2,4-DP
R= -CHCO ₂ H CH ₃	A = Cl B = Cl, C = H	2-(2,4,5-trichlorophenoxy)-propionate	2,4,5-TP
R= -CH ₂ CH ₂ CH ₂ CO ₂ H	A = Cl B = Cl, C = Cl	2,4,5-trichloro phenoxy acetate	2,4,5-T
R= -CH ₂ CH ₂ CH ₂ CO ₂ H	A = Cl B = Cl, C = H	4-(2,4-dichlorophenoxy)-butyrate	2,4-DB
R= -CH ₂ CH ₂ CH ₂ CO ₂ H	A = Cl B = Cl, C = Cl	4-(2,4,5-trichlorophenoxy)-butyrate	2,4,5-TB

2.4.4. Behaviour of Pesticide Residues in Soil

Soil is important for the agricultural production and for the preservation of ground water quality. In comparison with other environmental compartments, soil has relatively high tolerance against natural and anthropogenic contamination. This is due to its inherent chemical and biological degradation processes that lead to an elimination of contaminants and counteract their accumulation in soil. However, excessive and indiscriminate use of pesticide can still cause damages to soil fauna and flora and result in loss of soil quality. In this respect, the application of pesticides should have no sustained impact on the ecological balance.

Contamination of soil by pesticides is inevitable. Pesticides arrive in soil through intended soil applications such as pre-emergence or post-emergence applications of some herbicides and insecticides or fungicides, some active substances can unavoidably reach soil surfaces and contribute to the undesired soil contamination. Additionally, pesticide residues can be washed off from treated plant surfaces by precipitation events. Soil incorporation of pesticide contaminated plant residues is another source of soil pollution. Thus, soil is a sink for pesticides applied.

Pesticide residues undergo a series of complex physical, chemical, and biological processes in soil. They are often a combination of processes such as chemical and biological degradation, adsorption and desorption, leaching, as well as conversion to non-extractable residues. The fate of a given pesticide in soil depends on its physical-chemical properties and the soil properties. Numerous factors of environment and agricultural practice affect the behaviour of pesticide residues as well (BBA, 1986; BBA, 1990).

Residual herbicides are often applied to crops to provide season-long weed control. However, herbicidal activity is beneficial only for the time it is needed; longer herbicide activity can cause injury to subsequent crops. The length of time for a herbicide remains active in the soil is called soil residual life or soil persistence. Persistence in soils is noted for average conditions, and will be influenced by factors such as weather, soil pH, and crops grown.

2.4.5. Persistence

Most organochlorines are long-lived and persistent. Fifty percent of the DDT originally applied to a field might be found in the soil after three years. When pesticides are applied in the prescribed amounts, 95 percent of the original amount will disappear in the time ranges between years to weeks. In comparison, organophosphates are

unstable and most tend to degrade to harmless chemicals after several months. Greenhouse workers have been killed in situations where ventilation was poor.

Herbicides generally are removed from the soil by bacteria. The herbicide 2,4-D in small quantities and low concentrations is decomposed in a period of one to four weeks after application, while 2,4,5-T could take more than a year to decompose. The actual disappearance rate depends on concentration, soil type, moisture, temperature, and aeration. Most herbicides in the group to which 2,4-D belongs are water soluble, so they can be moved via surface water and streams to other areas if applied in high concentrations. Pesticides can be classified into four groups of various persistences (Anderson, 1987). Relative persistence of some pesticides in natural water is given in Table 2.5.

Table 2.5. Relative persistence of some pesticides in natural waters.

Readily Degradable, half-life less than 2 weeks	Slightly Persistent, half-life 2-6 weeks	Moderately Persistent, half-life 6-weeks	Persistent, half-life more than 6 months
Captan Carbaryl Chlorpyrifos Dichlone Dicrotophos Endotol Endosulfan Fenitrothion Malathion Methiocarb Methylparathion Phophamidon Propoxur 2,4-D Trifluralin	Chloramben Chlorpropham Dalapon Diazinon Disulfoton Fenuron MCPA Methoxychlor Munuron Phorate Propham Dichlorvos	Carbofuran Carboxin Chlordane Chlorfenvinfos Chloroxuron Dimethoate Diphenamid Diuron Ethion Fensulfothion Linuron Prometion Propazine Simazine Toxaphene	DDT Y-HCH Aldrin Dieldrin Heptachlor Isodrin Monocrotophos Benomyl

The persistent pesticides such as DDT, γ -HCH (Hexachlorocyclohexane), dieldrin, endrin and others have only slight solubility in water. However, they usually readily dissolve in fats, and for this reason they accumulate in the body tissue of birds, fish and mammals, and threaten the health of the organism. Because of the high persistence of pesticides, their consumption is decreasing in many countries. The degradation of process depends on temperature, water, pH and biota. The pH of the water is a significant factor, because very often hydrolysis is one stage of the biodegradation. A rise in temperature increases the rate of the chemical reaction and activity of microorganisms taking part in the biodegradation (Dojlido et al., 1993).

2.4.5.1. Factors Affecting Persistence of Herbicides in Soil

Herbicide soil persistence or residual life is the length of time a herbicide remains active in a soil. The soil persistence of a herbicide is often stated as “half-life,” which is the amount of time it takes to decompose 50 percent of the applied chemical to a herbicidally inactive form. The stated half-life of a herbicide is determined under standard conditions in the laboratory. The half-life of a herbicide in the field will vary depending on environmental and soil conditions. For example, a herbicide with a half-life of 4 weeks would be 50 percent decomposed, with 50 percent remaining in the soil 4 weeks after application (Figure 2.7). After 8 weeks, 75 percent of the herbicide would be degraded, with 25 percent remaining, and after 12 weeks, only 12.5 percent would remain. The time it takes to degrade half of the applied herbicide—half-life— is independent of the herbicide rate that is applied.

Factors affecting herbicide persistence and concentration in the soil (Figure 2.8) include:

- | | |
|----------------------------|--------------------------------|
| 1. Microbial decomposition | 2. Chemical decomposition |
| 3. Soil adsorption | 4. Volatilization |
| 5. Photodecomposition | 6. Plant uptake and metabolism |
| 7. Leaching | 8. Surface runoff |

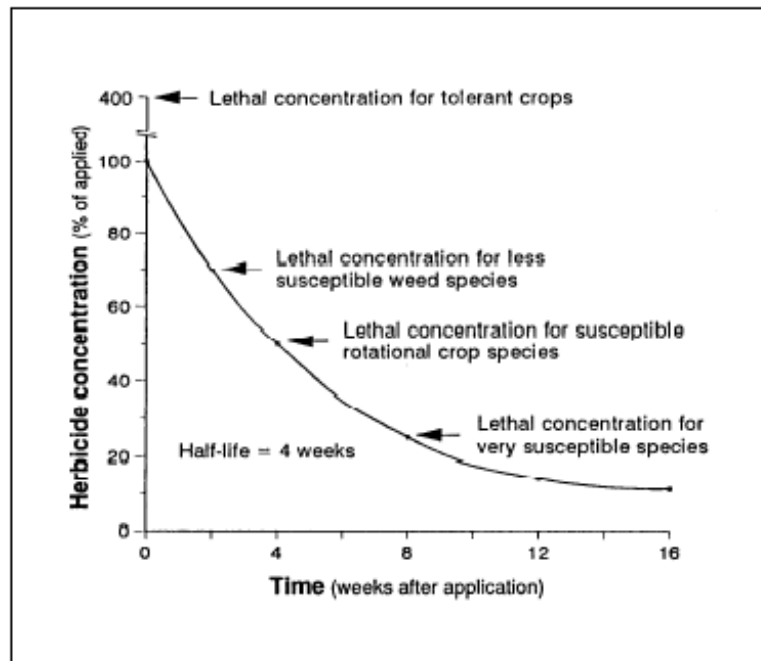


Figure 2.7. An example of how half-life and herbicide residues affect weed control and rotational crop injury.

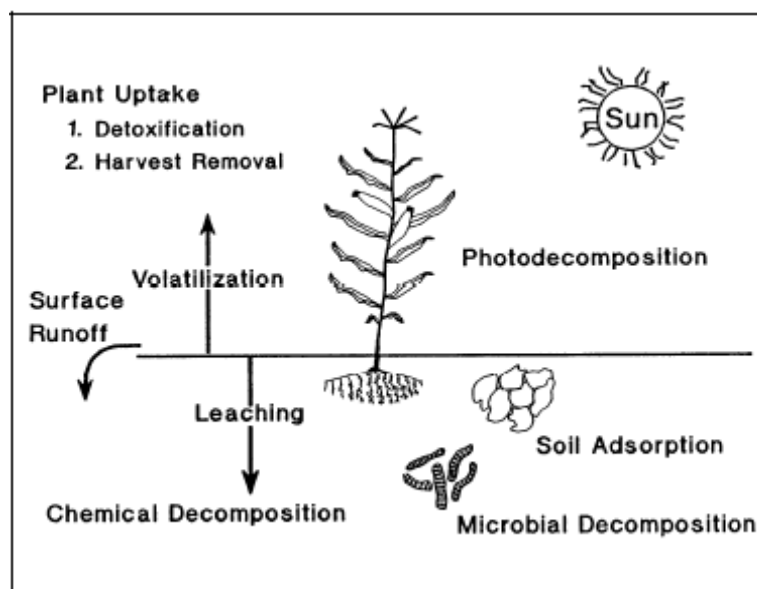


Figure 2.8. Factors affecting persistence of herbicides applied to crops.

2.4.6. Pesticides and Human Health

People ingest pesticides by eating food containing traces of pesticide residue or are exposed to pesticides through house dust, particularly in areas near orchards sprayed with pesticides. Once they enter the human system, pesticides can be detoxified and removed or retained in tissues. In trying to determine the effects of pesticides on people, scientists have found a trace of DDT in the fatty tissue of every person sampled. Eskimos who eat fatty foods from upper-level consumers have very high concentrations in their fatty tissue. This buildup has led the population biologist Paul Ehrlich to suggest that overweight people might not be able to reduce in the future because the release of fat-bound pesticides in their bodies could cause toxic effects.

The effects of pesticides on humans are variable. The World Health Organization maintains that the level of DDT causing death in humans is unknown. When volunteers ingested 0.5 milligram of DDT per kilogram of body weight per day, they developed a tolerance (Allman, 1985; Matthiessen, 1985; Anderson, 1987). Other studies have found that symptoms such as nausea, headache, and restlessness occur in people that ingest up to 6 milligrams per kilogram of body weight over a period of weeks.

Some forms of pesticides cause mutations in animal and plant species. For example, fumigants containing chlorine or iodines cause mutations in yeast; pesticides containing mercury cause genetic changes in flies; and organophosphates are known to induce mutations in yeast and bacteria. Many other pesticides appear to alter plant and animal chromosomes. There are some indications that mercury compounds cause chromosome breakage in humans. However, we need more information to ascertain the effects of pesticides on human genetics.

2.4.7. Pesticides in Water

Pesticides can very easily reach ponds, lakes or rivers by a variety of routes. They may be applied to water as aerial sprays to control pests such as mosquitoes, blackflies or midges, they may fall on water accidentally when applied as aerial treatments to control forest pests or agricultural pests, they may reach water by surface runoff from soil, they may be discharged with sewage effluents or industrial effluents or they may be carried down from the atmosphere in rain (Weidnass et. al., 1960; Edwards et.al., 1970; Gorham, 1961; Holden, 1966).

It is still difficult to assess the relative importance of sources of insecticide residues found in rivers, but Nicholson stated that the two principal sources of contamination are runoff from agricultural land and discharge of industrial wastes, either from industries that manufacture or formulate pesticides or from those that use these compounds in their manufacturing processes, e.g., moth-proofing chemicals. The latter source of residues may be important locally but aerial spraying probably contributes more to the steady replenishment of residues in rivers, particularly in the United States. Runoff from agricultural land is a steady source of residues in rivers, but amounts from this cause are relatively small. Careless applications of insecticides, and disposal or washing of insecticide containers may add to residues in contamination could be controlled, so that fewer pesticides reach fresh waters (Nicholson, 1969).

Chlorinated hydrocarbon insecticides are not usually in solution in the water because they are all of very low solubility, and the residues reported in the surveys are of insecticides carried on particulate matter suspended in the water. When an insecticide reaches natural waters, a large proportion disappears rapidly. For example, Weidnass et al. kept water containing DDT above soil covered with filter paper, and after six hours, 56% of the insecticide was in the soil; whereas, after 24 hours a further 22% had moved into the soil. In a study of the distribution of toxaphene in a lake after several days, there was a concentration of 0.01 to 0.28 ppm in the water, 0.04 to 0.13 in the bottom sediment, 0.4 to 18.3 in aquatic plants, and

2.5 to 15.2 in fish. Bridges et al followed the distribution of DDT in a pond and found that it was quickly concentrated into the bottom mud and vegetation. Lichtenstein et al. found that aldrin and gamma BHC were much less stable in water if it contained lake mud.

There is little information on the amounts of pesticides in sea water; indeed it is difficult to see how large amounts of pesticides could reach sea water. The most likely source would be through rain or dust in the atmosphere, or the outflow from major rivers into estuaries. The data quoted in the section on pesticides in air and rainwater show that the amounts that might reach the sea from the atmosphere are very small, and if diluted by the volume of water in the sea would be infinitesimal (Edwards, 1970).

2.4.8. Degradation

Water is a suitable medium for chemical reactions and is also itself chemically reactive (Crosby, 1973). In alkaline natural aquatic systems many pesticides may undergo alkaline hydrolysis. Other reactions which contribute to abiotic transformation of pesticides in water include reduction, elimination, decarboxylation, oxidation and isomerization (Crosby, 1973).

The extent of pesticide photodegradation in natural waters will be determined by factors such as light quality and quantity, water turbidity and pH, the presence of adsorbing surfaces, chemical reactants and agencies to remove photolysis products, also the presence of photosensitizing substances, a feature which may be particularly important (Crosby and Li, 1969). Biodegradation of pesticides is partly correlated with their solubility in water. Those organic pesticides, which readily dissolve in water, hydrolyze rapidly in water, and in general they degrade easily. The same pesticides are quickly washed out from the soil by rainwater and enter river waters. The solubility of some pesticides is given in Table 2.6.

2.4.8.1. Pesticides and Drinking Water

The quest for high-quality water has been an objective of human society going back to prehistoric times. Early humans gathered in locations with readily accessible sources of water and if the water was believed to be of questionable quality, entire settlements would be abandoned. The first documented drinking water treatment can be found in Egyptian hieroglyphics, describing procedures to purify water. The basic principles were the same then as they are today; boiling, chemical treatment and filtration were recommended treatments. Although the importance of drinking water quality was known, the specific contaminants would not be identified for centuries to come (Calderon, 2000).

Table 2.6. Solubility of some pesticides.

	Compound	Solubility(mg/L)
Organochlorine	DDT	0.0012
	Aldrin	0.01
	Heptachlor	0.056
	Methoxychlor	0.10
	Dieldrin	0.18
	Endrin	0.23
	Toxaphene	0.30
	Lindane	7.00
Organophosphorous	Parathion	24.0
	Disulfon	25.0
	Diazinon	40.0
	Chlorfenvinfos	145.0
	Malathion	145.0
	Methyl demeton	330.0
	Dichlorvos	10000.0
	Dimethoate	2500.0
Carbamates	Carbaryl	40.0
	Carbofuran	700.0
	Aldicarb	6000.0
Herbicides	Simazine	5.0
	Propazine	8.0
	Diuron	42.0
	2,4,5-T	280.0
	2,4-D	890.0
	Trifluralin	0.300
	Diquat	70.0
	Dalapon	80.0

Among the many chemicals encountered in drinking water (and other environmental media), pesticides occupy a unique position, since they are deliberately used to control the growing problem of pests. They comprise different classes, including insecticides, fungicides, herbicides and rodenticides, in addition to miscellaneous

other substances (e.g. nematocides, plant growth regulators, pheromones). Consequently, the use of pesticides requires careful selection and quantitation, as well as means of application that minimize effects on non-target organisms. In addition, many pesticides are persistent, and may therefore bioaccumulate in the environment (Clark and Kenna, 2001).

Because of their widespread use, pesticides leach into surface and groundwater, and are therefore present in drinking water. Persistent organic pesticides, though largely banned or severely restricted in their use worldwide, are still present in the environment and, therefore, also in drinking water (WHO, 1993). WHO has derived drinking water guidelines for some 40 pesticides (WHO, 1993, 1996, 1998).

2.4.9. The Use of Pesticide in World

The amount of produced pesticides is approximately 3 tons in the world. As seen from Figure 2.9, the herbicides are the most used pesticides with 47%. Insecticides have a ratio of 29% and fungicides have a ratio of 19% in the used pesticides. Above 70% percent of the used pesticides are herbicides and insecticides. The other pesticide groups have 5% ratio. In the world, North America has the highest pesticide market according to 1994 data (Figure 2.10).

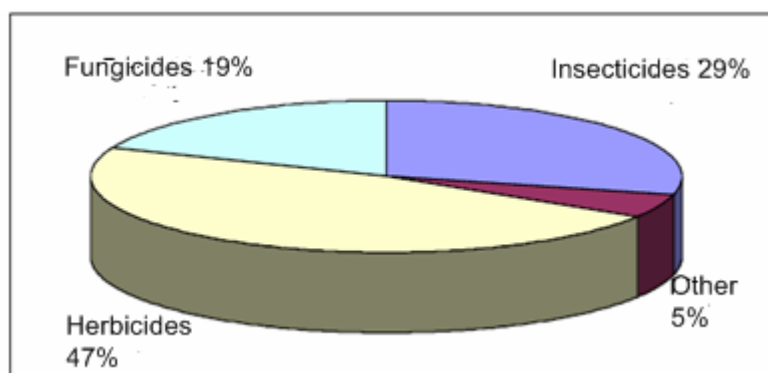


Figure 2.9. The distribution of pesticide consumption in the world according to pesticide groups (Delen et. al., 2005).

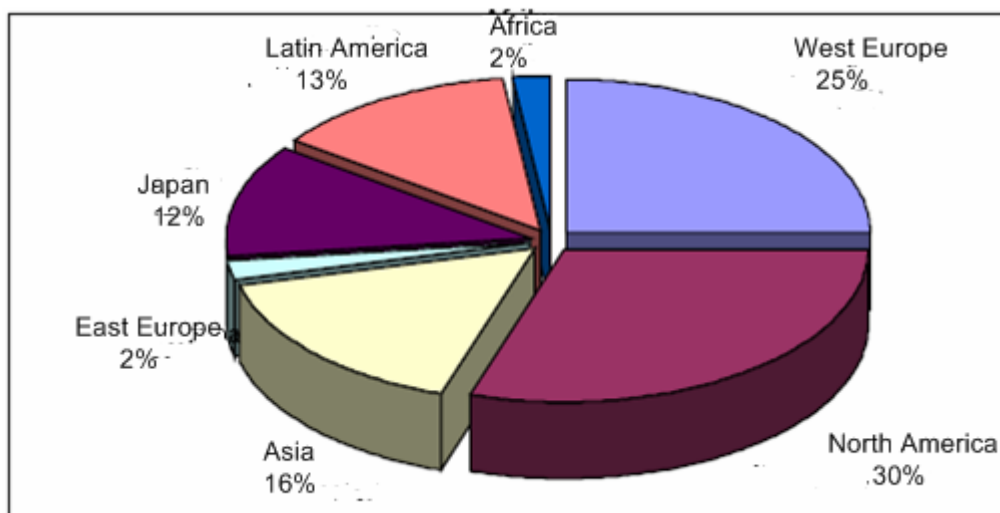


Figure 2.10. The regional distribution of pesticides (1994) (Delen et. al., 2005).

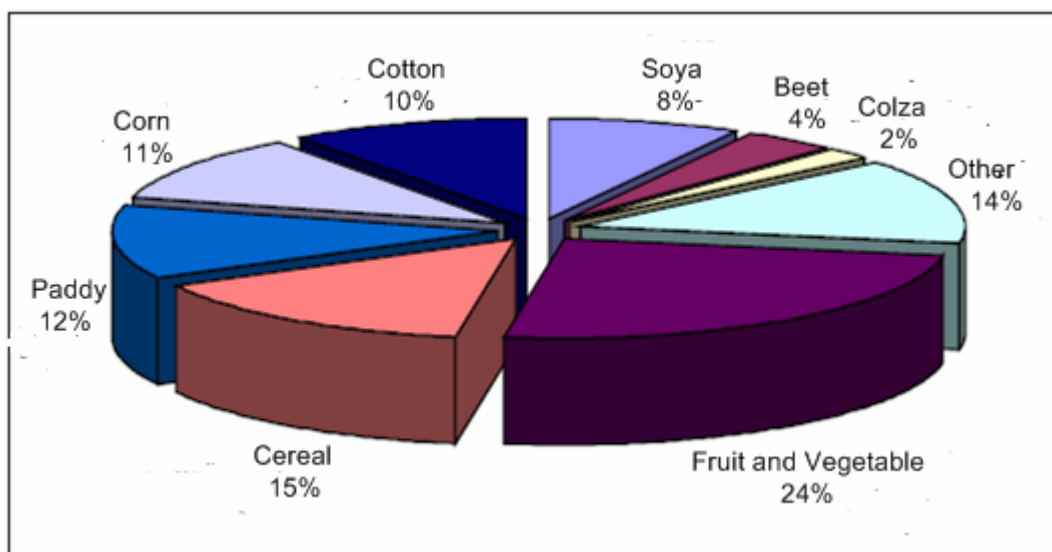


Figure 2.11. The consumption of pesticide distribution for products (1994) (Delen et. al., 2005).

As seen from Figure 2.11, it is observed that the most important applied pesticide groups in the world are vegetables and fruits (25%) and cereals (15%). In addition to these, paddy (12%), corn (11%) and cotton (10%) are important product groups which pesticides are applied.

2.4.10. The Use of Pesticide in Turkey

The agricultural struggle is the protection of herbs from illness, destructive and strange herbies in the economical scales and the increase of quality and production. It is easily understood that, with agricultural struggle, the aim is to increase the quality and the production (De Waard et al., 1993; Ragsdale, 1994). The unconscious and uncontrolled use of pesticides can cause the increase in the resistivity of the harmful organisms and the unfavorable effects on the health of the human beings and environment. In Table 2.7, the use of pesticides in Turkey are summarized according to their classes from 1979 to 2002.

Table 2.7. The consumption of pesticides in Turkey with years (kg or L).

Pesticide Groups	1979	1987	1994	1996	2002
Insecticides	2.287.658	3.303.446	2.064.991	3.027.380	2.250.898
Akaricides	203.107	240.360	192.279	223.857	296.809
Oils	1.594.526	2.147.106	2.147.106	2.871.160	2.428.238
Fumigant and Nematicide	315.665	322.227	530.738	1.076.661	1.559.489
Rodenticide and Mollucide	5.600	2.124	2.509	3.268	1.794
Fungicide	1.537.315	2.611.960	2.201.406	2.951.191	1.964.292
Herbicide	2.451.977	3.495.044	3.902.588	3.643.971	3.697.397
TOTAL	8.395.848	12.112.267	10.871.792	13.797.488	12.198.917

According to these statistical data, the pesticide use in Turkey increased 45.29% from 1979 to 2002. Although this increase, the use of pesticide in Turkey is very low compared with developed countries. In Akdeniz and Ege regions, extensive agriculture is popular so the use of pesticides in these regions are higher than the Turkey average. Although in Turkey low amount of pesticides are used, the most used pesticides are dangerous for health and environment.

The researches for pesticide residues in Turkey are not as widespread as developed countries. According to obtained data, the pesticide residues in agricultural products in Turkey are generally below the limits but the pesticide residues determined by

European Union countries is an important problem. Similar with the pesticide residues, the researches for the resistivity of the organisms to the pesticides are not enough.

2.5. Isolation and determination of pesticides

Solid-phase extraction developed from classical chromatography, which is the use of and adsorbing medium affinities for the sorbing medium. Chromatography is historically marked from the first work of Tswett in 1906 on the separation of plant pigments, using a tool he called “chromatography plant pigments with petroleum”. Tswett used calcium carbonate to sorb various plant pigments with petroleum ether as the mobile or moving phase through the column. This separation would be called a normal-phase separation by today’s nomenclature (Thurman, 1998).

Practically until 1946 only the residue of arsenic compounds and several inorganic insecticides impenetrable to plant tissue have been determined. Wide introduction of synthetic organic pesticides posed to chemists many new analytical tasks associated with the determination of these pesticides and the products of their decomposition which are frequently even more toxic than the original compounds. However, the analysis of residue requires methods capable of determining the analytes at the ppm, ppb, ppt or even lower levels.

The most common methods of preconcentration of pesticides from environmental samples are

- 1.liquid-liquid extraction (LLE)
- 2.solid-phase extraction (SPE)

Presently, three novel methods of isolation and enrichment of the analytes are being vigorously developed:

- 1.Supercritical fluid extraction (SFE) of samples preconcentrated on solid sorbents.
- 2.Solid-phase microextraction (SPME)
- 3.Extraction using hollow fiber membranes.

2.5.1. Solid Phase Extraction (SPE)

Solid phase extraction (SPE) is a method of sample preparation that concentrates and purifies analytes from solution by sorption onto a disposable solid phase cartridge, followed by elution of the analyte with a solvent appropriate for instrumental analysis. The mechanism of retention include reversed phase, normal phase and ion exchange. Traditionally, sample preparation consisted of sample dissolution, purification and extraction that was carried out with liquid-liquid extraction. The disadvantages with liquid-liquid extraction include the use of large volumes of organic solvent, cumbersome glassware, and cost. Furthermore, liquid-liquid extraction often creates emulsions with aqueous samples that are difficult to extract and liquid-liquid extraction is not easily automated. These difficulties overcome with solid phase extraction. Thus, solid phase extraction was invented in the mid 1970s as an alternative approach to liquid-liquid extraction.

Solid phase extraction columns are now typically constructed of polypropylene or polyethylene and filled with 40 μm packing material with different functional groups. A 20 μm polypropylene frit is used to contain from 50 mg to 10 g packing material. A liquid sample is passed through the column and analytes are concentrated and purified. The sample volume that can be applied ranges from 1 ml to over 1 L. The sample may be applied to the column by positive pressure or by vacuum manifold. After quantitative sorption of the analyte, it is removed with an appropriate elution solvent.

The goal of SPE is quantitatively remove the analyte from solution and completely recover it in an appropriate solvent. Purification consists of removing the analyte from interfering compounds and concentrating the analyte in a small volume of solvent. For example pesticides are concentrated from a water sample by SPE into a small volume of organic solvent for analysis by gas chromatography /mass spectrometry. Interfering substances, such as humic and fulvic acids, ionic metabolites and salts are removed (Thurman, 1998).

2.5.2. Sorbents and Modes of Interaction

The sorbents used for SPE are similar to those used in liquid chromatography, including reversed phase, normal phase, size exclusion (commonly called wide pore) and ion exchange. Normal phase sorbents consist of a stationary phase that is more polar than the solvent or sample matrix that is applied to the SPE sorbent. This means that water is not usually a solvent in normal phase SPE because it is too polar. Normal phase sorbents therefore are used in SPE when the sample is an organic solvent containing an analyte of interest.

Reversed phase sorbents are commonly used in SPE when aqueous samples are involved. The mechanism of interaction is van der Waals forces (also called non polar or hydrophobic) and occasionally secondary interactions such as hydrogen bonding and dipole dipole interactions. Size exclusion sorbents utilize a separation mechanism based on the molecular size of the analyte. It is a method only recently being used in SPE, usually in conjunction with reversed phase or ion exchange. Ion exchange sorbents isolate analytes based on the ionic state of the molecule either cationic or anionic.

The phenoxy alkanoic herbicides are anionic compounds that are moderately polar. The acid-herbicide family consists of compounds that are ionic or partially ionic at the pH of a typical water sample (pH = 7). Thus the capacity of these compounds for C18 is quite low without acidification of the water sample. Typically, the pH must be lowered to 2 pH units below the pK_a for effective recovery, usually not to be lower than pH 2. At pH units below this value, damage may occur to silica sorbent. Methanol is better eluent than ethyl acetate because of the ionic character of the analytes.

Phenols and chlorinated phenols are examples of ionic moderately polar compounds. They are ionic only at certain pH ranges. Phenol itself is actually a polar compound, while the chlorinated phenols are moderately polar. Thus, phenol would be best

isolated by an styrene divinyl benzene (SDB) sorbent, while the chlorinated phenols may be isolated effectively on C18 or SDB. The pK_a of these compounds varies from 8 to 10. Thus, it is critical that the pH of the sample be approximately 7, or less, for good retention of the nonionic species. These compounds are important industrial chemicals and phenol itself is listed on the EPA's contaminant list. The elution solvents that are miscible with water works best: acetone, acetonitrile and methanol. There may be the possibility of methylation if methanol is used and that should be considered during the analysis (Thurman, 1998).

2.5.3. Columns and Apparatus for Solid-Phase Extraction

SPE isolates analytes using the same principles as those used in liquid chromatography, though much less efficiently. The compounds are retained and eluted as a mobile phase transports them over a stationary phase (sorbent) that has been conditioned with an organic solvent to active it. In the most common use of SPE, the mobile phase is the aqueous sample to retain the analytes onto the sorbent. This technique's benefits are that it significantly reduces extraction times and solvent consumption and has a concentration step (Majors, 2001).

The vacuum manifold is used to draw the sample and eluting solvents through the syringe barrel under negative pressure by applying a vacuum to the manifold. Figure 2.12 shows a typical vacuum manifold system, which is fitted with a small vacuum pump and a waste receiver.

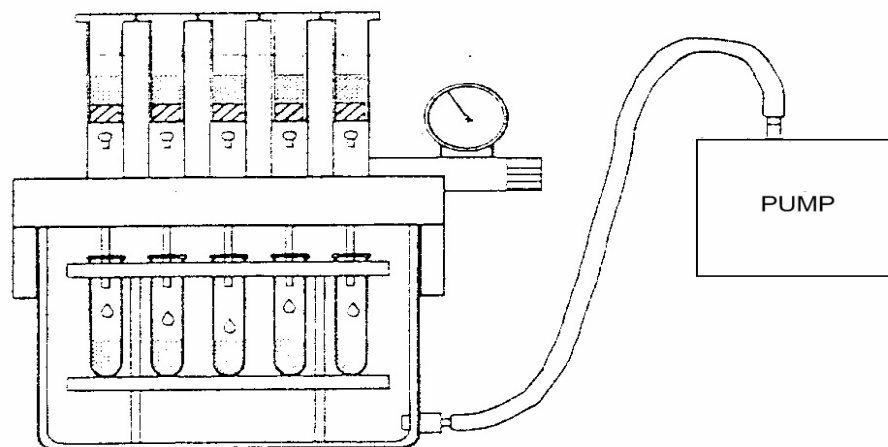


Figure 2.12. Process of solid-phase extraction.

2.6. Instrumental Analysis Methods Used in the Analysis of Pesticides

Important progress has occurred in the development and applications of various analytical tools including separation methods such as gas chromatography (GC) and high performance liquid chromatography (HPLC) and detection techniques such as electrochemistry, spectrophotometry and spectrofluorimetry. These techniques have allowed the identification and determination (at low concentration levels) of pesticide residues in a number of food and environmental samples.

GC remains the main analytical method for pesticide residue analysis because of its excellent separation and detection potential, especially when combined with MS. However, it has some drawbacks such as the need for pretreatment procedures in the case of weakly volatile and/or thermally labile pesticides. The second most utilized method is HPLC, with UV visible absorption detectors; it remains the technique of choice for screening work (Coly et al., 1998).

2.6.1. Gas Chromatography

Gas chromatography is a powerful technique for separating complex mixtures of organic compounds of a minimum volatility. It is now the standard technique for analysis of specific organics in waters and wastewaters. Gas chromatography first became commercially available in 1955. However, it wasn't until the 1970s before they were widely used in the analysis of waters and wastewaters.

Gas-liquid chromatography (GLC) accomplishes a separation by partitioning solutes between a mobile gas phase and a stationary liquid phase held on a solid support. Gas-solid chromatography (GSC) employs a solid adsorbent as the stationary phase.

The sequence of a gas chromatographic separation is as follows. A sample containing the solutes is injected into a heating block where it is immediately vaporized and swept as a plug of vapor by the carrier gas stream into the column inlet. The solutes are adsorbed at the head of the column by the stationary phase and then desorbed by fresh carrier gas. The sorption-desorption process occurs repeatedly as the sample is moved toward the column outlet by the carrier (mobile phase) gas. Each solute will travel at its own rate through the column. Their bands will separate so a degree chart is determined by the individual partition ratios and the extent of band spreading. The solutes are eluted sequentially in the increasing order of their partition ratios and enter a detector attached to the column exit. If a recorder is used, the signals appear on the chart as a plot of versus the composition of the carrier gas stream. The time of emergence of a peak is characteristic for each component; the peak area is proportional to the concentration of component in the mixture. Although gas chromatography is limited to volatile materials, about 15% of all organic compounds, the availability of column temperatures up to 450°C, pyrolytic techniques, and the possibility of converting non volatile materials into a volatile derivative extend somewhat the applicability of the method.

Basically, a gas chromatograph consists of six parts:

- 1) A supply of carrier gas in high pressure cylinder with attendant pressure regulators and flow meters, and a valve to introduce extra make-up gas to some detectors
- 2) A sample injection system
- 3) The separation column
- 4) The detector
- 5) An electrometer and strip-chart recorder (and integrator perhaps),
- 6) Separate thermostated compartments for housing the column and the detector so as to regulate their temperature, or to program the column temperature.

The components are shown in Figure 2.13.

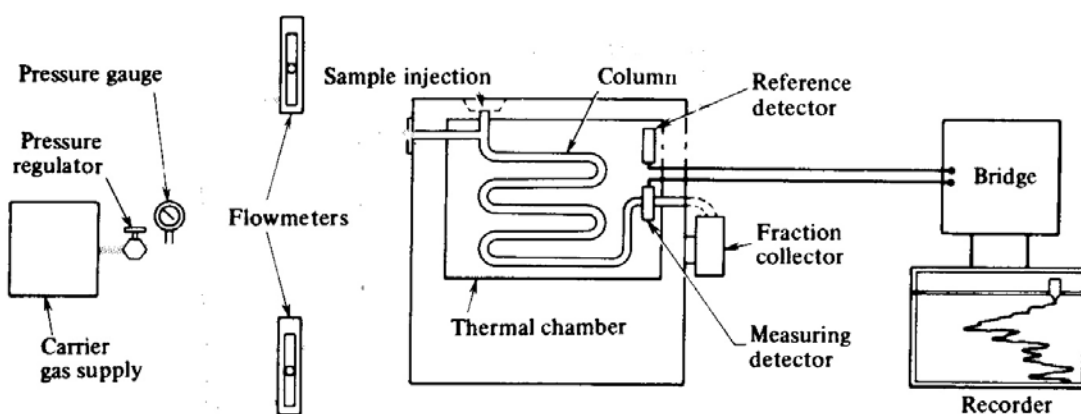


Figure 2.13. Schematic of a gas chromatograph.

Samples are introduced into the flowing gas stream by means of an injector. Separation of the constituents is achieved in the column. Finally, the detector measures the amount of each compound as it leaves the column. The major types of gas chromatography are gas-liquid chromatography and gas-solid chromatography. Most environmental applications employ gas-liquid chromatography. This means that the GC column contains a viscous liquid into which the solutes dissolve. This liquid is ultimately responsible for the separation of solute from the solvent and of the various solutes from each other. In gas-solid chromatography, the columns contain a solid packing material, which serves to adsorb solutes to its surface. In either case a phase change occurs: the former to a liquid, the latter to a solid (Williard et.al., 1981).

2.6.2. Mass Spectrometry

The first mass spectrometer dates back to the work in England of J.J. Thompson in 1912 and of F. W. Aston in 1919, but the instrument that served as a model for more recent ones was constructed in 1932. The mass spectrometer produces charged particles consisting of the parent ion and ionic fragments of the original molecule, and sorts these ions according to their mass/charge ratio. The mass spectrum is a record of the numbers of different kinds of ions-the relative numbers of each are characteristic for every compound, including isomers.

The main advantages of mass spectrometry as an analytical technique are its increased sensitivity over other analytical techniques and its specificity in identifying unknowns or for confirming the presence of suspected compounds. The enhanced sensitivity results primarily from the action of the analyzer as a mass filter to reduce background interference and from the sensitive electron multipliers used for detection. Sample size requirements for solids and liquids range from a few milligrams to subnanogram quantities as long as the material can exist in the gaseous state at the temperature and pressure existing in the ion source. The excellent specificity results from characteristic fragmentation patterns, which can give information about molecular weight and molecular structure. In addition, a mass spectrometer is an essential adjunct to the use of stable isotopes in investigating reaction mechanisms and in tracer work. Also, mass spectrometry has contributed greatly to a more detailed understanding of kinetics and mechanisms of unimolecular decomposition of molecules (Williard, 1981).

2.6.2.1. Components of Mass Spectrometers

There is no universal mass spectrometer. Certain designs and configurations lend themselves to the solution of specific problems better than do others. However a mass spectrometer can be divided into the following main parts:

- 1) Sample inlet system(s)
- 2) Ion source
- 3) Ion analyzer system
- 4) Ion detector
- 5) Spectrum recording system
- 6) Vacuum chamber and pumping system
- 7) Electronic power and control system
- 8) Interfacing a chromatograph with a mass spectrometer is often desirable.

2.6.2.2. Ionization Sources

The ion source is primary importance and must be considered as the heart of the mass spectrometer. In fact the ion source might be regarded as a chemical reaction vessel, and each source must chosen as appropriate to the sample. Ion sources have the dual function of producing ions without mass discrimination from the sample and accelareting them into the mass analyzer with ony a small spread of kinetic energies prior to acceleration. Sources that produce a large spread of energies in the ion beam must be used with double-focusing mass analyzers to obtain sufficient resolution.

All source designs have several features in common. There must be an ionization chamber in which the actual ionization of the sample occurs and there must be an ion withdrawal and focusing system in which the ions are removed electrostatically from the chamber and are accelerated toward the mass analyzer. Several pairs of focusing elements and slits then control the direction, shape, and width of the ion beam. Generally the source will have its own separate high vacuum pump.

The ionization efficiency of a source must be high so that a large portion of the neutral sample particles presented will become ions to be analyzed and detected as a mass spectrum. High efficiency is particularly important for the analysis of nanogram quantities of sample material and trace impurities in solids. An ion beam current of 10^{-10} A desirable source output.

The positive ions formed in the ionization chamber are drawn out by a small electrostatic field between the large repeller plate (charged positive) behind them—the original entrance to the ion source which did not affect the molecules while they were yet unionized—and the first accelerating slit (charged negative) (Figure 2.13). A strong electrostatic field between the first and second accelerating slit of 400–4000 V accelerates the ions of masses m_1 , m_2 , m_3 , and so on, to their final velocities. The ions emerge from the final accelerating slit as a collimated ribbon of ions with velocities and kinetic energies given by

$$eV = \frac{1}{2}mv_1^2 = \frac{1}{2}mv_2^2 = \frac{1}{2}mv_3^2 = \dots\dots\dots$$

Combinations of ion sources offer dual capabilities within one source housing. Sometimes both electron-impact and chemical ionization spectra (or field ionization spectra) are needed for a given compound. The chemical ionization or field ionization spectrum might show a molecular ion and the fragmentation of an electron-impact spectrum might identify the class of compound. Calibration of a mass spectrometer must be done with the electron-impact mode; perfluoroalkanes so often used as mass markers would deactivate emitter wires used in field ionization or field desorption, and chemical ionization would provide few if any fragment ions. Ionisation can be accomplished by one of the following methods:

Atmospheric Pressure Chemical Ionisation	(APCI)
Chemical Ionisation	(CI)
Electron Impact	(EI)
Electrospray Ionisation	(ESI)
Fast Atom Bombardment	(FAB)
Field Desorption / Field Ionisation	(FD/FI)
Matrix Assisted Laser Desorption Ionisation	(MALDI)
Thermospray Ionisation	(TSP)

There are a number of mass analyzers currently available, the better known of which include quadrupoles, time of flight (TOF) analysers and magnetic sectors. The type of detector is supplied to suit the type of analyser; the more common ones are the photomultiplier, the electron multiplier and the micro-channel plate detectors (Williard, 1981).

2.6.2.3. Electron-Impact Ionization

The electron-impact ion source is the most commonly used and highly developed ionization method. As shown in Figure 2.14 once past the molecular leak, the neutral molecules find themselves in a chamber that is maintained at a pressure of 0.005 torr and at a temperature of $200 \pm 0.25^\circ\text{C}$. Located perpendicular to the incoming gas stream is an electron gun. Electrons emitted from a glowing filament (rhenium, thoriated iridium, or carbonized tungsten) are drawn off by a pair of positively charged slits through which the electrons pass into the body of the chamber. An electric field maintained between these slits accelerates the electrons. The number of electrons is controlled by the filament temperature, whereas the energy of the electrons is controlled by filament potential. Ions are formed by the exchange of energy during the collision of the electron beam and sample molecules. This results in a Franck—Condon transition producing a molecular ion, which has an odd number of electrons and is usually in a high state of electronic and vibrational excitation.

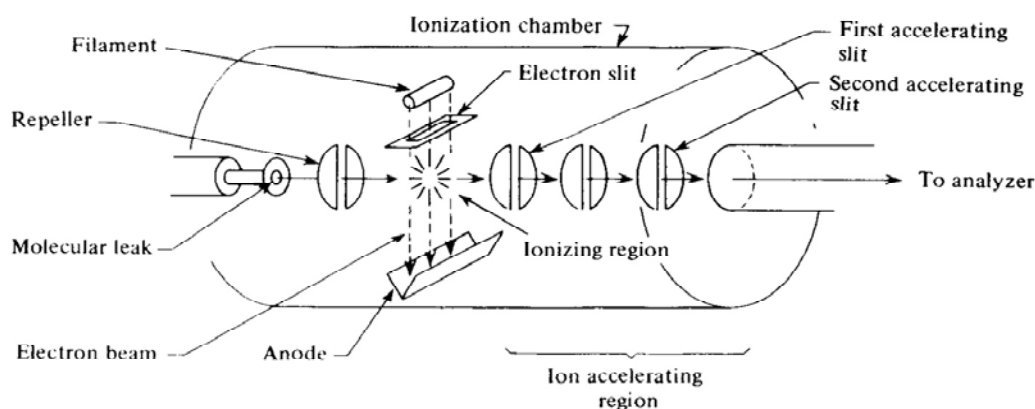


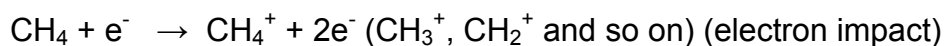
Figure 2.14. Electron-impact ion source and ion accelerating system.

The electric field can be varied from 6 to 100 V. A range from 6 to 14 V is employed in molecular weight determinations when it is desirable to avoid fragmentation. Also, little or no fragmentation is desirable when an analysis of a mixture of compounds is needed and the list of possible components is limited. A source operating at 70 V, the conventional operating potential, provides sufficient energy to ionize and cause the characteristic fragmentation of sample molecules. Minor fragmentation is helpful as

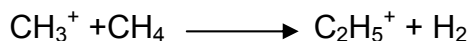
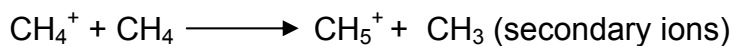
confirmatory identification, while moderate fragmentation can provide positive identification of an unknown. At 70 V the appearance of the spectrum is nearly independent of the electric field, and reproducibility for quantitative work is thereby secured. It is customary to form the ionizing electrons from the cathode into a tight helical beam by a small magnetic field, on the order of 100 G, which is confined within the ionization region. Many compounds do not give a molecular ion in an electron-impact source because of the excess ionization energy imparted to the molecule during the ionization step. This can be considered as a disadvantage of this source.

2.6.2.4. Chemical Ionization

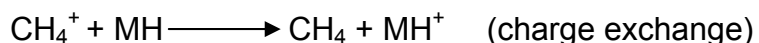
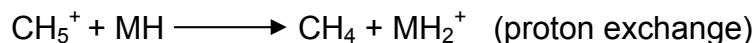
Chemical ionization results from ion-molecule chemical interactions involving a small amount of sample with extremely large amount of reagent gas. A two-part process occurs. First, a reagent gas (methane in our example) is ionized by electron-impact ionization in the source. The electron energy must be 200-500 V to ensure penetration of the ionization electrons into the active volume.



Primary reagent ionization is followed by second-order processes in which the primary ion reacts with additional reagent gas molecules to produce a stabilized reagent ion plasma



The second part of the chemical ionization process occurs when a reagent ion (CH_5^+ or C_2H_5^+) encounters a sample molecule (MH). Reagent ion and sample molecule may react via any of several modes:



2.7. GC-MS

Gas chromatography coupled with Mass Spectrometry (GC-MS) permits separation of complex mixtures into single components before ionisation and mass analysis. This is particularly useful when analysing relatively low levels of target compounds derived from complex biological matrices. The target analyte must be relatively volatile or must be susceptible to conversion to a volatile derivative to permit GC separation. In general, the derivatised analyte should have a molecular weight (MW) of less than 1000 Da in cases, where GC-MS can be successfully applied. In special cases, derivatised analytes with MW 1000-2000 Da can be successfully applied. In special cases, derivatised analytes with MW 1000-2000 Da can be investigated. The ionization methods that can be used are EI and CI in both positive and negative parts. This analysis is usually done at low resolving power or at high resolving power in case of known target compounds for proving compound presence (Williard, 1981).

2.8. Ion Chromatography

Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the corresponding resin. Its greatest utility is for the analysis of anions, for which there are no other rapid analytical methods. It is commonly used for the quantification of cations and biochemical species such as amino acids and proteins. Ion exchange separations are run with pumps and metal columns. Simple LC columns are used to separate one ion from others in ultra-trace analytical concentration. Figure 2.15 shows an Ion Chromatography System.

Ions in solution can be detected by measuring the conductivity of the solution. In ion chromatography, the mobile phase contains ions that create small background conductivity, making it difficult to measure the sole conductivity caused by the analyte ions as they exit the column. This problem can be largely reduced by selectively removing the mobile phase ions behind the analytical column and before the detector.

This is achieved by converting the mobile phase ions to a neutral form or removing them with an eluent suppressor, which consists of an other ion-exchange column or membrane. For cation analysis, the mobile phase is often HCl or HNO₃, which can be neutralized by an eluent suppressor that supplies OH⁻. The Cl⁻ or NO₃⁻ are either retained or removed by the suppressor column or membrane. The sample principle holds for anion analysis, where the mobile phase is often NaOH or NaHCO₃, and the eluent suppressor supplies H⁺ to neutralize the anion and retain or remove the Na⁺ ion. Molecular ions, such as proteins, that have absorption bands in the ultraviolet or visible spectral region may be easily detected by absorption spectroscopy .

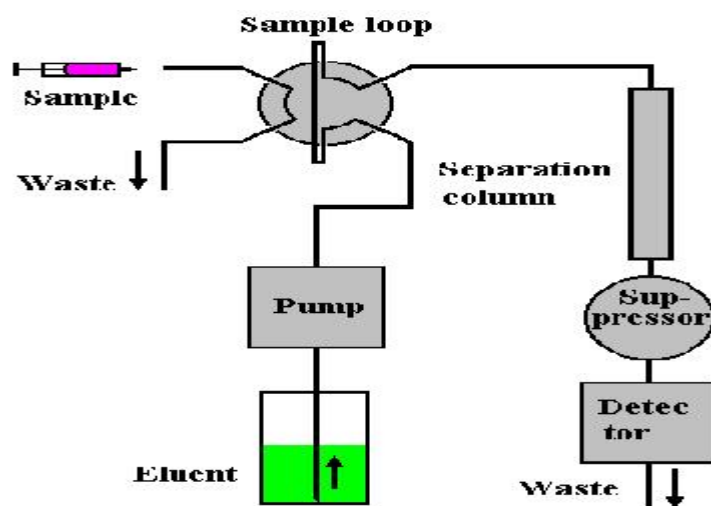


Figure 2.15. Scheme of Ion Chromatography System.

3. MATERIALS AND METHOD

3.1. Chemicals and Reagents

Pesticide standards were obtained always with purity higher than 95%. The internal standard (IS), methyl ester of 2,4-dichlorophenoxybutanoic acid for pesticides and 4-bromo phenol for phenolic compounds (98% purity) were supplied from Aldrich (Steinheim, Germany) and Fluka (Steinheim, Germany), respectively. Stock standard solutions (between 6 and 100 $\mu\text{g mL}^{-1}$) were prepared by exact weighting and dissolution in acetone. The following standards, 2,4-dichloro phenol (97% purity), 4-chloro phenol (99% purity) and 4-bromo phenol (98% purity) were supplied from Fluka (Steinheim, Germany), and catechol (99% purity), 3-chloro phenol (98% purity), resorcinol (99% purity) were obtained from Merck (Darmstadt, Germany), Sigma-Aldrich, (Steinheim, Germany), Fisher Scientific Company (New Jersey, USA), respectively.

The other standards, phenol (99% purity), 2-chloro phenol (99% purity), 2,3-dichloro phenol (98% purity), 2,6-dichloro phenol (99% purity), 4-chloro resorcinol (98% purity), 4,6-dichloro resorcinol (97% purity), 3,5-dichloro phenol (97% purity), 3,4-dichloro phenol (99% purity), 2,4-dichlorophenoxybutanoic acid (95% purity), 2,4-D (98% purity), 2,4-DP (95% purity), were supplied from Aldrich (Steinheim, Germany). The chemical structures of these two pesticides are given in Figure 3.1.

The standard working solutions were prepared by appropriate dilutions and stored in a refrigerator (4°C). Pesticide-quality solvents n-hexane (95% purity), methanol (99.5% purity), acetone (99% purity) were supplied by Merck (Darmstadt, Germany). Reagent-grade concentrated H_2SO_4 (95-98%, w/w) was also supplied by Merck (Darmstadt, Germany) and sodium chloride (99.9% purity) and HNO_3 (65%, w/w) for extraction of methyl esters of herbicides to n-hexane was obtained from BDH (Poole, England) and Fluka (Steinheim, Germany), respectively.

The used chemicals in the determination of ozone in aqueous phase, $K_2Cr_2O_7$ (Potassium dichromate) (99.5% purity), KI (Potassium iodide) (99% purity) and Starch, from potatoes, $Na_2S_2O_3 \cdot 5H_2O$ (sodium thiosulphate pentahydrate) (99% purity) were obtained from Merck (Darmstadt, Germany) and Riel de Haen (Seelze, Germany), and Fluka (Steinheim, Germany), Hopkin and Williams Limited (Essex, England), respectively.

The aliphatic acids which are possible intermediates produced during the irradiation of pesticides in the presence of air, H_2O_2 and O_3 , Chloroacetic acid (99% purity), Malic Acid (99% purity), Malonic acid (99% purity), Itaconic Acid (99% purity) were supplied from Fluka (Steinheim, Germany). 2-Chloropropionic acid (95% purity) and Maleic acid (99% purity) were obtained from Merck (Darmstadt, Germany). Acetic Acid (99.7% purity), Oxalic Acid, dihydrate (99% purity) and Formic Acid (90% purity) were used from Sigma-Aldrich (Steinheim, Germany) and BDH (Poole, England), respectively. Hydrogen peroxide (H_2O_2) (35% w/w) is supplied from Riel de Haen (Seelze, Germany).

The chemicals used in the determination of formaldehyde, chloride ions and total acid yield are Acetylacetone (98% purity), Ammonium Acetate (98% purity), Mercury (II) thiocyanate (99% purity), Iron (III) nitrate nonahydrate (98% purity), Sodium Hydroxide (97% purity) and they were supplied from BDH (Poole, England), Sigma-Aldrich (Steinheim, Germany), Fluka (Steinheim, Germany), Sigma-Aldrich (Steinheim, Germany), Merck (Darmstadt, Germany), respectively.

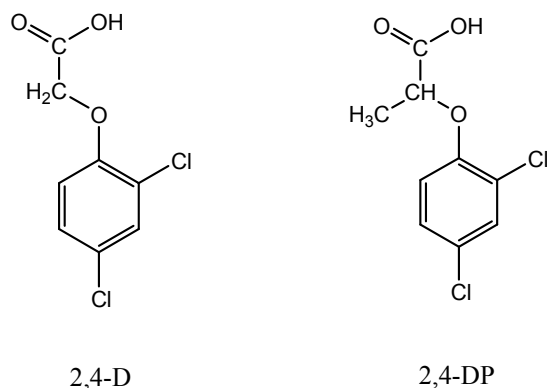


Figure 3.1. Chemical structures of the pesticides.

3.2. Materials Used for Solid Phase Extraction

Varian (vacuum manifold Varian 20) solid phase extraction system, a vacuum unity mode of glass for sample preparation with Solid Phase Extraction (SPE) cartridges. Varian octadecyl (C18) one way cartridges, end capped, 10 mL cartridge with 500 mg sorbent were purchased from Varian.

3.3. Instruments

3.3.1. Gamma Irradiation

Aqueous solutions of two chlorinated phenoxyacetic acid pesticides were prepared at low concentrations (3.0 ppm and 75.0 ppm). Final diluted pesticide solutions were irradiated in air at ambient temperature in a Gammacell 220 type γ -irradiator. Doses of 0.2-5.0 kGy were applied at a fixed dose rate of 0.07 kGy h^{-1} . Aqueous solutions of 2,4-D and 2,4-DP were irradiated in 200 mL glass conical flasks without deaeration. To investigate the effects of H_2O_2 and O_3 to degradation of pesticides, the same aqueous solutions were irradiated in the presence of H_2O_2 and O_3 . After the irradiation, samples diluted by water were extracted with n-hexane in appropriate v/v ratios and then analyzed by Gas Chromatography. The photograph of γ -source is given in Figure 3.2.

3.3.2. Ion Chromatography

The ion-chromatographic determinations of anions, aliphatic acids and chloride were performed using DX-3000 chromatograph from Dionex, equipped with electrochemical ultra anion self regenerating suppressor model ASRS 300, 4 mm, conductivity detector and AG9-HC guard column with analytical column IonPac AS9-HC. Ion chromatography: Aliphatic acids and chloride. DionexSeries 3000; columns: DionexIonpac AS9-HC (4x250mm) and AG9-HC (4x50 mm); injection volume: 500 μL ; flow rate: 1 mL/min; mobile phase: sodium carbonate in 10mM; detection: suppressed

conductivity, ASRS, auto suppression recycling mode. The photograph of Ion chromatography is given in Figure 3.3.



Figure 3.2. ⁶⁰Co-γ source.

Figure 3.3. Ion chromatography.

3.3.3. UV-Vis Spectrophotometer

The state of pesticide degradation was first followed by measuring the change of the absorption spectra of unirradiated and irradiated chlorinated phenoxyacetic acid pesticide solutions using Varian Cary 100 UV–VIS spectrophotometer. Changes of the spectra were observed at the maxima: 228 nm for both 2,4-D and 2,4-DP. The changes of the optical density (OD/cm) at these wavelengths was followed as a function of the absorbed dose γ -rays. Since the changes of 2,4-D and 2,4-DP absorption spectra and those of the formation of final products are overlapping, the observed OD/cm values served as indicator for the degradation process only. The photograph of UV-vis spectrophotometer is given in Figure 3.4.

3.3.4. GC/MS Analysis

The pesticide residues were analyzed by gas chromatography (GC-3900) method. A Saturn 2100T ion trap mass spectrometer from Varian Instruments (Sunnyvale, CA, USA) equipped and operated in the split mode and a VF5-MS (30 m x 0.25 mm i.d.),

0.25 μm film thickness, chromatographic column was employed. The ion trap mass spectrometer was operated in the electron ionization (EI) mode. The computer that controlled the system had an NIST library specially created for the target analytes under our experimental conditions. In addition, an NIST library was available which was used for building our own MS library. Helium (99.999%) at a flow-rate of 1 mL min^{-1} was used as carrier. The photograph of Gas chromatography/Mass-Mass spectrometer is given in Figure 3.5.



Figure 3.4. UV-Vis spectrophotometer. Figure 3.5. Gas chromatography and Mass-Mass spectrometer.

3.3.4.1. Instrumental Conditions

Sample aliquots of 1.0 μL were injected into the GC operating at a syringe injection flow-rate of 1.0 $\mu\text{L s}^{-1}$. To obtain a good separation between all the component peaks of interest, according to EPA 528 and EPA 8151 for intermediate products and phenoxy acid pesticides. Temperature programme in Table 3.1 was used. The ion-trap mass spectrometer was operated in EI-MS mode. Calibration of the mass spectrometer was done weekly. Non-resonant wave form was used for all compounds. Ionization mode (EI) was used, depending on the analyte, in the same run. The transfer line, manifold and trap temperatures were 280, 80 and 210 $^{\circ}\text{C}$, respectively. The analysis was performed with a filament through multiplier delay of 3.0 min to prevent instrument damage. The automatic gain control (AGC) was activated with an AGC-target of 20000 counts. The emission current for the ionisation

filament was set at 10 μ A, generating electrons with an energy of 70 eV. The axial modulation amplitude voltage was 4.0 V. GC/MS was applied for the quantification of two chlorinated phenoxyacetic acid pesticides. Used GC/MS system and its working conditions are given in Table 3.1.

Table 3.1. GC/MS system and its working conditions.

Apparatus	: Varian GC3900 Gas Chromatography and Varian Saturn 2100T Ion Trap Mass Spectrometer
Injector	: Split/splitless injector
Temperature	: 270°C
Injection volume	: 1 μ L
Separation column	: Factor four capillary column (Varian) 30m x 0.25mm x 0.25 μ m film thickness (Crosslinked 5% phenylmethylsilicone)
Temperature program	: 65°C(0min) $\rightarrow$ 10°C/min $\rightarrow$ 185°C (1 min) $\rightarrow$ 20°C/min $\rightarrow$ 275°C(5min) for intermediate products. 60°C(1min) $\rightarrow$ 30°C/min $\rightarrow$ 150°C (0 min) $\rightarrow$ 5°C/min $\rightarrow$ 190°C(3min) $\rightarrow$ 10°C/min $\rightarrow$ 270°C(1min) for phenoxy acid pesticides.
Detector	: Ion trap (IT)
Ionization	: Electron ionization (EI), 70 eV
Carrier gas	: Helium 9.32:1.0 mL/min
Septum purge	: 5.5 mL/min
Split	: 65.9 mL/min

3.4. Pesticide Extraction Method for Water

Solid Phase Extraction is a proven technique for traditional solvent extraction for the separation and enrichment of middle and strongly volatile organochlorine pesticides from water. Solid phase extraction (SPE) (Figure 3.6) is a specific extraction method that uses a solid phase and a liquid phase to isolate one type of analyte from a solution. It is usually used to clean up a sample before using a chromatographic or other analytical method to quantify the amount of analytes contained in the sample. The general procedure is to load the pesticide solution onto the SPE phase, column

wash away undesired components, and then wash off the desired analytes with another organic solvent into a collection tube.

Solid-phase extractions use the same type of stationary phases as are used in liquid chromatography columns. The stationary phase is contained in a glass or plastic column above a frit or glass wool plug. The column might have a frit on top of the stationary phase and might have a stopcock to control the flow of solvent through the column. Commercial SPE (Varian) cartridges have 1-10 mL capacities and are discarded after use. The SPE system used here contained a 10 mL cartridge connected to a vacuum line at the outlet, which increases the solvent flow rate through the cartridge. A collection tube is placed beneath the SPE cartridge (inside the vacuum system) to collect the final eluent containing the concentrated solution.

In this method, SPE vacuum manifold from Varian 20 model was used. C18 cartridge was assembled the solid phase vacuum manifold for multiple extraction. For conditioning, 6 mL n-hexane was passed through the C18 cartridge. C18 column was dried under vacuum for 1-2 minutes and then 12 mL methanol, 6 mL HPLC grade water was aspirated through C18 cartridge, respectively. 4 mL HPLC grade water was added to cartridge with the vacuum off. The real water sample (200 mL) was aspirated through the C18 cartridge at a flow rate of about 5 mL/min. C18 was washed with 1.0 mL of pure HPLC grade water. C18 cartridges were dried with stream of nitrogen (or under vacuum for an hour) for 20-25 minutes. Pesticides collected on C18 were eluted with 2.0 mL methanol by using the vacuum. 2.0 mL of extract was placed in 2 mL glass vial for GC analysis.

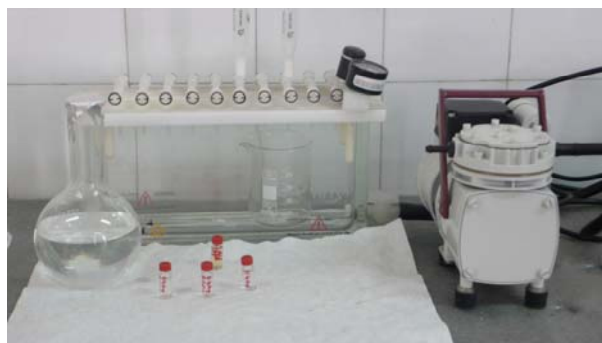


Figure 3.6. Vacuum manifold.

3.4.1. Derivatisation

Most acidic herbicides are not volatile and must be converted to volatile derivatives for GC analysis. The basic methods of derivatisation used for the purpose are transesterification, esterification, silylation, alkylation, extractive alkylation, and pyrolytic alkylation. The reagents used for derivatisation include methyl alcohol in the presence of concentrated H_2SO_4 , diazomethane, trimethylsulfonium hydroxide, trimethylanilinium hydroxide, benzyl bromide, pentafluorobenzyl bromide, (2-cyanethyl)dimethyl (diethylamino)silane, acetic anhydride, dimethyl sulfate, methyl iodide, tetraalkylammonium salts, and bis(trimethylsilyl) trifluoroacetamide. By selecting an appropriate reagent for a given detection system selectivity and sensitivity can be controlled. This is very important in trace analysis of environmental samples which are generally very complex. Some derivatisation reactions can be performed directly in the aqueous sample. When the reactive hydrogen in the acidic herbicide is replaced by a non-polar group directly in the sample higher recoveries of the analytes by means of SPE.

Acidic herbicides (with carboxyl and phenol groups) are widely used in agriculture and forestry. In Turkey, 65% of herbicides applied were phenoxy acids. Tens of compounds from different chemical classes are used as acidic herbicides. They are derivatives of: phenol (dinoseb, dinoterb, pentachlorophenol); benzoic acid (sodium and ammonium salts of 3,6-dichloro-2-methoxybenzoic acid, e.g. dicamba, and sodium and ammonium salts of 3-amino-2,5-dichlorobenzoic acid, e.g. chloramben); acetic acid [(2,4-dichlorophenoxy)acetic acid (2,4-D), (4-chloro-2-methylphenoxy)acetic acid (MCPA)]; propanoic acid [dichlorprop, 2-(4-chloro-2-methylphenoxy)propanoic acid (MCP), etc.]; butanoic acid [4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB)]; and other acids (e.g. potassium or triisopropylamine salts of 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid, e.g. picloram, triethylammonium 3,5,6-trichloro-2-pyridyloxyacetate – triclopyr-TEA). Characteristics and applications of acidic herbicides are described by Hornsby et al (Hornsby et al., 1996). Because of their high physiological activity and structural

diversity herbicides can be a great threat to non-target species. Acidic herbicides, an important group of herbicides can affect non-target species even if present at low concentrations. Acidic herbicides are relatively highly soluble in water, so they are readily washed from the soil (Rompa et. al., 2002) and they and their metabolites should be monitored in different environmental matrices.

The determination of low concentrations of acidic herbicides in inherently complex environmental samples requires application of sensitive and selective analytical techniques of high separating power, such as chromatography (Rimmer, 1996; Namiesnik, 2001). Acidic herbicides can dissociate in water and are not usually volatile (herbicides with carboxyl groups); for gas chromatographic (GC) analysis they must therefore be derivatised (Brondz, 1992).

Derivatisation is usually performed after pre-concentration and clean-up of extracts (Namiesnik and Gorecki, 2001). Better extraction efficiency can be expected if acidic herbicides are converted to less polar derivatives (e.g. acids to esters, phenols to ethers, etc.). Methods based on incorporating derivatisation and extraction into one step have also been proposed.

In general, derivatisation of herbicides with carboxyl and phenol groups is aimed at converting them to compounds which:

- are more volatile,
- are more thermally stable,
- give larger and more selective analytical response,
- are less polar (symmetrical GC peaks, low adsorption on the different parts of the equipment and hence small losses even at low concentrations),
- can be more efficiently extracted into organic solvents,
- can be more selectively and efficiently trapped on solid sorbents and in liquid phases coated on solid supports.

An optimal reagent for derivatisation should be very reactive and ideally give only one product which is of sufficient stability; if any by-products are formed they should be easily removed from the reaction mixture (Namiesnik and Gorecki, 2000). Derivatising reagents generally have two halves; an organic portion which determines the properties of the product and a reactive group which provides the means by which the organic chain is attached to the analyte.

The aim, method, and place of derivatisation depend, to some extent, on the chromatographic technique used. Most often acidic herbicides are first extracted from water into an organic solvent and then derivatised. Some reagents are used to convert acidic herbicides in organic solvent extracts in a GC injection port, kept at high temperature. Such an approach, called pyrolytic alkylation is very convenient. With some reagents derivatisation can be performed directly in aqueous samples. This improves the efficiency of extraction into organic solvents. Sometimes derivatisation is accompanied by extraction into an organic solvent, this is so-called extractive alkylation. For example, in analysis based on solid-phase extraction (SPE) preconcentration and GC separation and detection (Zygmunt, 2001), three different approaches can be applied:

- in-situ derivatisation, based on adding a derivatising reagent to a sample and SPE extraction of the derivatives from the headspace (HS) (Pan, 1995);
- derivatisation in a GC injector port – derivatisation of the analytes extracted on an SPE fibre proceeds at high temperature in a GC injection port (Pan, 1997).
- derivatisation in an SPE fibre coating in which conversion of the analytes to their derivatives takes place in the stationary phase coated on the SPE fibre.

The fibre is first immersed in a reagent solution and then in a sample. The analyte is extracted and converted to a derivative in the SPE coating. The reverse order can also be applied; first the analytes are extracted into the fibre which is then immersed in the reagent solution for derivatisation (Boy-Boland et.al., 1994).

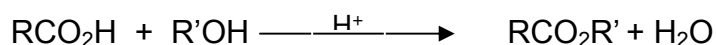
3.4.1.1. Basic Types of Derivatisation Reaction

Most derivatisation reactions used in GC analysis of acidic compounds belong to four categories, i.e. acylation, alkylation, esterification, and silylation. The reactions are as follows:

1. Transesterification with use of:

- H₂SO₄/*n*-propanol in the case of methyl esters of 2,4-D, 2,4,5-T, and MCPA;
- H₂SO₄/methanol in the case of *iso*-octyl esters of 2,4-D and 2,4,5-T.

2. Acid-catalysed esterification (reaction with alcohols):



In our experiments, the following method was followed for esterification of 2,4-D and 2,4-DP and the esterification mechanisms are given in Figure 3.7.

Esterification method: After irradiation or ozonation, aqueous pesticide samples are acidified with concentrated nitric acid to pH=1 to convert the ionized pesticide samples into the molecular form. This step is necessary because ionized pesticide molecules can not be trapped with C18 cartridges in means of SPE. After SPE and drying of cartridges, the trapped pesticide molecules are eluted with 2 mL methyl alcohol. This alcoholic solution is acidified with concentrated sulfuric acid for acid catalyzed esterification. This solution is mixed enough to complete esterification and diluted to 10 mL with water. 4 mL of hexane is added into the system as an upper phase to extract methyl ester. 2 grams of sodium chloride is added into the aqueous phase to force methyl ester of pesticide to be extracted into hexane (Gökmen,1999).

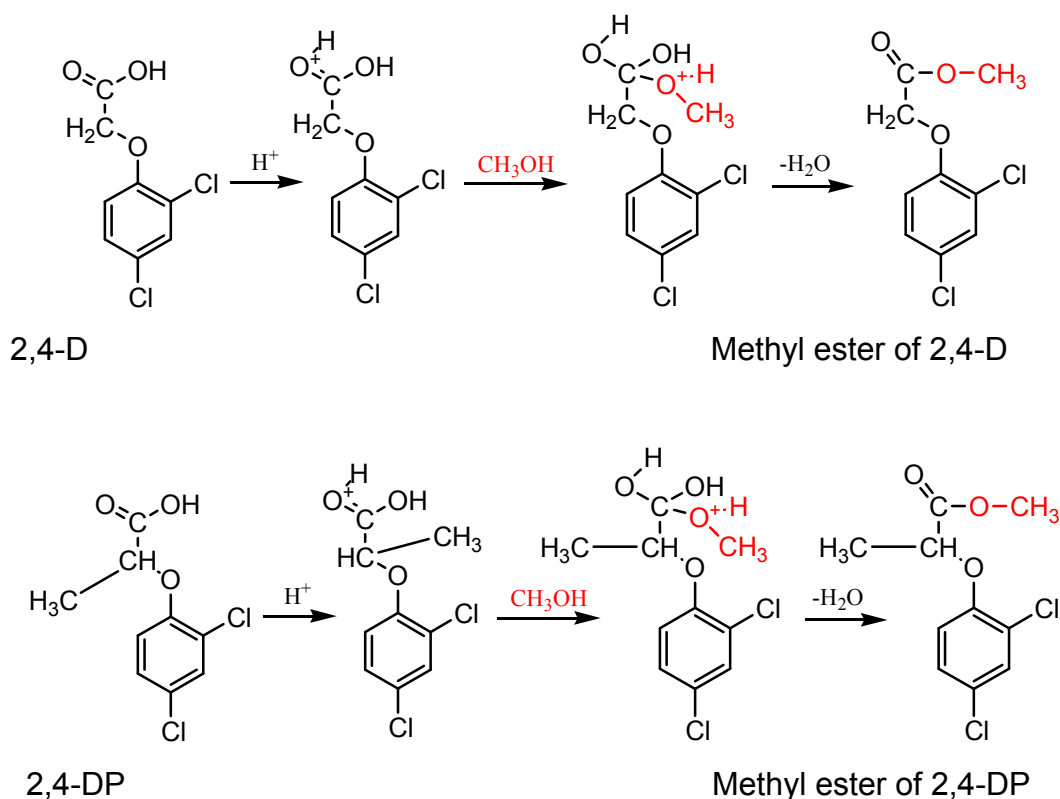


Figure 3.7. Esterification mechanisms of 2,4-D and 2,4-DP.

3. Silylation in which the acidic hydrogen of a herbicide is substituted by a silyl group – a mixture of *N,O* bis(trimethylsilyl) acetamide (80%) and trimethylchlorosilane (20%) is a very efficient formulation for silylation of carboxylic acids and phenols (De Ruiter et. al., 1991).

4. Extractive alkylation in which extraction and derivatisation are incorporated into one step in which anions of carboxylic acids and phenols are transferred as ion pairs from an aqueous phase to an organic solvent which contains an alkylating reagent. For ion pair formation, tetraalkylammonium hydroxides are most often used (Suzuki, 1991). The process can proceed as follows:



5. Alkylation, in which the acidic hydrogen is replaced by an alkyl or aryl group:



Pyrolytic alkylation, which is also used, is the process whereby a volatile alkyl derivative of an acidic compound is formed by thermal decomposition of a quaternary ammonium salt of the acid in the heated injector of a gas chromatograph.

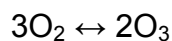
Gas chromatography is a very efficient tool for analysis of organic compounds and is widely applied in the analysis of acidic herbicides. A wide spectrum of reagents has been used to convert these herbicides to GC-analysable derivatives. The most common derivatisation reactions for herbicides with carboxyl and phenol groups are based on formation of esters and ethers, respectively. Methyl derivatives are the most volatile and, therefore, most often produced. The other aim of derivatisation is to improve sensitivity and selectivity and in this way to reduce detection limits (Cserhati, 1998).

A simple procedure for extraction and analysis of chlorinated phenoxy acids was described by Hodgeson et al. (Hodgeson et al., 1994). In their procedure two extraction disks (47 mm in diameter), one packed with SDB and the other with silica gel bonded C18, were used to isolate these pollutants from different water samples (reagent water, dechlorinated tap water, biologically active surface water, high humectant water). Analytes were eluted from the sorbent with a mixture of methanol and methyl-*tert*-butyl ether (MTBE). The extract was dried by passing it through a pipette packed with anhydrous sodium sulfate.

3.5. Ozone Generator

Ozone is such a strong oxidant, it will react with many organic and inorganic compounds present in the water. Ozone is used to remove tastes and odors by breaking down organic compounds. Once ozone gas is transferred into water, the dissolved ozone reacts with the organic and inorganic constituents, including any pathogens. Ozone not transferred into the process water during contacting is

released from the contactor as off-gas. Ozone is an unstable molecule, it should be generated at the point of application for use in water treatment. It is generally formed by, combining an oxygen atom with an oxygen molecule (O_2):



This reaction is endothermic and requires a considerable input of energy. Ozone can be produced several ways, although one method, corona discharge, predominates in the ozone generation industry. Ozone can also be produced by irradiating an oxygen-containing gas with ultraviolet light, electrolytic reaction and other emerging technologies as described by Rice (Rice,1996).

In this study, ozone was generated from dried atmospheric air by OGN 20 model Opal Ozone generator. The photograph of Ozone generator is given in Figure 3.8.

The technique properties of OGN 20 model Opal Ozon generator:

Maximum temperature of water for ozonization	: 30 °C
Ozone output	: 10 g.ozone / hour
Electric consumption	: 3000 W/hour
Power requirements	: 220 Volt, 50 Hz

3.6. Dissolved Oxygen Meter

3.6.1. Dissolved Oxygen

The life of animals and plants is dependent on their energy, which is obtained when their food is oxidized and decomposed with atmospheric oxygen. Thus, oxygen is indispensable to life. The life of aquatic animals and plants is similarly dependent on dissolved oxygen. Thus, dissolved oxygen is critical for living organisms. This means that the life of aquatic animals and plants is greatly affected by the concentration of

dissolved oxygen. Therefore, water with a low concentration of dissolved oxygen is considered to be dirty. Oxygen is supplied to water directly from the air or from the oxygen generated through photosynthesis by phytoplankton.

3.6.2. Measuring Principle of Dissolved Oxygen Meter

Dissolved oxygen can be measured with membrane-type dissolved oxygen electrodes using a galvanic cell or membrane-type dissolved oxygen electrodes using a polarograph.

1) Membrane-type dissolved oxygen electrodes using a galvanic cell: The membrane-type dissolved oxygen electrodes using a galvanic cell are configured as illustrated in Figure 3.9. In this study, WTW Microprocessor Oxi 3000 Oxygen Meter was used. The working electrode uses a noble metal (Ag), and the opposite electrode uses a base metal (Pb). For the electrolyte, an alkaline solution is used. For the membrane, a highly oxygen-permeable Teflon membrane is used. Oxygen which has passed through the membrane is reduced with the working electrode. A reduction current in proportion to the concentration of the dissolved oxygen is generated, and then the dissolved oxygen is measured.

2) Membrane-type dissolved oxygen electrodes using a polarograph The membrane-type dissolved oxygen electrodes using a polarograph are configured as illustrated below. The working electrode uses a noble metal (Pt), and the opposite electrode uses Ag. For the electrolyte, a potassium chloride solution is used, and for the membrane, a Teflon membrane is used. Voltage is applied between the two electrodes so that the threshold diffusion current for oxygen is generated there. The oxygen which has passed through the membrane is reduced with the working electrode. A reduction current in proportion to the dissolved oxygen is generated, and then the dissolved oxygen is measured.

In either case, the current which has flowed in proportion to the concentration of the dissolved oxygen is processed with the current amplifier, and then the concentration of the dissolved oxygen is measured.



Figure 3.8. Ozone generator.

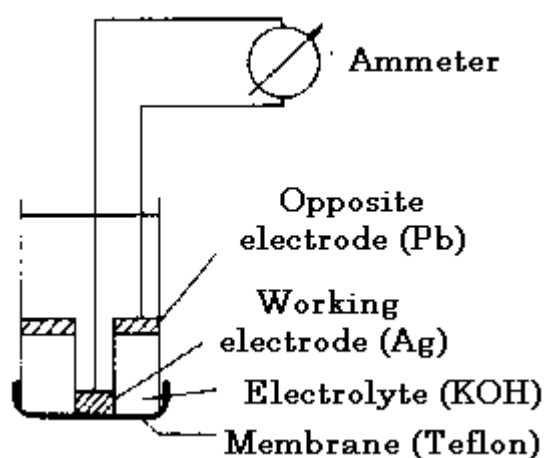


Figure 3.9. Membrane-type dissolved oxygen electrodes using a galvanic cell.

3.7. Analytical Methods

3.7.1. Absorption Spectra

The UV-absorbances at the wavelength of maximum absorbance of the irradiated and unirradiated 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenoxypropionic acid pesticide solutions were measured by a Carry 100 model UV-vis spectrophotometer. The percent degradation was estimated from the reduction in optical density. Deionized water was used to prepare different concentrations (3-75 mg/L) for 2,4-

dichloro phenoxyacetic acid and 2,4-dichlorophenoxypropionic acid pesticide solutions. pH of the irradiated and unirradiated pesticide solutions were measured by ISTEK NeoMet pH-200L model pH meter. The degradation process of these two phenoxyacid pesticides were followed by the changes in their absorption spectra, it was established that the absorption spectrum of the radiolytic products was superimposed with that of the substrate. Therefore, the GC/MS-MS method was used for the precise determination of the 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenoxypropionic acid pesticides degradation as well as for the identification and quantification of the major resulting products and residual pesticides.

3.7.2. Analysis of Degradation, Residual Pesticides, Intermediate and Final Products

Gas chromatograph (GC/MS-MS) was used to identify some degradation products of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) pesticides after and before irradiation in air, H_2O_2 and O_3 . 2,4-D and 2,4-DP pesticides and some intermediate species and final products were analyzed by gas chromatography with Factor Four Capillary Column (Varian) 30 m x 0.25 mm x 0.25 μ m film thickness and a mass spectrometry detection. For extraction, depending on the concentration of 2,4-D and 2,4-DP pesticides and some intermediate species and final products, 200 mL of samples were eluted under vacuum on C18 cartridges and then recovered with 2 mL of methyl alcohol and acetone for pesticides and intermediate species, respectively. Methyl ester of 2,4-DB and 4-bromo phenol were used as internal standard for pesticides and intermediate species, respectively. The accuracy of determinations was routinely checked by using standard samples containing known amounts of phenoxyacid pesticides and chlorinated phenols.

3.7.3. Ozonation and Determination of Dissolved Ozone in Aqueous Phase

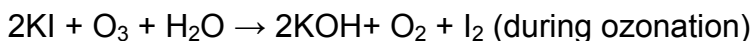
3.7.3.1. Ozonation

Ozone was generated from atmospheric air by a prototype corona discharge generator (OPAL OGN-20, Turkey), and driven by air pump with flow rate of 0.078 L min^{-1} . Air was used as the generator feed gas. Production rate was $10 \text{ g O}_3 \text{ h}^{-1}$. Phenoxyacid pesticide solutions (400 mL) were ozonized in a cylindrical glass reactor (volume 500 mL) by bubbling ozone/air mixture into the solution through a sinterized glass filter (pore size 50-80 mm). Due to small reactor volume, 400 mL fresh phenoxyacid pesticide sample (stock solution) was used for each reaction time period studied (10-1200 sec or 0.17-20 min). Excess ozone leaving the reactor was trapped by three-sequential bubblers containing KI aqueous solution (2%). Then an iodometric titration procedure (APHA, 1992) was performed to measure the ozone concentration, trapped in the KI solutions, and this value was used to calculate the transferred ozone (produced ozone - trapped in KI). All experiments were conducted at room temperature ($298 \pm 1 \text{ K}$).

3.7.3.2. Iodometric Method

The methods for measuring residual ozone consist of the indigo colorimetric method, acid chrome violet K method, the iodometric method, Bis-(Terpyridine)Iron(II) method and UV absorption. In this study, the iodometric method was followed. Iodometric procedures have been used for all of the ozone concentration ranges encountered in water treatment plants (Gordon et al., 1992). This includes measurement of ozone directly from the generator and of ozone as stripped from aqueous solution. For the iodometric method, the ozone containing gas is passed into an aqueous solution containing excess potassium iodide. All other oxidizing materials except ozone act as interferences with iodometry (Gordon et al., 1992). Nitrogen oxides (that may be present when ozone is generated in air) also act as interferences to iodometric methods. The effects of nitrogen oxides may be eliminated by passing the ozone-

containing gas through absorbents such as potassium permanganate that are specific for nitrogen oxide gases. The iodometric method is based on oxidation of iodide ion with ozone.



Since the amount of produced I_2 is equal to the amount of consumed O_3 in moles, the amount of produced iodine in moles found with titration against sodium thiosulphate with starch as indicator is equal to the amount of trapped ozone in moles.



The amount of dissolved ozone in phenoxyacid pesticide solutions is found with subtraction of trapped ozone amount in KI solutions from produced ozone in generator (10 g/h). Sodium thiosulphate is not a primary standard, so, it is standardized against potassium dichromate.

3.7.4. Determination of Some Ionic Species

Inorganic and organic anions which include different aliphatic acids were determined by ion chromatography (IC Dionex DX3000) operated in auto suppression recycle mode (ASRS-300 4mm) and equipped with a conductivity detector. Samples of 500 μL injected at a flow rate of 1.0 mL min^{-1} through an IonPac AS9-HC analytical column (Dionex, 4X250 mm) and an IonPac AG9-HC guard column (Dionex, 4X50 mm). The analyses were carried out in triplicate and data analysis was made using software Chromeleon Version 6.80 SP2 Build 2284 (Dionex).

3.7.5. Determination of Chloride Ions

Chloride ion also appeared to be one of the major degradation products. The formation of the free Cl^- ions was measured using the mercury (II)-thiocyanide method, where the complex absorption was registered at 460nm (Florence and Farror, 1971). In this case too, a calibration curve was used for the determination of

the yield. The amount of free Cl^- ions was determined with ion chromatography. The results were controlled with mercury (II)-thiocyanide method.

3.7.6. Determination of Formaldehyde

Formaldehyde was determined by the Hantzsch method (Nash, 1973). The formation of formaldehyde is measured spectrophotometrically at $\lambda_{\text{max}} = 412 \text{ nm}$. The obtained yields were calculated by means of a calibration curve.

3.7.7. Determination of Total Acid Yield

The total acid yield was measured with titrimetric method by using 0.01 M NaOH which is standardized against 0.01 M oxalic acid as a function of the absorbed dose for irradiated and unirradiated phenoxy acid pesticides in air, H_2O_2 and O_3 .

4. RESULTS AND DISCUSSION

Three analytical techniques were used to monitor chlorinated phenoxy pesticides degradation: (1) A UV-Vis spectrophotometer was used to determine the changes in UV-vis spectra of the irradiated chlorinated phenoxy pesticides or determine the degradation of these pesticides and record all spectra. (2) A Gas chromatography/Mass-Mass spectrometer (GC/MS-MS) was used to separate by-products and examine the evolution of breakdown products. (3) An ion chromatograph (IC) was employed to observe and determine the anions and the other ionic species which for during the irradiation (Gauch, 2001; Vel Leitner, 1999).

4.1. Evolution of UV Absorption Spectra

The UV absorption spectrum of 2,4-dichlorophenoxyacetic acid (2,4-D) solutions (75 mg/L at 0.07kGy/h) in our experimental conditions presents a maximum at 228 nm (Figure 4.1). After 2,4-D solutions irradiated at different irradiation doses we observed a decrease about 83% in the height characteristic peak (228 nm) of the UV 2,4-D spectrum (Figure 4.2). The absorption band at 228 nm decreased with the increasing irradiation dose and disappeared almost completely at 3.0 kGy. For the same experimental conditions cited above during irradiation the absorbance of 2,4-dichlorophenoxypropionic acid (2,4-DP) solution was determined at 228 nm (Figure 4.3). Results presented in Figures 4.1- 4.6 indicate that the absorbance is decreased with increasing radiation dose. The absorption spectra of the unirradiated and irradiated 75 mg/L 2,4-D and 50 mg/L 2,4-DP solutions in air at 0.07 kGy/h dose rate are shown in Figure 4.1 and Figure 4.4. While the absorption band at 228 nm decreased with increasing dose and disappeared completely at 2.5 and 2.0 kGy in air for 2,4-D and 2,4-DP solutions (Figure 4.2 and 4.5), respectively. The absorption spectra of 2,4-DP were also similar to each other.

The effect of irradiation dose in kGy on the different concentrations of 2,4-D and 2,4-DP solutions was studied. 2,4-D (3-75) mg/L and 2,4-DP solutions at (3-50) mg/L concentrations were subjected to different irradiation doses at 0.07 kGy/h dose rate in

air and the decrease in absorbance at maximum wavelengths and percent degradation versus irradiation doses at different concentrations are shown in Figures 4.2 and 4.5. In the Figures 4.3 and 4.6 it can be seen that the percent degradation of 2,4-D and 2,4-DP was increased with the irradiation dose. The modification of the absorbance spectra during the degradation shows us that there is a transformation in the molecule structure of 2,4-D and 2,4-DP and the formation of by-products.

To investigate the effect of irradiation dose on the pH of the 75 ppm and 50 ppm 2,4-D and 2,4-DP solutions at 0.07 kGy/h dose rate, pH values of the unirradiated and irradiated herbicide solutions were measured. The pH values of the unirradiated and irradiated solutions are given in Tables 4.1 and 4.2. Tables show that pH of the solutions decreased with the irradiation dose. The pH of the solutions was lower at the low herbicide concentrations than the higher herbicide concentrations. The change of pH depends on the structure of herbicide and types of intermediate molecules (Sanchez, 2002). When the maximum absorbance or the percent degradation (%) of two herbicide solutions which have different concentrations compared with each other, the increase in the percent degradation (%) was more rapidly for the lowest concentration (3 mg/L) pesticide solutions than for the higher concentrations.

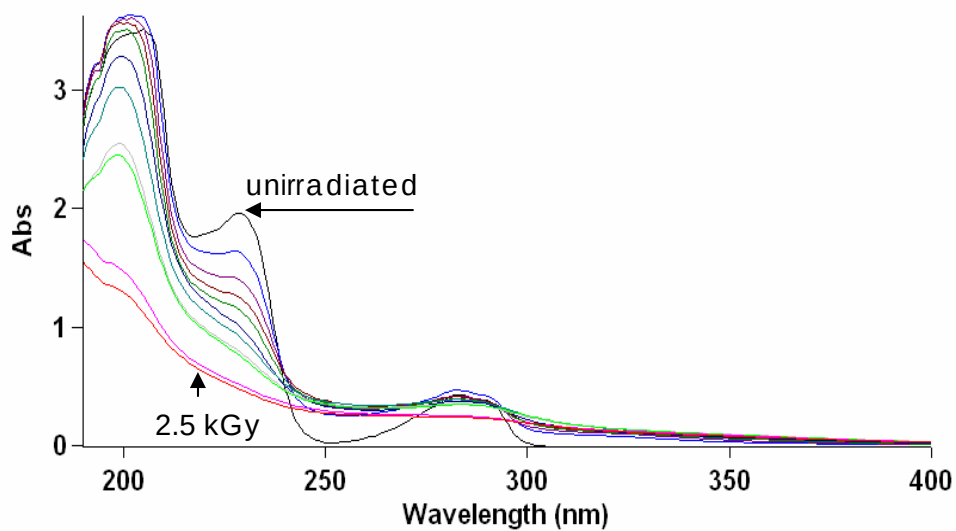


Figure 4.1. Absorption spectra of unirradiated and irradiated 2,4-D solutions. [2,4-D]: 75 mg/L. ($\lambda_{\text{max}} = 228 \text{ nm}$) Dose rate: 0.07 kGy/h.

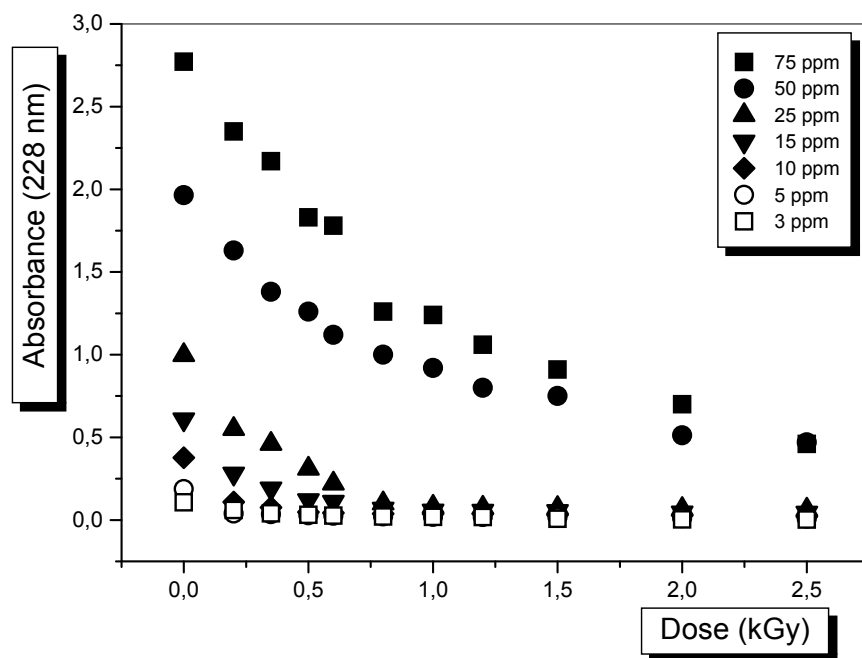


Figure 4.2. Change of the absorbance at 228 nm as a function of irradiation dose (kGy) at various concentrations of 2,4-D in air. Dose rate: 0.07 kGy/h.

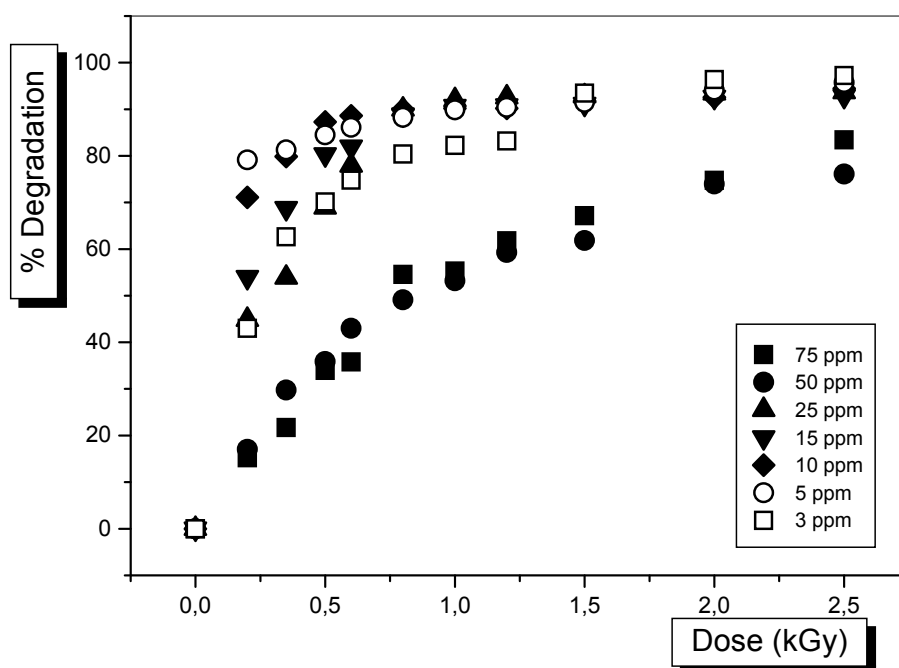


Figure 4.3. The percent degradation as a function of irradiation dose (kGy) at various concentrations of 2,4-D in air. Dose rate: 0.07 kGy/h.

Table 4.1. The change of pH as a function of irradiation dose (kGy) at various concentrations of 2,4-D in air. Dose rate: 0.07 kGy/h.

Dose (kGy)	Concentration (ppm)						
	3	5	10	15	25	50	75
0.0	5.90	5.60	4.91	4.43	4.15	3.90	3.87
0.20	6.33	5.70	5.24	4.26	3.75	3.67	3.44
0.35	6.1	5.01	4.56	3.92	3.75	3.54	3.49
0.50	6.01	4.65	3.99	3.78	3.57	3.60	3.40
0.60	5.93	5.86	4.06	3.82	3.66	3.47	3.42
0.80	5.64	4.42	3.92	3.65	3.57	3.58	3.28
1.00	6.05	5.45	4.87	3.76	3.52	3.43	3.31
1.20	4.97	4.46	3.91	3.70	3.53	3.42	3.19
1.50	5.93	5.23	3.92	3.71	3.52	3.40	3.19
2.00	4.22	4.29	3.83	3.67	3.49	3.34	3.27
2.50	4.54	4.37	3.98	3.72	3.51	3.32	3.12

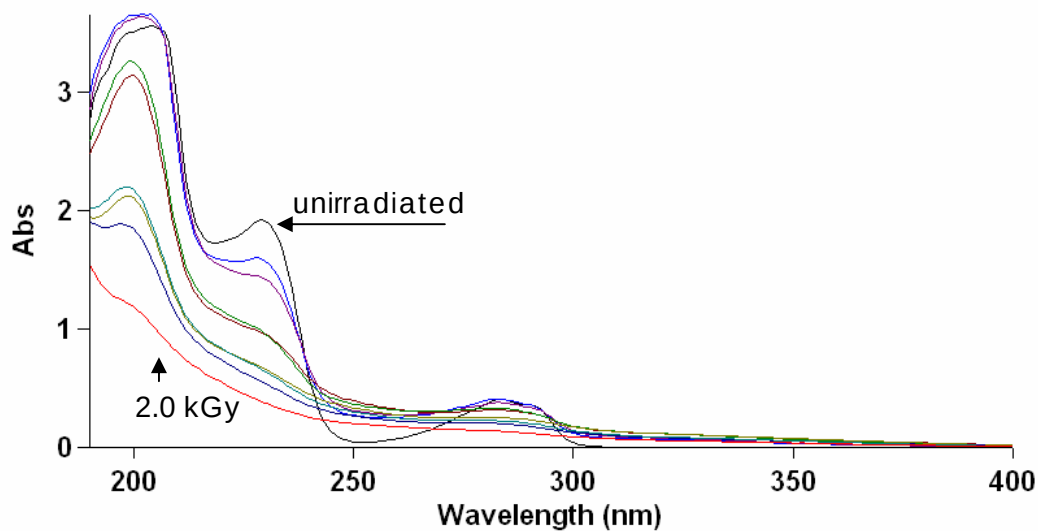


Figure 4.4. Absorption spectra of unirradiated and irradiated 2,4-DP solutions. [2,4-DP]: 50 mg/L. ($\lambda_{\text{max}} = 228 \text{ nm}$) Dose rate: 0.07 kGy/h.

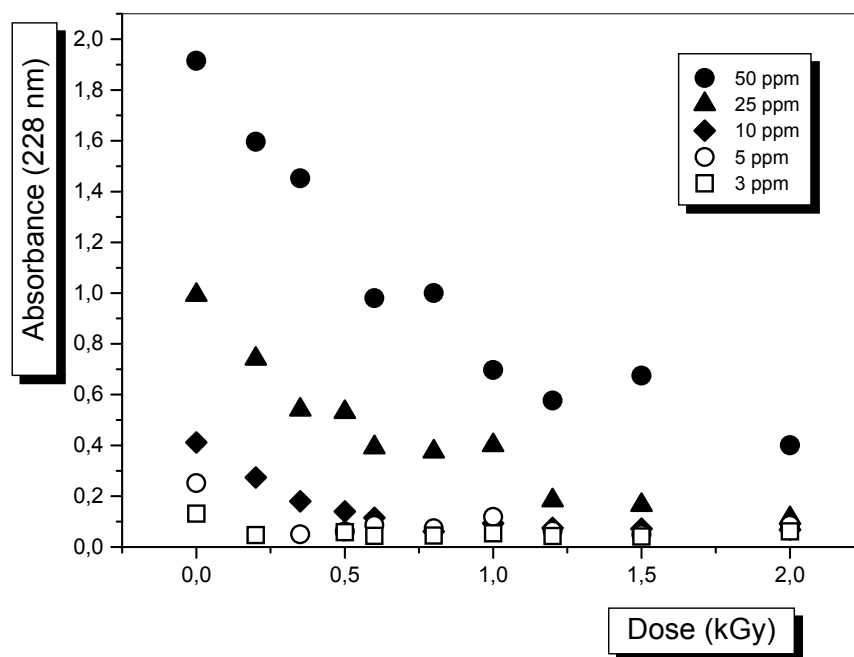


Figure 4.5. Change of the absorbance at 228 nm as a function of irradiation dose (kGy) at various concentrations of 2,4-DP in air. Dose rate: 0.07 kGy/h.

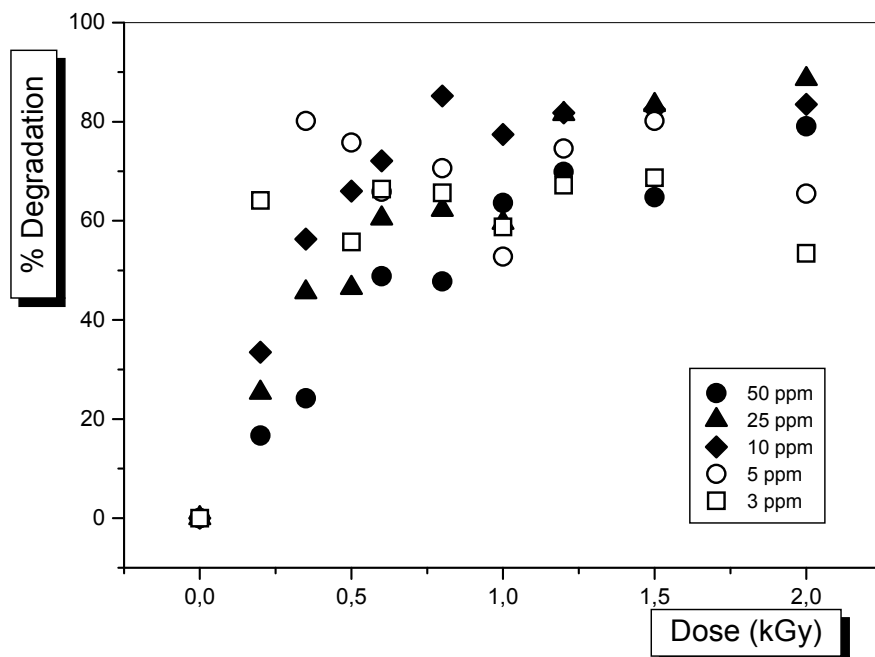


Figure 4.6. The percent degradation as a function of irradiation dose (kGy) at various concentrations of 2,4-DP in air. Dose rate: 0.07 kGy/h.

Table 4.2. The change of pH as a function of irradiation dose (kGy) at various concentrations of 2,4-DP in air. Dose rate: 0.07 kGy/h.

Dose (kGy)	Concentration (ppm)				
	3	5	10	25	50
0.00	6.15	6.15	5.34	4.62	4.16
0.20	4.75	4.94	4.38	4.11	3.75
0.35	5.03	4.33	4.26	3.89	3.72
0.50	4.32	4.21	4.02	3.83	3.67
0.60	4.41	4.27	4.02	3.77	3.54
0.80	4.48	4.63	4.11	3.88	3.64
1.00	4.34	4.34	4.08	3.80	3.53
1.20	4.20	4.21	4.01	3.67	3.49
1.50	4.37	4.14	3.99	3.67	3.49
2.00	4.12	4.08	3.99	3.65	3.39

4.2. Evolution of Gas Chromatography/Mass-Mass Spectrometry Results

Acidic herbicides are relatively highly soluble in water. The determination of low concentrations of acidic herbicides in inherently complex environmental samples requires application of sensitive and selective analytical techniques of high separating power, such as chromatography (Rompa, 2002). Acidic herbicides can dissociate in water and are not usually volatile (herbicides with carboxyl groups); for gas chromatographic (GC) analysis they must therefore be derivatised (Brondz, 1992). Derivatisation is usually performed after pre-concentration and clean-up of extracts (Namiesnik, 2001). By selecting an appropriate reagent for a given detection system selectivity and sensitivity can be controlled.

The herbicides present in water are at a trace level, mixed with other contaminants at higher concentrations. Their analysis requires first an extraction and a concentration. For the extraction step, several methods are available. The best known is liquid–liquid extraction. Its advantages are simplicity and implementation easiness, but it requires time, large sample volumes and consumes a lot of solvent. Another more recent method is more and more used because it pollutes less: solid phase extraction (SPE). It offers the advantages to consume much less solvent and to be automatisable, but requires substantial investment in equipment and extraction cartridges which are not reusable. In this study, we present an application of the SPE/ GC for the analysis of chlorinated phenoxy herbicides in water (Boussahel, 2002).

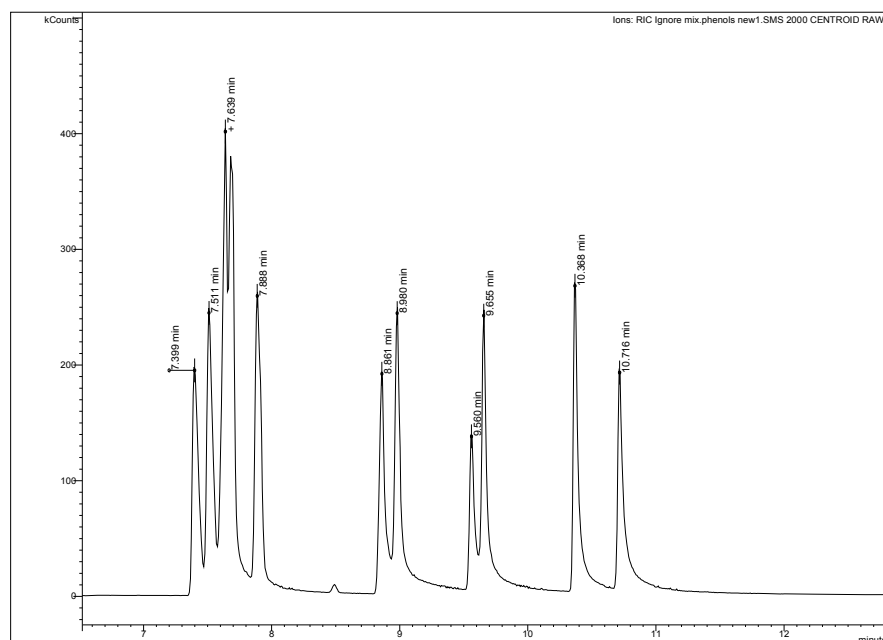
Some derivatisation reactions can be performed directly in the aqueous sample. When the reactive hydrogen in the acidic herbicide is replaced by a non-polar group directly in the sample higher recoveries of the analytes by means of SPE could be achieved. Some attempts were also made to incorporate extraction and derivatisation into one step. A wide variety of reagents can be used to derivatise acidic herbicides at different steps of the analysis. This makes the approach applicable to many environmental samples.

Currently, gas chromatography mass spectrometry (GC–MS) remains the main analytical technique used for pesticide residue analysis, combining the power of separation allowed by GC, with the sensitivity, selectivity, and identification capability of MS (Fillion, 2000; Garcia, 1995). In the few years, tandem MS (MS–MS) using bench top ion-trap systems has been shown to be a relevant approach in pesticide residue analysis, providing increased selectivity and sensitivity (Martinez, 2002; Schachterle, 1996). However, one of the main goals in the development of new GC–MS methods is an increase in analysis speed to reduce the analysis time. The relatively slow multiresidue methods currently used in pesticide residue laboratories restrict the number of analyses per day. The main aim of this study was to demonstrate the ability of a multiresidue and GC–MS–MS method for the determination of herbicides in surface and ground waters. This method is based on a simple and fast solvent extraction steps before analysis. The results obtained by this approach were compared to those obtained using H₂O₂ and O₃.

4.2.1. Determination of Working Conditions

The GC conditions were determined according to EPA methods. For preconcentration and to extract intermediates and undecomposed herbicides from aqueous media to organic phase, solid phase extraction method was used. To obtain a good separation between all the component peaks of interest, according to EPA 528 and EPA 8151 for intermediate products and phenoxy acid herbicides, temperature programme in Table 3.1 was used. For quantitative determination, 4-bromo phenol and methyl ester of 2,4-dichlorophenoxybutanoic acid was used as an internal standards for phenolic compounds and for undecomposed 2,4-D residues, respectively. The gas chromatogram of the standard phenol mixtures, internal standards and their retention times are given in Figure 4.7. a, b and Table 4.3 and the gas chromatogram of methyl esters of 2,4-D, 2,4-DB (IS) and 2,4-DP, 2,4-DB(IS) and their mass spectra of 2,4-D, 2,4-DP are given in Figure 4.8 a,b and 4.9 a,b. m/z data are seen in their mass spectra.

a)



b)

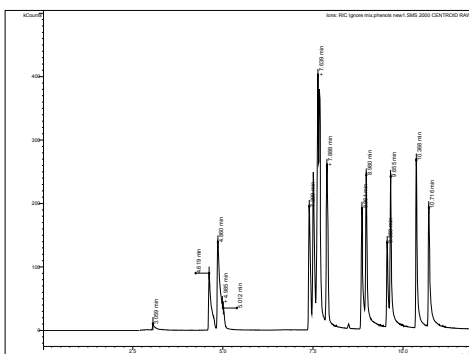


Figure 4.7. Gas chromatogram of the standard phenol (4-bromophenol as internal standard) mixtures. The amounts of all standards are 50 ppm except resorcinol (170 ppm) and catechol (220 ppm). Retention time interval a) 0-12.5 min, b) 6-13 min.

Table 4.3. Retention times of phenol standards.

Retention time (min)	Name of the standards
4.619	Phenol
4.860	2-Chloro phenol
7.399	2,3-Dichlorophenol
7.511	2,4-Dichlorophenol
7.639	Catechol
7.889	4-Chlorophenol and 3-Chlorophenol
7.888	2,6-Dichlorophenol
8.861	Resorcinol
8.980	4-Bromophenol
9.560	4-Chloro resorcinol
9.655	4,6-Dichlororesorcinol
10.368	3,5-Dichlorophenol
10.716	3,4-Dichlorophenol

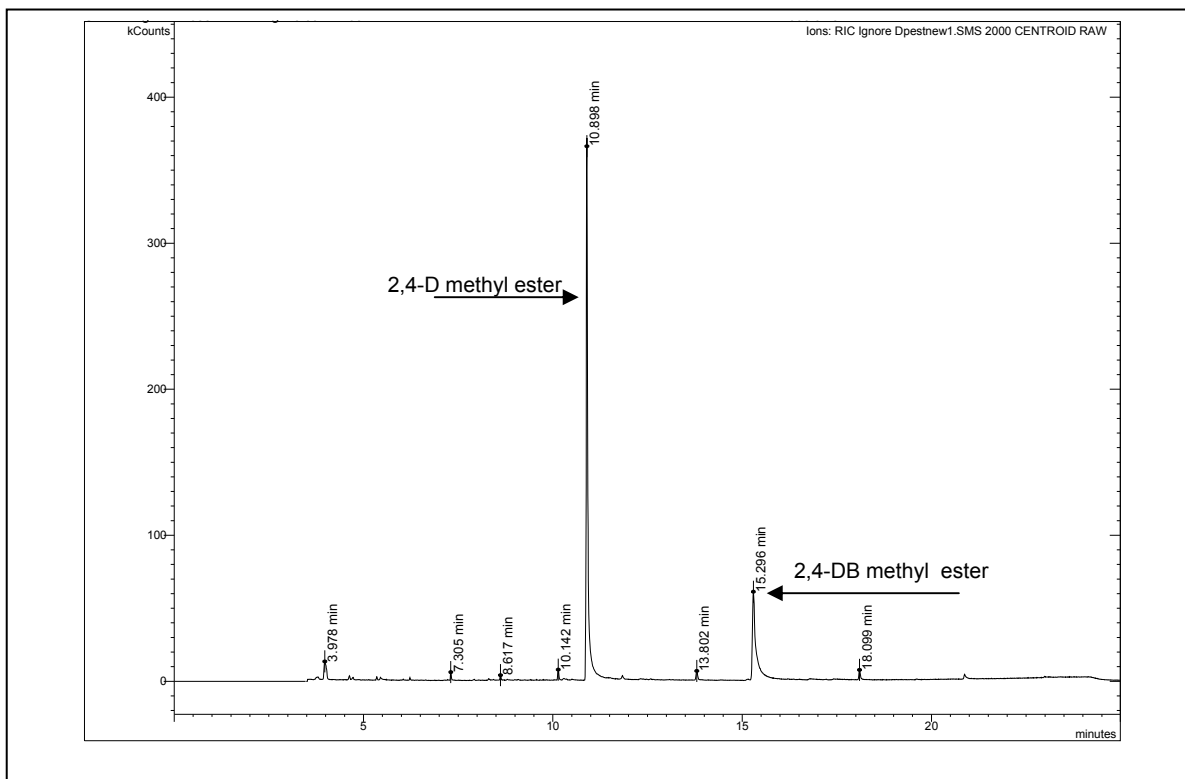


Figure 4.8.-a) Gas chromatogram of methyl esters of 2,4-dichlorophenoxyacetic acid (25 ppm) and 2,4-dichlorophenoxybutanoic acid (10 ppm) (IS).

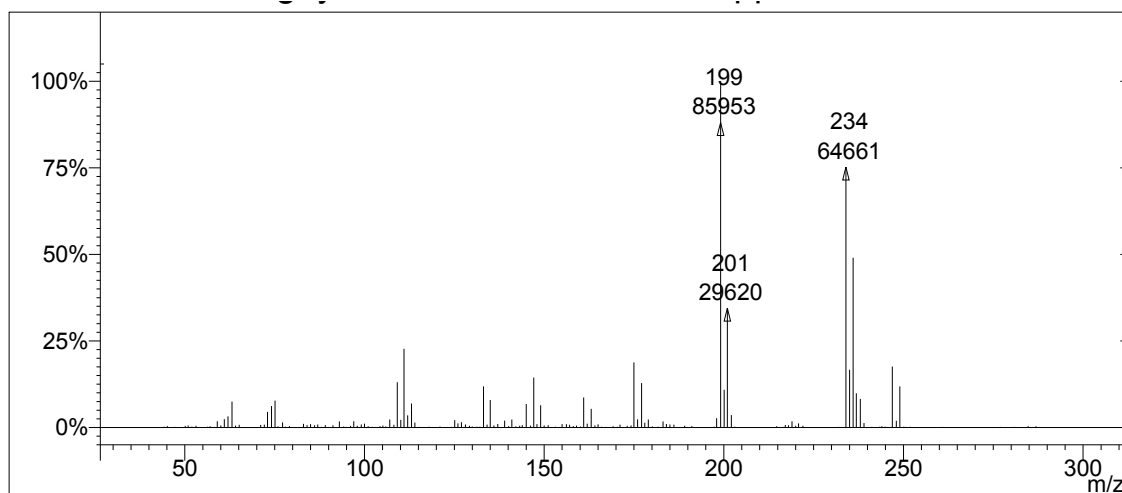


Figure 4.8.-b) Mass spectrum of methyl ester of 2,4-D (10.898 min.)

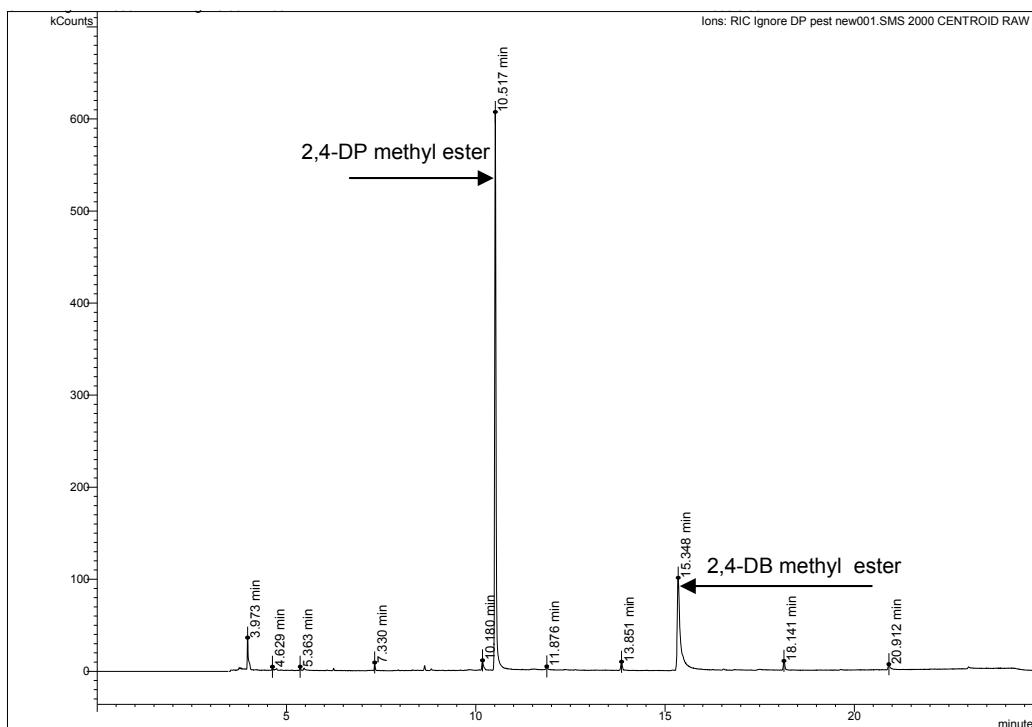


Figure 4.9.a) Gas chromatogram of methyl esters of 2,4-dichlorophenoxy propionic acid (25 ppm) and 2,4- dichlorophenoxybutanoic acid (10 ppm) (IS)

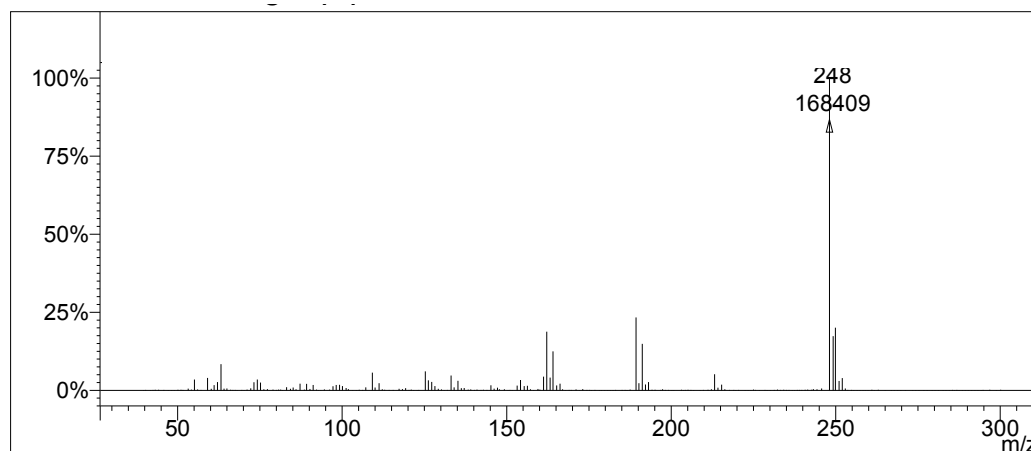


Figure 4.9.b) Mass spectrum of methyl ester of 2,4-DP (10.517 min.)

4.2.2. Effect of Gamma Irradiation on Degradation of 2,4-D and 2,4-DP

Groundwater consists of potable water with percent of 0.58 in the world. The organic substances and microorganism content of groundwater respect to the surface water, and its chemical structure and temperature doesn't change in the course of time. As a result of the strong development of various industries as well as the growth of the world population, the contamination of the environment has been increasing in the last few decades, especially in the water resources. The disposal of untreated wastes in lakes, rivers, seas and also the use of fertilizers, pesticides, etc. in the modern agriculture are the major contributors of the water pollution (Sanchez,2002). Many of the pesticides are fairly mobile in soil and readily migrate into ground-water. Because of their widespread use, pesticides leach into surface and groundwater, and are therefore present in drinking water (Younes, 2000).

Among the numerous agrochemicals in use today, the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) have been widely also used in Turkey. After application, it can be easily transferred into natural waters due to its high solubility. In 1982, the World Health Organization considered 2,4-D as moderately toxic (classII) and recommended a maximum 2,4-D concentration of 100 ppb in drinking water (Zona, 2002; Hoover, 1986).

Ionizing radiation is an efficient process for oxidative removal of water pollutants (Wang, 1994; Lin et.al., 1995; Woods, 1994; Gehringer, 1996). Numerous methods can be employed for removal of various classes of environmental pollutants. In recent years, more attention is being paid to various advanced oxidation processes (AOPs), which are based on the use of in situ formed reactive free radicals, that can effectively decompose organic pollutants without an additional separation step. The most common AOPs are ozonation, UV photolysis, photocatalysis and Fenton reactions, and etc. Radiation processes are very powerful AOPs, where irradiation with a beam of accelerated electrons or gamma-radiation is employed for degradation of various pollutants. Numerous papers have been published that are devoted to the

degradation of organic compounds by ionizing radiation (Cooper et al., 1998) but in only few of them, was toxicity controlled during the radiation processes. Because of the possibility of transient formation of more toxic pollutants during irradiation (or other AOPs applied), the toxicity measurements are very valuable in assessment of real environmental value of applied treatment processes. Compared to other AOPs, ionizing radiation has the advantage that no chemicals have to be added to the water samples.

The effect of ionizing radiation on water results among other things in the formation of almost equal amount of hydroxyl radicals ($\text{OH}\cdot$) and solvated electrons (e^-_{aq}). Therefore, γ -irradiation can be used to study both the action of oxidizing and reducing free radical species to solutes in water. Beside the primary species generated during water irradiation the effect of some secondary species like $\text{O}^{\cdot-}_2$ (originating from the scavenging of e^-_{aq} by oxygen). The use of $\text{OH}\cdot$ for pollutants degradation has been studied more intensively because there are also some other processes (so-called Advanced Oxidation Processes AOPs) which generate and use $\text{OH}\cdot$ for organics removal, e.g. O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2$, TiO_2/UV and others (Vel Leitner, 1999).

To investigate the effect of irradiation dose, 50 ppm ($2.26 \times 10^{-4} \text{ mol L}^{-1}$) 2,4-D and 50 ppm ($2.13 \times 10^{-4} \text{ mol L}^{-1}$) 2,4-DP solutions were subjected to 0.2-4.5 and 0.2-5.0 kGy irradiation doses at 0.07 kGy/h dose rate in air at ambient conditions, respectively. For preconcentration and to extract intermediates and undecomposed herbicides from aqueous media to organic phase, solid phase extraction method was used. For determination of acidic groups, such as undecomposed herbicides, methyl alcohol was used for organic phase extraction. The analytes that include carboxylic acid groups can not be observed in GC-MS system, so the derivatives of these groups such as methyl esters, have to be injected to the system. These groups were converted to methyl esters in methyl alcohol with excess concentrated sulphuric acid and methyl esters were extracted into hexane for injection into GC-MS system. The GC chromatograms, mass spectra of possible intermediates of 0.2, 4.5 kGy irradiated 2,4-D solutions and 0.2-5.0 kGy irradiated 2,4-DP solutions after solid-phase

extraction in acetone and probable degradation products from the irradiated samples are given in Figures 4.10 a, b, 4.11, 4.12 and Figures 4.13 a,b, 4.14, 4.15.

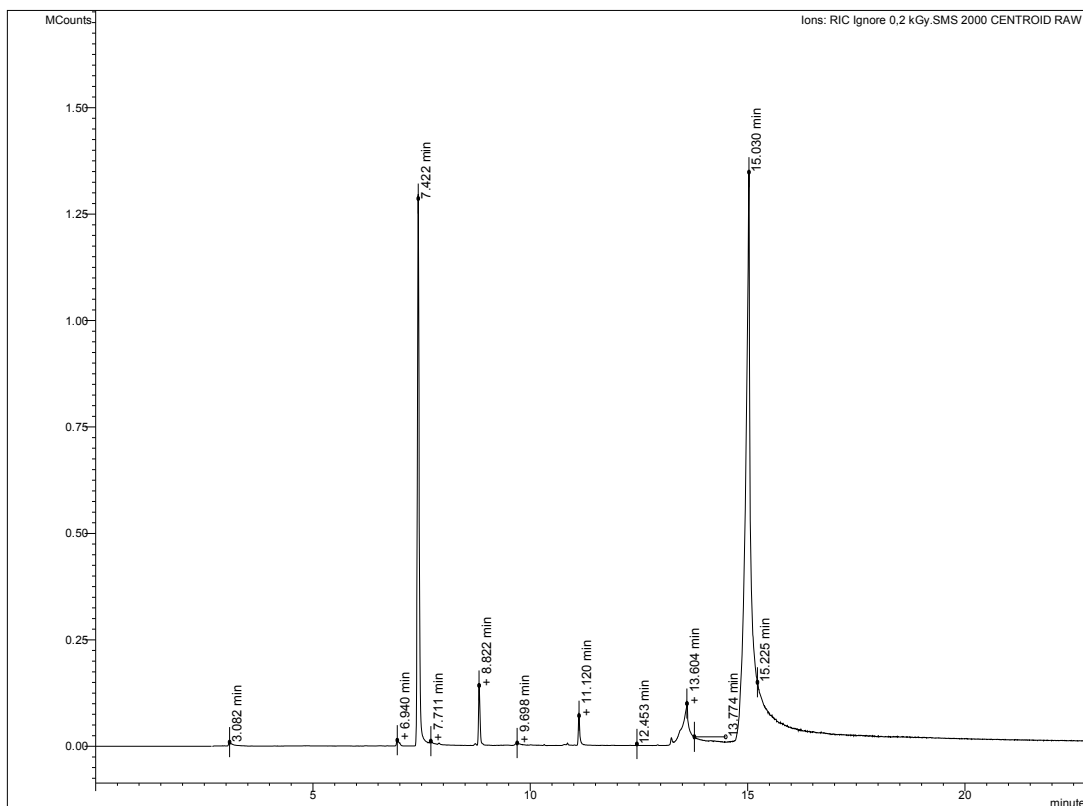


Figure 4.10.-a) GC chromatogram of the 0.2 kGy irradiated 2,4-D (50 ppm) samples after eluted from C18 cartridges in acetone.

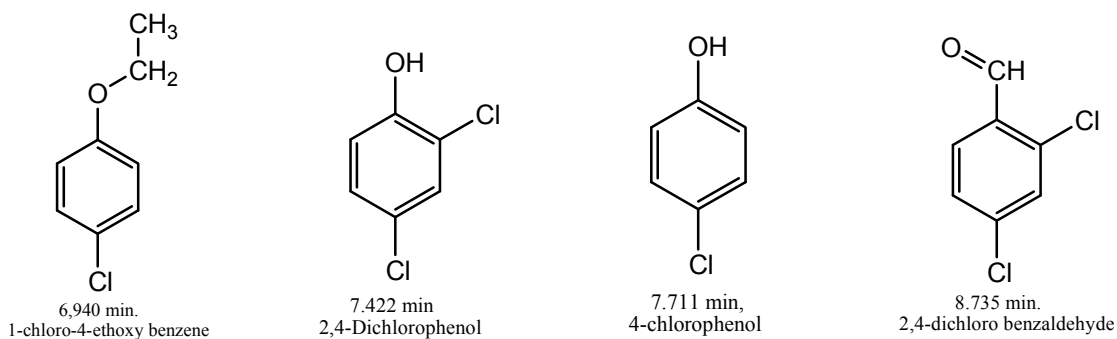


Figure 4.10.-b) Possible intermediates for 0.2 kGy irradiated 2,4-D (50 ppm) samples after eluted from C18 cartridges in acetone.

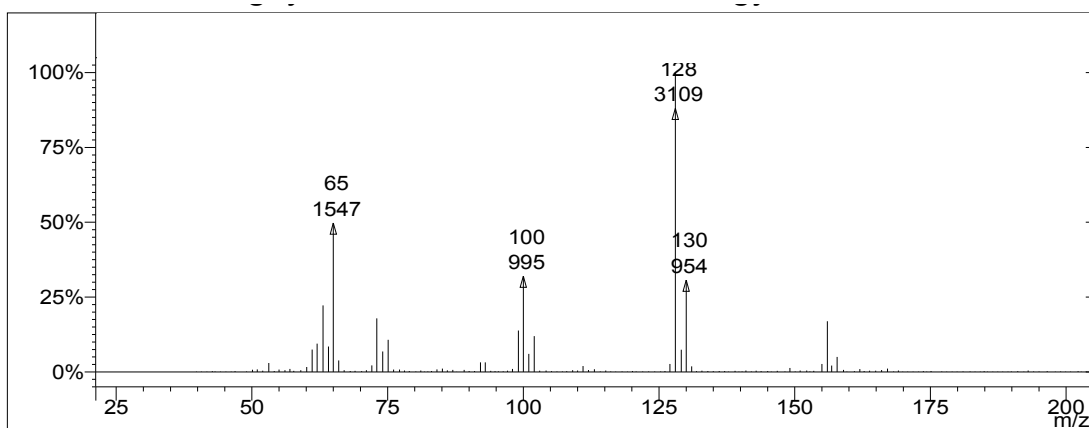


Figure 4.11.a) Mass spectrum of intermediate 1-chloro-4-ethoxy benzene (6.940 min.)

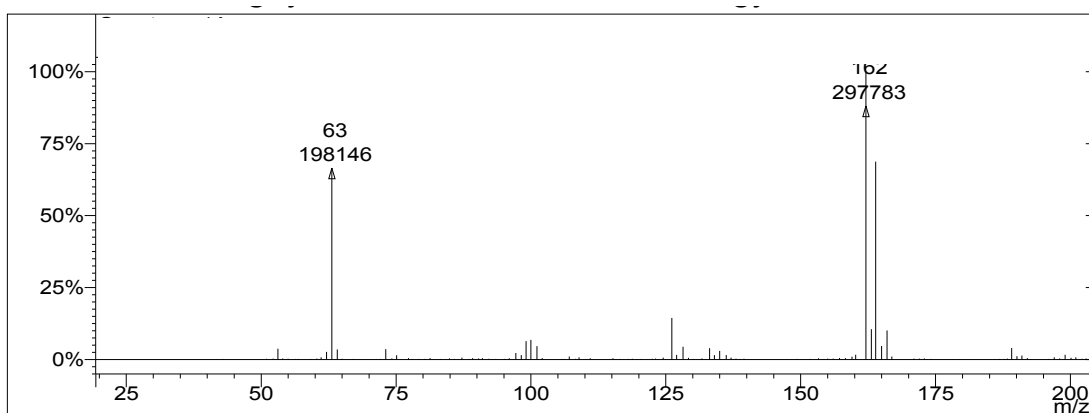


Figure 4.11.b) Mass spectrum of intermediate 2,4-dichlorophenol (7.422 min.)

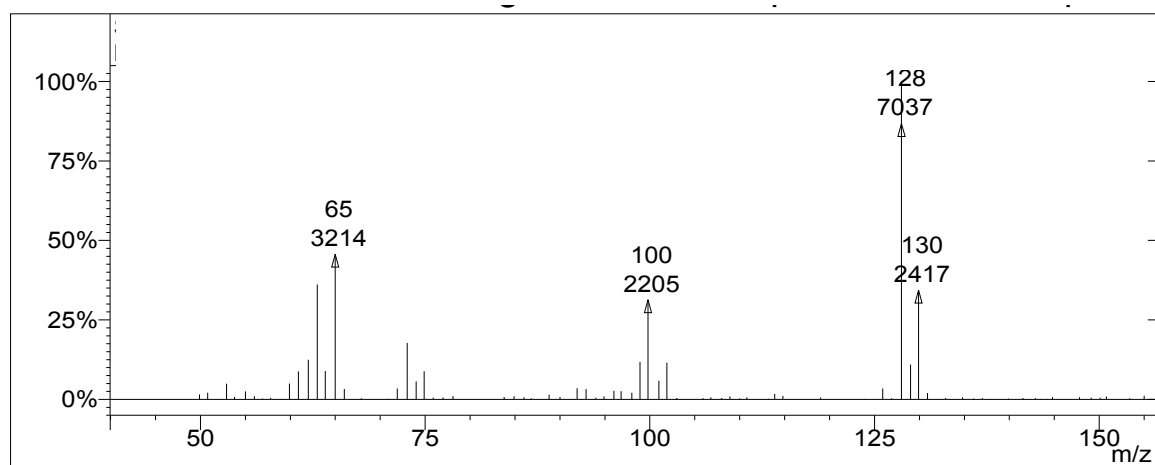


Figure 4.11.c) Mass spectrum of intermediate 4-chlorophenol (7.711 min.)

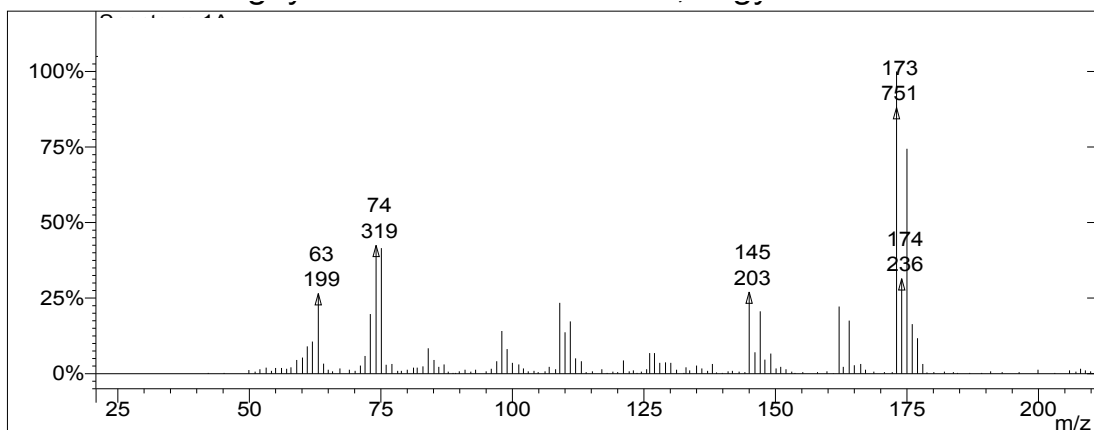


Figure 4.11.d) Mass spectrum of intermediate 2,4-dichlorobenzaldehyde (8.735 min)

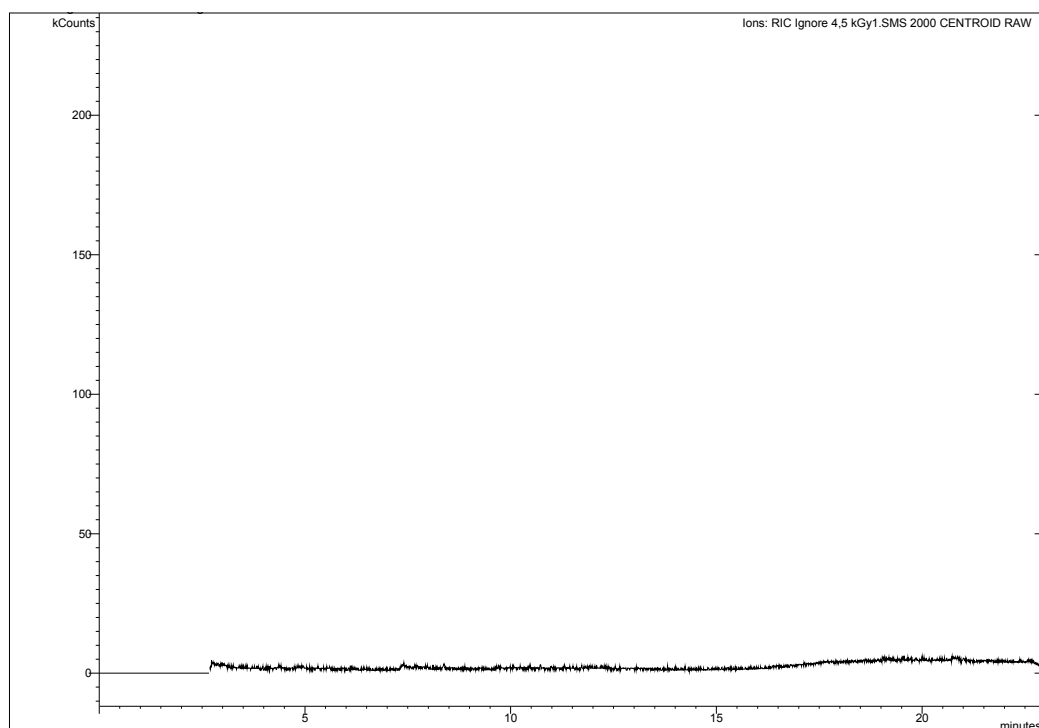


Figure 4.12. GC chromatogram of 4.5 kGy irradiated 2,4-D (50 ppm) samples after eluted from C18 cartridges in acetone.

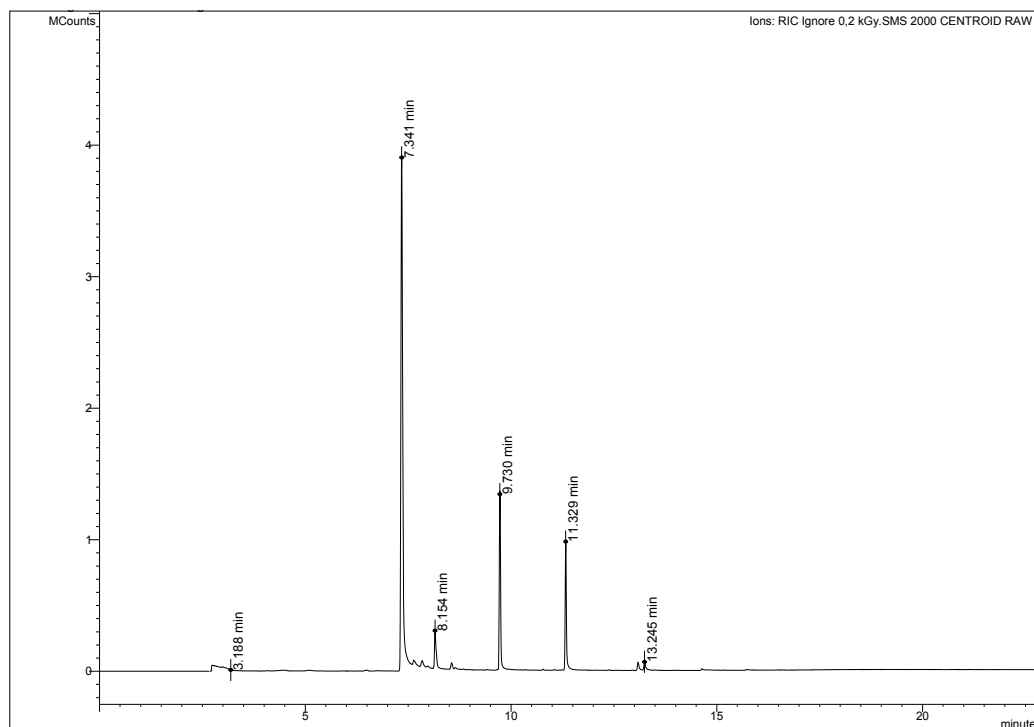


Figure 4.13.a) GC chromatogram of the 0,2 kGy irradiated 2,4-DP (50 ppm) samples after eluted from C18 cartridges in acetone.

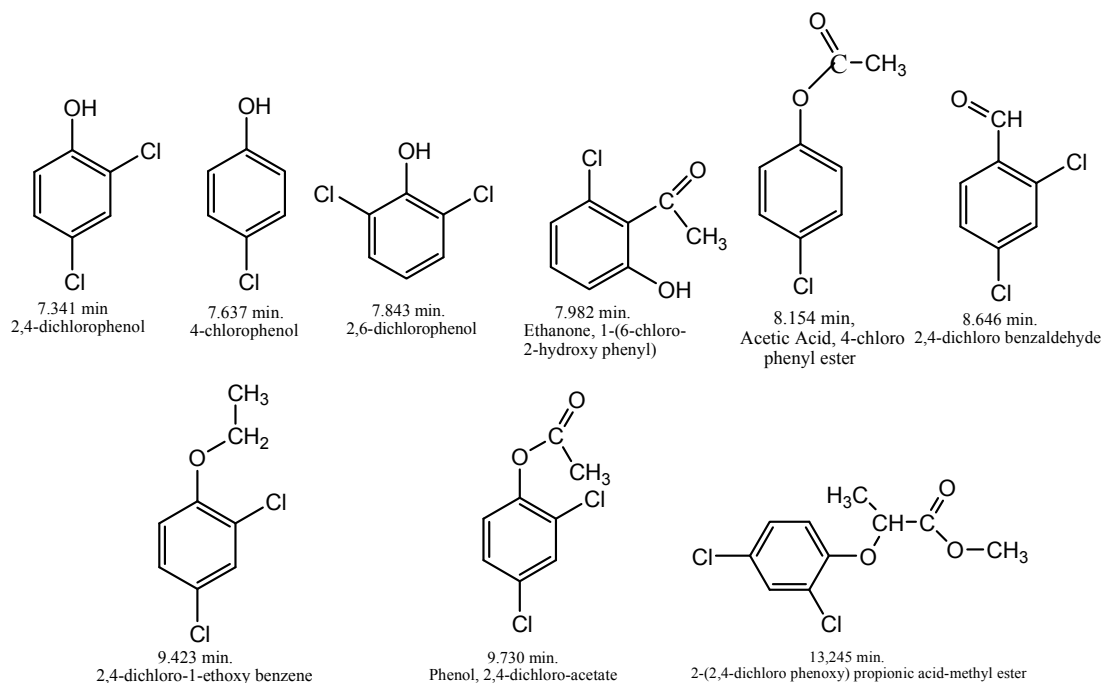


Figure 4.13.b) Possible intermediates for 0.2 kGy irradiated 2,4-DP(50 ppm) samples after eluted from C18 cartridges in acetone.

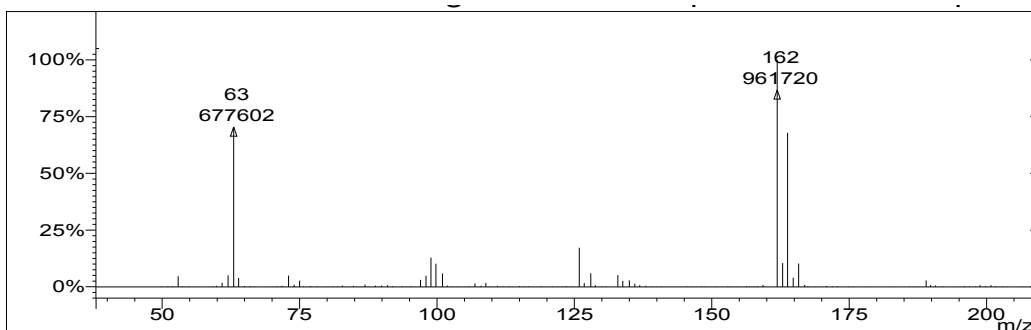


Figure 4.14.a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.341 min.)

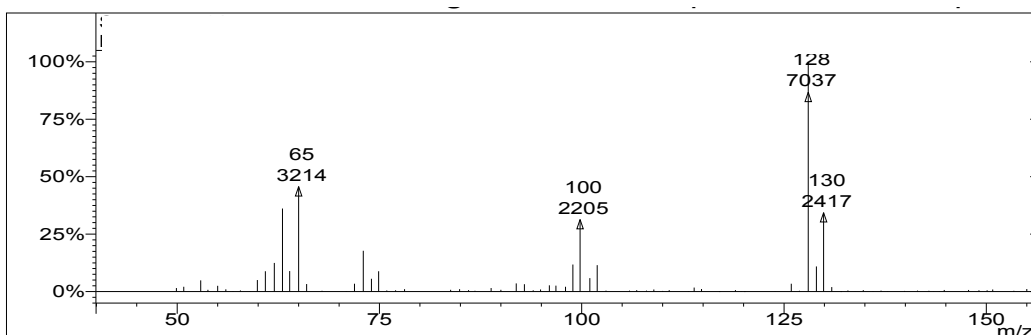


Figure 4.14.b) Mass spectrum of possible intermediate 4-chloro phenol (7.637 min.)

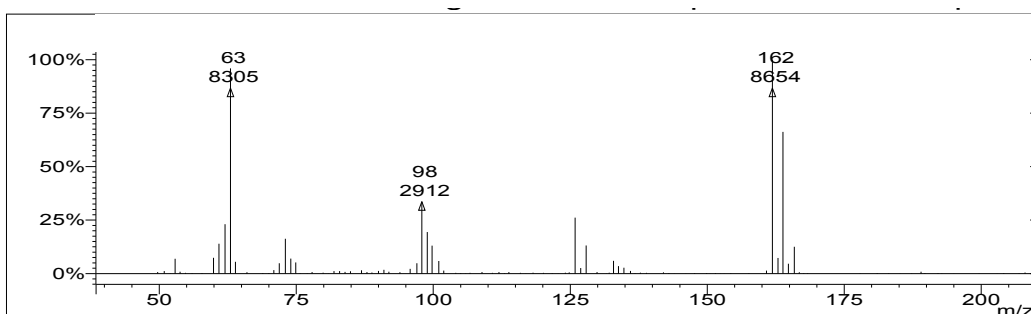


Figure 4.14.c) Mass spectrum of possible intermediate 2,6-dichloro phenol (7.843 min.)

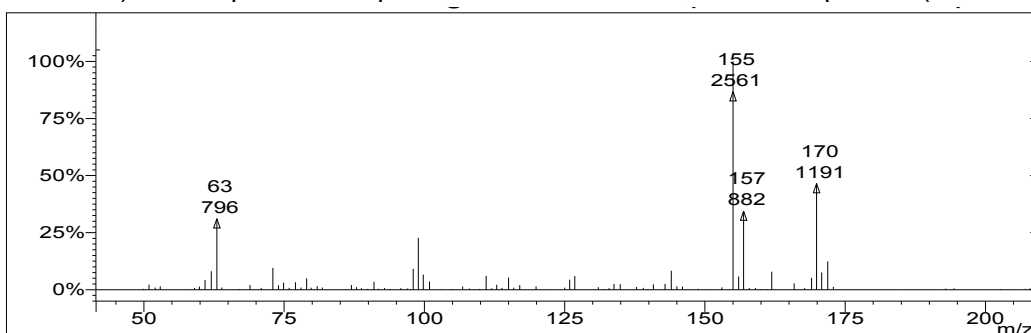


Figure 4.14.d) Mass spectrum of possible intermediate Ethanone 1-(6-chloro-2-hydroxy phenyl) (7.982 min).

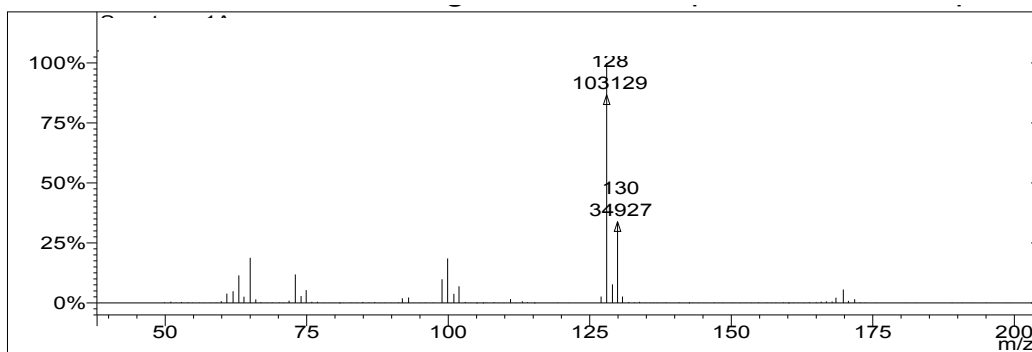


Figure 4.14.e) Mass spectrum of possible intermediate Acetic acid, 4-chloro phenyl ester (8.154 min).

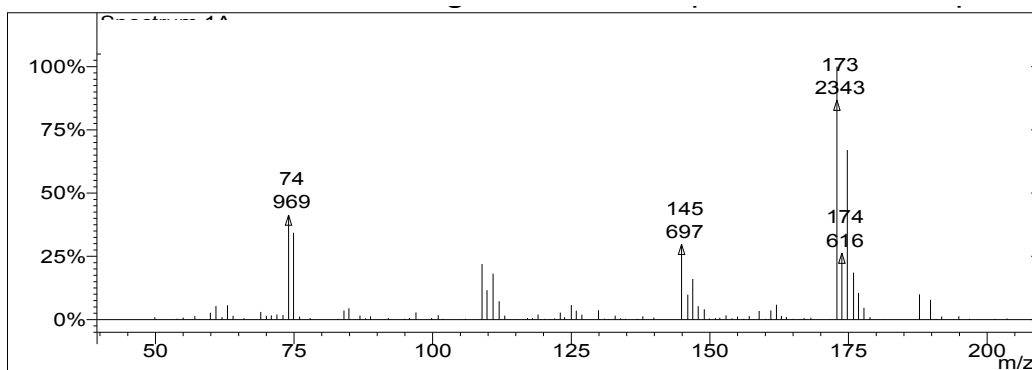


Figure 4.14.f) Mass spectrum of possible intermediate 2,4-dichloro benzaldehyde (8.646 min).

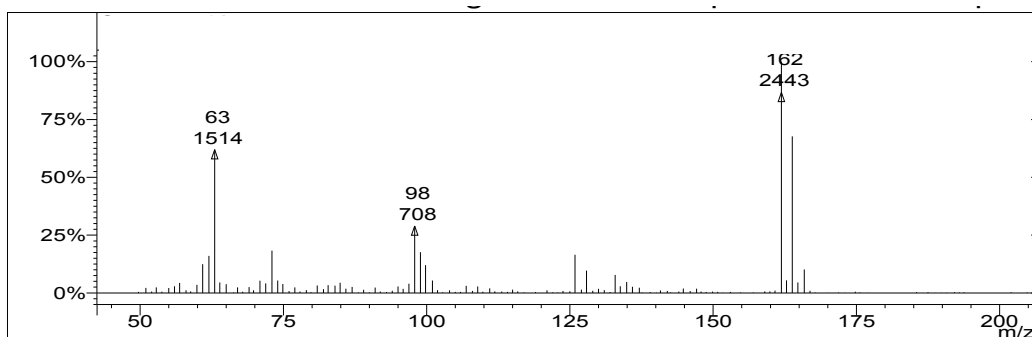


Figure 4.14.g) Mass spectrum of possible intermediate 2,4-dichloro-1-ethoxy-benzene (9.423 min.).

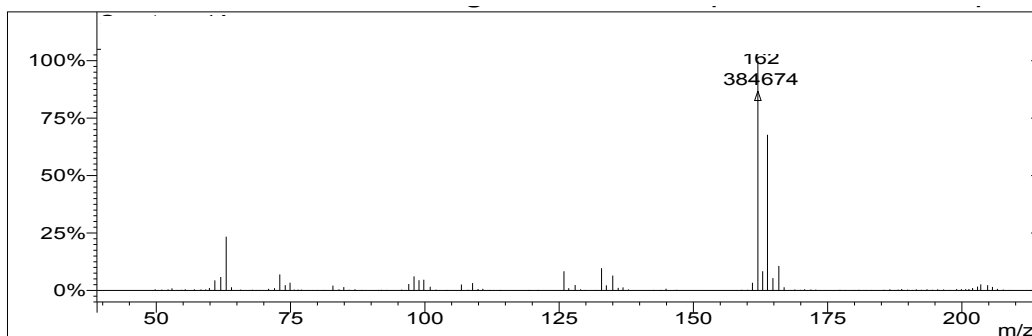


Figure 4.14.h) Mass spectrum of possible intermediate Phenol, 2,4-dichloro acetate (9.730 min.).

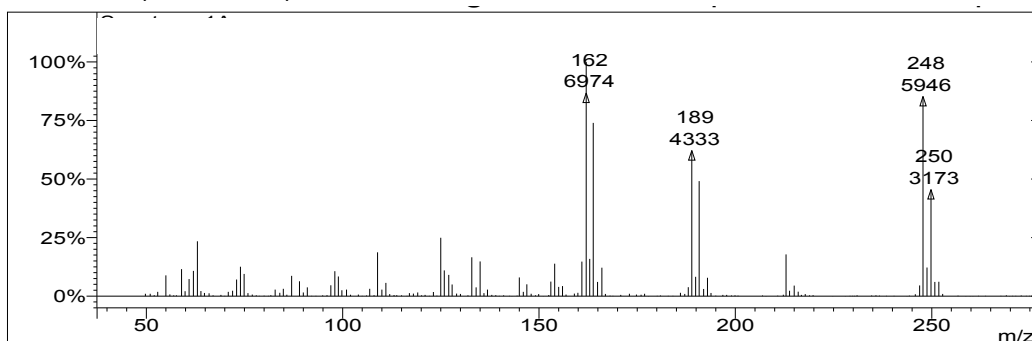


Figure 4.14.i) Mass spectrum of possible intermediate 2-(2,4-dichloro phenoxy) propionic acid methyl ester (13.245 min.).

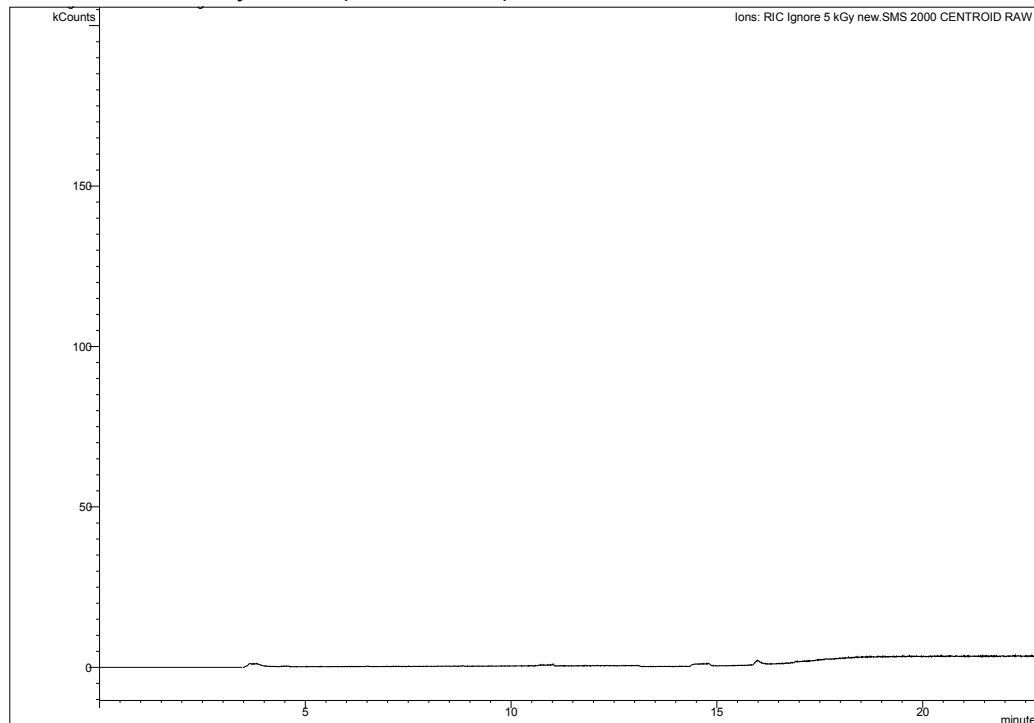


Figure 4.15. GC chromatogram of the 5.0 kGy irradiated 2,4-DP (50 ppm) samples after eluted from C18 cartridges in acetone.

4.2.3. Effect of H₂O₂ on Degradation of 2,4-D and 2,4-DP

The aim of this work was (i) to determine the impact of solvated electrons (e^-_{aq}), superoxide radical anions ($O_2^{\cdot-}$) and hydroxyl radicals ($OH^\cdot$) on the removal of 2,4-D and 2,4-DP in aqueous solution and (ii) to study the changes of some chlorinated phenoxyacetic acid characteristics induced by different ionizing radiation conditions in the absence and in the presence of H₂O₂ and O₃.

Figure 4.16 a and b shows the effect of hydrogen peroxide on radiation induced degradation of 2,4-D. The GC chromatograms, mass spectra of possible intermediates of 0.2 and 3.5 kGy irradiated 2,4-D solutions after solid-phase extraction in acetone and probable degradation products from the irradiated samples are given in Figures 4.17 a, b, 4.18 and 4.19. The amounts of intermediate (2,4-DCP) increased up to definite irradiation doses and decreased with the increasing irradiation dose and finally disappeared almost completely at 4.5 and 3.0 kGy for 2,4-D solutions in the absence and presence of H₂O₂. The amounts of intermediate (4-CP) disappeared completely at 4.5 and 3.5 kGy for 2,4-D solutions in the absence and presence of H₂O₂.

Figure 4.20 a and b shows the effect of hydrogen peroxide on radiation induced degradation of 2,4-DP. The GC chromatograms, mass spectra of possible intermediates of 0.2 and 4.0 kGy irradiated 2,4-DP solutions after solid-phase extraction in acetone and probable degradation products from the irradiated samples are given in Figures 4.21 a, b, 4.22 and 4.23. The amounts of intermediates (2,4-DCP and 4-CP) increased up to definite irradiation doses and decreased with the increasing irradiation dose and disappeared almost completely at 5.0 and 4.0 kGy for 2,4-DP solutions in the absence and presence of H₂O₂.

The effect of the hydrogen peroxide was examined in degradation of 2,4-D and 2,4-DP with the irradiation doses up to 3.0 and 3.5 kGy. The H₂O₂ concentration was set at 1.2 mM. The H₂O₂ was added to level of 1.2 mM in each solution irradiated with

the different irradiation doses. Figures 4.24-4.29 show the effect of H_2O_2 on 2,4-D and 2,4-DP degradations, as well as changes of several intermediates of degradation of target herbicide. As shown by obtained data, almost at each absorbed dose the addition of hydrogen peroxide affected positively the degradation process. The complete degradations of 2,4-D and 2,4-DP were obtained at 3.0 and 3.5 kGy in the absence of H_2O_2 and 2.0 and 2.5 kGy irradiation doses were sufficient for complete degradations of 2,4-D and 2,4-DP in the presence of H_2O_2 . Substantial positive effect of addition of H_2O_2 was observed in case of degradation of 2,4-dichlorophenol (2,4-DCP) and 4-chlorophenol (4-CP).

2,4-D (50 ppm) and 2,4-DP (50 ppm) are weak organic acids with a pK_a values of 2.80 and 2.95. Complete degradation was observed at 3.0 kGy and 2.0 kGy in the absence and presence of 1.20 mM H_2O_2 for 2,4-D. The initial pH values of the unirradiated solutions for 50 ppm 2,4-D and 2,4-DP are 3.90 and 4.16 and in the presence of 1.20 mM H_2O_2 , pH values of the 2,4-D and 2,4-DP solutions are 3.81 and 4.05. pH of the solution is not adjusted so these pH values are due to pure 50 ppm 2,4-D and 2,4-DP solutions. Due to the acidic behaviour of 2,4-D and 2,4-DP, solutions were irradiated in acidic media.

The degradation pathway and efficiency of degradation is strongly depended on the radiolysis products of water which reacts with 2,4-D and 2,4-DP and have a different ratio at different pH values. 2,4-D and 2,4-DP are found as in acidic form and ionized form in aqueous solutions, but the efficiency of decomposition is affected mostly by a kind of reactive species present, and not by degree of protonation (Bojanowska-Czajka, 2007).

In acidic conditions, $\text{H}^\cdot$ is predominant than $\text{OH}^\cdot$ and e^-_{aq} , since e^-_{aq} is converted to $\text{H}^\cdot$ when reacts with H^+ (Getoff, 1985). Some researchers observed for 4-chloro-2-methyl phenoxy acetic acid (MCPA), a minor effect of pH of irradiated solutions on the yield of MCPA decomposition (Bojanowska-Czajka, 2007). In the presence of oxygen, all reducing species produced during irradiation as a result of the radiolysis of water

such as e_{aq}^- and $H^\cdot$ are scavenged to form $O_2^{\cdot-}$ and $HO_2^\cdot$ (Equation 2.12 and 2.7) (Buxton et al., 1988; Von Sonntag, 1997)

They are not very reactive toward most of the organic compounds, except quinones. The main species that plays an important role in the radiolytic degradation of phenoxy herbicides in solution is the $OH^\cdot$ radical. In investigations of radiolytic decomposition of several different organic pollutants based on reaction with hydroxyl radical, it has been shown that in some cases the effectiveness of decomposition can be improved by addition of hydrogen peroxide to irradiated solutions (Bojanowska-Czajka, 2006).

As mentioned above, in the presence of 1.20 mM H_2O_2 , the efficiency of degradation is more favorable since H_2O_2 decomposes to give $OH^\cdot$ radicals which are most efficient for degradation of 2,4-D. Addition of 1.20 mM hydrogen peroxide into 50 ppm aqueous solution of 2,4-D causes to the degradation of 0.8 ppm 2,4-D (1.6%). Enhancement of effectiveness of radical decomposition of organic compounds with hydroxyl radicals is possible in the presence of ozone or hydrogen peroxide (Bojanowska-Czajka, 2006).

The hydrogen peroxide reacts with $H^\cdot$ ($k_{(20^\circ C)} = 2.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$) and e_{aq}^- ($k_{(20^\circ C)} = 1.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) as in equations 2.22 and 2.23 (Zona, 2003; Jankowska, 2004):

In the presence of excess of hydrogen peroxide in solution it can scavenge the hydroxyl radicals with rate constant $k_{(20^\circ C)} = 3.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$), according to reactions in equations 2.24-2.26.

The estimation of optimum amount of hydrogen peroxide needed in order to enhance given process is difficult, as it is involved in numerous reactions with radicals formed during radiolytic degradation of target compounds and secondary products (Bojanowska-Czajka, 2006). The degradations of 2,4-D and 2,4-DP and their intermediates were observed at higher irradiation doses at lower H_2O_2 concentrations.

Because of the reaction shown in equation 2.15, the higher H_2O_2 concentrations were not used.

G_i values of 2,4-D solutions (50 ppm) in the absence and presence of 1.20 mM H_2O_2 were calculated as 1.42 and 2.72, respectively. (G value is the number of decomposed molecules per 100 eV absorbed energy.) G_i value is the initial G value. Getoff concluded that the higher starting solute concentration, the higher G_i value (Getoff, 1985). It is observed that the degradation of 2,4-D is more efficient in 1.20 mM added H_2O_2 solution. The initial degradation rate of 2,4-D is more than at higher irradiation doses. This may be due to the chloride ions that are cleaved from 2,4-D. At higher doses, more chloride ions are present in solution and chloride ions are efficient scavenger of hydroxyl radicals. (Yu and Barker, 2003).

Also, another affect for this different degradation rate may be at higher irradiation doses, amount of dissolved oxygen decreases. Dissolved oxygen accelerates the formation of polyhydroxybenzenes from phenol and formation of aliphatic acids from polyhydroxybenzenes (Getoff, 1986). The other reason is mineralization, formation of carbonate and bicarbonate causes decrease in effective concentration of hydroxyl radicals that facilitates the decomposition of 2,4-D. (Buxton et. al., 1988).

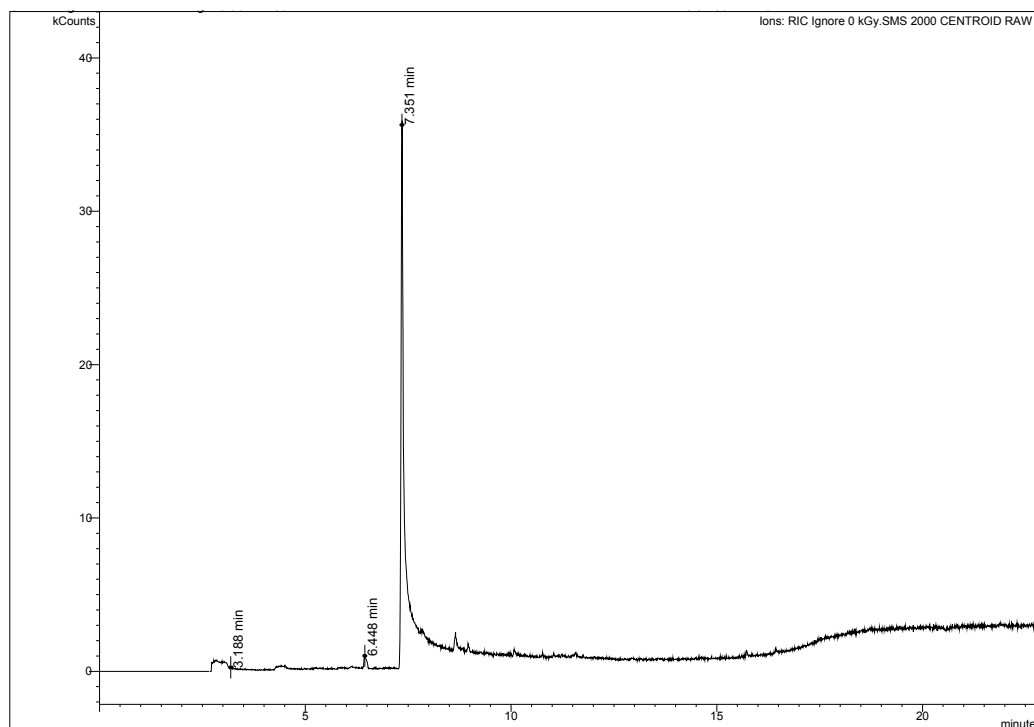


Figure 4.16.a) GC chromatogram of the unirradiated 2,4-D (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

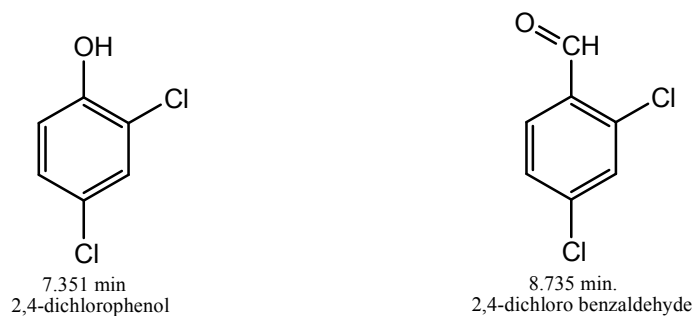


Figure 4.16.b) Possible intermediates for the unirradiated 2,4-D (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

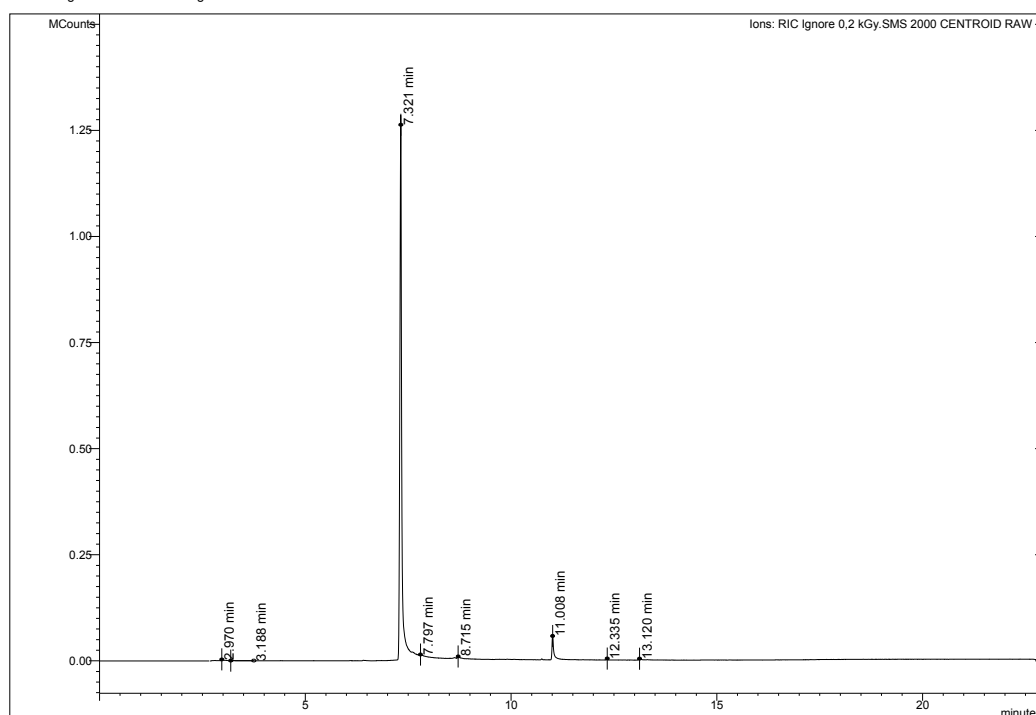


Figure 4.17.a) GC chromatogram of 0.2 kGy irradiated 2,4-D (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

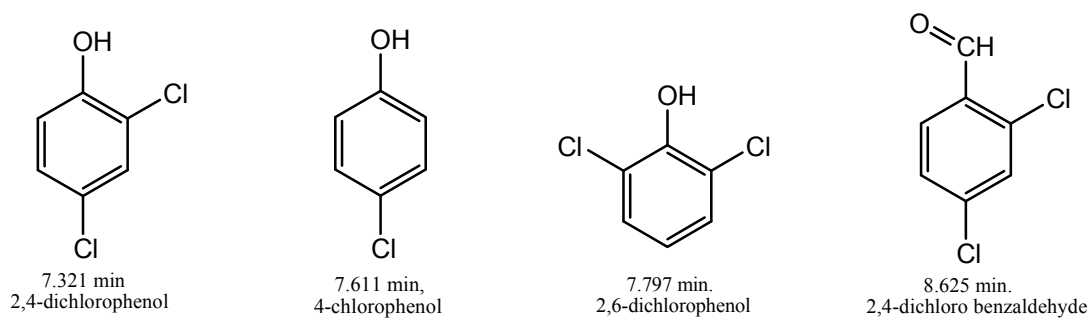


Figure 4.17.b) Possible intermediates for 0.2 kGy irradiated 2,4-D (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

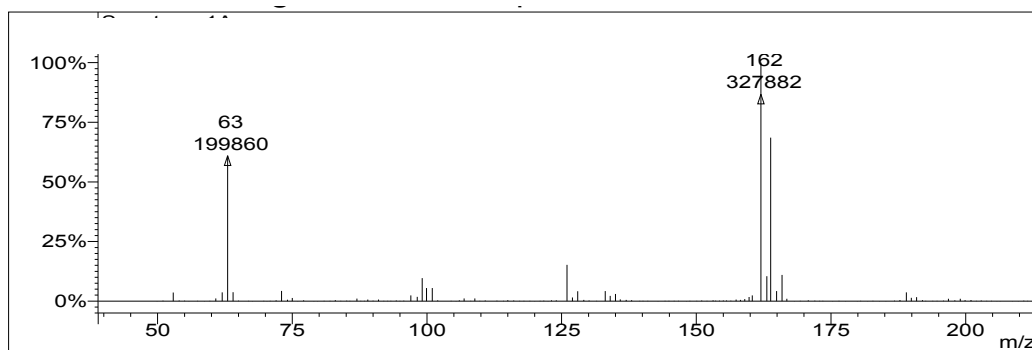


Figure 4.18.-a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.321 min.)

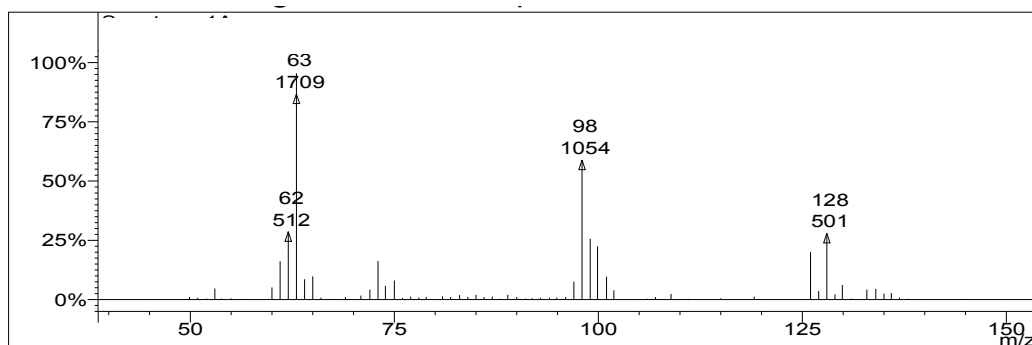


Figure 4.18.-b) Mass spectrum of possible intermediate 4-chloro phenol. (7.611 min.)

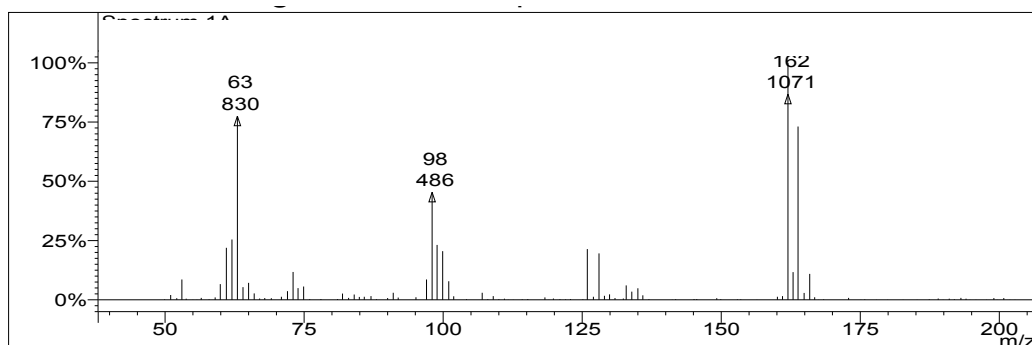


Figure.4.18.-c) Mass spectrum of possible intermediate 2,6- dichloro phenol (7.797 min.)

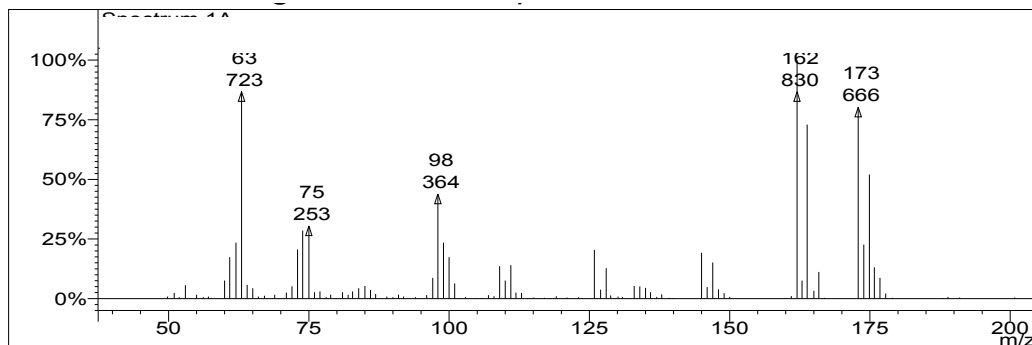


Figure 4.18.d) Mass spectrum of possible intermediate 2,4-dichloro benzaldehyde (8.625 min.)

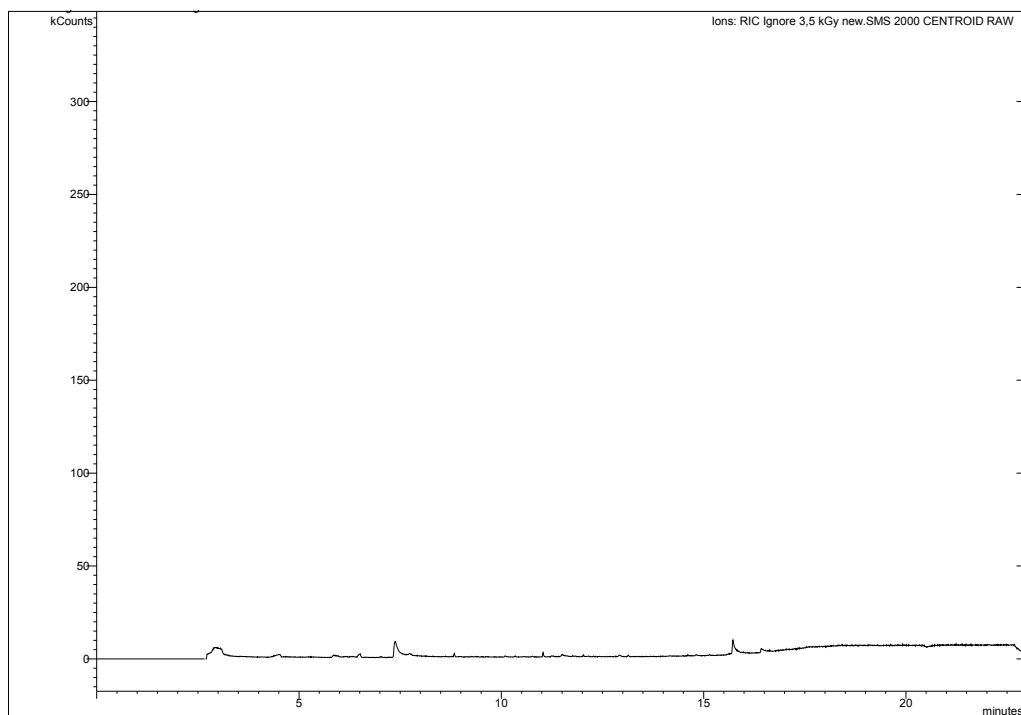


Figure 4.19. GC chromatogram of 3,5 kGy irradiated 2,4-D (50 ppm) in the presence of hydrogen peroxide (1.20 mM) samples after eluted from C18 cartridges in acetone.

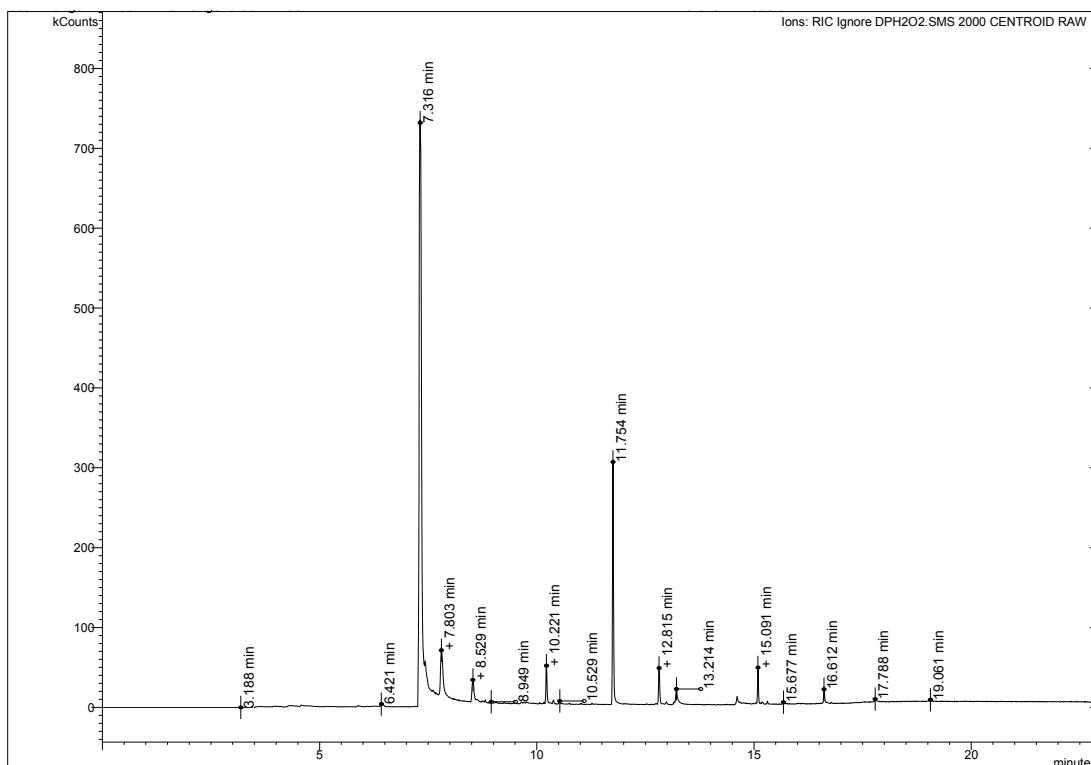


Figure 4.20.a) GC chromatogram of the unirradiated 2,4-DP (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

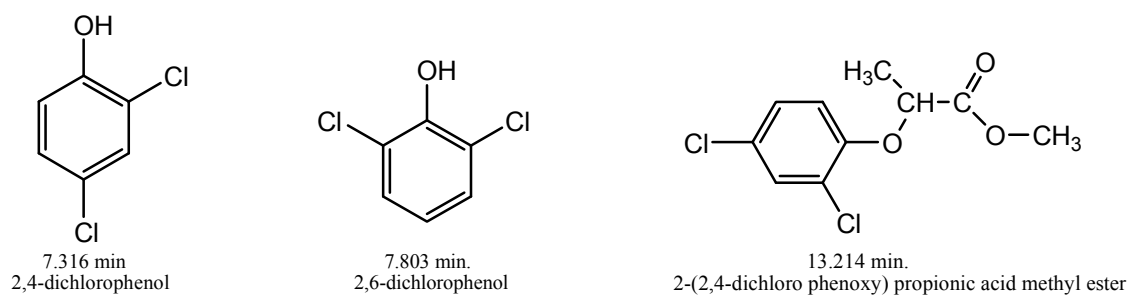


Figure 4.20.b) Possible intermediates for the unirradiated 2,4-DP (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

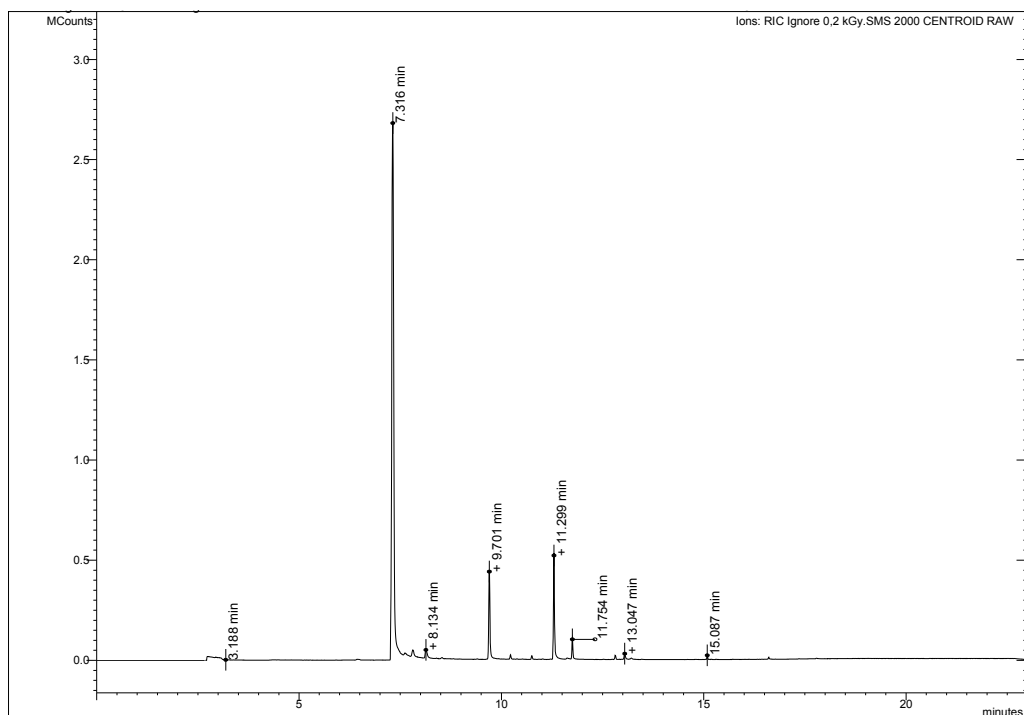


Figure 4.21.a) GC chromatogram of the 0.2 kGy irradiated 2,4-DP (50 ppm) samples in the presence of hydrogen peroxide (1.20mM) after eluted from C18 cartridges in acetone.

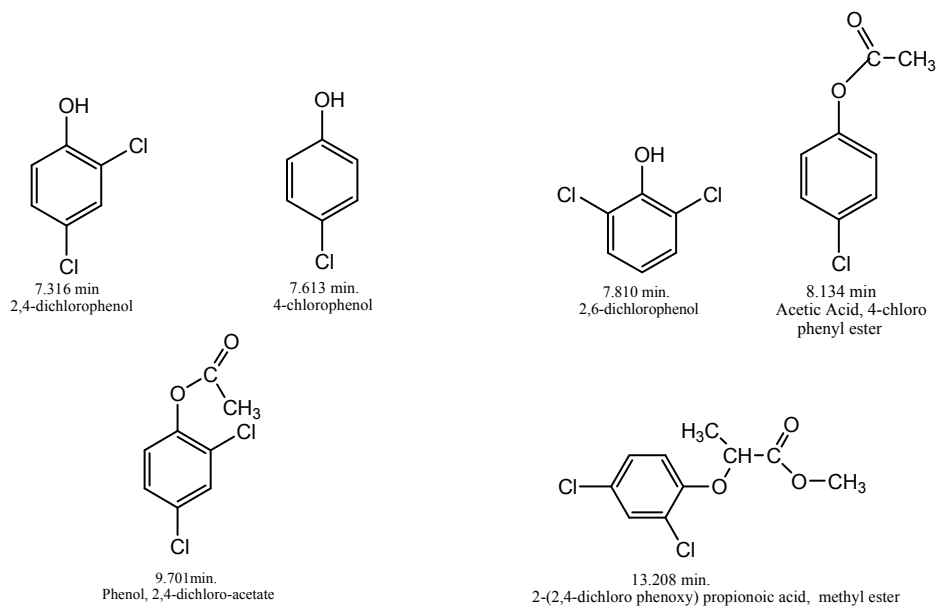


Figure 4.21.b) Possible intermediates for the 0.2 kGy irradiated 2,4-DP (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

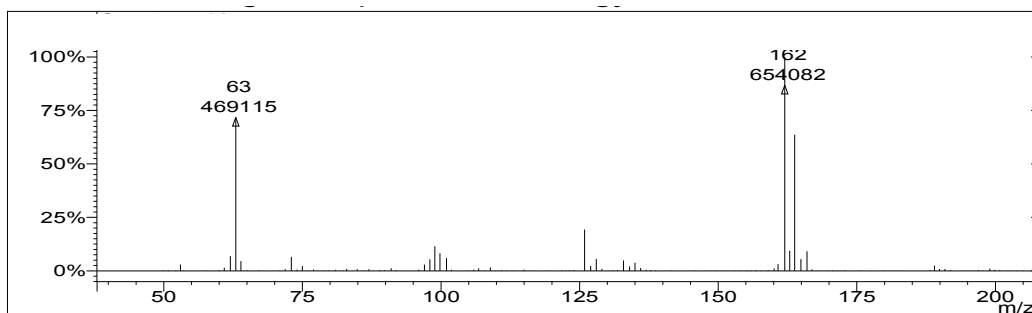


Figure 4.22.a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.316 min.).

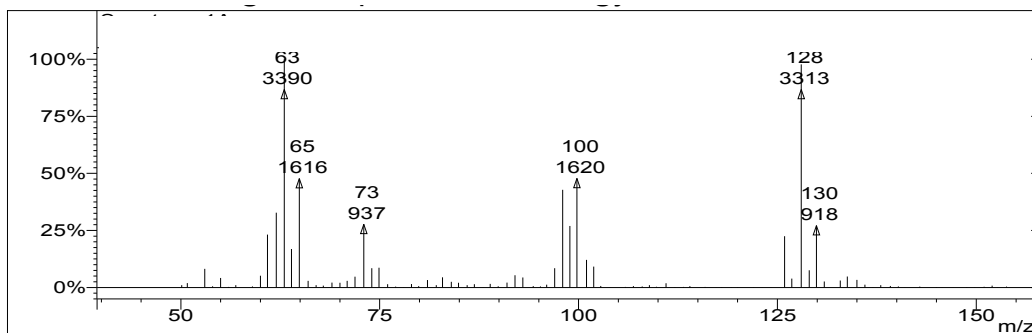


Figure 4.22.b) Mass spectrum of possible intermediate 4-chloro phenol (7.613 min.).

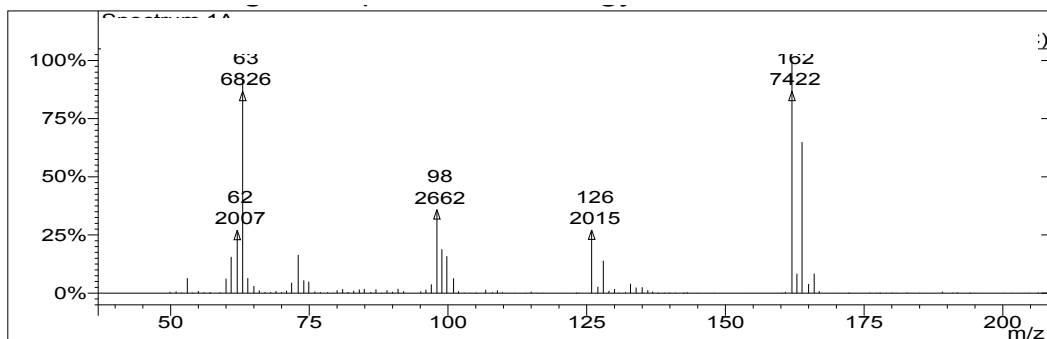


Figure 4.22.c) Mass spectrum of possible intermediate 2,6-dichloro phenol (7.810 min.).

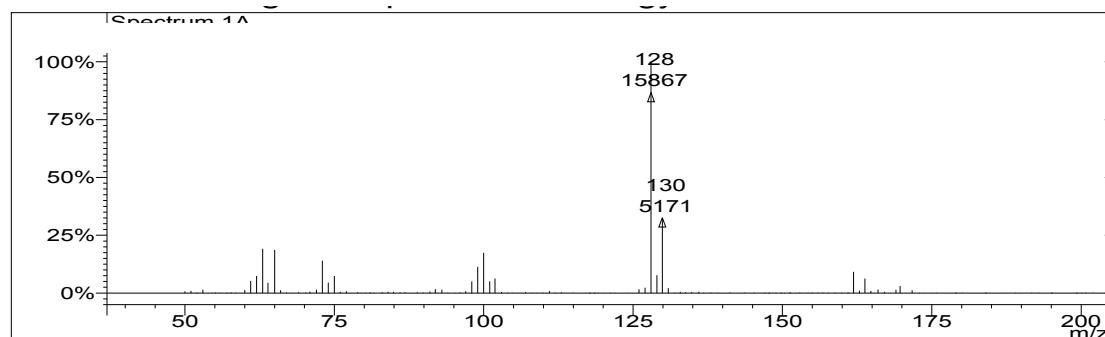


Figure 4.22.d) Mass spectrum of possible intermediate Acetic acid,4-chloro phenylester (8.134 min.).

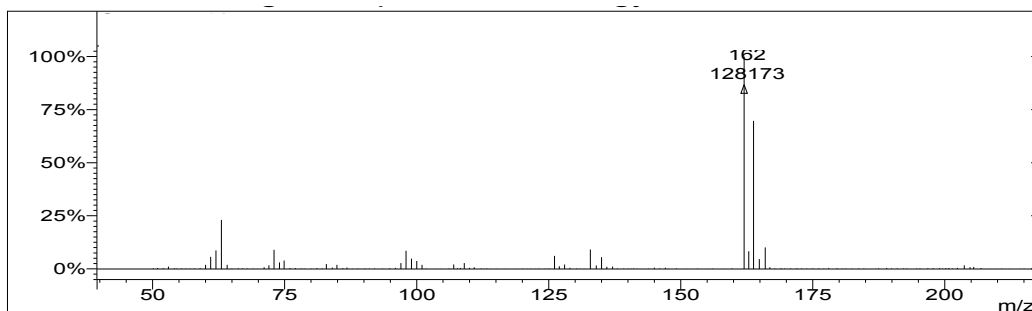


Figure 4.22.e) Mass spectrum of possible intermediate Phenol, 2,4-dichloro acetate (9.701 min.).

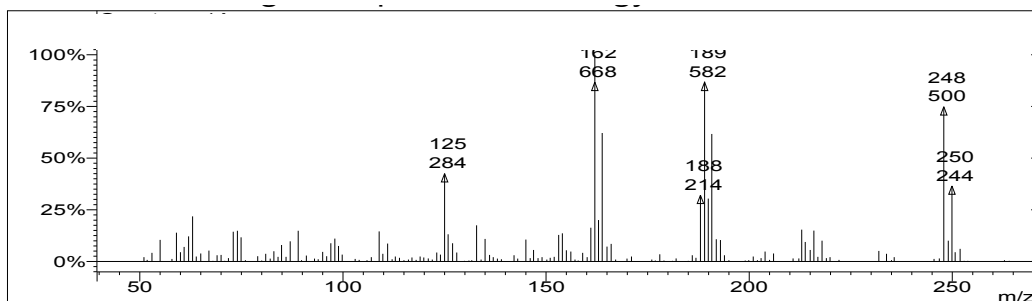


Figure 4.22.f) Mass spectrum of possible intermediate, 2-(2,4-dichloro phenoxy) propionic acid methyl ester (13.245 min.).

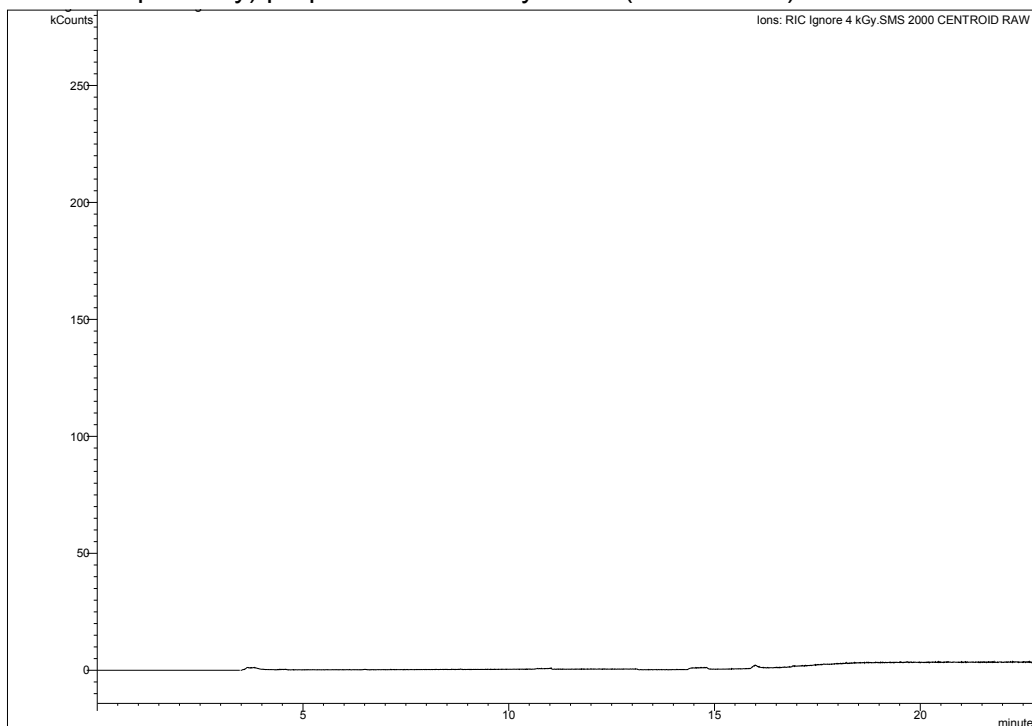


Figure 4.23. GC chromatogram of the 4.0 kGy irradiated 2,4-DP (50 ppm) samples in the presence of hydrogen peroxide (1.20 mM) after eluted from C18 cartridges in acetone.

4.2.4. Analysis of Residual 2,4-D, 2,4-DP and Intermediate Products

The analysis of herbicide residues in water is typically done by gas chromatography (Heberer et al., 1994). Methods employing more recent techniques have been developed. Gas chromatography is very useful for simultaneous determination of several pesticides at trace level, and in general higher sensitivity can be obtained (Juhler, 2001).

2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP) are a common herbicides widely used in agriculture, on pastures and lawns, in parks and for protection of rail roads. In living organisms, as well as in natural environment, as result of metabolic processes of 2,4-D and 2,4-DP, various toxic and cancerogenic chloroorganic compounds are formed, mostly 2,4-dichloro phenol (2,4-DCP). One of severe environmental problems is a storage of unused and unwanted expired pesticides including large amounts of 2,4-D and 2,4-DP. They are stored in concrete tombs and their leakage to soil and underground waters has been already reported because of aging and gradual destruction of all protective materials used.

The aim of this work was to study the effect of various experimental factors on effectiveness of radiolytic degradation of 2,4-D and 2,4-DP. The efficiencies of degradation for 2,4-D and 2,4-DP can be substantially enhanced in the presence of other sources of hydroxyl radical.

2,4-D was taken as an example herbicide. The GC chromatograms obtained after irradiation of 2,4-D solution with different irradiation doses are shown in Figure 4.10 a,b and 4.12. At dose 0.2 kGy, besides 2,4-DCP-the main compound of degradation, small amounts of 4-CP were also detected. About 80% of the initial amount of herbicide was decomposed at doses up to 1,2 kGy and its total removal was obtained with 3.0 kGy in the absence of H_2O_2 . The GC chromatograms obtained after irradiation of 2,4-DP solution with different applied doses are shown in Figure 4.13 a,b and 4.15. At dose 0.2 kGy, 2,4-DCP is the main compound of degradation but small

amounts of intermediates in very low concentrations were detected. All amount of 2,4-DP herbicide was decomposed at 3.5 kGy in the absence of H_2O_2 .

In these conditions, 2,4-DCP was the main product of irradiation. Among the chlorophenols 2,4-dichlorophenol (2,4-DCP) and also 4-chlorophenol (4-CP) are especially toxic and resistant towards biodegradation (Ikehata and Nicell, 2000; Drzewicz et al., 1999; Trojanowicz et al., 2000). The obtained results showed that with the increasing irradiation dose the degradation of chlorophenoxy acid proceeds during radiolytic degradation of 2,4-DCP (Getoff, 1996).

Figure 4.24 shows the effect of hydrogen peroxide on radiation-induced degradation of 2,4-D. 2,4-D can also be degraded in the presence of 1.20 mM hydrogen peroxide before irradiation, the amount of residual herbicide at 0 kGy for this condition is 49.2 ppm. Also, at 2.0 kGy, no residual herbicide is observed in H_2O_2 medium although this condition is satisfied at 3 kGy in the absence of H_2O_2 . Addition of hydrogen peroxide into the unirradiated 50 ppm 2,4-D solution causes the formation of 2,4-DCP as a phenolic intermediate. G_i values for degradation of 2,4-D in the absence and presence of 1.20 mM H_2O_2 are 1.42 and 2.72, respectively.

The results for 2,4-DP are presented in Figure 4.25. 2,4-DP can also be degraded in the presence of 1.20 mM hydrogen peroxide before irradiation, the amount of residual herbicide at 0 kGy for this condition is 49.4 ppm. Also, at 2.5 kGy, no residual herbicide is observed in H_2O_2 medium although this condition is satisfied at 3.5 kGy in the absence of H_2O_2 . Addition of hydrogen peroxide into the unirradiated 50 ppm 2,4-DP solution causes also the formation of 2,4-DCP as a major phenolic intermediate. G_i values for degradation of 2,4-DP in the absence of 1.20 mM H_2O_2 is 1.20 and 2.42, respectively.

All phenolic intermediates from 2,4-D degraded during irradiation at 4.5 kGy in the absence of H_2O_2 . Figures 4.26 and 4.27 show the change in the amount of 2,4-DCP with the irradiation dose. Up to 0.6 kGy, the amount of 2,4-DCP from 2,4-D increases

but at further doses, it degrades and at 4,5 kGy all of 2,4-DCP degraded in the absence of H_2O_2 . When the amounts of 2,4-DCP formed from 2,4-D and 2,4-DP compared we can say that the amount of 2,4-DCP which form from 2,4-DP is higher than those of 2,4-D herbicide. Figures 4.28 and 4.29 show the change in the amount of 4-CP with the irradiation dose. Amount of 4-CP also increases up to 1,6 kGy and at 4,5 kGy no 4-CP observed in the absence of H_2O_2 . Some intermediates may be more toxic than 2,4-D and 2,4-DP but at further irradiation doses, they all decomposed (Trojanowicz, et. al., 2002; Zona et. al., 2003). The amount of 4-CP from 2,4-DP is also higher than those of 2,4-D herbicides. 4-CP is possible intermediate of 2,4-DCP. It is expected the higher amount of 4-CP from 2,4-DP rather than those of from 2,4-D.

The more heavily used herbicides in Turkey and in the world are 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenoxypropionic acid (2,4-DP). These herbicides belong to a larger class of herbicides known as the chlorinated phenoxy herbicides, which have provided control of broad leaf weeds in both agricultural fields and non-cropland grasses for the past 50 years. The major degradation products of 2,4-D and 2,4-DP are 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP). The major breakdown product, 2,4-DCP, is likely a more toxic compound and often more resistant to oxidative degradation (Peller, 2004).

These dependences on 2,4-D and other herbicides by the agricultural industry will not decline, guaranteeing the continued application of these compounds in large amounts (millions of pounds per year) (Aspelin, 1997). This massive reliance on herbicides has led to measurable herbicide levels in natural bodies of water, which supply the human population with fresh drinking water (Hapeman, 2002; Goolsby, 1997; Schottler, 1994). An additional concern is the undesirable and often more toxic and/or persistent intermediates formed in the natural degradation pathways of herbicides and pesticides that can accumulate in the ecosystem in even higher concentrations (Kalkoff, 1998; Zimmerman, 2002; Kolpin, 2001; Kolpin, 1996; Barbash, 1999). The half-life of 2,4-D can be as short as 4-10 days; however, 2,4-D and/or its natural degradation products may persist for several weeks.

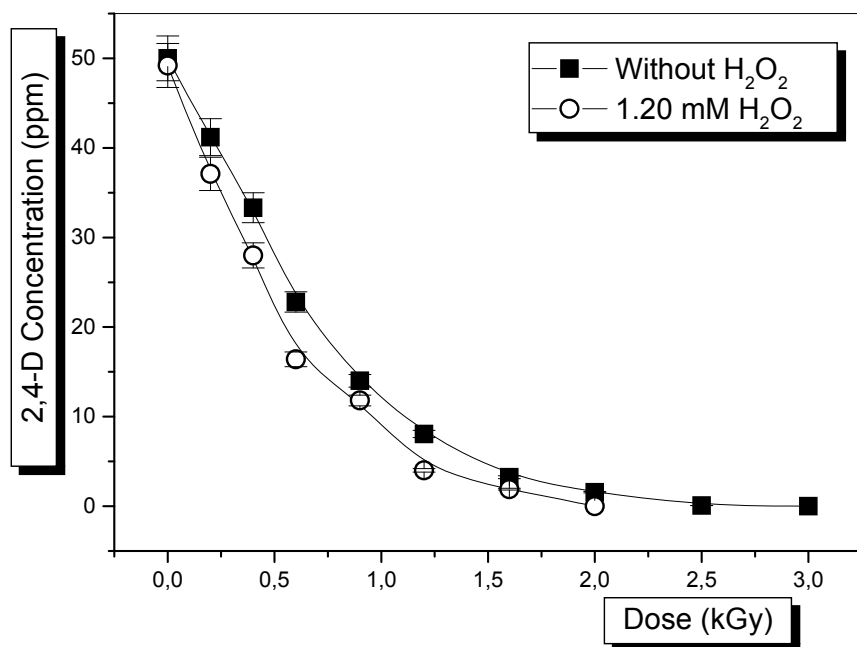


Figure 4.24. The effect of hydrogen peroxide (1.20mM) on radiation-induced degradation of 2,4-D (50 ppm).

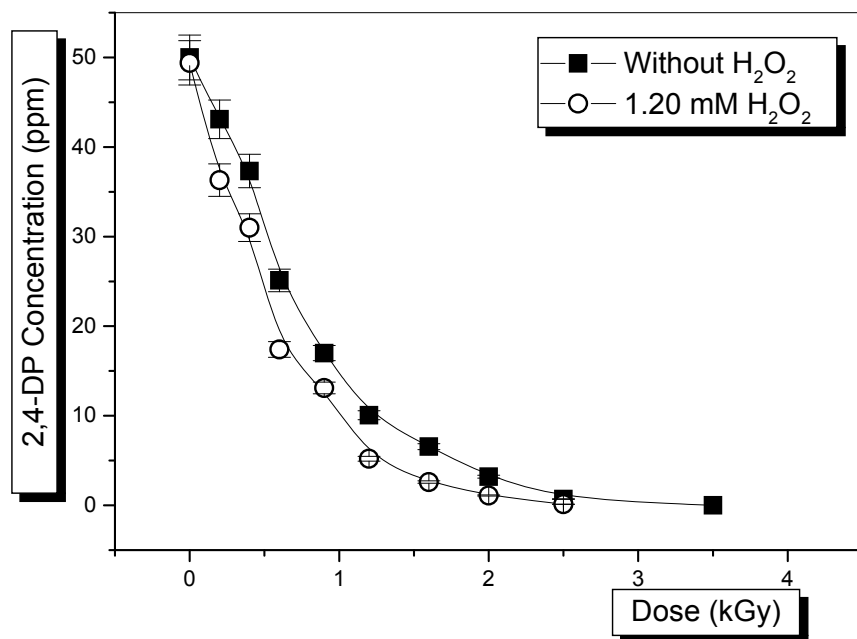


Figure 4.25. Effect of hydrogen peroxide (1.20 mM) on radiation-induced degradation of 2,4-DP (50 ppm).

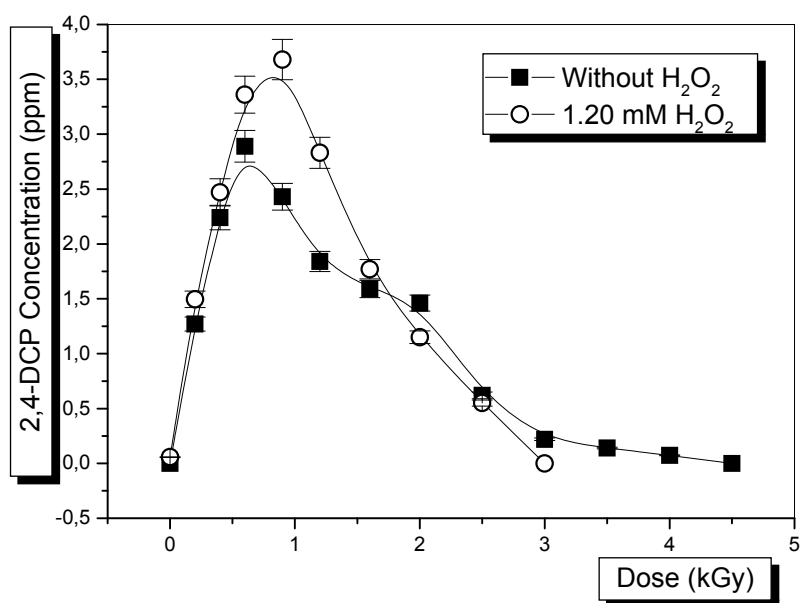


Figure 4.26. Change in the amount of intermediate 2,4-dichlorophenol with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

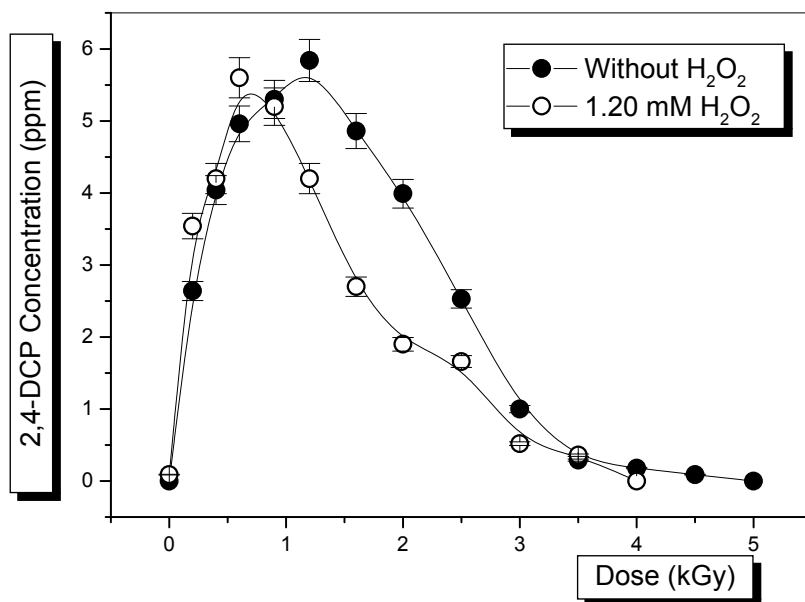


Figure 4.27. Change in the amount of intermediate 2,4-dichlorophenol with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

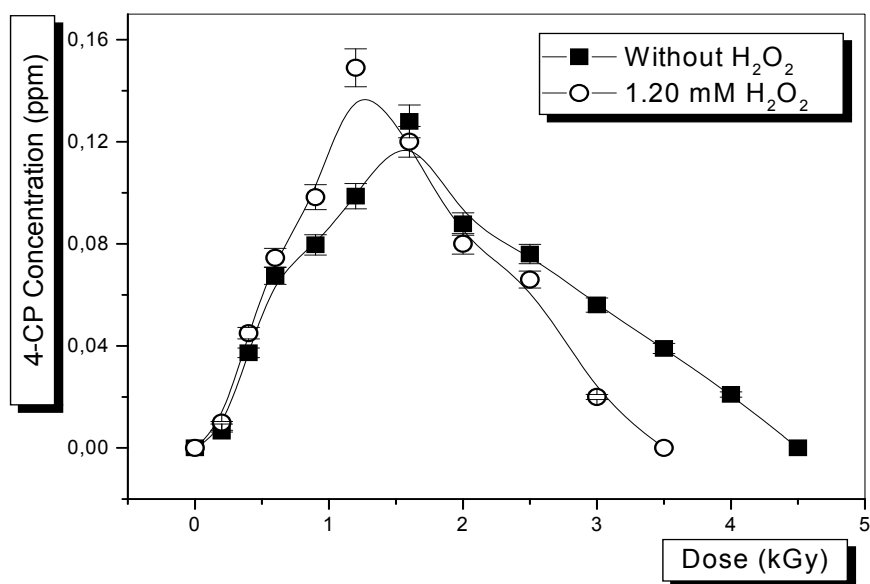


Figure 4.28. Change in the amount of intermediate 4-chlorophenol with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

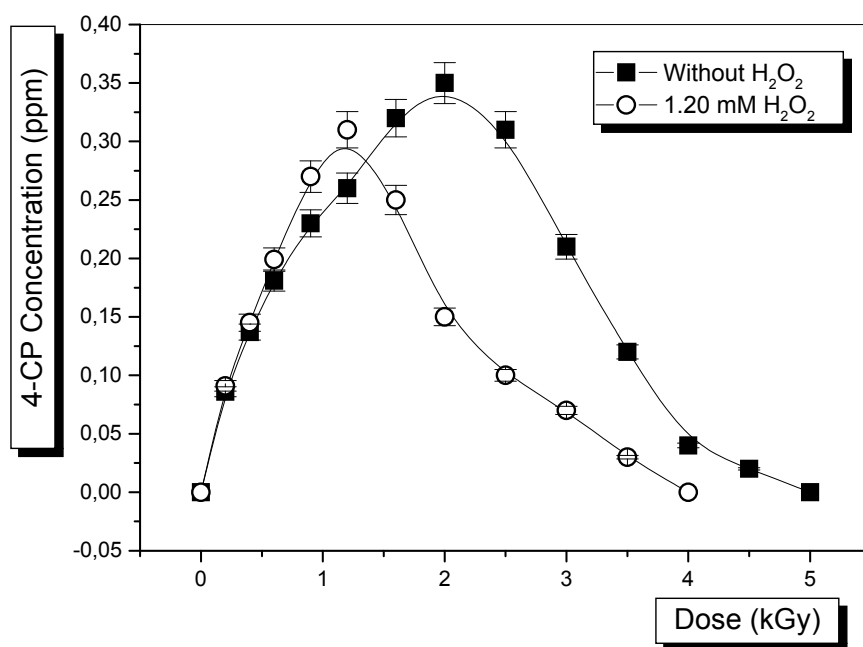


Figure 4.29. Change in the amount of intermediate 4-chlorophenol with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

2,4-Dichlorophenol (2,4-DCP) is a toxic compound and the main intermediate in the 2,4-D degradation pathway (Garcia-Valcarcel, 1999). The O-H bond present on the 2,4-DCP molecule is slightly acidic with a pKa value of 7.89. The oxidation potential of the 2,4-DCP differs from that of the herbicide 2,4-D and from other chlorinated compounds (Clark, 1999; Nikolaou, et.al., 2004).

The breakdown of 2,4-D represents a pathway where a toxic intermediate, 2,4-dichlorophenol (2,4-DCP), is formed in the hydrolysis of the herbicide 2,4-D. 2,4-DCP is also a problematic industrial contaminant because it is formed from phenolic compounds when water undergoes chlorination treatment. The monitoring of herbicides/pesticides in natural bodies of water obviously requires an awareness of the natural breakdown products and toxicities associated with the degradation pathways (Kolpin, 2001; Panshin, 2000).

The formation of 2,4-DCP is due to the attack of hydroxyl radicals on 2,4-D. In the presence of 1.20 mM H_2O_2 , the attack of hydroxyl radicals on 2,4-D is more effective and the produced 2,4-DCP amount is higher as expected. An addition of 1.20 mM H_2O_2 into 50 ppm 2,4-D and 2,4-DP solutions caused the formation of 0.057 and 0.090 ppm 2,4-DCP. The reaction of hydroxyl radical with 2,4-D is not pH dependent. In both protonated and deprotonated forms, addition of the $\text{OH}^\cdot$ to the aromatic ring is the only reaction that takes place, forming the hydroxycyclohexadienyl radical of 2,4-D (Peller, 2005).

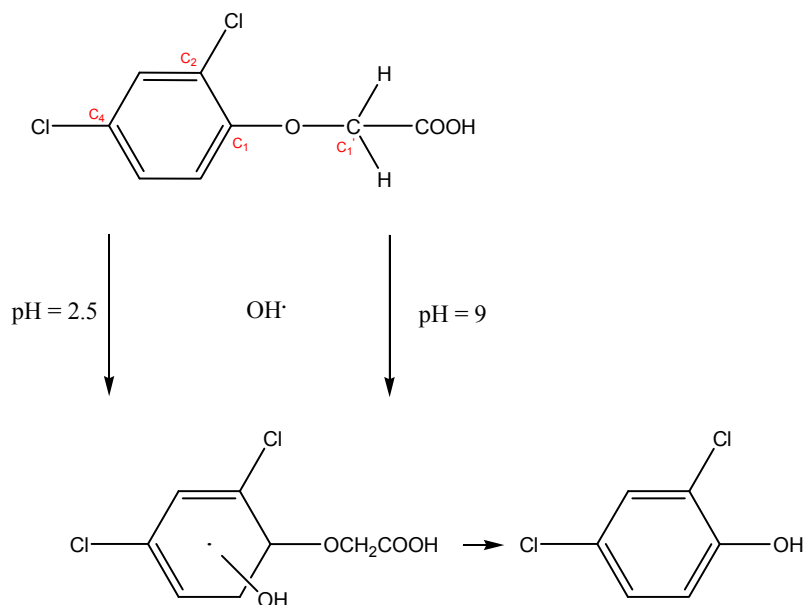


Figure 4.30. Reaction between 2,4-D and hydroxyl radical.

In all experimental oxidative transformations, the single most prevalent intermediate in the reaction between $\text{OH}^\cdot$ and 2,4-D is 2,4-DCP. Formation of 2,4-DCP is due to the addition of $\text{OH}^\cdot$ followed by the loss of alkoxy moiety of 2,4-D (Peller, 2003).

In the hydroxyl radical transformations of 2,4-D, the single most prevalent intermediate in the reaction, regardless of the technique used to form the $\text{OH}^\cdot$, is 2,4-dichlorophenol (Sun, 1993; Sun, 1995; Pignatello, 1992; Pichat, 1993; Muller, 1998; Brillas, 2003). Peller's group explained that the formation of this intermediate implies a high degree of selectivity for $\text{OH}^\cdot$ addition to the 2,4-D ring. It is envisioned that an $\text{OH}^\cdot$ attack at C_1 (Figure 4.30) of the aromatic ring followed by the loss of an alkoxy radical or anion to form 2,4-DCP takes place. Alternatively, hydrogen abstraction from the methylene carbon, followed by trapping of the ensuing radical and breaking of the $\text{C}_1'\text{-O}$ bond, by analogy to the mechanism proposed in an earlier study by Li and Jenks, is also possible (Li, 2000). These two pathways differ by which C-O bond, $\text{C}_1\text{-O}$ or $\text{C}_1'\text{-O}$, is broken. Results of the experiments using the O-18 labeled water discussed above clarify the site of $\text{OH}^\cdot$ attack on 2,4-D. The hydroxyl radicals formed from the labeled water were incorporated into the structure of the intermediate 2,4-

DCP. It can therefore be concluded that the formation of 2,4-DCP proceeds via hydroxyl radical addition to the ring in the first step of the mechanism, followed by the loss of the alkoxyl group. No hydroxylated intermediates of 2,4-D were detected in any of the experiments (Peller 2003).

The degradation of 2,4-DCP is expected mainly due to the reactions with hydroxyl radicals. The yield of degradation depended essentially on the position of chlorine atom relative to OH in the molecule (Schmid et. al., 1997). According to the results of Trojanowicz et al., for 50 ppm 2,4-DCP, up to 1 kGy, 40% is decomposed and 10 kGy is necessary for complete degradation of 2,4-DCP although 50 ppm 2,4-D completely degrades at 3kGy in our study. 2,4-DCP degrades to monochlorophenols, catechol compound, hydroxylated 2,4-dichloro phenols and mainly some carboxylic acids (Bojanowska-Czajka et. al., 2006; Getoff, 1997; Zona, 2003; Trojanowicz, 2002).

4-CP is also one of the radiolytic intermediate observed in the degradation of 2,4-D. Although its amount is not as high as 2,4-DCP, its amount is considerable with respect to other aromatic compounds. For 4-CP, the efficiency of formation and degradation is higher for 1.20 mM H₂O₂ added solution. The amount of 4-CP for 2,4-D is 0.128 ppm at 1.6 kGy for without H₂O₂ addition and the amount of 4-CP is 0.149 ppm at 1.2 kGy for 1.20 mM H₂O₂ added solution. Because of reactivity of hydroxyl radicals, formation amount of 4-CP is higher for 1.20 mM H₂O₂ added solution than without added. Also, the degradation of 4-CP is completed at lower doses for 1.20 mM H₂O₂ added solution, which is 3.5. For the solution, without H₂O₂, the complete degradation is observed at 4.5 kGy. The formation of 4-CP can be due to 4-chlorophenoxyacetic acid (4-CPA), as an intermediate of 2,4-D (Zona, 2002; Zona, 2003; Hamburg et.al., 2001). In the case of 4-CPA, like 2,4-DCP, an attack of hydroxyl radical on 4-CPA may cause the formation of 4-CP. Another possibility is that radiolytic degradation of 2,4-DCP formed 4-CP (Drzewicz et.al.,1999). Dehalogenation of 4-chloro phenol leads to the formation polyhydroxy benzenes and then opening an aromatic ring and formation of various carboxylic acids (Getoff,

1986). The addition 1.20 mM H₂O₂ into unirradiated solution can not be effective in the formation of 4-CPA.

4.2.5. Determination of Free Chlorine

The determination of free chloride ions was performed by using both mercury thiocyanate method (the reaction is the following) and ion chromatography. The visible spectrum for determination of free chloride ions is given in Figure 4.31.

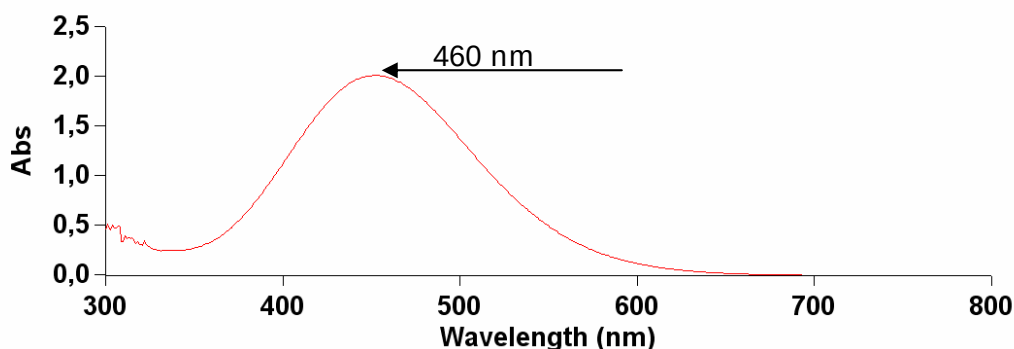
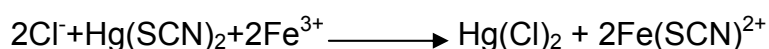


Figure 4.31. Visible spectrum of Fe(SCN)²⁺ complex (λ_{max} =460nm.).

The ion-chromatography measurements provide more information about the mechanisms of 2,4-D and 2,4-DP degradation and other side processes. The determination of chloride indicates that the complete degradation has been observed at 3.5 kGy and 5.0 kGy irradiation doses and 4.5 and 5.0 kGy in the presence and absence of H₂O₂, depending on the initial concentration of 2,4-D and 2,4-DP (Figure 4.32 and 4.33). Figures 4.32 and 4.33 show the changes in the amount of free chloride ions in solutions with the irradiation dose. At 4.5 kGy and 3.5 kGy for 2,4-D and 5.0 kGy and 4.5 kGy for 2,4-DP all of the chlorine atoms are found as free chloride ions in the absence and presence of H₂O₂, respectively. Bonded chlorine atoms may be a constituent of acids, phenolic compounds or aldehydes.

Chloride ions were detected for irradiated and unirradiated solutions of 1.20 mM H_2O_2 added solution and without 1.20 mM H_2O_2 added solution. It is observed that, an addition of 1.20 mM H_2O_2 can not cleavage Cl atoms from 2,4-D and 2,4-DP. It is observed that the release of Cl^- is completed at 3.5 kGy and 5.0 kGy in the presence and absence of H_2O_2 for 2,4-D. Some researchers resulted the formation of Cl^- is due to the attack of solvated electrons (e_{aq}^-). e_{aq}^- leads to a quantitative scission of the C-Cl bond resulting in Cl^- ion. Prompt formation of Cl^- as a sequence of $\text{H}^\cdot$ -attack on the substrate is insignificant (<2%) and the direct observation of Cl^- ions as a result of the $\text{OH}^\cdot$ with chloro phenols is nearly 5%. The highest Cl^- yield was obtained in the absence of oxygen for chlorinated olefins which was detected since most of e_{aq}^- and $\text{H}^\cdot$ are scavenged by O_2 (reactions 4.1 and 4.2) (Getoff, 1989).

At higher irradiation doses, the yield of dechlorination decreases although oxygen is consumed, since the Cl^- yield exhibits a strong dependence on the substrate concentration and in these dilute solutions the majority of free radicals react with each other, with other molecules or with chloro-organic compounds through reactions that do not result in chlorine removal. This reduction of efficiency may also be due to the reaction of e_{aq}^- with oxalate or oxalic acid. Some researchers found that the dechlorination rate in the pre-irradiated solution is lower (Taghipour, 1997).

The positions of the chlorine atoms did not affect the removal rate of chlorine from the compounds (Buxton et. al., 1988). The reactivity of chloro-organic compounds with the e_{aq}^- increases in the presence of neighbouring electron withdrawing groups. It is observed 4-chlorophenol rather than 2-chlorophenol in our study, since ortho position of Cl^- is easily released because of electron withdrawing groups. The release of chloride ions may be due to elimination of HCl if $\text{OH}^\cdot$ attacks on the carbon bonded to chloride atom (Piera et.al., 2000).

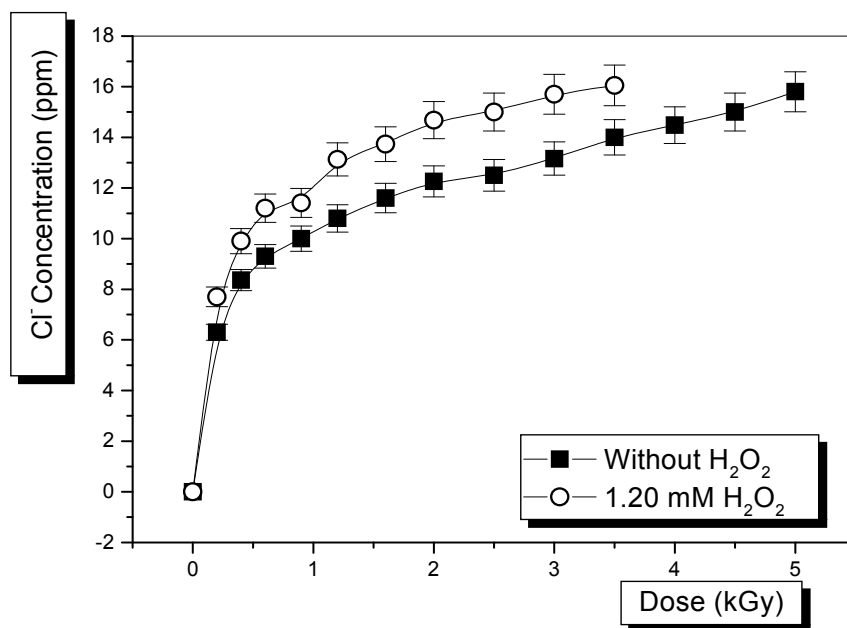


Figure 4.32. Change in the amount of intermediate free chloride ions with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

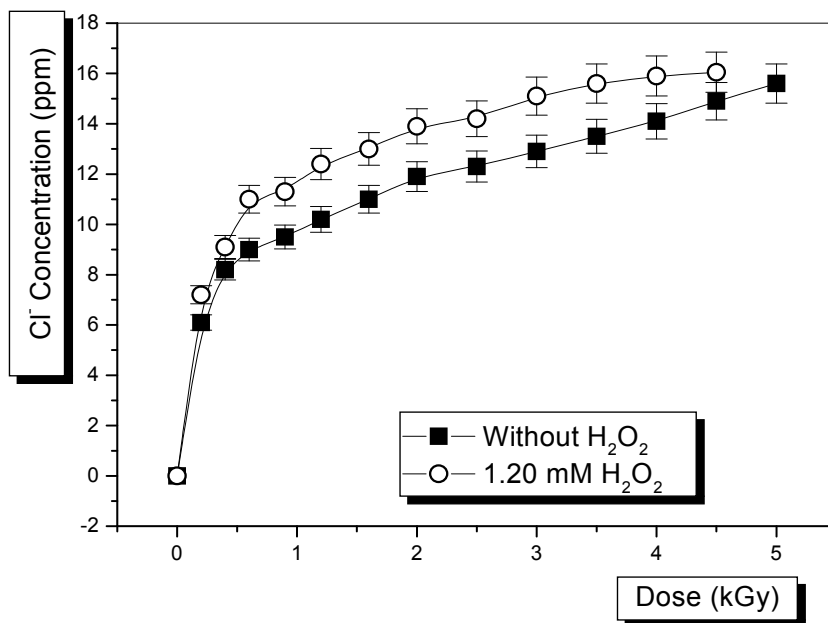


Figure 4.33. Change in the amount of intermediate free chloride ions with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

4.2.6. Determination of Dissolved Oxygen

In the absence and presence of H_2O_2 , the change in the amount of dissolved oxygen were followed by using oxygen meter during irradiation for 50 ppm 2,4-D and 2,4-DP solutions and the results are presented in Figures 4.34 and 4.35. The amount of dissolved oxygen for distilled water is also same with unirradiated 50 ppm 2,4-D and 2,4-DP, it is 3.50 mg/L for both of them. The oxygen consumption was observed as 0.55 and 0.51 mg/L for 2,4-D and 2,4-DP, before irradiation in the presence of H_2O_2 . This may be due to formation of 0.41 ppm acetic acid, 0.40 ppm formic acid, 0.024 ppm formaldehyde for 2,4-D and 0.13 ppm acetic acid, 0.09 ppm formic acid, 0.021 ppm formaldehyde for 2,4-DP. According to measured values the amount of dissolved oxygen was decreased up to 0.6 kGy irradiation dose and then it is constant in the range of 0.25-0.36 mg/L for 2,4-D and 2,4-DP. During the irradiation O_2 which can be in the medium was used to degrade 2,4-D and 2,4-DP up to 0.6 kGy.

In the presence of oxygen, even in a very small amount, the primary products of water radiolysis, e^-_{aq} and $\text{H}\cdot$ will attack on substrate, such as irradiated 2,4-D and 2,4-DP solutions in air, and the H-atoms are converted into hydroperoxy radicals ($\text{HO}_2\cdot$), whereas e^-_{aq} results in peroxide radical anion ($\text{O}_2^{\cdot-}$). We can not use all of these primary products from water radiolysis to degrade 2,4-D and 2,4-DP herbicides (Sanchez, 2002). The reducing radicals $\text{H}\cdot$ and e^-_{aq} are scavenged to form $\text{HO}_2\cdot$ and $\text{O}_2^{\cdot-}$ with oxygen. Oxygen is further consumed by its addition to carbon centered radicals and causes to ring fragmentation to form aliphatic acids or hydroxylation (Pan et. al., 1993). Oxygen enhances the degradation of organic pollutant. G_i values for consumption of dissolved oxygen is 2.1 and 2.6 for 2,-D, and 2.04 and 2.48 for 2,4-DP in the absence and presence of 1.20 mM H_2O_2 , respectively.

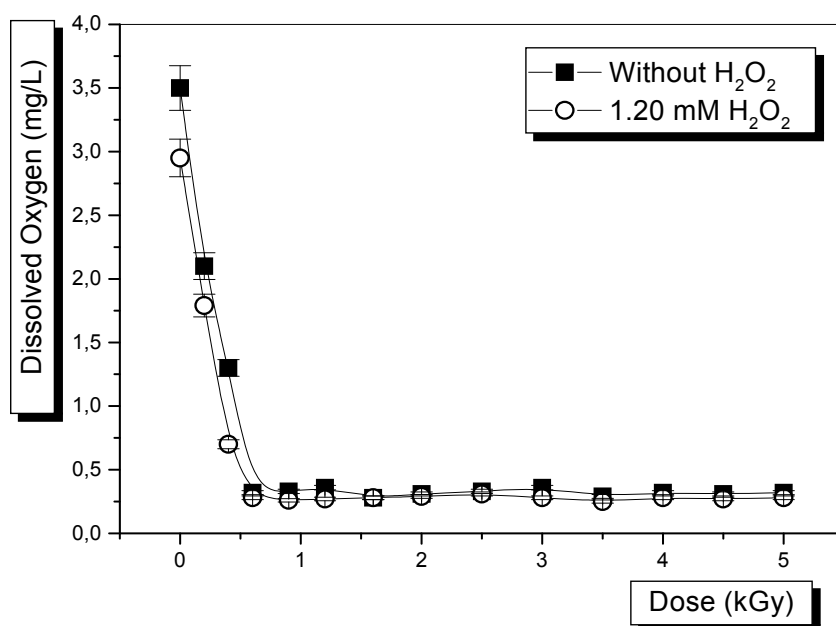


Figure 4.34. Change in the amount of dissolved oxygen with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

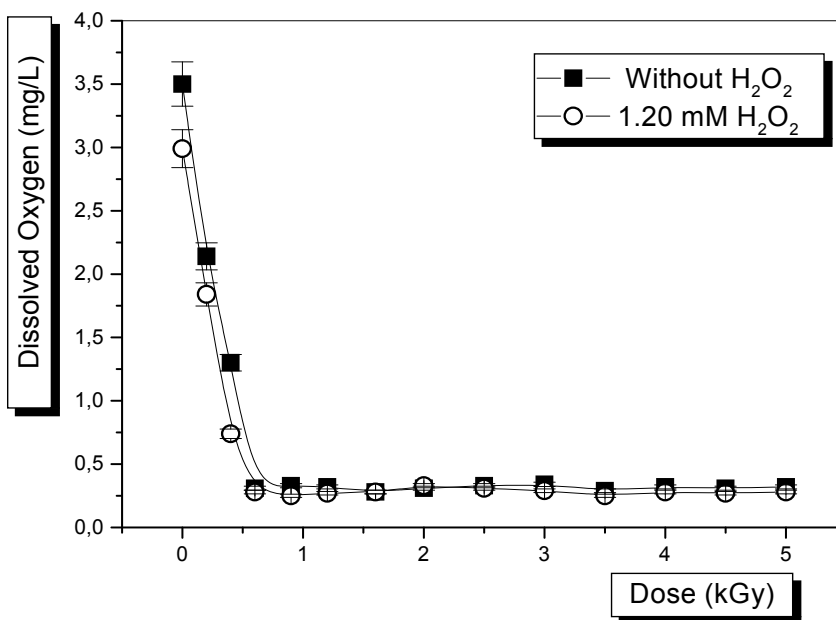


Figure 4.35. Change in the amount of dissolved oxygen with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

4.2.7. Determination of Formaldehyde

Figure 4.36 shows the UV-vis spectra of formaldehyde and acetaldehyde complexes. Formaldehyde complex has a maximum absorption at 412 nm (Nash, 1973).

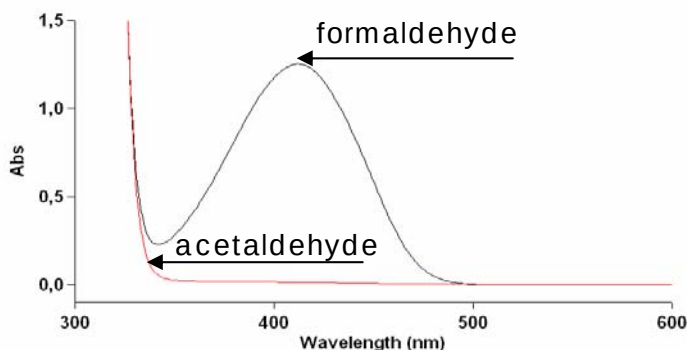


Figure 4.36. UV-visible spectra of formaldehyde complex ($\lambda_{\max} = 412$ nm) and for acetaldehyde complex.

The formation of formaldehyde as a function of the irradiation dose was studied in 2,4-D and 2,4-DP solutions in the absence and presence of H_2O_2 . The amount of formaldehyde formed in solutions in the absence and presence of H_2O_2 as a function of the irradiation dose is presented in Figures 4.37 and 4.38. The formation of formaldehyde in the presence of 1.20 mM H_2O_2 is higher than in the absence of H_2O_2 during irradiation for 2,4-D and 2,4-DP. The observed formaldehyde formation amounts are 0.024 and 0.021 ppm for 2,4-D and 2,4-DP before irradiation in the presence of H_2O_2 . The amount of formaldehyde at 5.0 kGy is 0.74 and 0.80 ppm for 2,4-D and 0.84 and 0.99 ppm for 2,4-DP in the absence and presence of 1.20 mM H_2O_2 , respectively.

Formaldehyde is also one of the radiolytic fragmentation product of the benzene ring as an attack of O_2 . Formaldehyde is consumed during the irradiation and further irradiation may convert formaldehyde to formic acid (Sanchez et. al., 2002). Formaldehyde is also the one of the last stage of degradation with CO_2 and H_2O_2 before formic acid formation (Schuchmann et. al., 1985). The formation of formaldehyde is an identification of the strong degradation of aromatic ring (Winarno, 2002). The aldehydes are toxic and, hence, dangerous to human health. With higher

irradiation doses, the aldehydes may also be converted into carboxylic acids (reaction (4.11)). The remaining can be decomposed to H₂O and CO₂ at higher absorbed doses.



4.2.8. Determination of Total Acidity and pH

Figures 4.39 and 4.41 show the change in the total acidity of 2,4-D and 2,4-DP solutions with the irradiation dose. The unirradiated 2,4-D and 2,4-DP herbicides were degraded to organic acids and/or aliphatic acids, the amount of total acids for unirradiated 2,4-D is 0.23×10^{-3} M and 0.322×10^{-3} M in the absence and presence of H₂O₂. The amount of total acids for unirradiated 2,4-DP is 0.21×10^{-3} M and 0.325×10^{-3} M in the absence and presence of hydrogen peroxide, respectively. It was observed that there is an increase in total acidity up to 5.0 kGy irradiation dose in the absence and presence of hydrogen peroxide. At 5.0 kGy irradiation dose, total acidity is 0.0011 M and 0.00142 M for 2,4-D and 0.0011 and 0.00142 M for 2,4-DP in the absence and presence of H₂O₂, respectively. The increase in acidity with the irradiation dose is due to the radiolytic fragmentation products of the benzene ring (Pan et. al., 1993). The pH values of 2,4-D and 2,4-DP solutions are given in Figures 4.40 and 4.42. When we compared the change of pH and total acidity of 2,4-D and 2,4-DP solutions (50 ppm) with the irradiation dose, the results are agreement with each other. An addition of 1.2 mM H₂O₂ to 50 ppm 2,4-D solution caused decrease in pH from 3.9 to 3.81, for 2,4-DP pH changed from 4.16 to 4.05. This is due to the reaction of hydroxyl radicals with pesticide and the formation of radiolytic products. When the total acidity increased, pH of 2,4-D and 2,4-DP solutions decreased with the irradiation dose. During the process of the radiation-induced degradation of 2,4-D and 2,4-DP pH values of the solutions gradually decreased with the increasing irradiation. These facts indicate the formation of carboxylic acids (formic acid, oxalic acid, etc.) in addition to chloride ions.

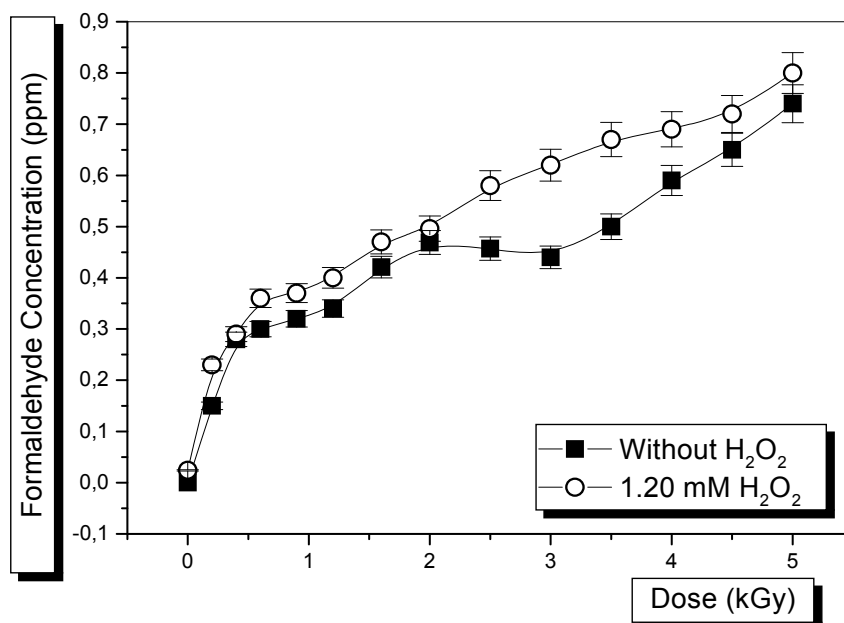


Figure 4.37. Change in the amount of formaldehyde with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

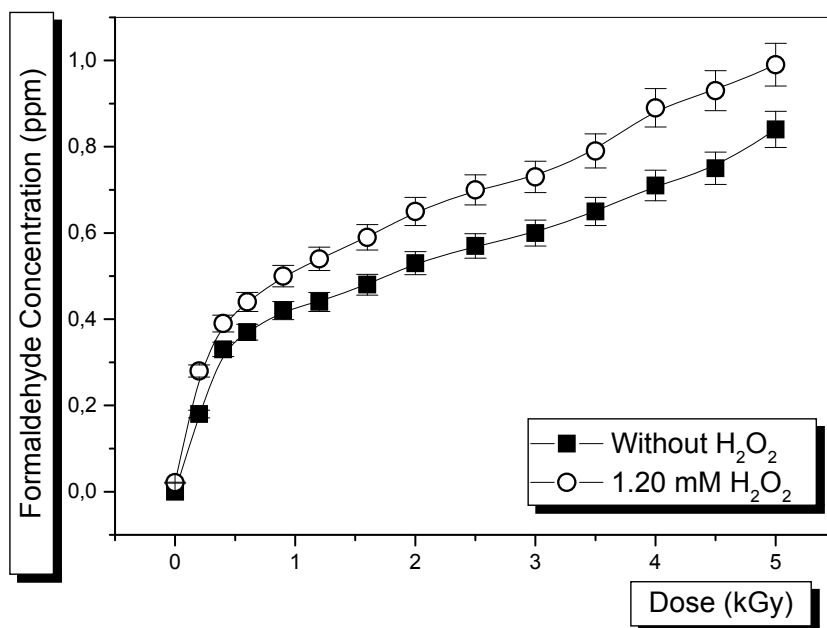


Figure 4.38. Change in the amount of formaldehyde with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

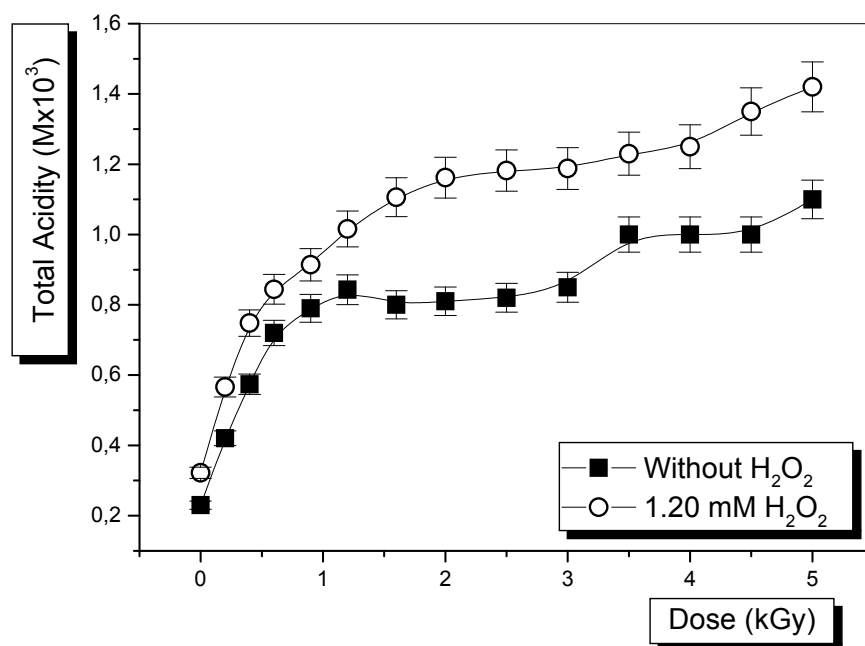


Figure 4.39. Change in the amount of total acidity with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

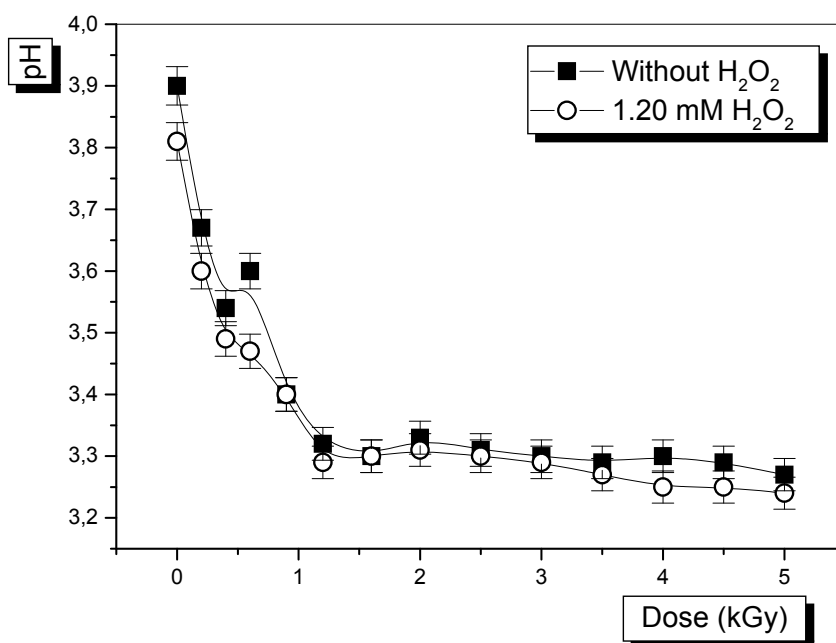


Figure 4.40. Change of pH with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-D (50 ppm).

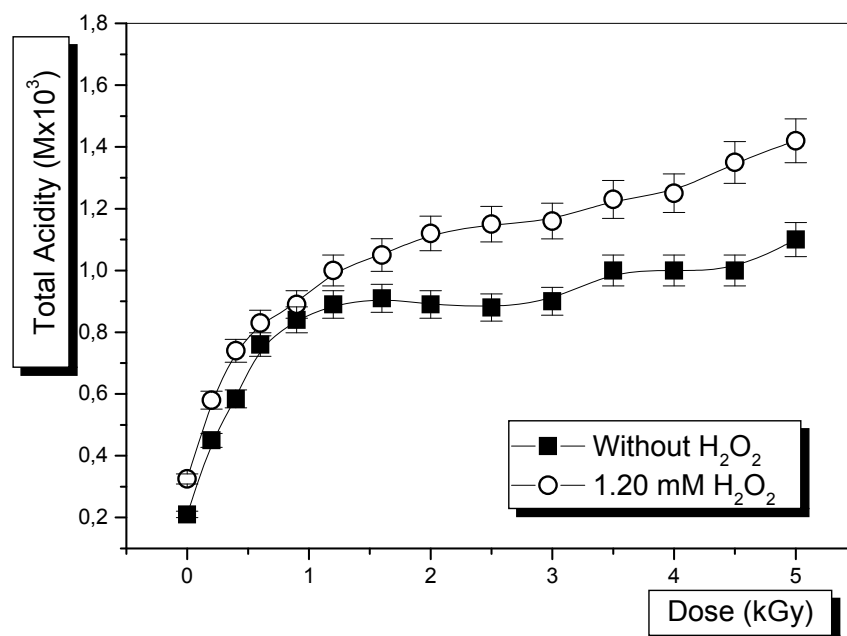


Figure 4.41. Change in the amount of total acidity with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

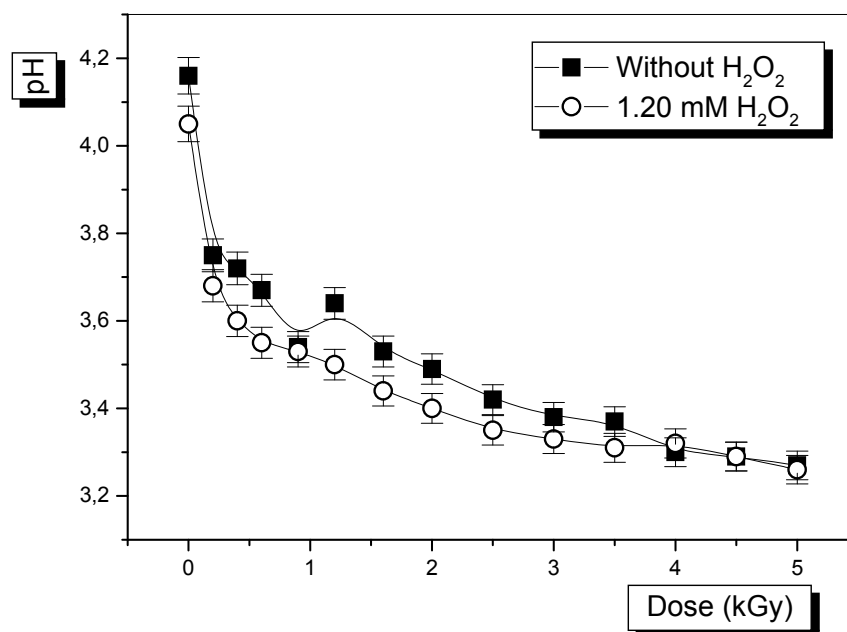


Figure 4.42. Change of pH with the irradiation dose in the absence and presence of hydrogen peroxide(1.20 mM) during irradiation of 2,4-DP (50 ppm).

4.2.9. Determination of Aliphatic Acids

Using ion chromatography, it was shown that the amount of inorganic chloride is almost all of expected from the degradation of the compounds. The intermediates from the radiolysis of 2,4-D and 2,4-DP after dehalogenation were determined mostly with ion chromatography. This method allows the determination of inorganic anions as well as anions of simple carboxylic acids. The degradation in steady-state radiolysis initially formed various intermediates and that leads to the formation of simple carboxylic acids (formic, oxalic, acetic etc.) (Getoff, 1990). At 3.0, 2.0 kGy and 3.5, 2.5 kGy in the absence and presence of H_2O_2 , all of 2,4-D and 2,4-DP herbicides are degraded and phenolic intermediates, 2,4-DCP and 4-CP from 2,4-DP are degraded at 4.0 and 5.0 kGy in the absence and presence of H_2O_2 . 2,4-DCP from 2,4-D is degraded at 3.0 and 4.0 kGy and 4-CP from 2,4-D is degraded at 3.5 and 4.5 kGy in the presence and absence of H_2O_2 , respectively.

The acetic acid, formic acid and oxalic acids were determined also by using ion chromatography. Firstly, ion chromatogram of standards of known aliphatic acids were recorded and their ion chromatographs and their retention times are given in Figure 4.43 and Table 4.4. For 1.2 kGy irradiated 2,4-D and 2,4-DP solutions in the absence and presence of H_2O_2 (1.2 mM), ion chromatograms are obtained and they are shown in Figures 4.44-4.47. The retention times of aliphatic acids are given in Tables 4.5-4.8. The changes in the amount of acetic acid, formic acid and oxalic acid with the irradiation dose in the absence and presence of 1.2 mM H_2O_2 during irradiation of 50 ppm 2,4-D and 2,4-DP solutions are shown in Figures 4.48-4.53.

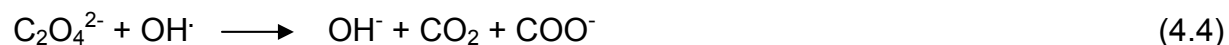
The formation of acetic acid and formic acid up to 1.2 kGy and 1.5 kGy irradiation doses for 2,4-D and 2,4-DP herbicides and after the maximum amount reached they decreased but the formation of oxalic acid increased continuously up to 5.0 kGy irradiation dose for two herbicides. Acetic acid was observed in all stages of irradiation. The formation of acetic acid is lower in the presence of H_2O_2 because the degradation of acetic acid is dominant.

Formic acid formation from 2,4-D and 2,4-DP is observed also up to 1.2 kGy in the absence and presence of H₂O₂ and after this irradiation dose, formic acid starts to decompose, but not efficient decomposition observed. Formic acid was observed in all stages of irradiation. If we compared the effect of H₂O₂ on the formation of aliphatic acids during the irradiation, we can concluded that in the presence of H₂O₂ in the medium the OH[•] radicals will increase and it will cause to form aliphatic acids and degrade 2,4-D herbicide.

It is well-known that the OH[•] radicals are strong oxidizing agents in aqueous systems and can play an important role on the degradation of aromatic compounds. These transients can add oxygen, forming peroxy radicals, which can further lead to ring opening. As a result of these reaction steps, aldehydes, carboxylic acids and many other products are obtained (Getoff,1997; Schuchmann, 1985; von Sonntag, 1997). During the process of the radiation-induced degradation of 2,4-D, the pH-values of the solutions gradually decreased with the increase of the absorbed dose. This fact indicates the formation of carboxylic acids (acetic acid, formic acid, oxalic acid, etc.) in addition to chloride ions.

The formation of acetate and formate anions is the last step before complete mineralization of organic substances to CO₂. In contrast to major component acetate, the other acids are typical radiolytic fragmentation products of the benzene ring. The production of acetic acid starts immediately after irradiation. Reaction of OH[•] with acetic acid results partly in decarboxylation. The second order decay of acetate peroxy radicals ([•]OOCH₂COO⁻) follows two major pathways, formation of glyoxylic acid and H₂O₂, and formation of formaldehyde, CO₂ and H₂O₂. Formic acid represents the last step before mineralization (Buxton et. al., 1988; Buxton, 1987).

Oxalic acid is one of the last intermediate of degradation. It decomposes to CO₂ and carbonate species (Draganic, 1966).



2,4-D (50 ppm) and 2,4-DP (50 ppm) solutions which contain H_2O_2 caused no affect on the formation of oxalic acid. During irradiation, an amount of oxalic acid increases up to 5 kGy. Increase in the amount of oxalic acid in the presence of hydrogen peroxide is higher than that of in the absence of hydrogen peroxide. At 5 kGy, The amounts of oxalic acid are 5.22 and 7.12 ppm from 2,4-D and 3.16 and 3.85 ppm from 2,4-DP in the absence and presence of H_2O_2 , respectively. Oxalic acid is observed in all stages of irradiation.

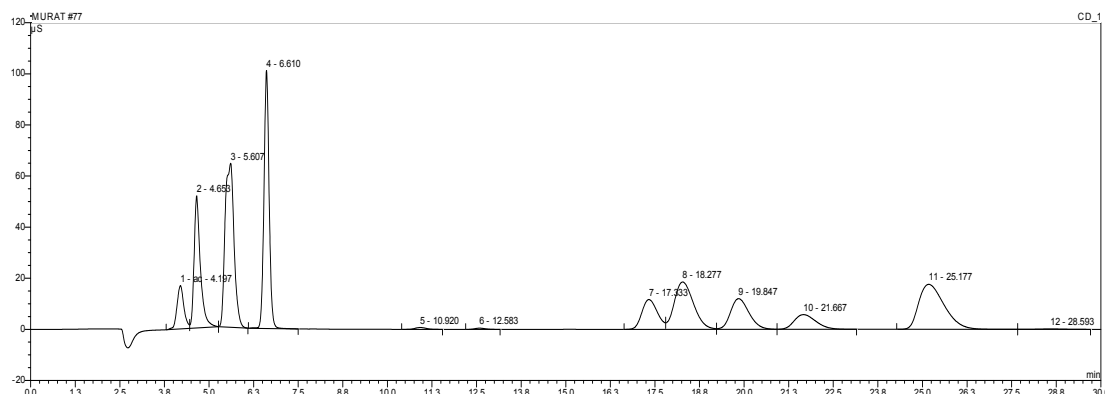


Figure 4.43. Ion chromatogram of the aliphatic acid standards (each 25 ppm).

Table 4.4. Retention times of the aliphatic acid standards.

Retention Time (min.)	Name of the Standard
4.197	Acetic Acid
4.653	Formic Acid
5.550	Chloro acetic acid
5.607	2-chloro propionic acid
6.610	Chloride
17.333	Malic Acid
18.277	Malonic Acid
19.847	Maleic Acid
21.667	Itaconic Acid
25.177	Oxalic Acid

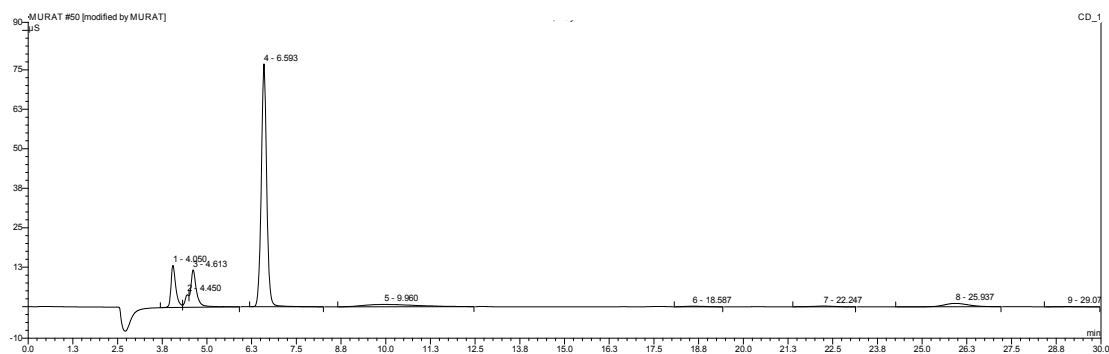


Figure 4.44. Ion chromatogram of 1.2 kGy irradiated 2,4-D.

Table 4.5. Retention times of aliphatic acids formed from 1.2 kGy irradiated 2,4-D.

Ret. Time (min.)	Name of the Intermediate
4.050	Acetic Acid
4.613	Formic Acid
6.593	Chloride
25.937	Oxalic Acid

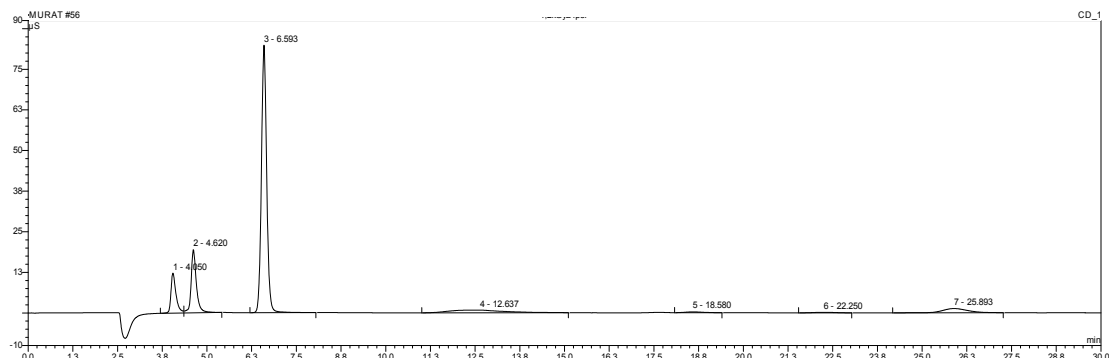


Figure 4.45. Ion chromatogram of 1.2 kGy irradiated 2,4-D in the presence of hydrogen peroxide (1.20 mM).

Table 4.6. Retention times of aliphatic acids formed from 1.2 kGy irradiated 2,4-D in the presence of hydrogen peroxide (1.20 mM).

Ret. Time (min.)	Name of the Intermediate
4.050	Acetic Acid
4.620	Formic Acid
6.593	Chloride
25.893	Oxalic Acid

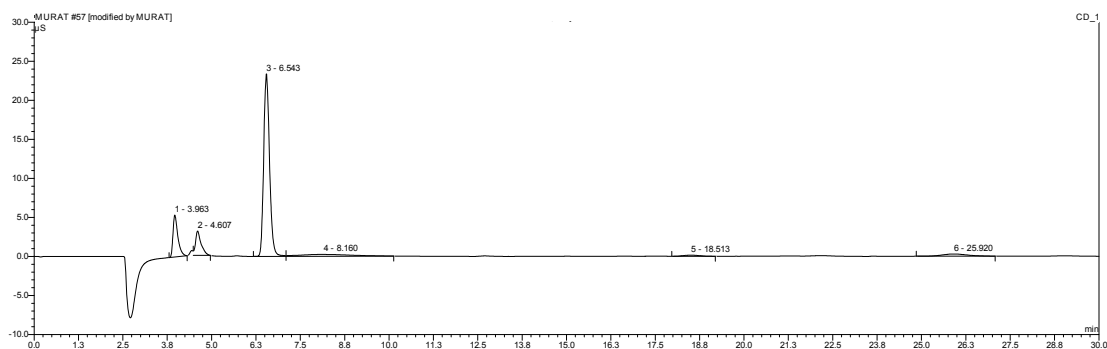


Figure 4.46. Ion chromatogram of 1.2 kGy irradiated 2,4-DP.

Table 4.7. Retention times of aliphatic acids formed from 1.2 kGy irradiated 2,4-DP.

Ret. Time (min.)	Name of the Intermediate
3.963	Acetic Acid
4.607	Formic Acid
6.543	Chloride
25.920	Oxalic Acid

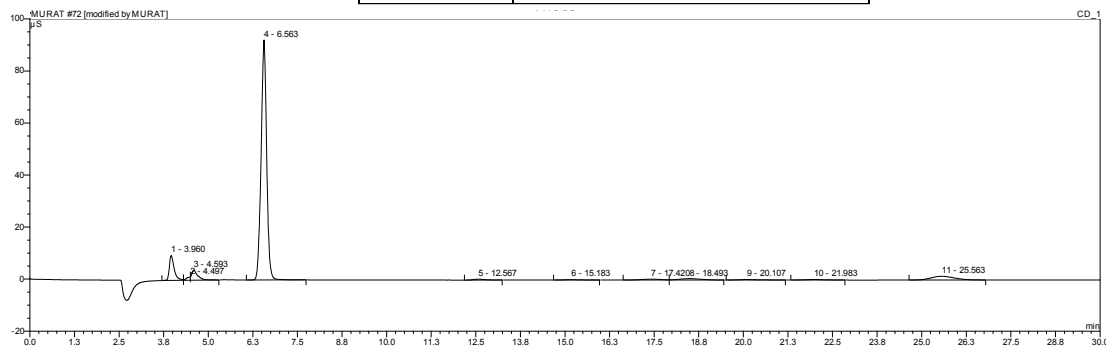


Figure 4.47. Ion chromatogram of 1.2 kGy irradiated 2,4-DP in the presence of H_2O_2 (1.2 mM).

Table 4.8. Retention times of aliphatic acids formed from 1.2 kGy irradiated 2,4-DP in the presence of H_2O_2 (1.2 mM).

Ret. Time (min.)	Name of the Intermediate
3.960	Acetic Acid
4.593	Formic Acid
6.563	Chloride
25.563	Oxalic Acid

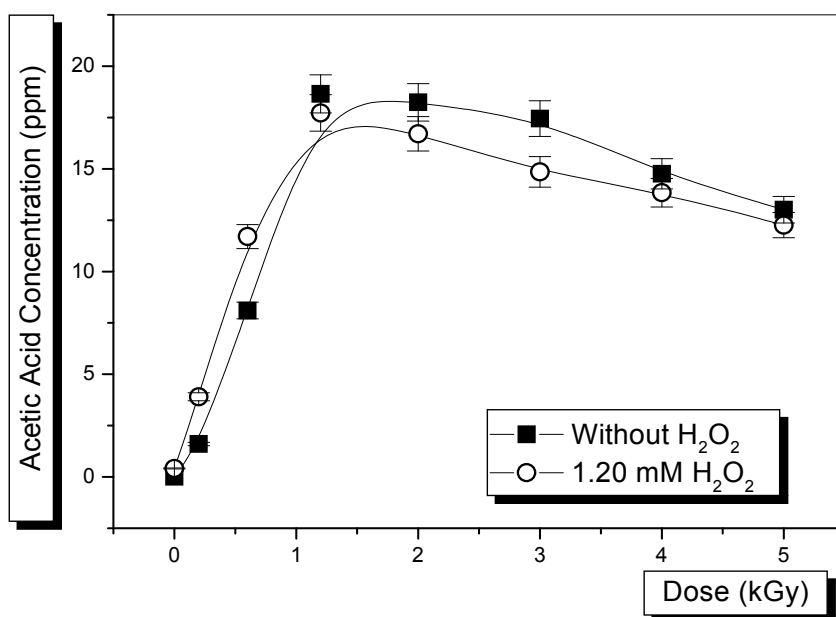


Figure 4.48. Change in the amount of acetic acid with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during the irradiation of 2,4-D (50 ppm).

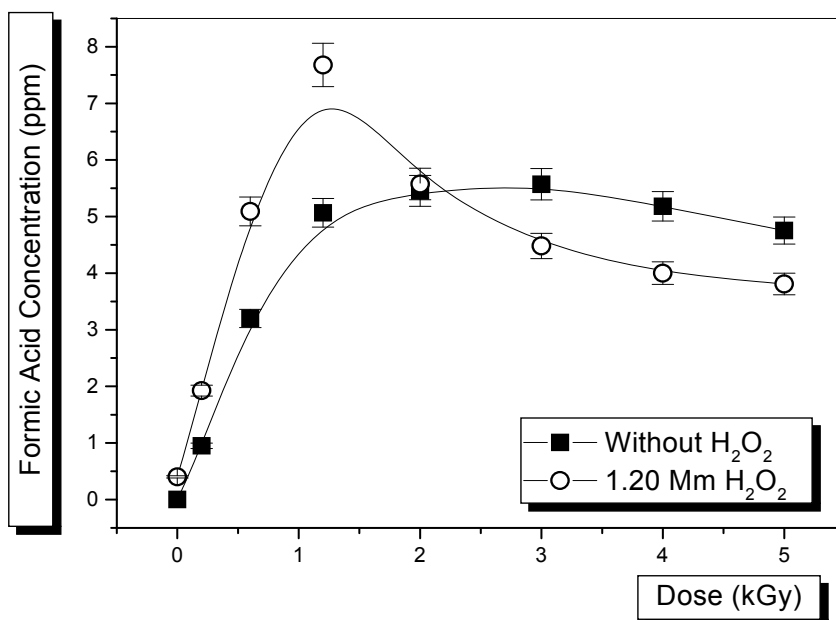


Figure 4.49. Change in the amount of formic acid with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during the irradiation of 2,4-D (50 ppm).

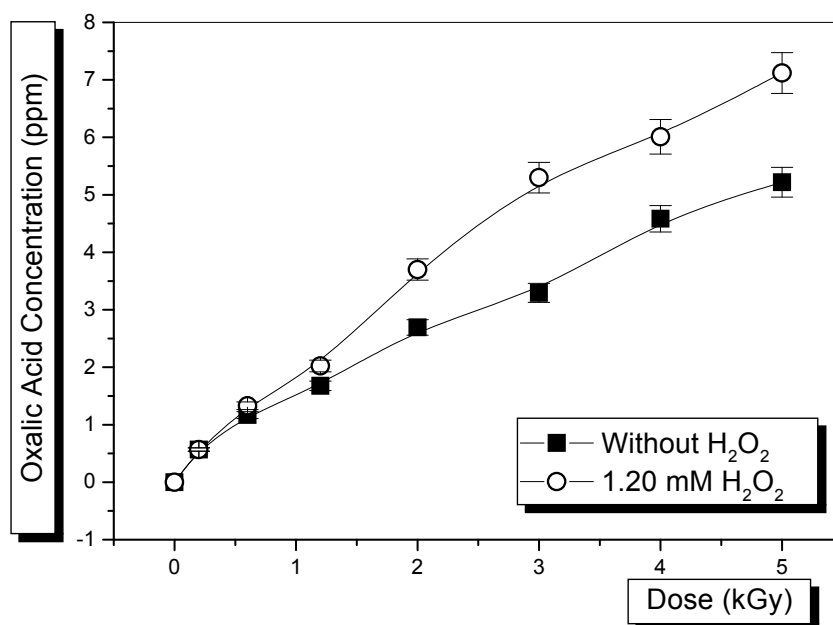


Figure 4.50. Change in the amount of oxalic acid with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during the irradiation of 2,4-D (50 ppm).

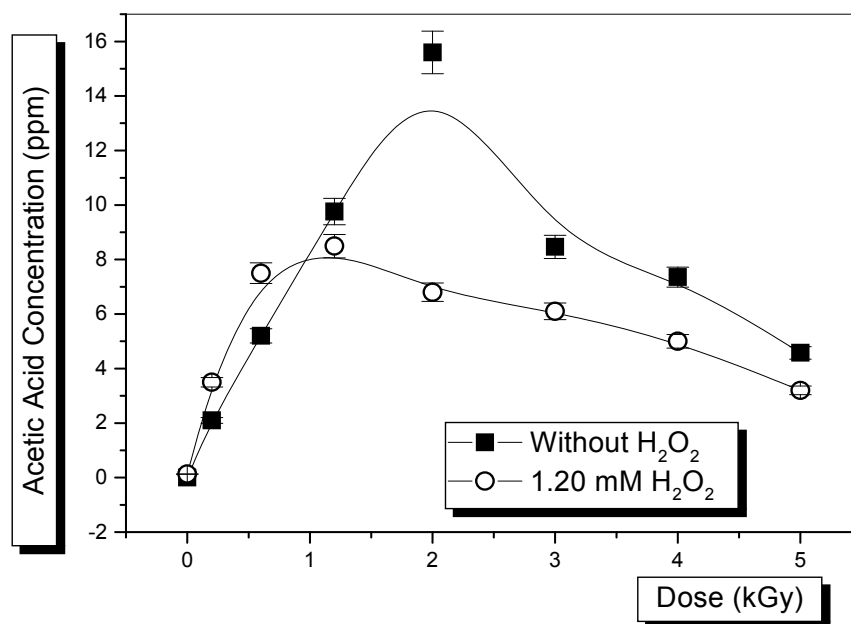


Figure 4.51. Change in the amount of acetic acid with the irradiation dose in the absence and presence of hydrogen peroxide (1.20 mM) during irradiation of 2,4-DP (50 ppm).

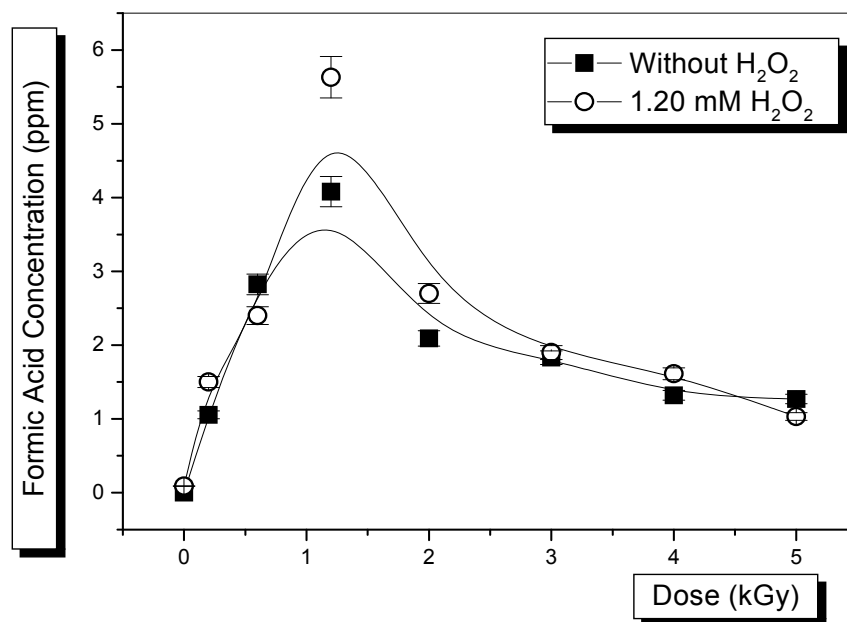


Figure 4.52. Change in the amount of formic acid with the irradiation dose in the absence and presence of hydrogen peroxide (1.2 mM) during irradiation of 2,4-DP (50 ppm).

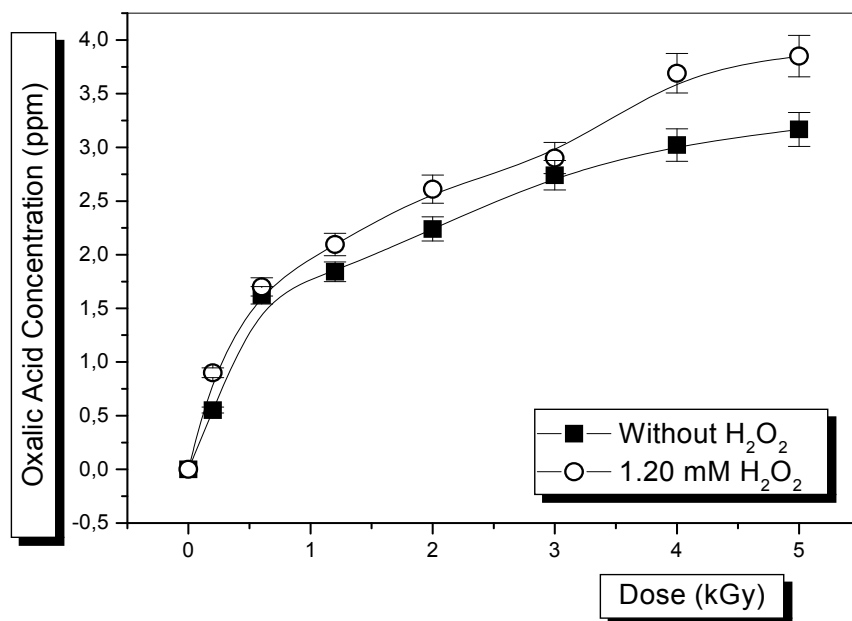


Figure 4.53. Change in the amount of oxalic acid with the irradiation dose in the absence and presence of hydrogen peroxide (1.2 mM) during irradiation of 2,4-DP (50 ppm).

4.2.10. Effect of Ozone on Degradation of 2,4-D and 2,4-DP

Human population is constantly exposed to numerous chemical species present in the environment. Among these compounds, chlorophenoxy acid herbicides are of significant importance because of their wide distribution and extensive use as plant growth regulators. When applied, they are easily transferred to surface and groundwaters due to their polar nature and relatively good solubility. Although their decomposition in the presence of oxygen is relatively fast, these herbicides are persistent under reductive conditions and their extended use can lead to pollution of surface and groundwaters. Microbiological decomposition of chlorophenoxy acid herbicides is only practicable because of their low concentration (Hoover, 1986). Among the chlorophenols, 2,4-dichlorophenol is especially toxic and resistant towards biodegradation. So, the development of analytical procedures for the simultaneous determination of chlorophenoxy acid herbicides and phenolic compounds is important. Advanced oxidation processes for toxic compounds recently utilized a variety of combination of irradiation, oxidants and catalysts to produce reactive oxidants such as hydroxyl radical $\text{OH}^\cdot$ for water treatment (Drzewicz, 1999; Lee, 2003).

Although its advantageous, ozone has also some serious limitations. First of all, it is not stable and in higher concentrations it is even explosive. Therefore, it cannot be stored and has always to be produced on site. It can be applied in low concentrations, usual concentrations in the gas flow should be low. It is a gas. Its transfer to the aqueous phase is technically not easy—especially in combination with irradiation—and, moreover, its solubility in water (109 mg O_3 /L at 25°C) is not very good. Last but not the least it is toxic and, above all, it is expensive (Gehring, 2002).

To analysis irradiated 2,4-D and 2,4-DP solutions in the presence of O_3 we used Gas chromatography-Mass-Mass spectrometer. GC/MS-MS remains the main analytical method used for herbicide residue analysis because of its excellent separation and detection potential, especially when combined with mass spectrometry detection.

4.2.10.1. Ozonation of 2,4-D and 2,4-DP

As mentioned in the experimental part, the ozone concentration in the herbicide solutions was adjusted by preliminary experiment in the range of (0.17-20) minute or (0.0695 -5.52) g O₃/L . During the treatment, a gas flow rate of 0.078 L min⁻¹ O₃ was passed through the solutions. Under these conditions it was observed that after about 20 min peaks for methyl esters of 2,4-D and 2,4-DP at 10.898 and 10.517 (Figures 4.8 a and 4.9 a) retention times disappeared, indicating that the 2,4-D and 2,4-DP degradations are completed. Samples after certain treatment times were taken and analyzed by GC/MS-MS-method and the obtained results are shown in Figures 4.54-4.65.

For unirradiated and ozonized 2,4-D and 2,4-DP solutions GC chromatograms of these solutions were obtained to investigate the effect of ozone on degradation of these herbicides. Figure 4.54 a and b shows the effect of ozone on degradation of 2,4-D. The GC chromatograms, mass spectra of possible intermediates of 1.3 and 13.3 minute (0.556 and 5.52 g O₃/L) ozonized 2,4-D solutions are presented in Figures 4.54 a,b, 4.55 and 4.56. Figures 4.57 a,b, 4.58 and 4.59 show the effect of ozone on radiation induced degradation of 0.2 kGy irradiated 2,4-D.

The major intermediate is 2,4-DCP but there are the other intermediates at very low concentrations. The intermediates were decreased with the increasing of ozonation time and disappeared almost completely at 13.3 and 8.3 minute (5.52 and 3.475 g O₃/L) ozonation times for unirradiated and irradiated 2,4-D and 2,4-DP. In the presence of ozone firstly intermediates are degraded and then 2,4-D and 2,4-DP herbicides. In the absence and presence of H₂O₂ we had reverse results. For 2,4-DP herbicide we have similar GC chromatograms and mass spectra for unirradiated and irradiated 2,4-DP samples in the presence of ozone in Figures 4.60-4.65.

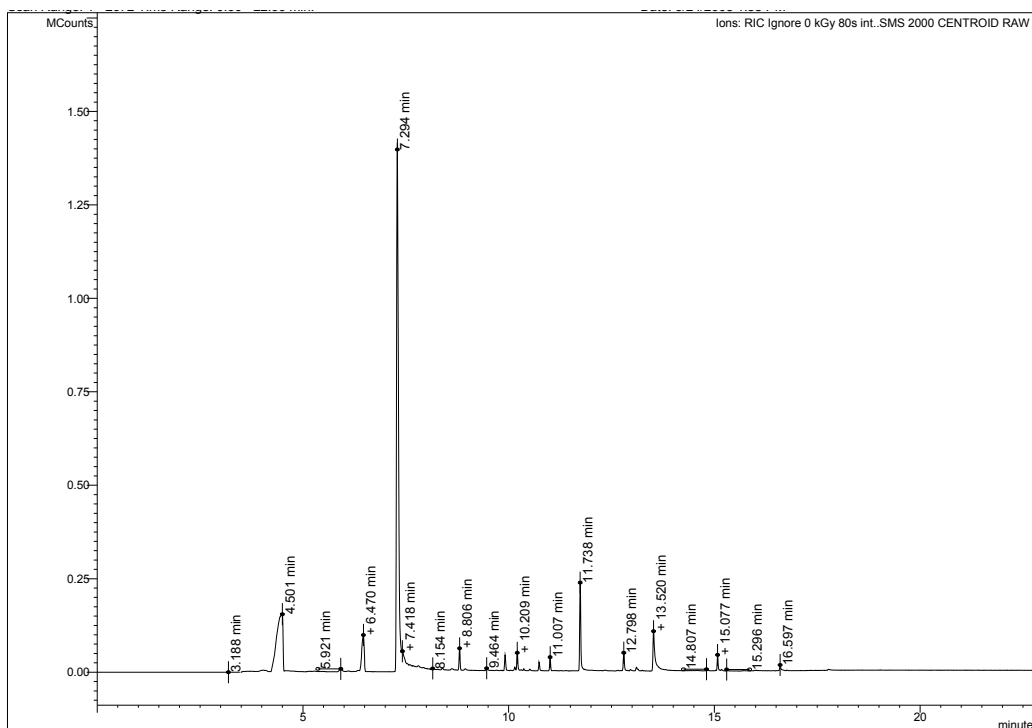


Figure 4.54.a) GC chromatogram of the ozonized 1.3 minute (0.556 g O₃/L) and unirradiated 2,4-D (50ppm) sample after eluted from C18 cartridges in acetone.

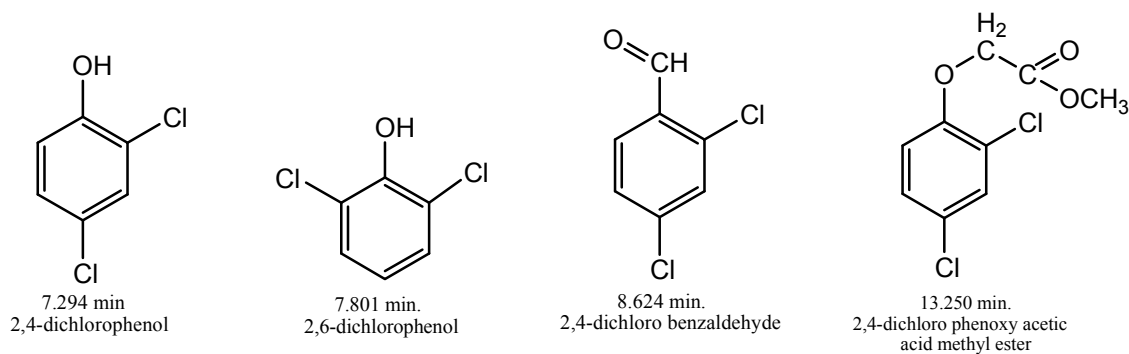


Figure 4.54.b) Possible intermediates for the ozonized 1.3 minute (0.556 g O₃/L) and unirradiated 2,4-D (50 ppm) sample after eluted from C18 cartridges in acetone.

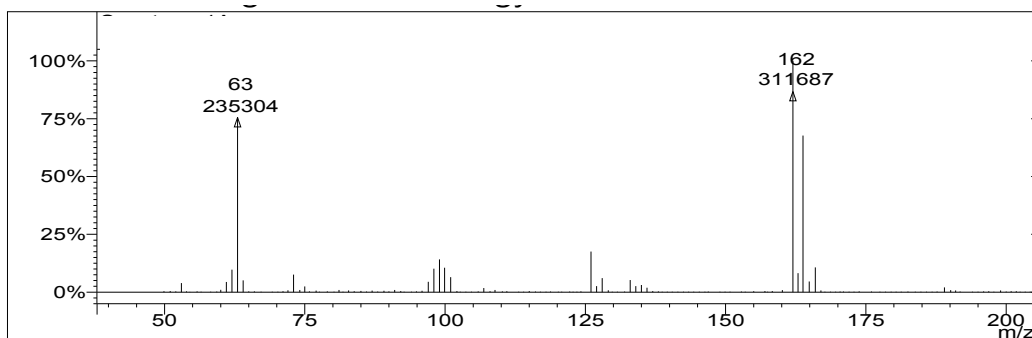


Figure 4.55.a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.294 min.)

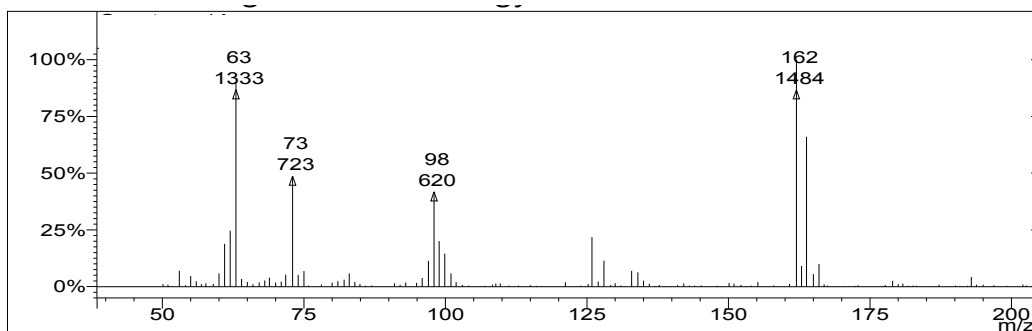


Figure 4.55.b) Mass spectrum of possible intermediate 2,6-dichloro phenol (7.801 min.)

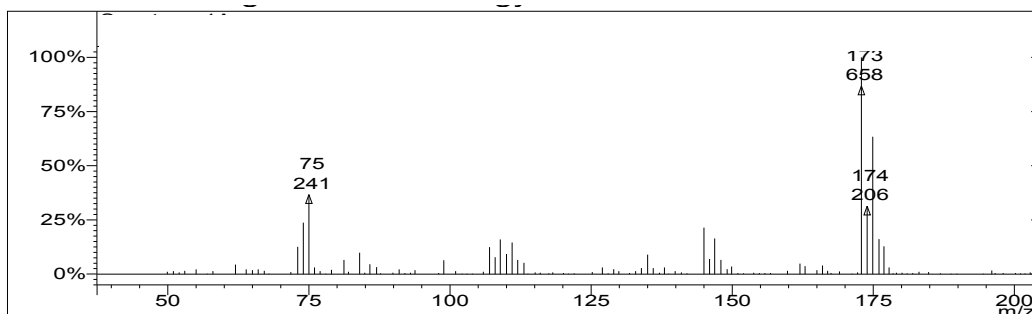


Figure 4.55.c) Mass spectrum of possible intermediate 2,4-dichloro benzaldehyde (8.624 min.)

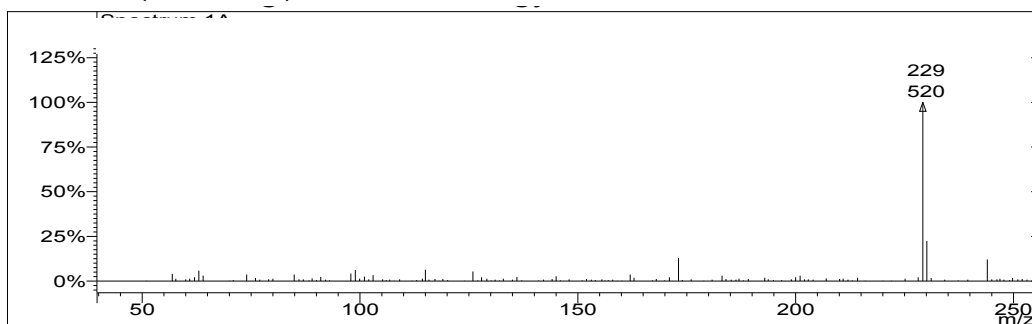


Figure 4.55.d) Mass spectrum of possible intermediate 2,4-dichloro phenoxy acetic acid methyl ester (13.250 min.)

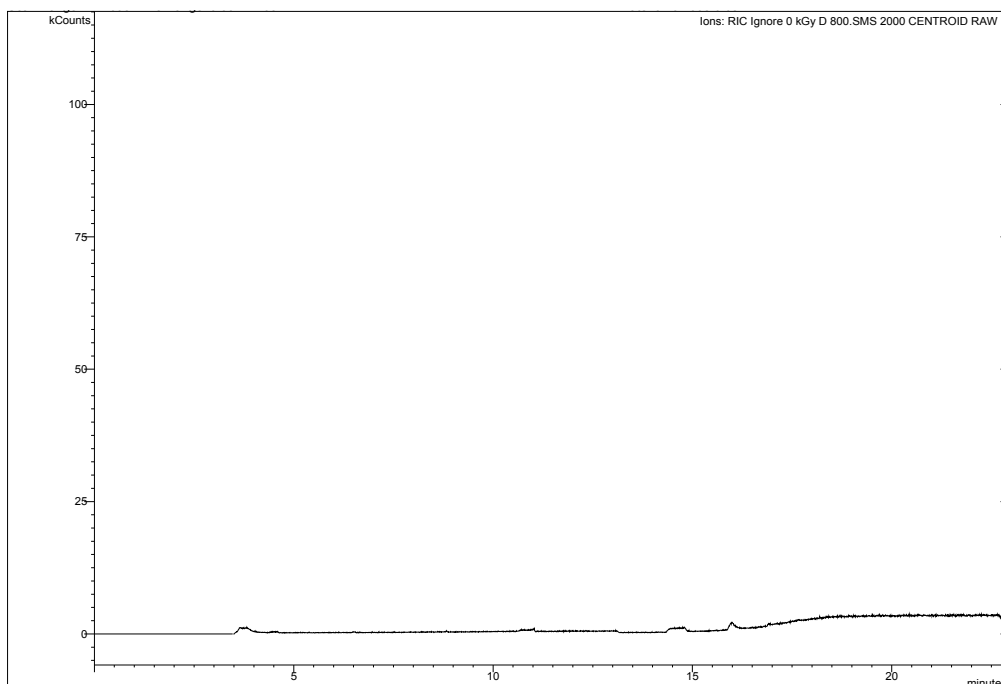


Figure 4.56. GC chromatogram of the ozonized 13.3 minute (5.52 gO₃/L) and unirradiated 2,4-D (50 ppm) sample after eluted from C18 cartridges in acetone.

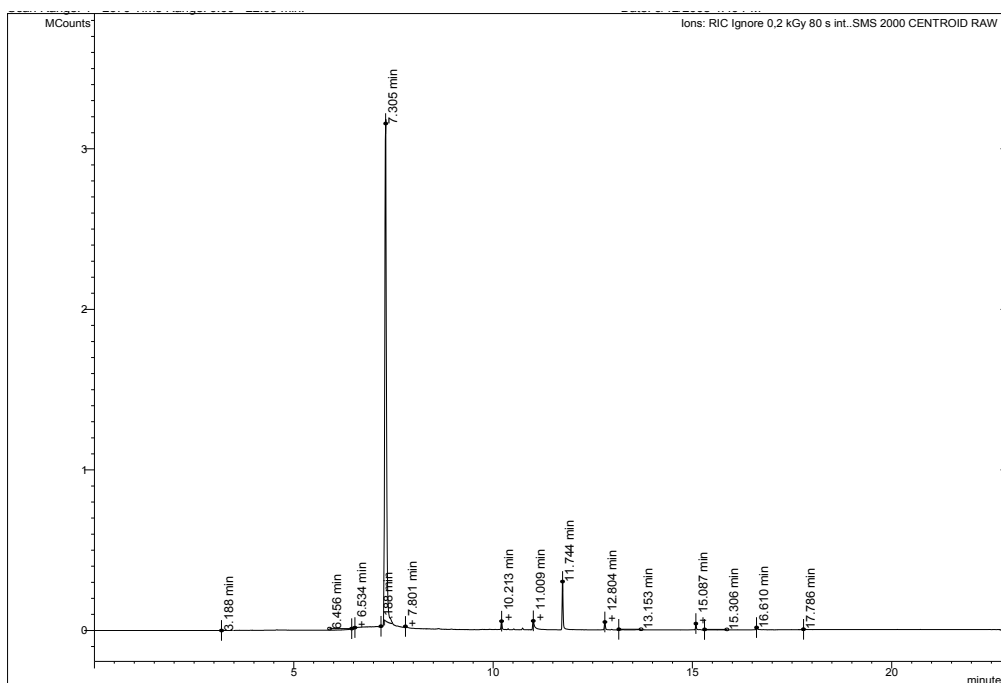


Figure 4.57.a) GC chromatogram of the ozonized 1.3 minute (0.556 g O₃/L) and 0.2 kGy irradiated 2,4-D (50 ppm) sample after eluted from C18 cartridges in acetone.

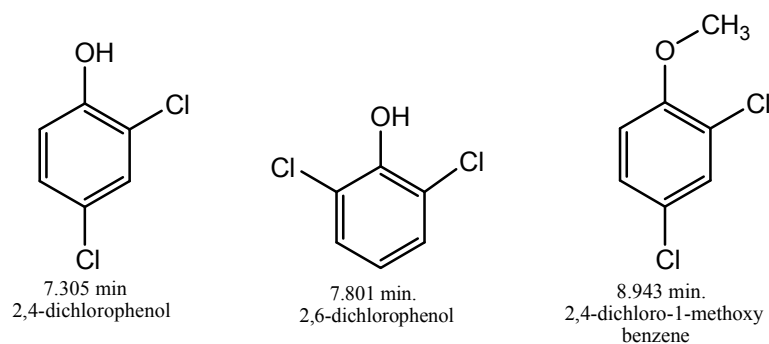


Figure 4.57.b) Possible intermediates for the ozonized 1.3 minute (0.556 g O₃/L) and 0.2 kGy irradiated 2,4-D (50 ppm) sample after eluted from C18 cartridges in acetone.

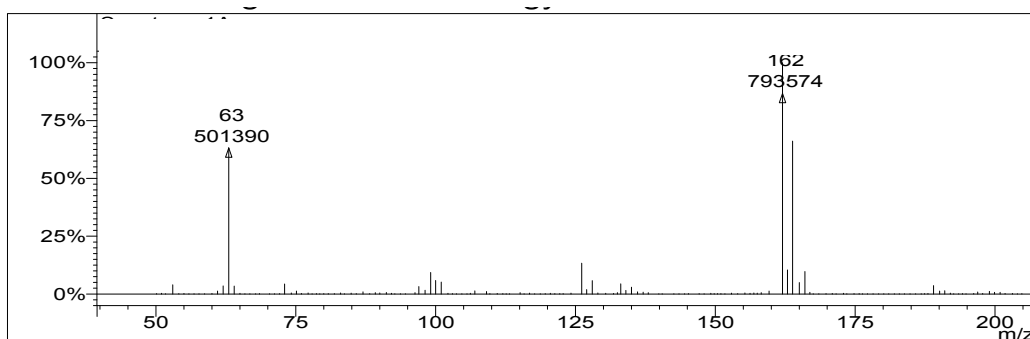


Figure 4.58.a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.305 min.)

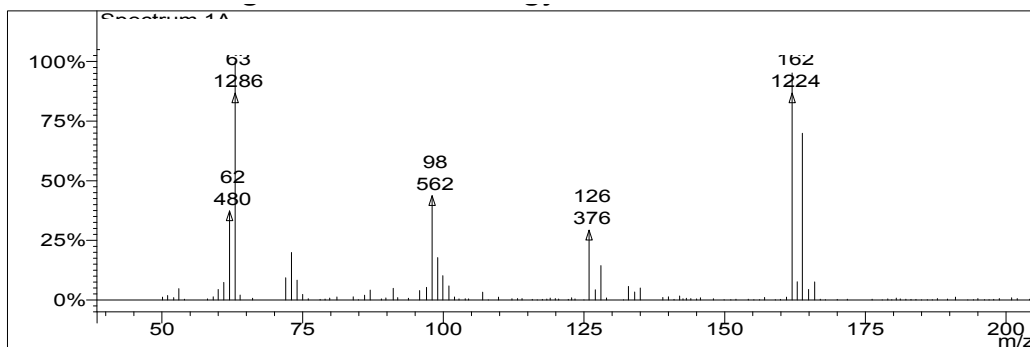


Figure 4.58.b) Mass spectrum of possible intermediate 2,6-dichloro phenol (7.805 min.)

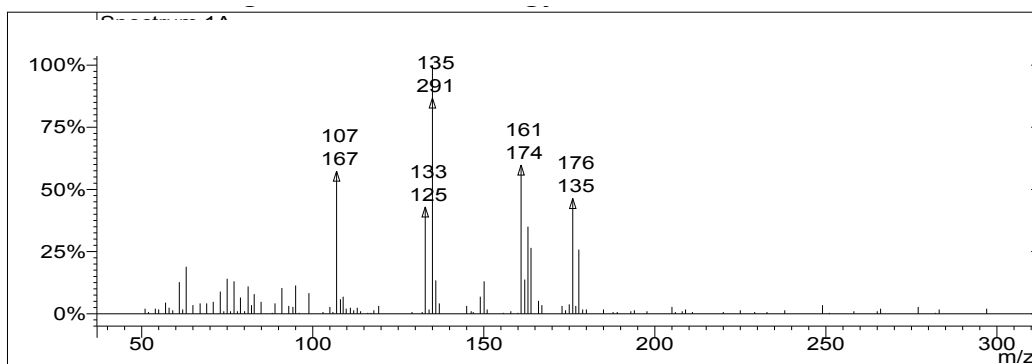


Figure 4.58.c) Mass spectrum of possible intermediate 2,4-dichloro-1-methoxybenzene (8.943 min.)

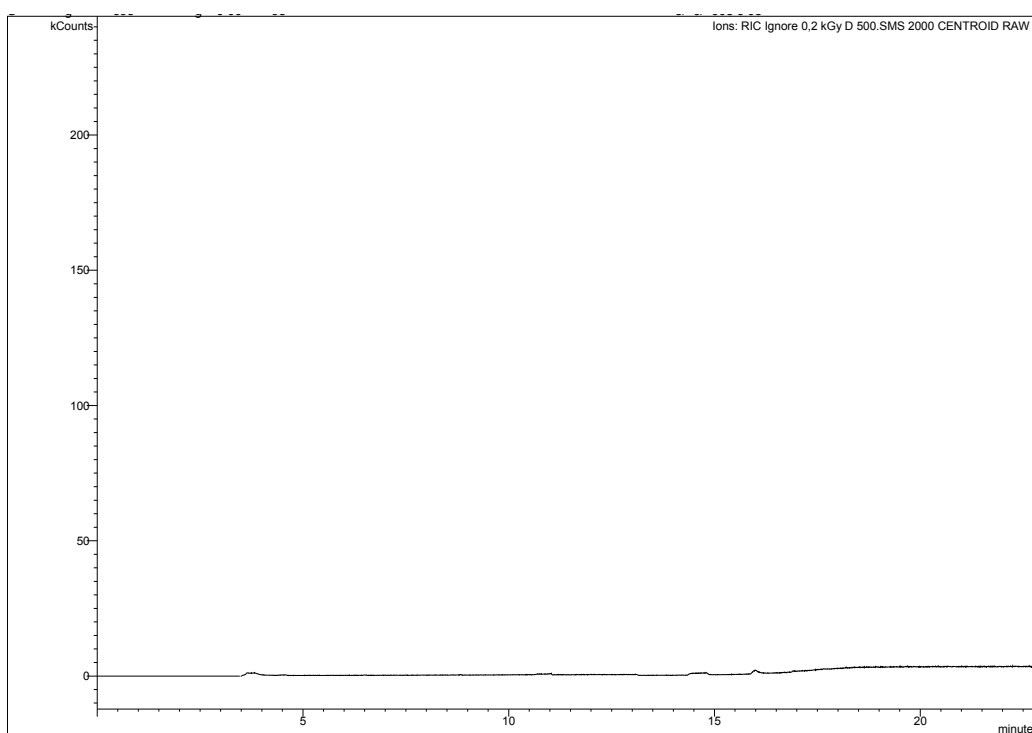


Figure 4.59. GC chromatogram of the ozonized 8.3 minute (3.475 g O₃/L) and 0.2 kGy irradiated 2,4-D (50 ppm) sample after eluted from C18 cartridges in acetone.

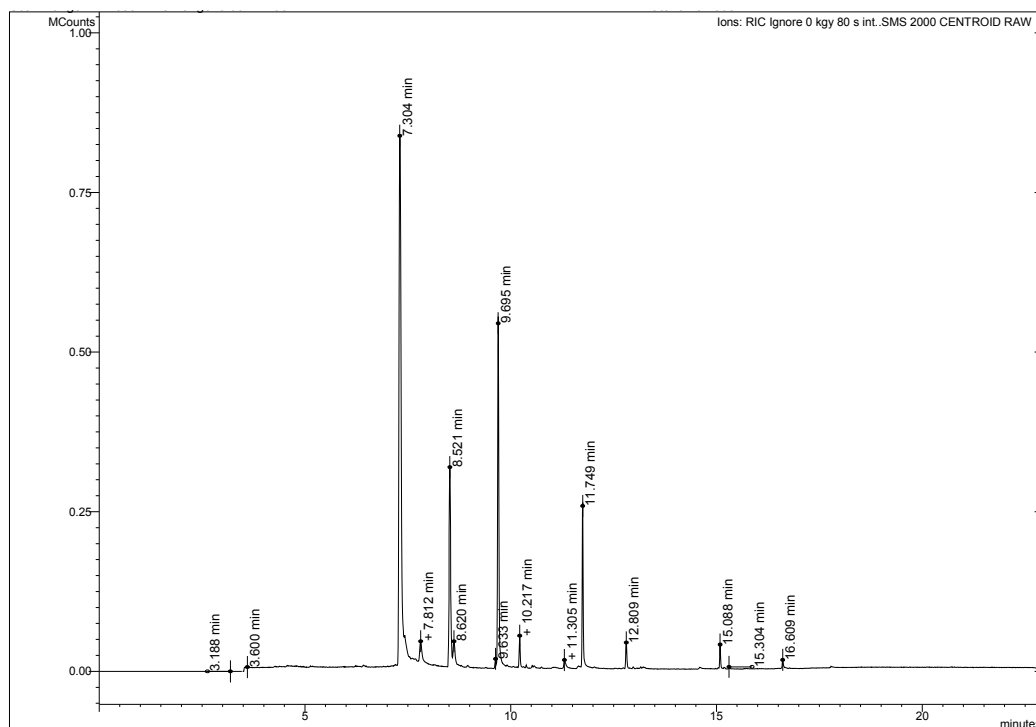


Figure 4.60.a) GC chromatogram of the ozonized 1.3 minute (0.556 g O₃/L) and unirradiated 2,4-DP (50 ppm) sample after eluted from C18 cartridges in acetone.

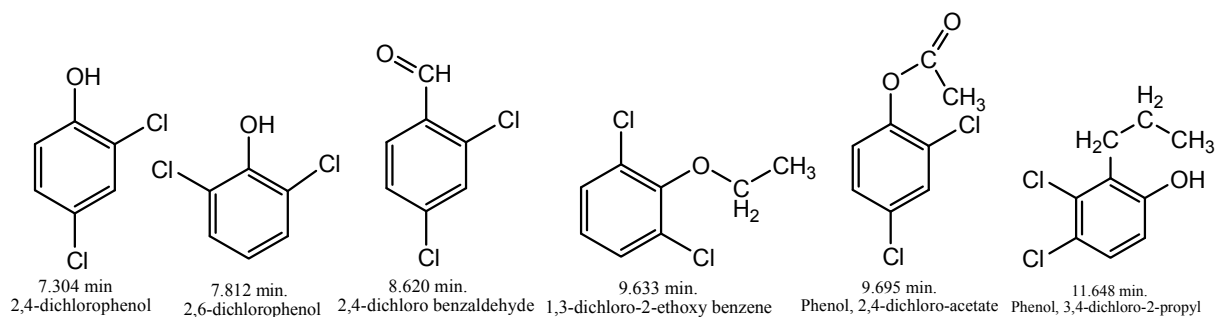


Figure 4.60.b) Possible intermediates for ozonized 1.3 minute (0.556 g O₃/L) and unirradiated 2,4-DP (50 ppm) sample after eluted from C18 cartridges in acetone.

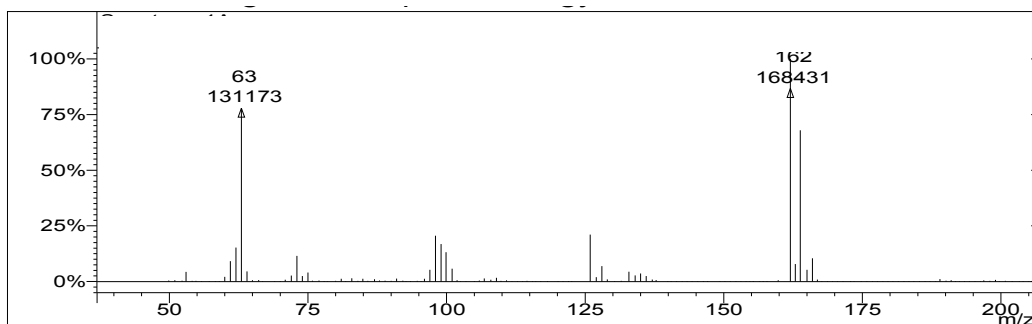


Figure 4.61.a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.304 min.).

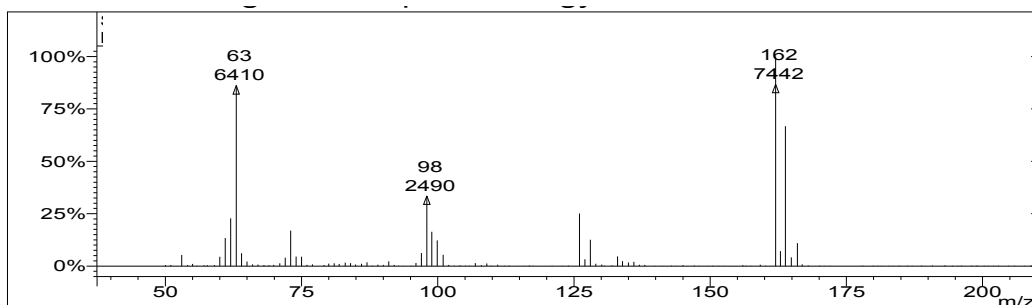


Figure 4.61.b) Mass spectrum of possible intermediate 2,6-dichloro phenol (7.812 min.).

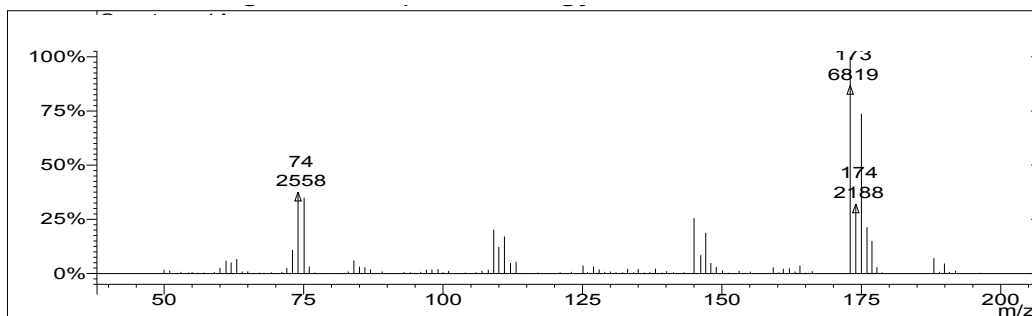


Figure 4.61.c) Mass spectrum of possible intermediate 2,4-dichloro benzaldehyde (8.620 min.).

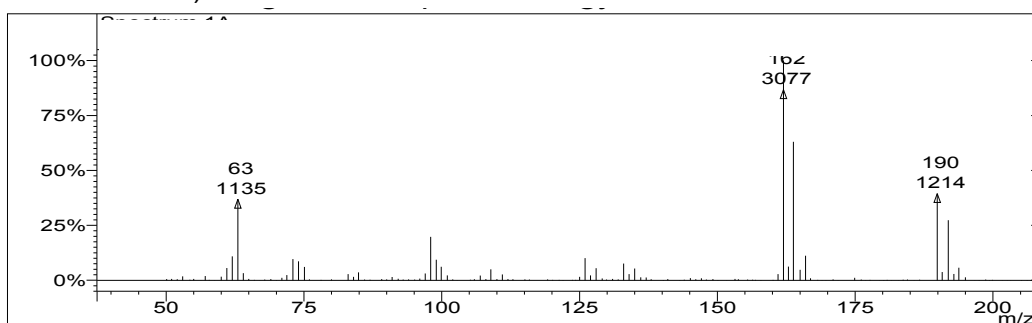


Figure 4.61.d) Mass spectrum of possible intermediate 1,3-dichloro-2-ethoxy benzene (9.633 min.).

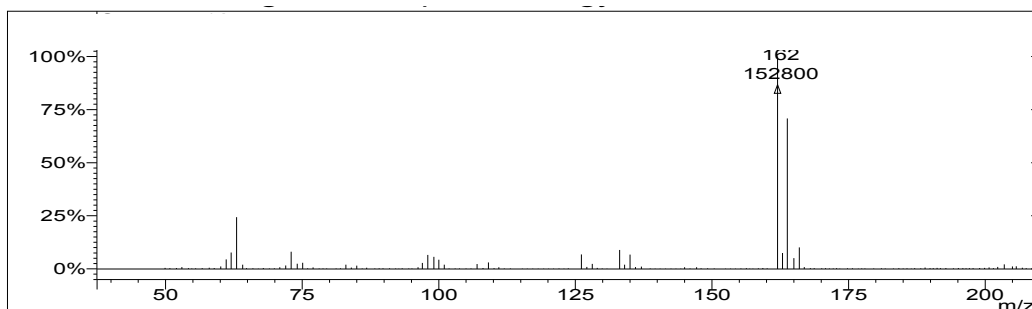


Figure 4.61.e) Mass spectrum of possible intermediate Phenol, 2,4-dichloro acetate (9.695 min.).

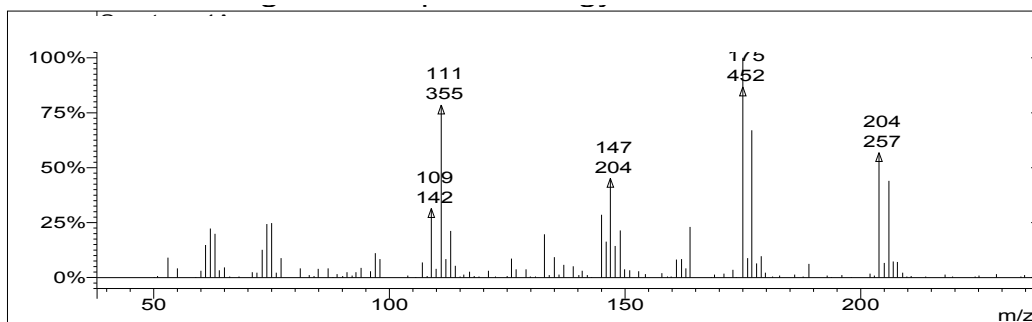


Figure 4.61.f) Mass spectrum of possible intermediate Phenol, 3,4-dichloro-2-propyl (11.648 min.).

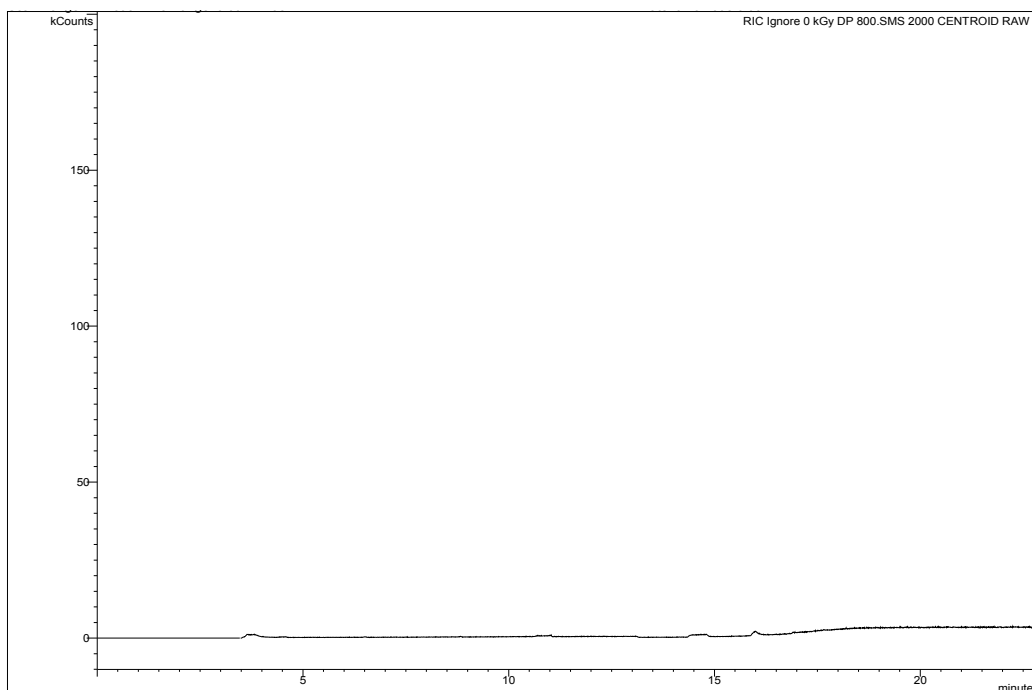


Figure 4.62. GC chromatogram of the ozonized 13.3 minute (5.52 g O₃/L) and unirradiated 2,4-DP (50 ppm) sample after eluted from C18 cartridges in acetone.

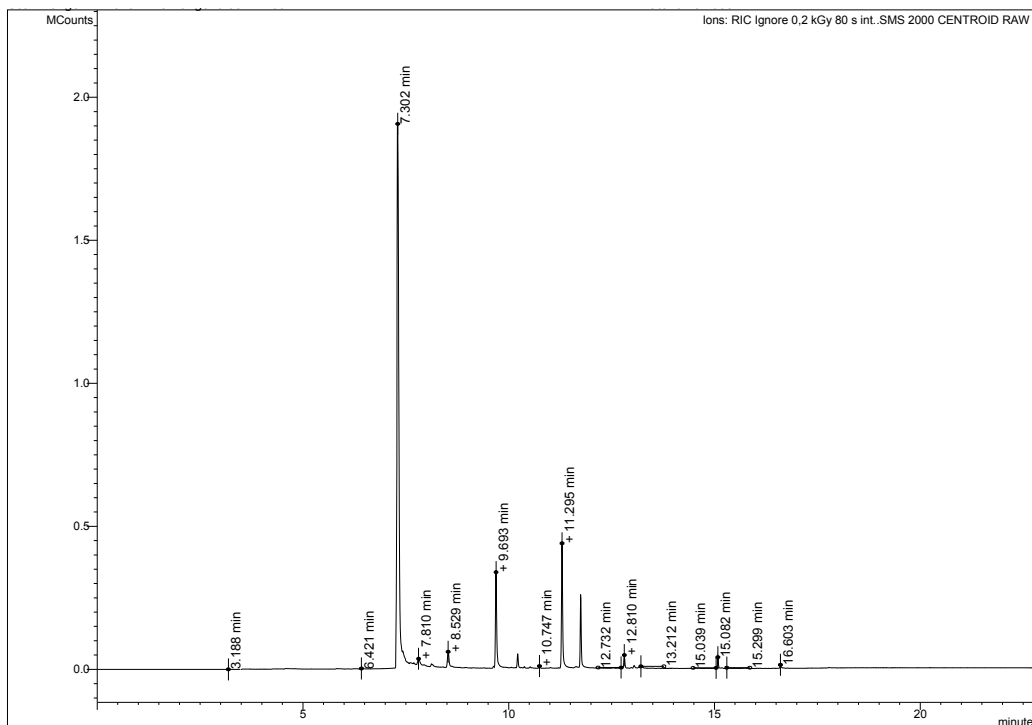


Figure 4.63.a) GC chromatogram of the ozonized 1.3 minute (0.556 g O₃/L) and 0.2 kGy irradiated 2,4-DP (50ppm) sample after eluted from C18 cartridges in acetone.

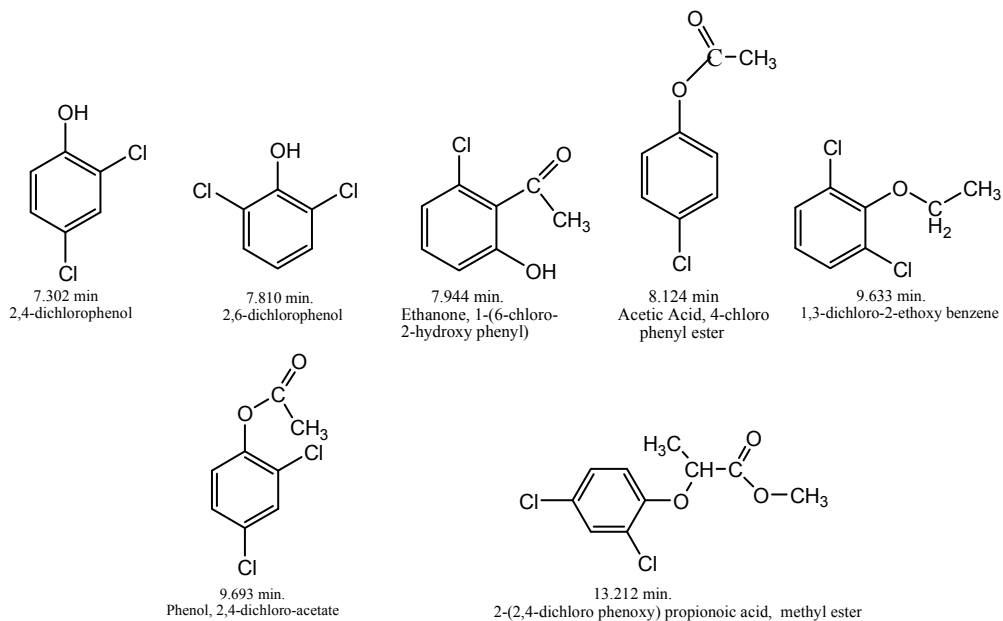


Figure 4.63.b) Possible intermediates for ozonized 1.3 minute (0.556 g O₃/L) and 0.2 kGy irradiated 2,4-DP(50ppm) after eluted from C18 cartridges in acetone.

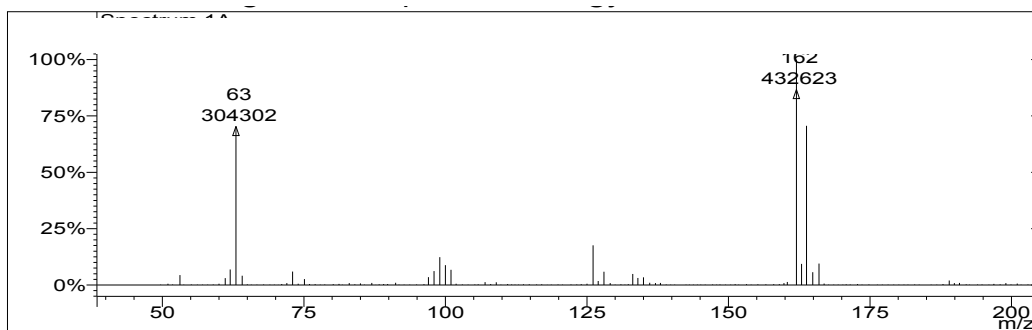


Figure 4.64.a) Mass spectrum of possible intermediate 2,4-dichloro phenol (7.302 min.).

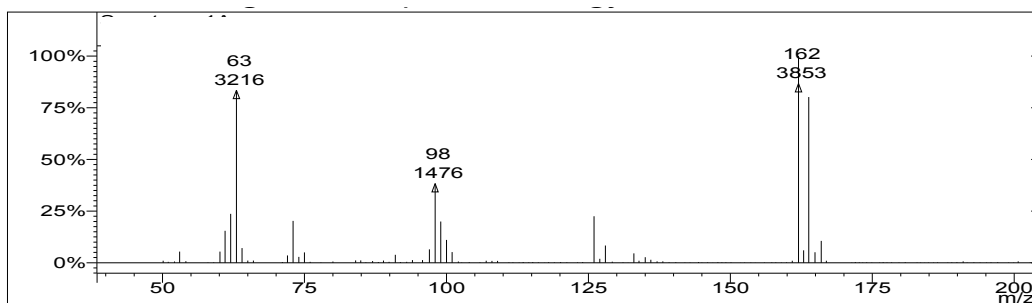


Figure 4.64.b) Mass spectrum of possible intermediate 2,6-dichloro phenol (7.810 min.).

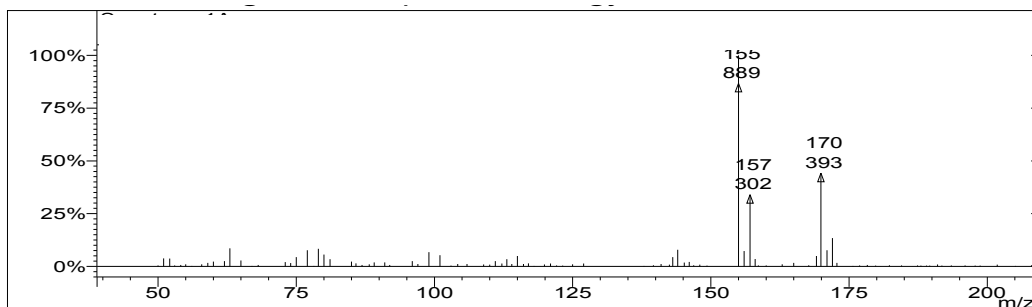


Figure 4.64.c) Mass spectrum of possible intermediate Ethanone, 1-(6-chloro-2-hydroxy phenyl) (7.944 min.).

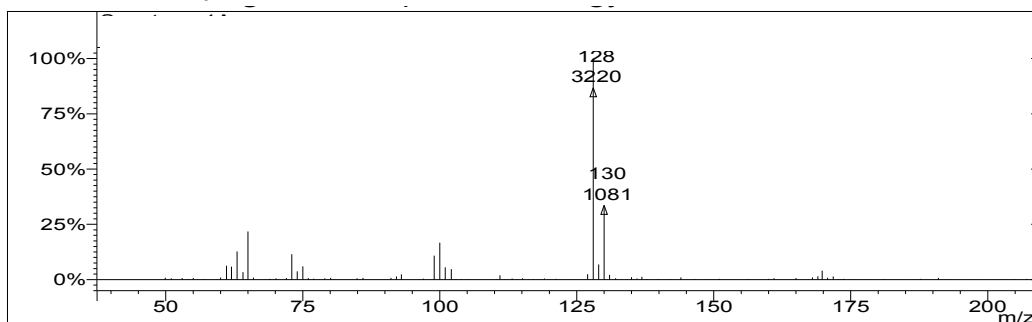


Figure 4.64.d) Mass spectrum of possible intermediate Acetic acid, 4-chloro phenyl ester (8.124 min.).

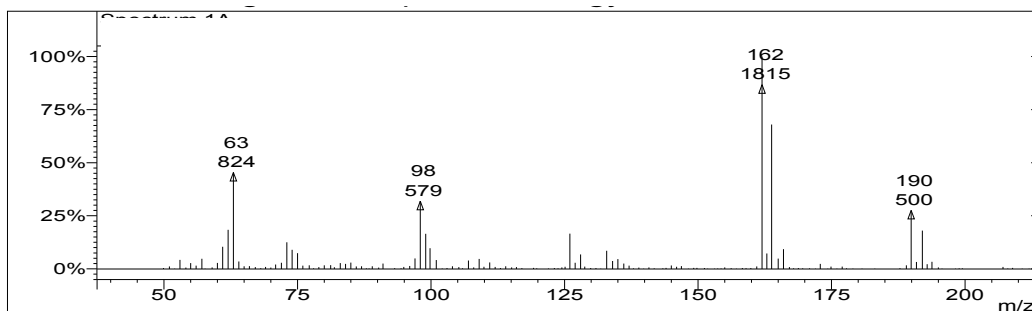


Figure 4.64.e) Mass spectrum of possible intermediate Phenol, 2,4-dichloro acetate(9.693 min.).

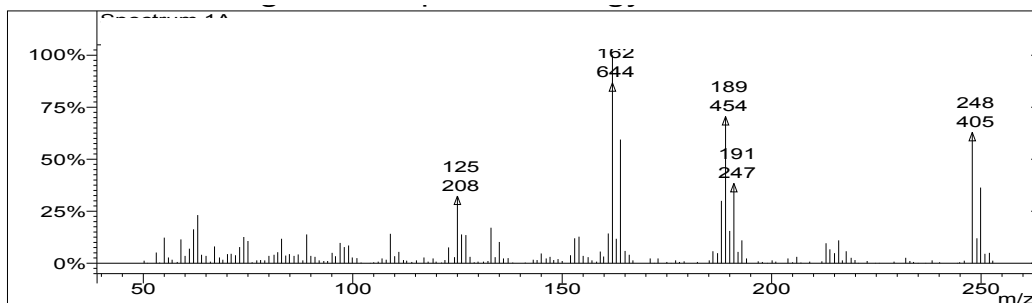


Figure 4.64.f) Mass spectrum of possible intermediate 2-(2,4-dichloro phenoxy) propionic acid methyl ester(13.212 min.).

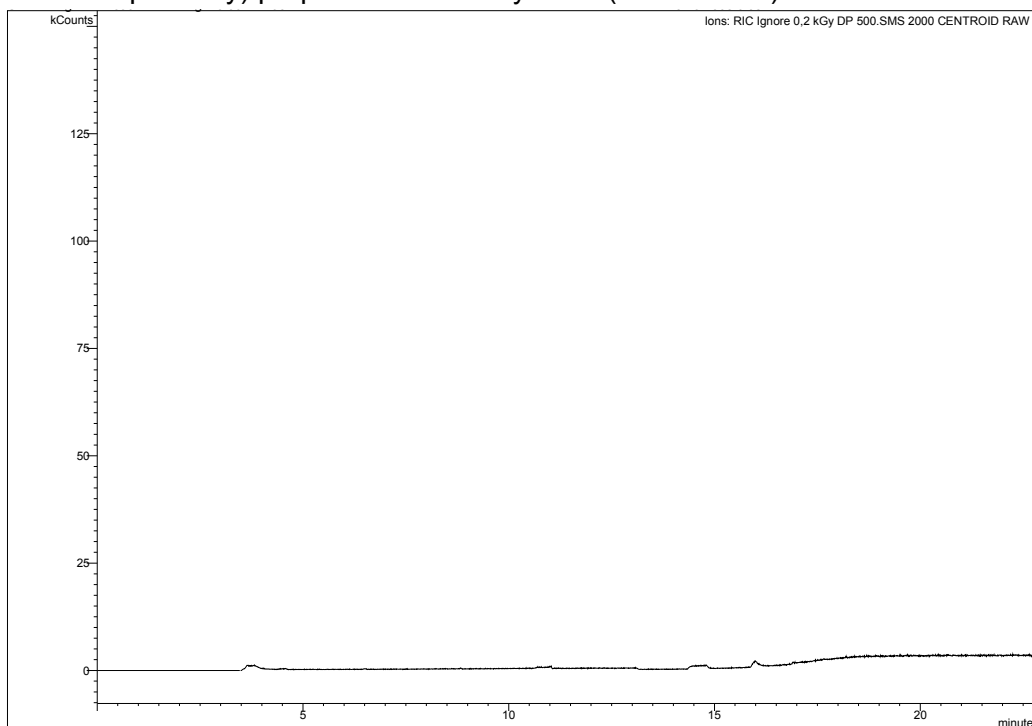


Figure 4.65. GC chromatogram of the ozonized 8.3 minute (3.475 g O₃/L) and 0.2 kGy irradiated 2.4-DP(50ppm) sample after eluted from C18 cartridges in acetone.

4.2.11. Effect of Ozone and Analysis of Residual 2,4-D, 2,4-DP, Intermediates

The irradiation dose was chosen as 0.2 kGy. The O_3 was passed from each herbicide solutions. Complete degradations of unirradiated 2,4-D and 2,4-DP which contain O_3 were obtained at high ozonation time. Addition of only O_3 had important effect on decomposition of intermediates, while 2,4-DCP, major intermediate, is increased up to 1.3 minute ozonation time and decreased and finally decomposed at 8.3 and 13.3 minute ozonation times on irradiated and unirradiated herbicides. Although the major degradation product, 2,4-DCP, is likely a more toxic compound and often more resistant to oxidative degradation, it degraded before herbicides. Data obtained for residual 2,4-D, 2,4-DP and intermediate from the γ irradiation/ O_3 process are given in Figures 4.66-4.69. The γ -irradiation/ O_3 system indicate that 2,4-D and 2,4-DP degradation results from both $OH^\cdot$ and O_3 (Yao and Haag, 1991).

To be effective in the treatment of groundwater and surface water containing trace amounts of pollutants, high hydroxyl free radical concentration is necessary. Combination of ozone with gamma irradiation/electron beam-which represents ionizing radiation- is able to produce much more higher free radical concentrations than the AOPs mentioned before because in this combination the hydroxyl free radicals originate from two different but simultaneously working sources: (1) directly from the water to be purified by action of the gamma or electron beam irradiation (so-called water radiolysis) , and (2) from ozone decomposition accelerated by reducing species formed during water radiolysis (Pikaev, 2000). Table 2.2 shows the most important steps of all ozone based AOPs. From this table it comes out clearly that two completely different mechanisms for $OH^\cdot$ free radical generation occur. UV radiation is absorbed by ozone while the energy of the fast electrons is totally absorbed by water and not by any solute. In other words, under the conditions given, UV irradiation represents the direct effect of radiation while gamma/electron beam irradiation stands for the indirect effect of radiation. It is obvious that ozone/ionizing radiation is the most attractive AOPs for groundwater and surface water. Radiation energy is absorbed by water not by any solutes. There are two $OH^\cdot$ sources

simultaneously: water radiolysis PLUS ozone decomposition higher OH[•] concentration.

Ozonation of phenoxy acids proceeds through the aromatic ring cleavage leading to aliphatic acids depending on pH (Benitez et. al., 1999). As well known, O₃ is added preferentially on double bonds, resulting in unstable ozonides which undergo hydrolysis under formation of various products (Getoff, 1997; Hoigne, 1983b). Ozone may react with solutes either by direct oxidation or by indirect reaction, whereby OH[•] radicals resulting from the decomposition of O₃ serve as oxidant (Getoff, 1997). Ozone can react with radiolysis products of water and possible reactions are (Pikaev, 2000):



Hence, an additional amount of OH[•] radicals which are capable of oxidizing aromatic compounds, appears in the system. The reaction of e_{aq}⁻ with ozone can also proceed as follows:



In acidic conditions, conversion of ozone to hydroxyl radical is enhanced. So, for the 50 ppm 2,4-D, pH 3.90, is suitable for this reaction. It is observed that irradiated 50 ppm 2,4-D and 2,4-DP with ozonized is more easily decomposed than unirradiated and ozonized in Figures 4.66 and 4.67, since for the first case, irradiation enhances additional reactive radicals which are OH[•], HO₂[•]/ O₂^{•-} radicals. During 1.17 minute ozonation, the amounts of 2,4-D and 2,4-DP are 43.2 ppm, 37.1 ppm and 44.7, 38.41 ppm for unirradiated and irradiated samples, respectively. Degradation of 50 ppm 2,4-D and 2,4-DP is efficient with ozone rather than in the absence of ozone and than hydrogen peroxide since the reducing species are converted to reactive species with ozone, attack of these reactive species both alkoxy group and, especially ozone, the double bond in aromatic ring. G_i values are 1.48 and 2.81 for unirradiated and

irradiated 2,4-D and 1.09 and 2.38 for unirradiated and irradiated 2,4-DP, respectively.

The amount of intermediate 2,4-DCP obtained for irradiated 2,4-D and 2,4-DP are higher than those of unirradiated samples since the irradiation in the presence of O_3 enhances the formation of $OH^\cdot$ radicals which increases the formation rate of 2,4-DCP. In the case of unirradiated sample, ozone and double bond selective radicals are predominant, so, the low amount of $OH^\cdot$ radicals can not produce 2,4-DCP and acids and aliphatic compounds are in excess. Also, 2,4-DCP decomposed at lower ozonized levels than 2,4-D. This may be due to attack of ozone more selectively on the double bond of 2,4-DCP which is dilute than 2,4-D. 4-CP wasn't observed for ionizing radiation/ O_3 process, this may be due to the lack of e^-_{aq} in ozone which is converted to more reactive species. 2,4-DCP is more resistant towards ozone compared to 4-CP (Manojlovic, 2007). It is possible that 4-CP degraded simultaneously during ozonation so, it couldn't be monitored.

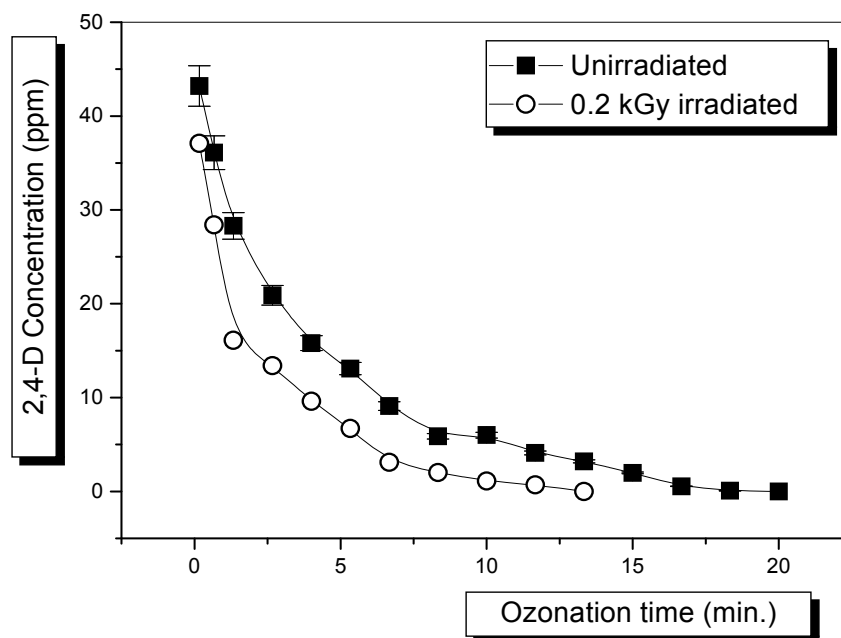


Figure 4.66. Effect of the presence of ozone on yield of 2,4-D (50 ppm) decomposition by γ -irradiation.

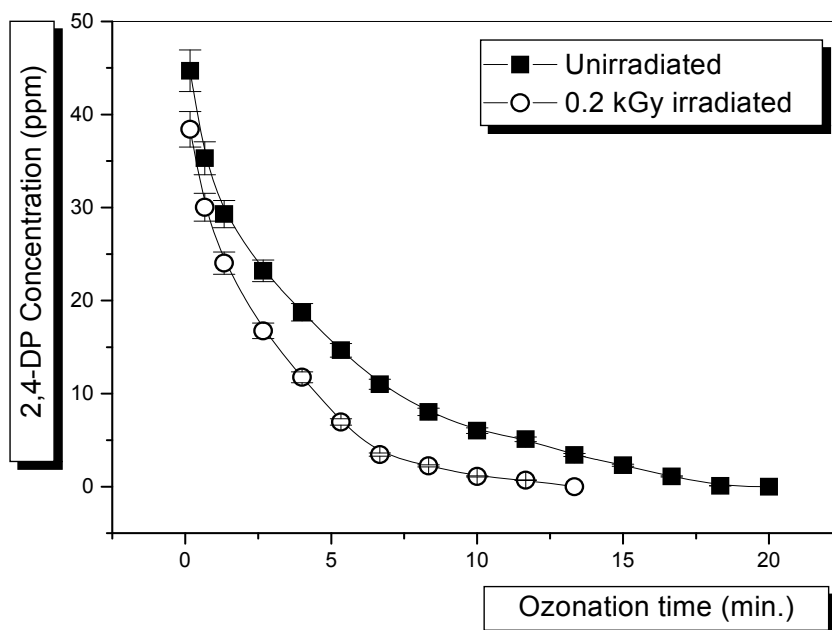


Figure 4.67. Effect of the presence of ozone on yield of 2,4-DP (50 ppm) decomposition by γ -irradiation.

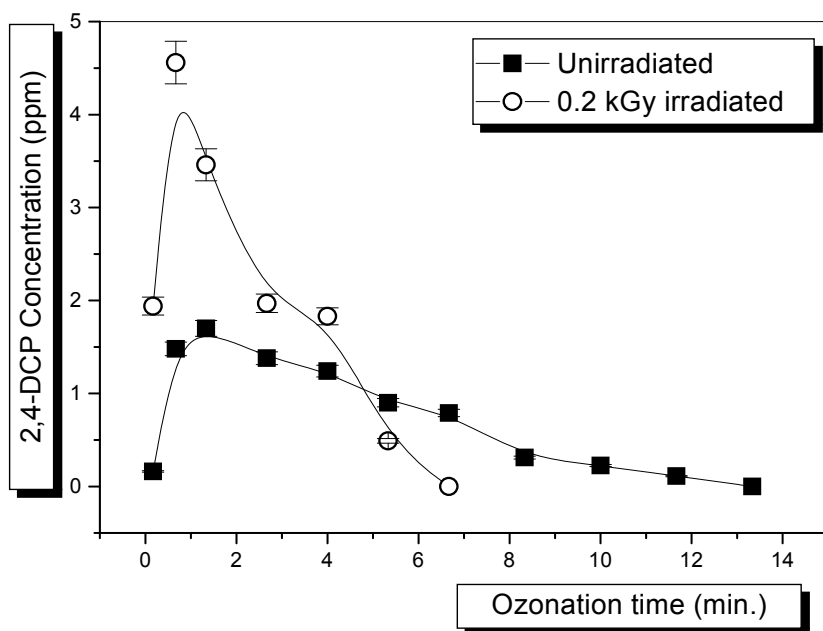


Figure 4.68. Effect of the presence of ozone on the change of formation of 2,4-DCP on yield of 2,4-D (50 ppm) decomposition by γ -irradiation.

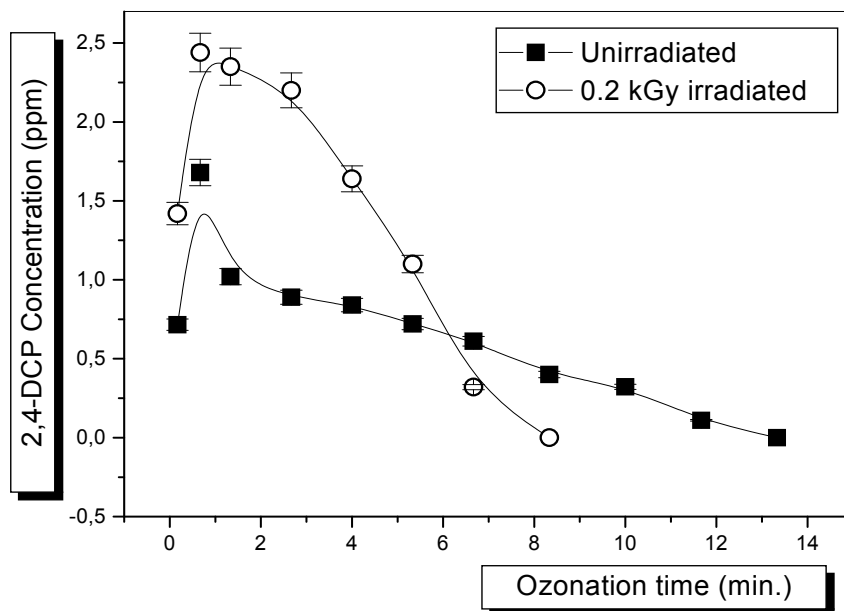


Figure 4.69. Effect of the presence of ozone on the change of formation of 2,4-DCP on yield of 2,4-DP (50 ppm) decomposition by γ -irradiation

4.2.12. Formation of Final Products

4.2.12.1. Free Chlorine

As a result of the degradation process of 2,4-D and 2,4-DP, a number of final products are formed. Their yields strongly depend on the kind of the applied degradation method. The observed Cl^- yields by ionizing radiation/ozone method can be taken as an indicator for the degradation of 2,4-D and 2,4-DP. The amounts of chloride are 2.75 ppm, 1.02 ppm and 3.77 ppm, 1.02 ppm for irradiated and unirradiated 50 ppm 2,4-D and 2,4-DP at 0.17 minute ozonation time, respectively. From the course of the corresponding curves (Figure 4.70 and 4.71) for unirradiated and 0.2 kGy irradiated two different herbicides it is obvious that at 20 and 16.7 minute ozonation times about 91.5 and 95.3 % of the Cl^- atoms in 2,4-D and 2,4-DP are splitting up in the combination of ozonation and radiolysis. Ozone can be added on double bonds too and hence can lead to other products, e.g. in addition to splitting of Cl^- atom, etc. Drzewicz et al. concluded that degradation of 2,4-D and chloride release is lower in ozone only compared to ozone and electron beam (Drzewicz, 2004).

4.2.12.2. Determination of Dissolved Oxygen

The amount of dissolved oxygen was followed by using oxygen meter during irradiation for 50 ppm 2,4-D and 2,4-DP solutions and the results are presented in Figures 4.72 and 4.73. According to decomposition of ozone (Table 4.9), oxygen will produce and when the amount of ozone which pass from 2,4-D and 2,4-DP solutions is increased the amount of dissolved oxygen is increased. The amounts of dissolved oxygen are 8.74, 11.36 mg/L and 8.5, 11.0 mg/L for irradiated and unirradiated 50 ppm 2,4-D and 2,4-DP solutions at 0.17 minute ozonation time, respectively. For 20 minute ozonation time, these amounts are 15.8 and 20.3 mg/L for irradiated and unirradiated 2,4-D, respectively. Increase in dissolved oxygen concentration for unirradiated and irradiated 2,4-D and 2,4-DP solutions is due to the reactions of decomposition of ozone. The lower amounts for irradiated 2,4-D and 2,4-DP solutions are due to the usage of O_2 for some reactions with radiolytic products of water.

4.2.12.3. Determination of Formaldehyde

The highest yields of formaldehyde as degradation product of 2,4-D and 2,4-DP are observed in unirradiated herbicides than irradiated in the presence of ozone (Figures 4.74 and 4.75). The formation of formaldehyde is an indication of the strong degradation of the aromatic ring. Formaldehyde is also one of the radiolytic fragmentation product of the benzene ring as an attack of O_2 . Formaldehyde is consumed during the irradiation and further irradiation may convert aldehydes to carboxylic acids (Sanchez et. al., 2002). With higher ozone amounts, the aldehydes may also be converted into carboxylic acids (such as in reactions (4.4 and 4.5)). The remaining can be decomposed to H_2O and CO_2 at higher absorbed doses. The amounts of formaldehyde increased up to 0.45 and 0.361 ppm for unirradiated and 0.2 kGy irradiated 2,4-D solutions at 9.7 and 5.2 minute ozonation times. The amounts of formaldehyde increased up to 0.42 and 0.33 ppm for unirradiated and 0.2 kGy irradiated 2,4-DP solutions at 8.3 and 5.2 minute ozonation times.

4.2.12.4. Determination of Total Acidity and pH

Figures 4.76 and 4.78 show the change in the total acidity of 2,4-D and 2,4-DP solutions with the different ozonation times. Up to 6.7 min. ozonation time, the total acidity is increased but in 0.2 kGy irradiated samples it is lower than those of unirradiated samples. The pH values of 2,4-D and 2,4-DP solutions are given in Figures 4.77 and 4.79. When we compared the change of pH and total acidity of 2,4-D and 2,4-DP solutions (50 ppm) with the irradiation dose, the results are agreement with each other. These facts indicate the formation of carboxylic acids (formic acid, oxalic acid, etc.) in addition to chloride ions. The decreasing of pH indicates the formation of acids. The pH of the irradiated and unirradiated samples of 50 ppm 2,4-D at 0.17 minute ozonation time are 3.7 and 3.8 respectively. For unirradiated 50 ppm 2,4-D, initial pH was 3.90. This means small amounts of acids are formed. The pH of the irradiated and unirradiated of 50 ppm 2,4-D at 20 minute ozonation time are 3.16

and 3.19 respectively. In the case of 2,4-DP solutions, we have approximately similar results but the initial pH of the unirradiated 50 ppm 2,4-DP was 4.16.

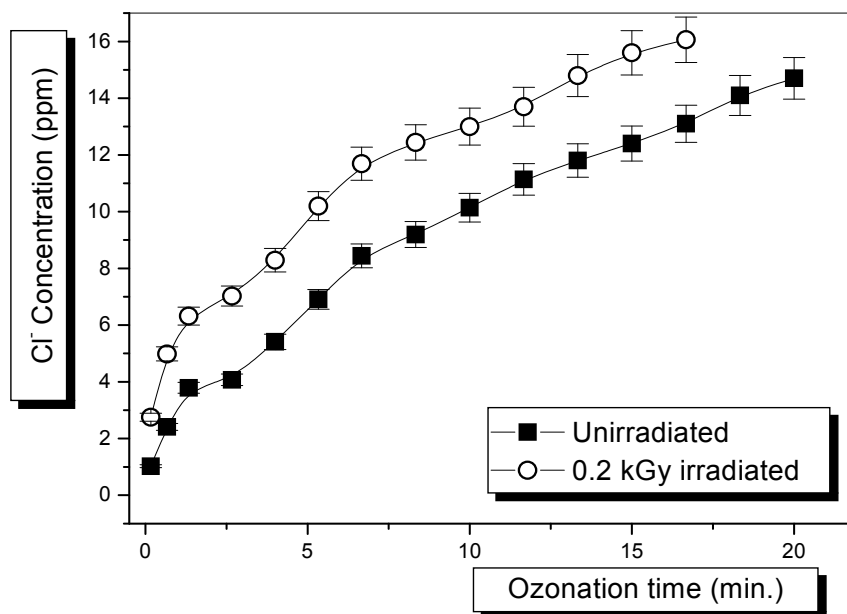


Figure 4.70. Change in the amount of free chloride ions with the ozonation time during irradiation of 2,4-D (50 ppm).

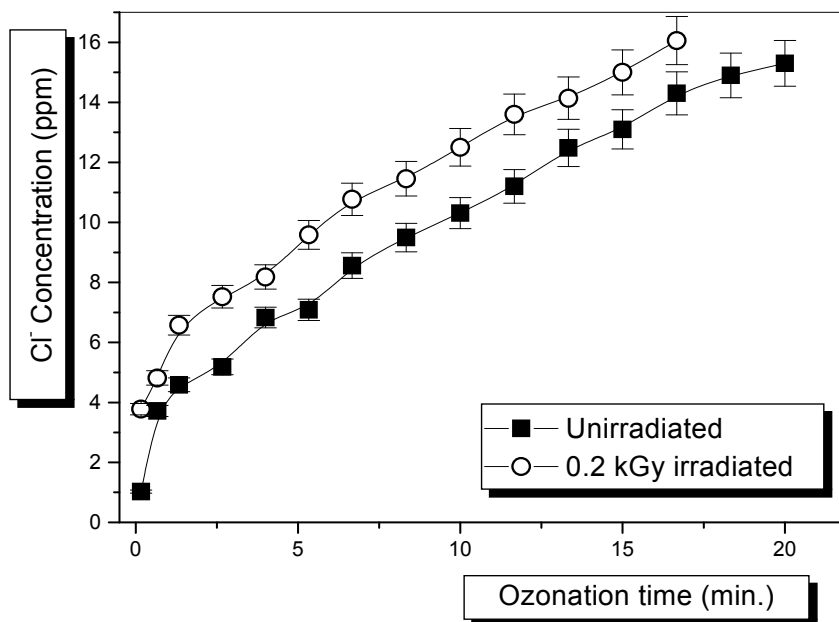


Figure 4.71. Change in the amount of free chloride ions with the ozonation time during irradiation of 2,4-DP (50 ppm)

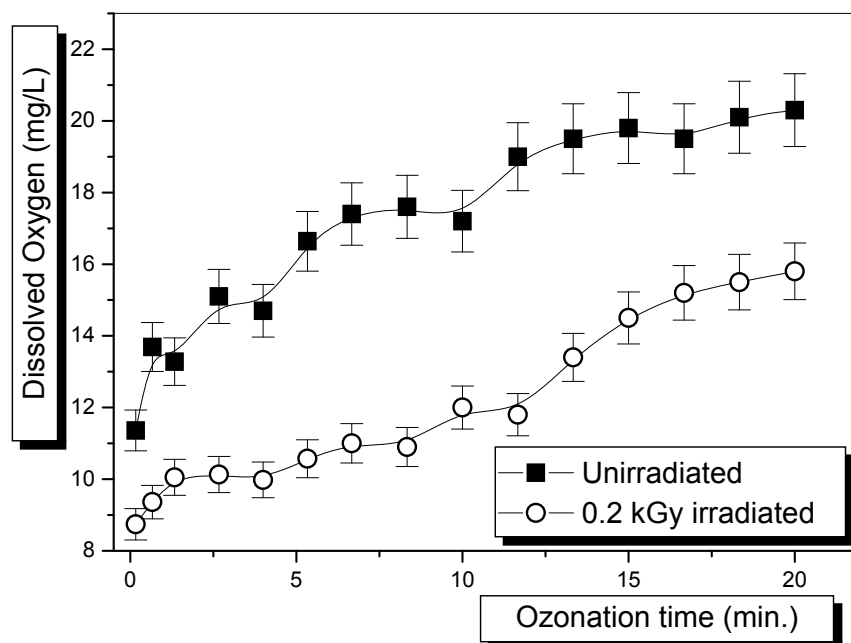


Figure 4.72. Change in the amount of dissolved oxygen with the ozonation time during irradiation of 2,4-D (50 ppm).

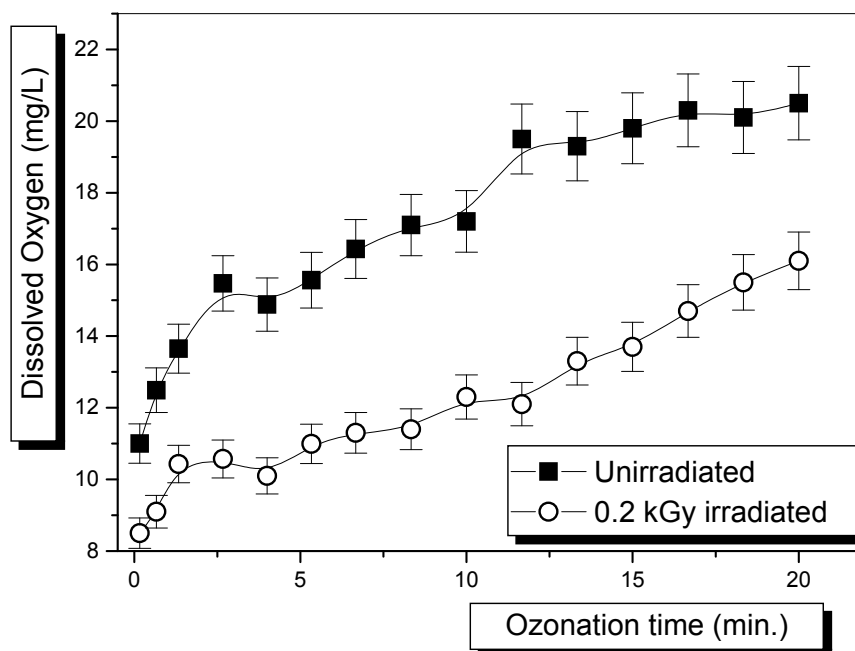


Figure 4.73. Change in the amount of dissolved oxygen with the ozonation time during irradiation of 2,4-DP (50 ppm).

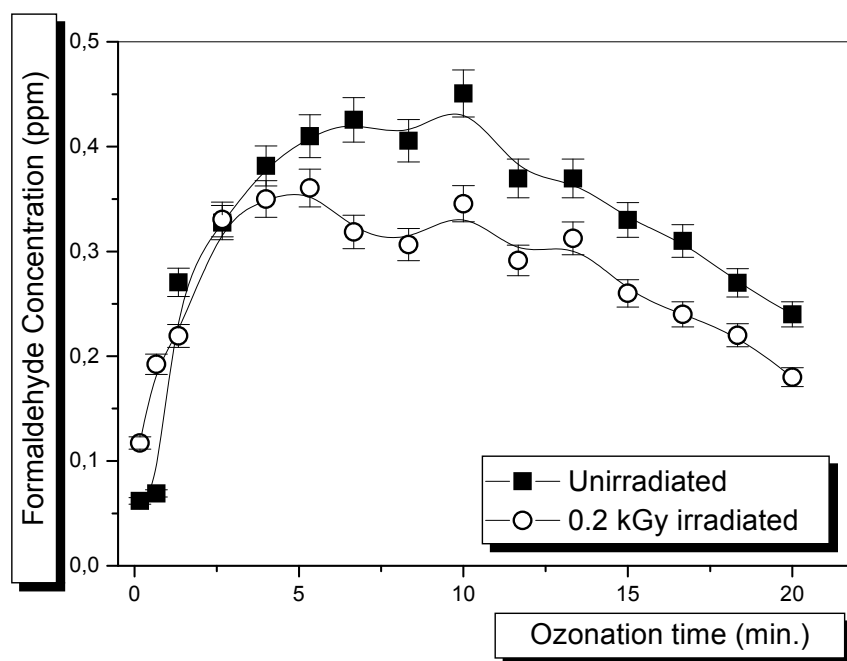


Figure 4.74. Change in the amount of formaldehyde with the ozonation time during irradiation of 2,4-D (50 ppm).

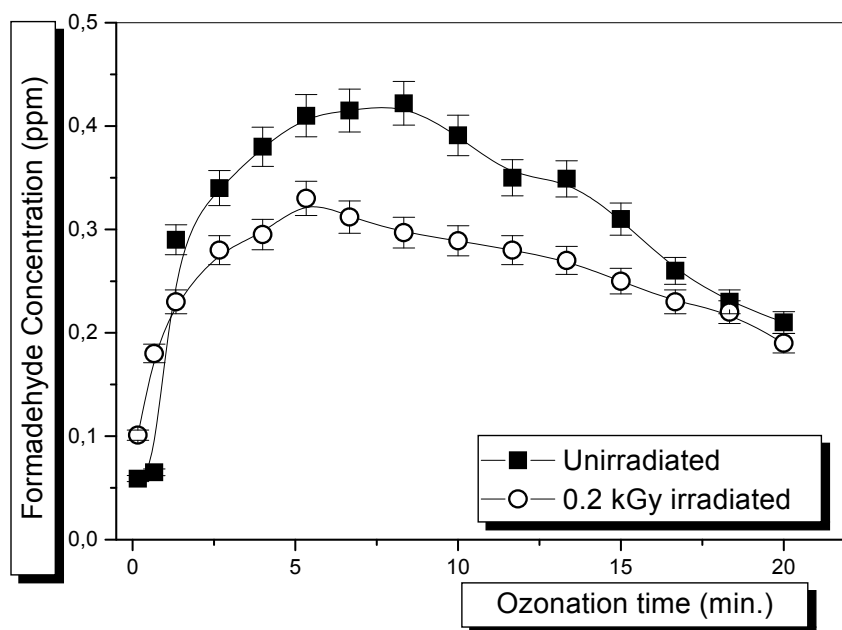


Figure 4.75. Change in the amount of formaldehyde with the ozonation time during irradiation of 2,4-DP (50 ppm).

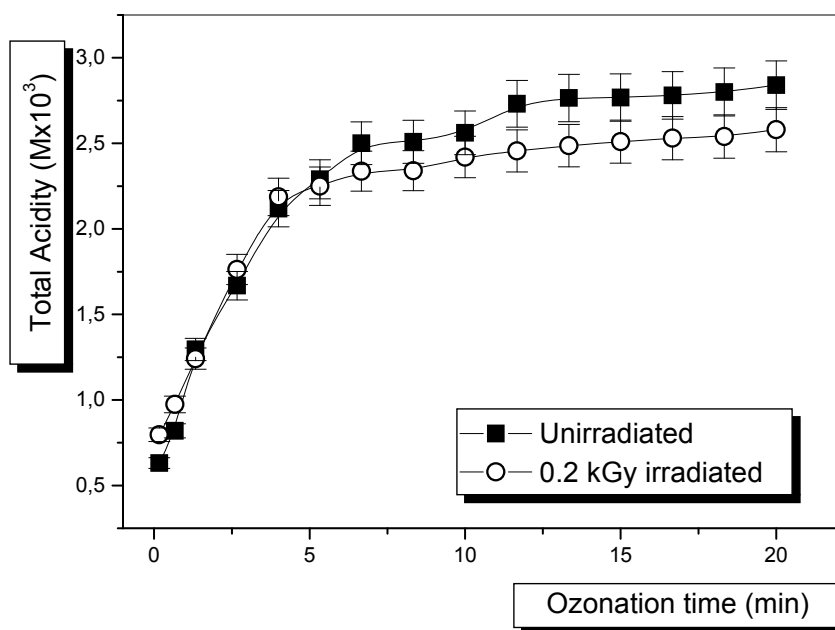


Figure 4.76. Change in the amount of total acidity with the ozonation time during irradiation of 2,4-D (50 ppm).

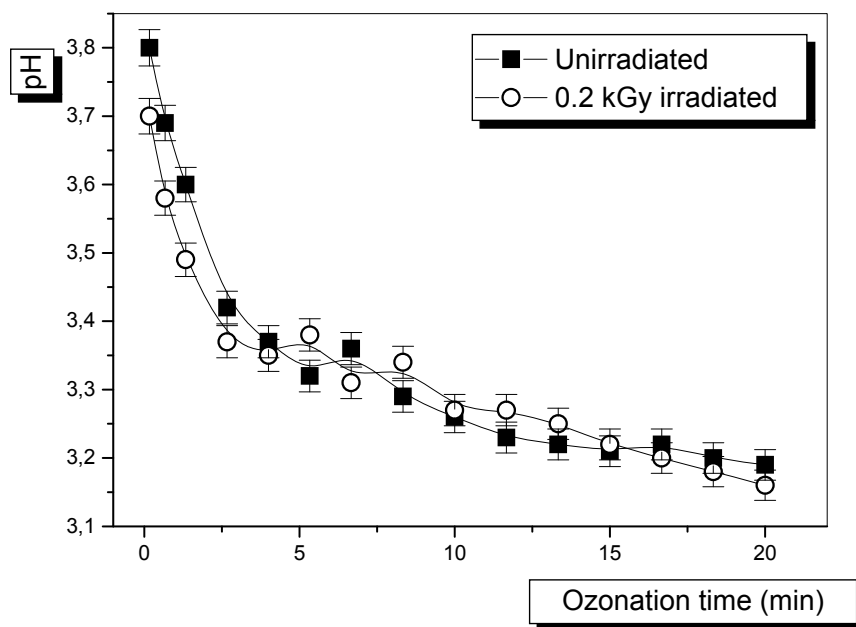


Figure 4.77. Change in the pH with the ozonation time during irradiation of 2,4-D (50 ppm).

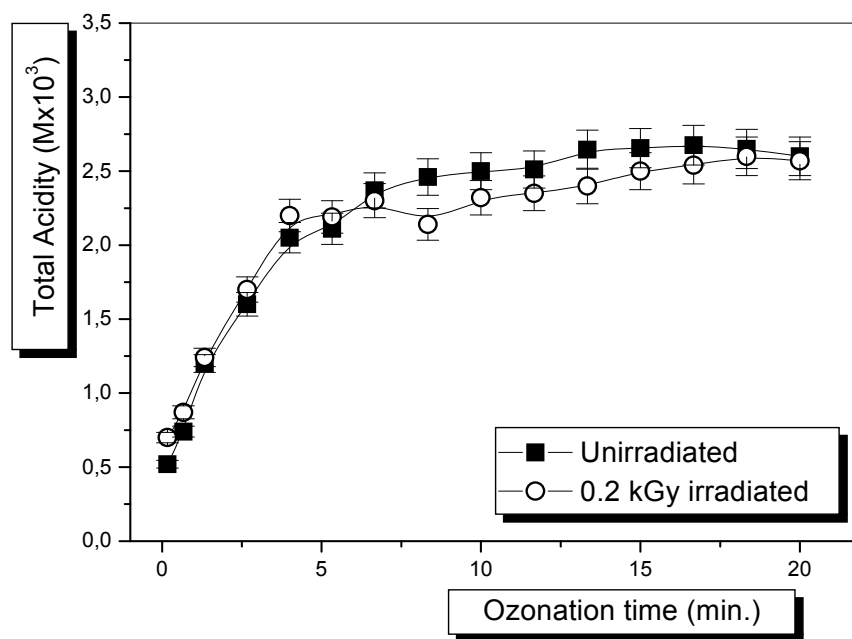


Figure 4.78. Change in the amount of total acidity with the ozonation time during irradiation of 2,4-DP (50 ppm).

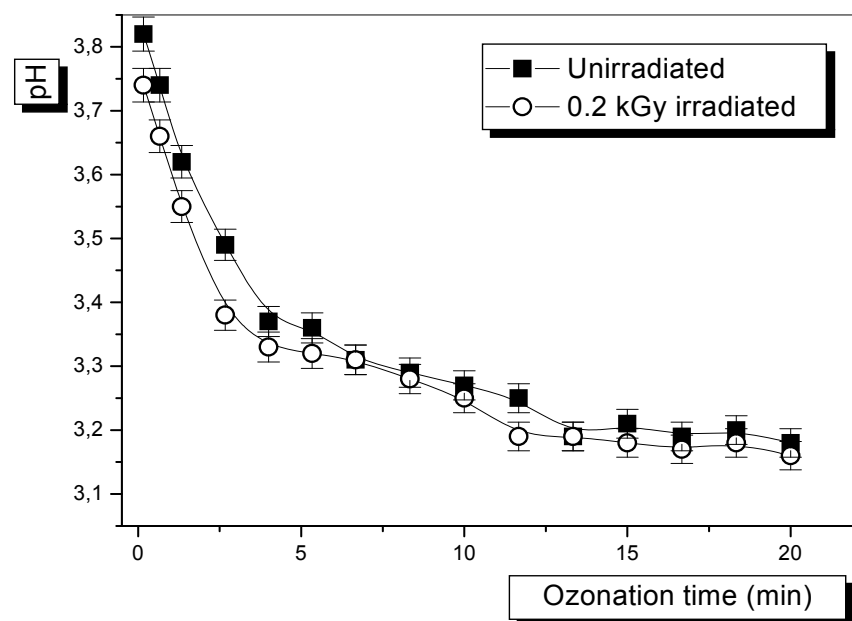


Figure 4.79. Change in the pH with the ozonation time during irradiation of 2,4-DP (50 ppm).

4.2.12.5. Determination of Aliphatic Acids

Ozone is a powerful oxidizing agent and a great number of organic pollutants in water can be decomposed by ozonation. Ozone may react with solutes either by direct oxidation (O_3 attack takes place on the electron rich site of the solute) or by indirect reaction, whereby $OH^\cdot$ radicals resulting from the decomposition of O_3 serve as oxidant (Balcioglu, 1998). The direct O_3 reactions are highly selective in terms of the solutes having double bonds. However, above some critical pH value (usually at pH >6), $OH^\cdot$ radicals become the predominant oxidants. It was observed that as the result of 2,4-D and 2,4-DP degradation under the applied strong oxidizing conditions a carboxylic acids mixture is formed. The total yield of the acids was followed also by the pH-decrease. In addition to this the individual yield of oxalic acid formed in the γ -rays/ O_3 -systems as a function of ozonation time has been determined. The oxalic acid resulting in the γ -rays/ O_3 system has a higher yield and passes a maximum at about 20 minute. The delayed formation in both cases indicates that the oxalic acid is a product of consecutive degradation reactions.

The acetic acid, formic acid and oxalic acid were determined by using ion chromatography. Firstly, ion chromatogram of standards of known organic acids were recorded and their ion chromatographs and their retention times are given in Figure 4.40 and Table 4.4. For 13.3 minute ozonized/unirradiated and 8.3 minute ozonized/0.2 kGy irradiated 2,4-D solutions, ion chromatograms are obtained and they are shown in Figures 4.80-4.81. The retention times of aliphatic anions are given in Tables 4.9 and 4.10. For 13.3 minute ozonized/unirradiated and 8.3 minute irradiated 2,4-DP solutions, ion chromatograms are obtained and they are shown in Figures 4.82-4.83. The retention times of aliphatic anions are given in Tables 4.11 and 4.12. The changes in the amount of acetic acid, formic acid and oxalic acid with the ozone amount during ozonation of 50 ppm 2,4-D and 2,4-DP solutions are shown in Figures 4.84-4.89. The formation of acetic acid and formic acid is increased up to approximately 6.7 minute ozonation time for 2,4-D and 2,4-DP herbicides and after

the maximum amount reached they decreased but the formation of oxalic acid increased continuously up to 20 minute ozonation time for two herbicides.

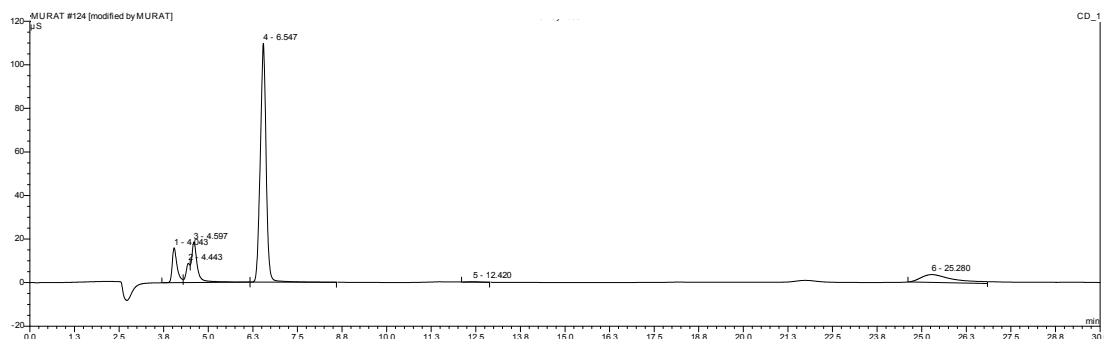


Figure 4.80. Ion chromatography of ozonized(13.3 min)/unirradiated 2,4-D.

Table 4.9.Retention times of intermediates of ozonized(13.3 min)/unirradiated 2,4-D.

Ret. Time (min.)	Name of the Intermediate
4.043	Acetic Acid
4.597	Formic Acid
6.547	Chloride
25.280	Oxalic Acid

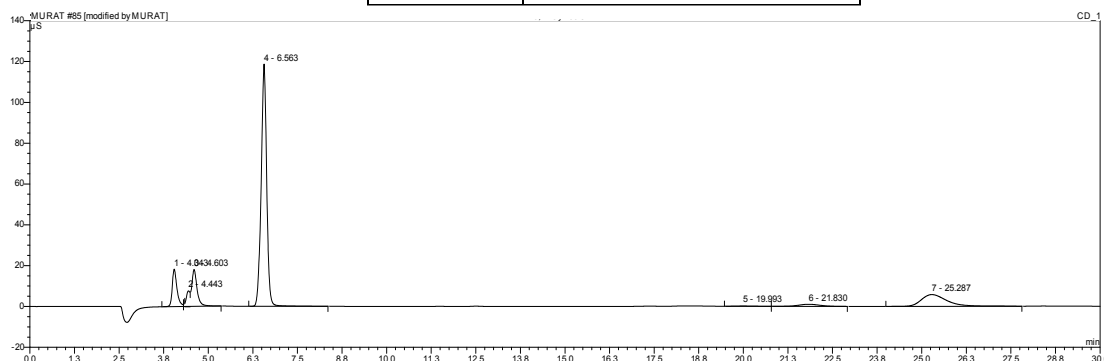


Figure 4.81. Ion chromatography of ozonized (8.3 minute)/0.2 kGy irradiated 2,4-D.

Table 4.10. Retention times of intermediates of ozonized (8.3 minute)/0.2 kGy irradiated 2,4-D.

Ret. Time (min.)	Name of the Intermediate
4.034	Acetic Acid
4.443	Formic Acid
6.563	Chloride
25.287	Oxalic Acid

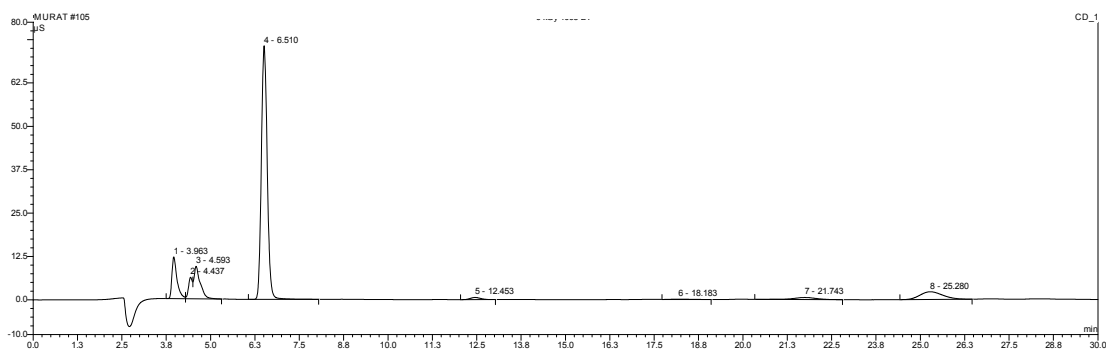


Figure 4.82. Ion chromatography of ozonized (13.3 min)/unirradiated 2,4-DP.

Table 4.11. Retention times of intermediates of ozonized (13.3 min)/unirradiated 2,4-DP.

Ret.Time (min.)	Name of the Intermediate
3.963	Acetic Acid
4.593	Formic Acid
6.510	Chloride
25.280	Oxalic Acid

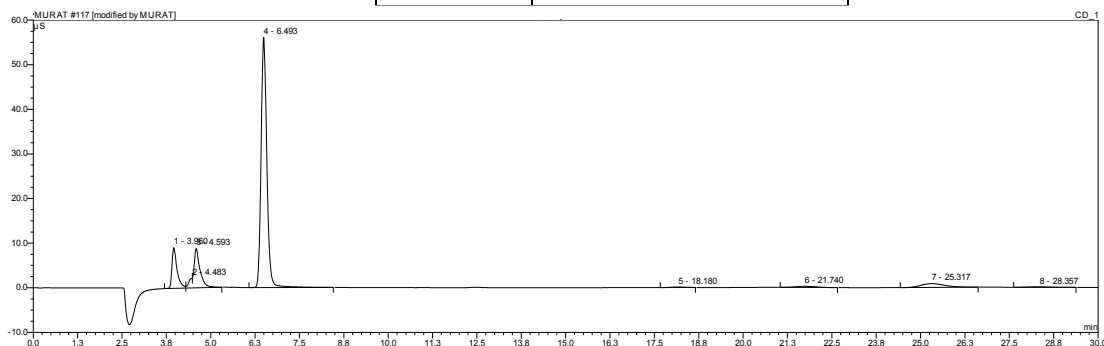


Figure 4.83. Ion chromatography of ozonized (8.3 min)/0.2 kGy irradiated 2,4-DP.

Table 4.12. Retention times of intermediates of ozonized (8.3 min)/0.2 kGy irradiated 2,4-DP.

Ret Time (min.)	Name of the Intermediate
3.960	Acetic Acid
4.593	Formic Acid
6.493	Chloride
25.317	Oxalic Acid

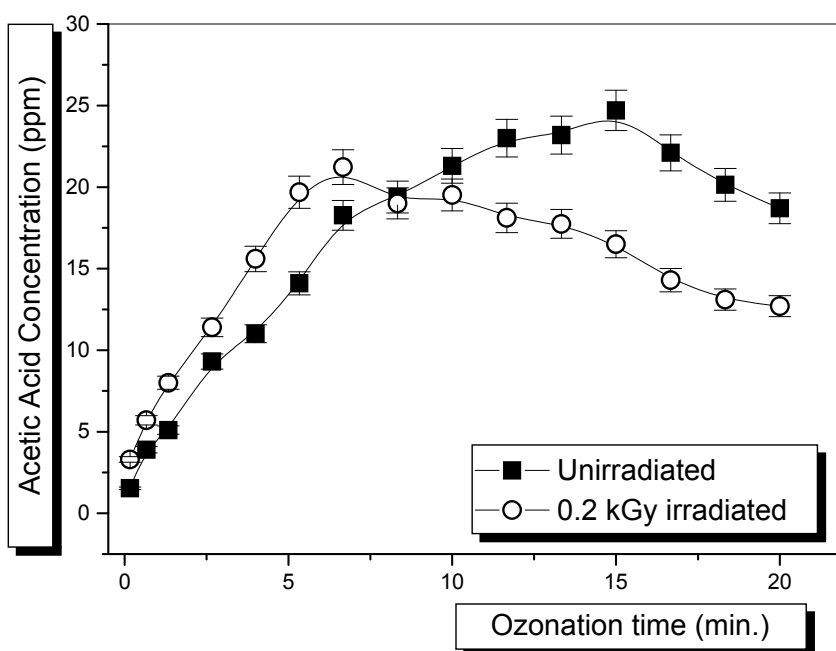


Figure 4.84. Change in the amount of acetic acid with the ozonation time during irradiation of 2,4-D (50 ppm).

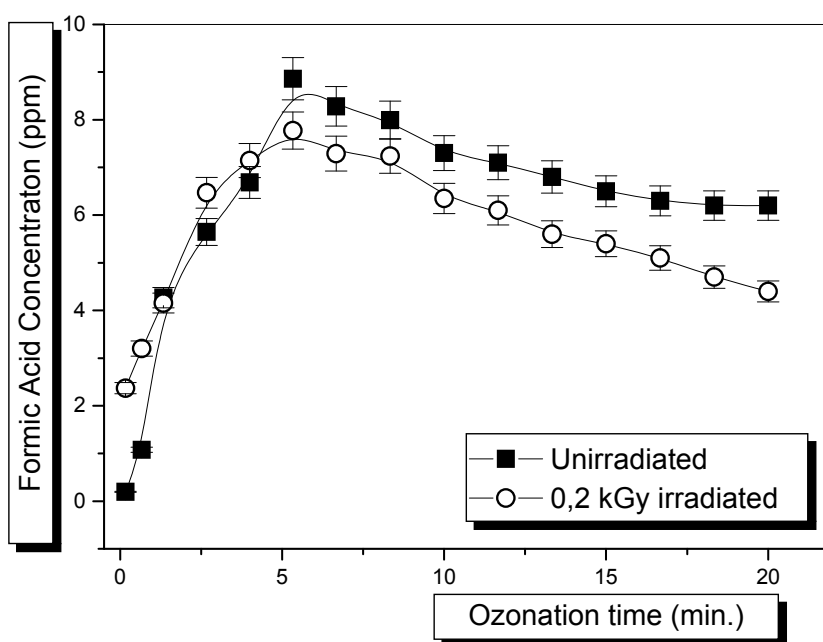


Figure 4.85. Change in the amount of formic acid with the ozonation time during irradiation of 2,4-D (50 ppm).

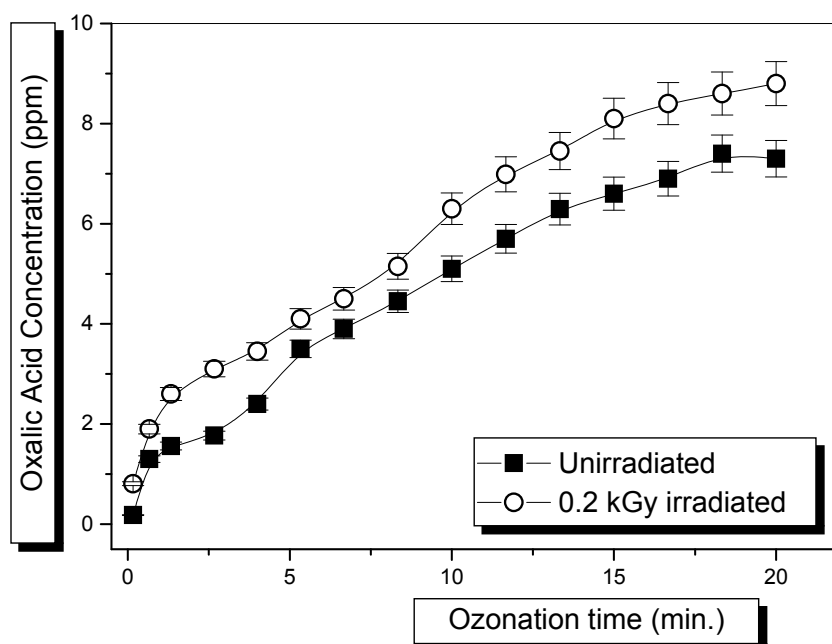


Figure 4.86. Change in the amount of oxalic acid with the ozonation time during irradiation of 2,4-D (50 ppm).

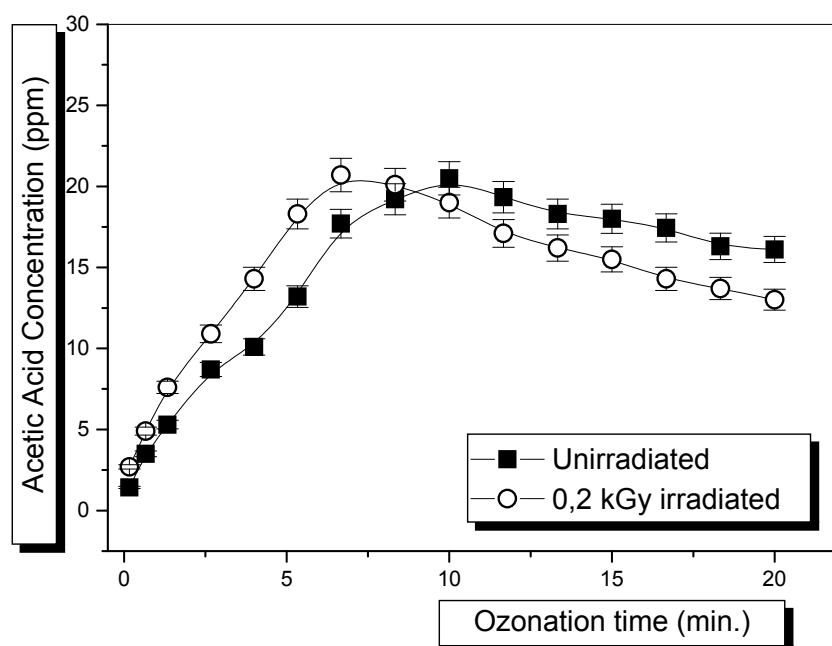


Figure 4.87. Change in the amount of acetic acid with the ozonation time during irradiation of 2,4-DP (50 ppm).

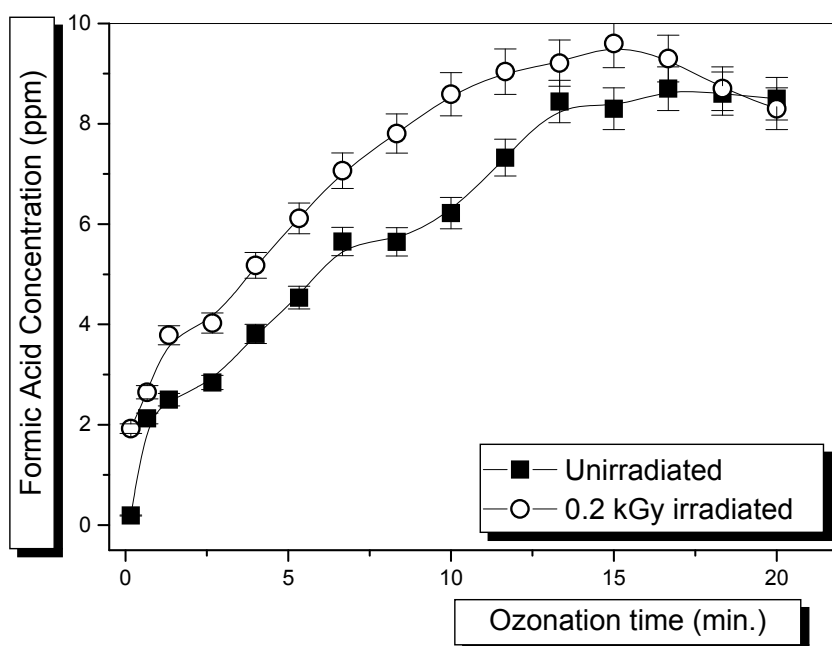


Figure 4.88. Change in the amount of formic acid with the ozonation time during irradiation of 2,4 DP (50 ppm).

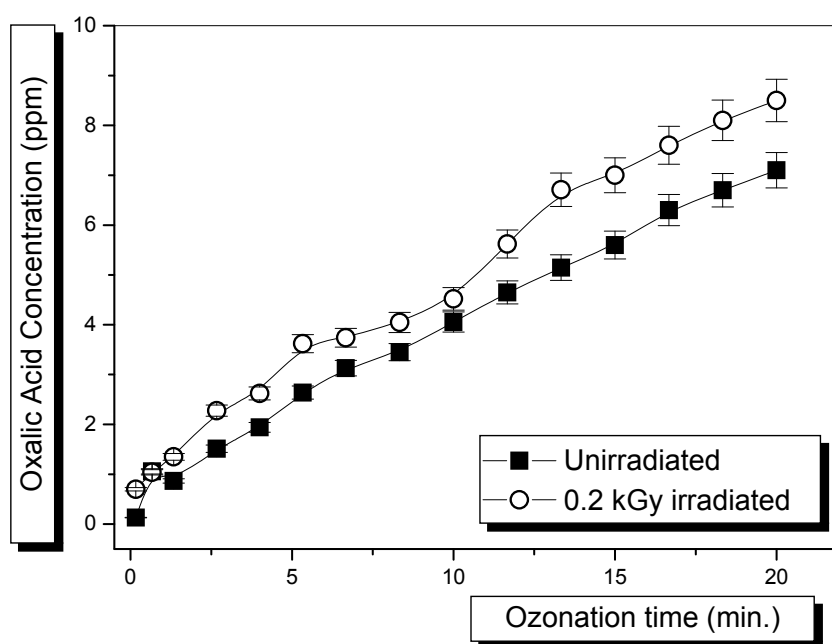


Figure 4.89. Change in the amount of oxalic acid with the ozonation time during irradiation of 2,4 DP (50 ppm).

The total amounts of acetic, formic and oxalic acids were calculated and determined as total aliphatic acids. The total acidities were found for each irradiation doses and ozonation times. The amounts of 2,4-D and 2,4-DP were calculated at each condition. There may be a relationship between the total acidity and the total amount of aliphatic acid. The difference may be the amounts of other organic acids, HCl and carbonic acids in the last step for minerilization. The results are given in Tables 4.13-4.16. From these tables, a trend in the increase of other organic acids, HCl and carbonates is observed. The ion chromatography may not be sensitive to the other organic acids.

Table 4.13. Change in the amounts of total acidity, 2,4-D, aliphatic acids and carbonates and HCl with the irradiation dose during irradiation of 50 ppm 2,4-D in the absence and presence of H_2O_2 .

Dose (kGy)	Total Acidty (M)		Remaining amount of 2,4-D (M)		Total aliphatic acid (Acetic,Formic,Oxalic) (M)		Carbonates , HCl and other organic acids(M)	
	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2
0	0.00023	0.000322	0.000230	0.000223	0	1.554×10^{-5}	0	8.38×10^{-5}
0.2	0.00042	0.000566	0.000186	0.000168	5.99×10^{-5}	0.00012	0.00017	0.00028
0.6	0.00072	0.000844	0.000103	7.42×10^{-5}	0.00023	0.00034	0.00039	0.00044
1.2	0.00084	0.0012	3.65×10^{-5}	1.81×10^{-5}	0.000458	0.00051	0.00035	0.00068
2	0.00081	0.00162	7.06×10^{-6}	0	0.000482	0.00048	0.00032	0.0011
3	0.00085	0.00188	0	0	0.000485	0.00046	0.00037	0.0014
4	0.001	0.00125	0	0	0.00046	0.00045	0.00054	0.00079
5	0.0011	0.00142	0	0	0.000436	0.00045	0.00066	0.00097

Table 4.14. Change in the amounts of total acidity, 2,4-DP, aliphatic acids and carbonates and HCl with the irradiation dose during irradiation of 50 ppm 2,4-DP in the absence and presence of H_2O_2 .

Dose (kGy)	Total Acidty (M)		Remaining amount of 2,4-DP (M)		Total aliphatic acid (Acetic,Formic,Oxalic) (M)		Carbonates , HCl and other organic acids(M)	
	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2	Absence of H_2O_2	Presence of H_2O_2
0	0.00021	0.000325	0.00021	0.00020	0	4.12×10^{-6}	0	0.000111
0.2	0.00045	0.00058	0.00018	0.000154	7.01×10^{-5}	0.000111	0.0002	0.000315
0.6	0.00076	0.00083	0.000107	7.45×10^{-5}	0.000184	0.000214	0.00047	0.000541
1.2	0.00089	0.001	4.28×10^{-5}	2.211×10^{-5}	0.000292	0.00031	0.00056	0.000668
2	0.00089	0.00112	1.36×10^{-5}	4.68×10^{-6}	0.000355	0.000229	0.00052	0.000885
3	0.00089	0.00116	3.83×10^{-7}	0	0.000242	0.00021	0.00065	0.000953
4	0.001	0.00125	0	0	0.000218	0.0002	0.00078	0.00105
5	0.0011	0.00142	0	0	0.000174	0.00016	0.00093	0.00126

Table 4.15. Change in the amounts of total acidity, 2,4-D, aliphatic acids and carbonates and HCl with the ozonation time during 0.2 kGy irradiation of 50 ppm 2,4-D.

Ozone (g/L)	Total Acidty (M)		Remaining amount of 2,4-D (M)		Total aliphatic acid (Acetic,Formic,Oxalic) (M)		Carbonates and HCl and other organic acids(M)	
	Unirradiatedd	0.2 kGy irradiated	Unirradiatedd	0.2 kGy irradiated	Unirradiatedd	0.2 kGy irradiated	Unirradiatedd	0.2 kGy irradiated
0.0695	0.00063	0.00080	0.00019	0.00017	3.38×10^{-5}	0.00012	0.00040	0.00051
0.278	0.00082	0.00097	0.00016	0.00013	0.00012	0.00021	0.00054	0.00064
0.556	0.0013	0.0012	0.00013	7.29×10^{-5}	0.00021	0.00028	0.00096	0.00089
1.12	0.0017	0.0018	9.46×10^{-5}	6.06×10^{-5}	0.00032	0.00040	0.0013	0.0013
1.668	0.0021	0.0022	7.15×10^{-5}	4.34×10^{-5}	0.00038	0.00049	0.0017	0.0017
2.224	0.0023	0.0023	5.93×10^{-5}	3.03×10^{-5}	0.00051	0.00059	0.0017	0.0016
2.78	0.0025	0.0023	4.12×10^{-5}	1.4×10^{-5}	0.00057	0.00061	0.0019	0.0017
3.475	0.0025	0.0023	2.66×10^{-5}	9.1×10^{-6}	0.00059	0.00059	0.0019	0.0017
4.17	0.0026	0.0024	2.71×10^{-5}	5.02×10^{-6}	0.00063	0.00060	0.0019	0.0018
4.865	0.0027	0.0025	1.86×10^{-5}	3.17×10^{-6}	0.00066	0.00059	0.002	0.0019
5.52	0.0028	0.0025	1.45×10^{-5}	0	0.00067	0.00058	0.0021	0.0019
6.25	0.0028	0.0025	8.91×10^{-6}	0	0.00070	0.00057	0.0021	0.0019
6.95	0.0028	0.0025	2.44×10^{-5}	0	0.00066	0.00054	0.0021	0.0020
7.65	0.0028	0.0025	3.17×10^{-7}	0	0.00063	0.00051	0.0022	0.0020
8.33	0.0028	0.0026	0	0	0.00061	0.00050	0.0022	0.0021

Table 4.16. Change in the amounts of total acidity, 2,4-DP, aliphatic acids and carbonates and HCl with the ozonation time during 0.2 kGy irradiation of 50 ppm 2,4-DP.

Ozone (g/L)	Total Acidty (M)		Remaining amount of 2,4-DP (M)		Total aliphatic acid (Acetic,Formic,Oxalic) (M)		Carbonates and HCl and other organic acids(M)	
	Unirradiatedd	0.2 kGy irradiated	Unirradiatedd	0.2 kGy irradiated	Unirradiatedd	0.2 kGy irradiated	Unirradiatedd	0.2 kGy irradiated
0.0695	0.00052	0.0007	0.00019	0.00016	3.81×10^{-5}	0.00010	0.00030	0.00043
0.278	0.00074	0.00087	0.00015	0.00013	0.00013	0.00016	0.00046	0.00058
0.556	0.0012	0.0012	0.000125	0.00010	0.00016	0.00024	0.00091	0.0009
1.12	0.0016	0.0017	9.87×10^{-5}	7.12×10^{-5}	0.00024	0.00032	0.0013	0.0013
1.668	0.0021	0.0022	7.97×10^{-5}	5.0×10^{-5}	0.00029	0.00041	0.0017	0.0017
2.224	0.0021	0.0022	6.24×10^{-5}	2.96×10^{-5}	0.00038	0.00052	0.0017	0.0016
2.78	0.0024	0.0023	4.69×10^{-5}	1.47×10^{-5}	0.00049	0.00058	0.0018	0.0017
3.475	0.0025	0.0021	3.42×10^{-5}	9.53×10^{-6}	0.00052	0.00059	0.0019	0.0015
4.17	0.0025	0.0023	2.56×10^{-5}	4.68×10^{-6}	0.00057	0.00060	0.0019	0.0017
4.865	0.0025	0.0024	2.2×10^{-5}	2.98×10^{-6}	0.00058	0.00061	0.0019	0.0017
5.52	0.0026	0.0024	1.45×10^{-5}	0	0.00060	0.00062	0.0020	0.0018
6.25	0.0027	0.0025	9.79×10^{-6}	0	0.00060	0.00062	0.0020	0.0019
6.95	0.0027	0.0025	4.68×10^{-6}	0	0.00062	0.00061	0.0020	0.0019
7.65	0.0027	0.0026	3.79×10^{-7}	0	0.00061	0.00060	0.0020	0.0020
8.33	0.0026	0.0026	0	0	0.00061	0.00059	0.0020	0.0019

4.3. The degradation mechanisms of 2,4-D and 2,4-DP

2,4-D and 2,4-DP herbicides followed the same degradation mechanism in the presence of O_2 and H_2O_2 . In the presence of O_2 , firstly $OH^\cdot$ attacks on the aromatic ring of phenoxyacid herbicides, resulting the formation of 2,4-DCP and alkoxy moiety. Intermediate 2,4-DCP degradation follows two possible steps: one of them is attack of e_{aq}^- to 2,4-DCP and formation of 4-CP. An attack of $OH^\cdot$ and then O_2 to aromatic ring caused the formation of mucconaldehyde and mucconic acid, then oxalic acid, one of the last stage (Getoff, 1990). The other step is addition of $OH^\cdot$ and then O_2 to aromatic ring of 2,4-DCP caused the formation of muccon aldehyde or mucconic acid. With hydroxyl group attack to mucconic acid, HCl elimination is possible. Final product is again oxalic acid and finally oxalic acid decomposes to CO_2 . The reaction of side chain, alkoxy moiety decomposed to formic acid and acetic acid. Formic acid decomposes to CO_2 with $OH^\cdot$ and O_2 . Acetic acid decomposes to formaldehyde and CO_2 , formaldehyde converted to formic acid then CO_2 . These reactions and some possible reactions are given in Figures 4.90 and 4.91.

In the presence of O_3 , there are two possible pathways: one of them is addition of $OH^\cdot$ to herbicides and formation of 2,4-DCP. Ozone selectively adds on the double bond of the aromatic ring of intermediate 2,4-DCP to form mucconic acid and mucconaldehyde and HCl. The other possibility is O_3 adds on the double bond of the aromatic ring of 2,4-D and 2,4-DP herbicides and to form mucconaldehyde and mucconic acid, HCl elimination is possible. Final products are acetic acid, formic acid and oxalic acid. The products and mechanism of formation of acetic acid, oxalic acid, formic acid and side group alkoxy moiety is the same with in the case of O_2 media. These reactions and some possible reactions are given in Figures 4.92 and 4.93.

The mechanism of addition of $OH^\cdot$ radicals on aromatic ring of chlorophenoxyacid herbicides and further degradation reactions and possible intermediates and final products can be generalized in Figure 4.94.

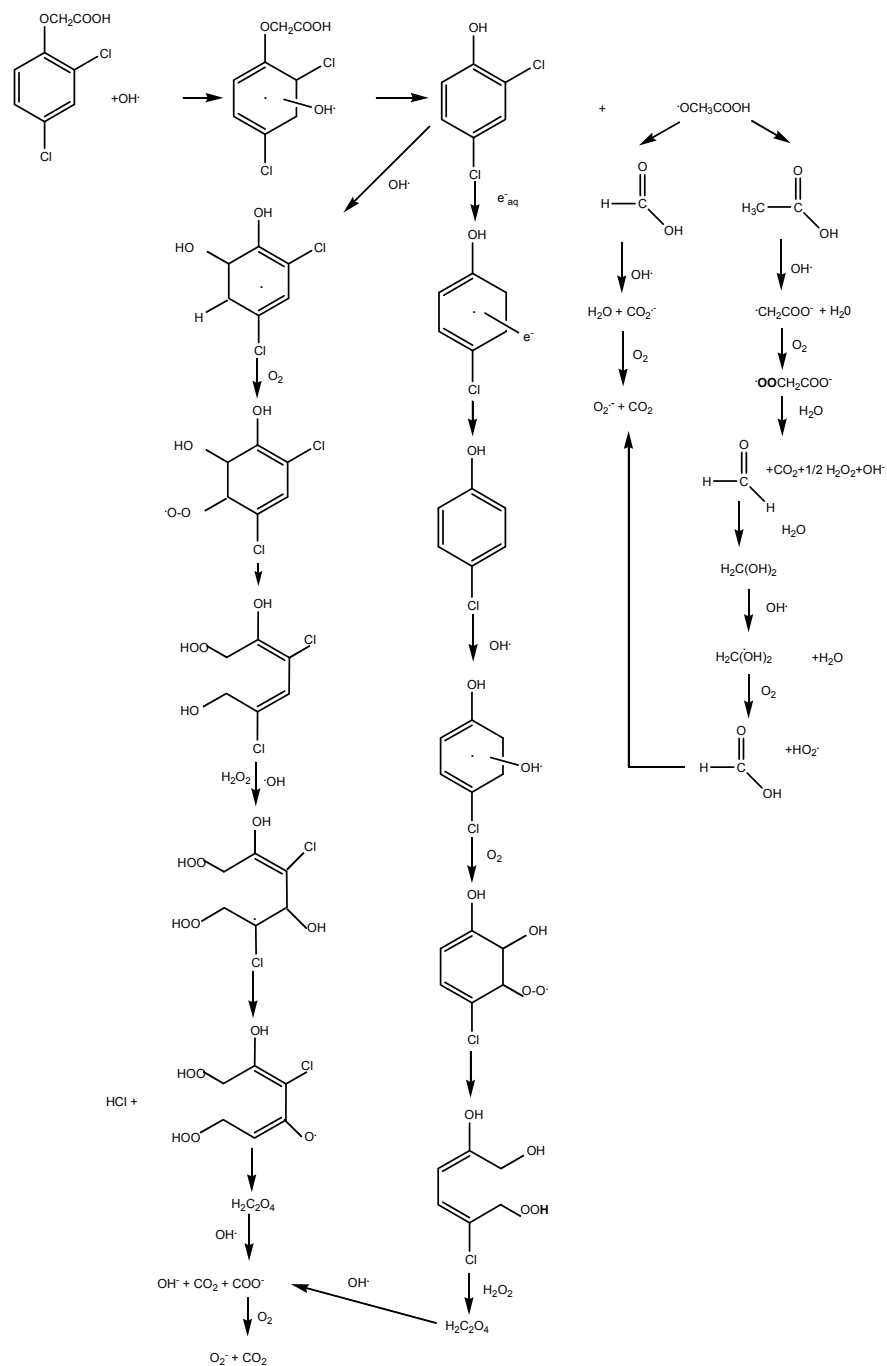


Figure 4.90. The probable degradation pathway of 2,4-D in the presence of O_2 and H_2O_2 .

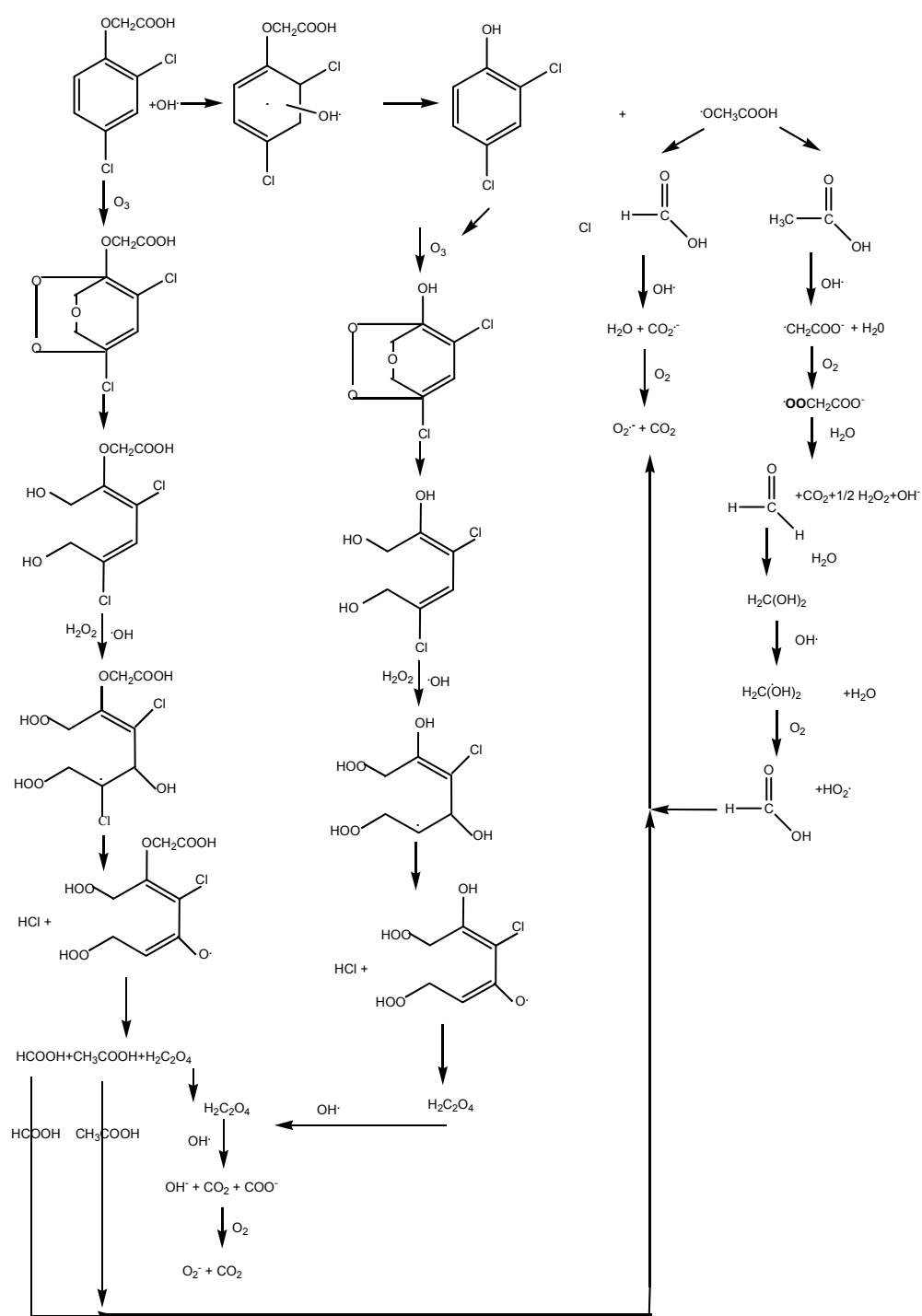


Figure 4.92. The probable degradation pathway of 2,4-D in the presence of O_3 .

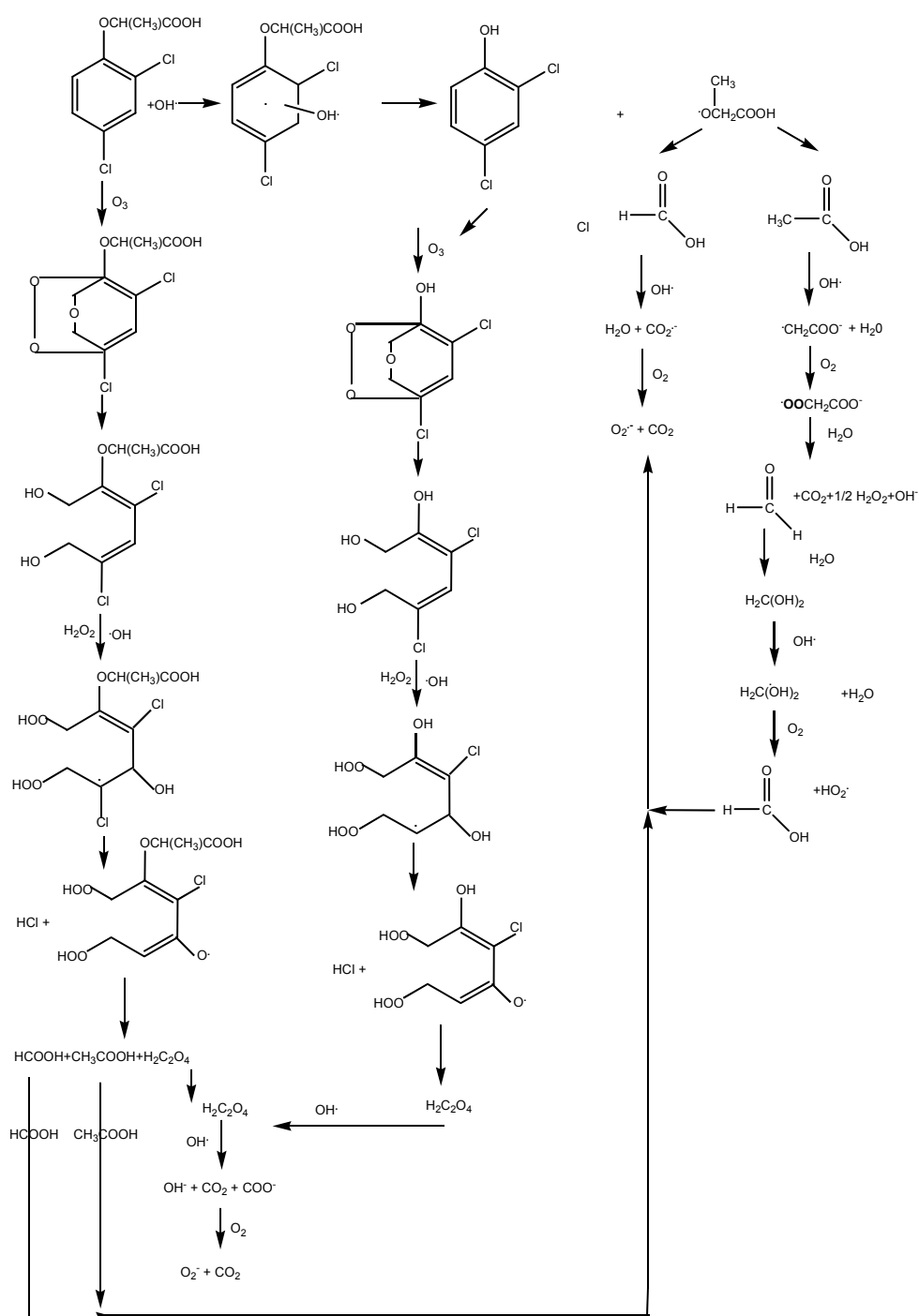


Figure 4.93. The probable degradation pathway of 2,4-DP in the presence of O₃.

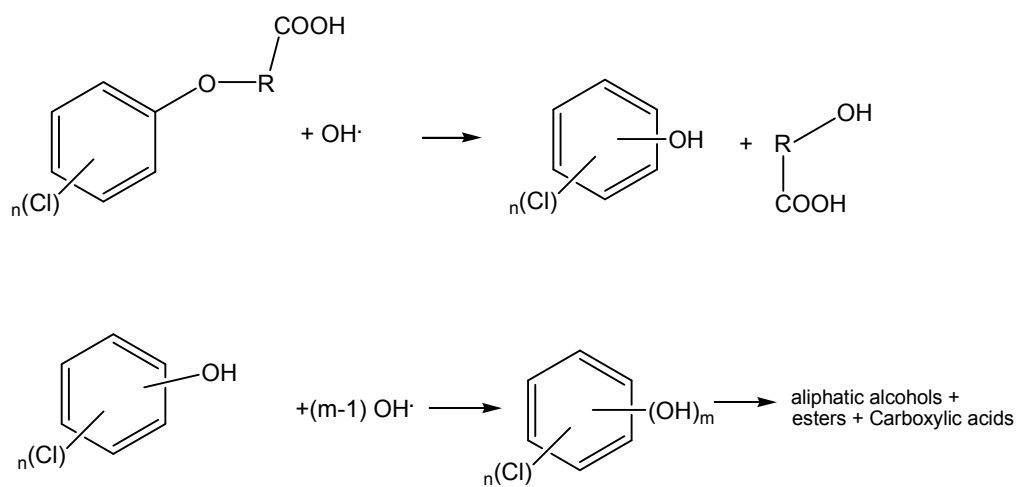


Figure 4.94. The generalized degradation pathway of 2,4-D and 2,4-DP herbicides.

5. CONCLUSION

- In this study, the removal of chlorinated phenoxyacid herbicides in surface and groundwaters at various conditions was investigated and we focused on 2,4-D and 2,4-DP herbicides which are widely used in agricultural activities in Turkey and in the world.
- The degradation of 2,4-D and 2,4-DP by gamma-irradiation was followed by using UV-Vis spectrophotometer as a function of irradiation dose and initial concentrations of them. It was found that the degradation of these herbicides was increased with the irradiation dose and initial concentration of herbicides. The decrease in the pH of these aqueous solutions of herbicides with the irradiation dose and initial concentrations was observed.
- For preconcentration and to extract intermediates and undegraded herbicides from aqueous media to organic phase, solid phase extraction method was used.
- The GC-MS-MS conditions were determined according to EPA methods for analysis of the remaining 2,4-D and 2,4-DP herbicides and intermediates after the irradiation in the absence and presence of some oxidants.
- The gas chromatograms, mass spectra and retention times of the derivatives (their methyl esters) and internal standards were recorded for speciation and quantitative determination of undegraded 2,4-D and 2,4-DP herbicides.
- The gas chromatograms, mass spectra and retention times of the phenolic and internal standards were recorded for speciation and qualitative and quantitative determination of possible intermediates.

- In order to increase the efficiency of degradation of herbicides and intermediates which may be toxic, H_2O_2 and O_3 were used as hydroxyl radical (oxidizing agents) sources in addition to water radiolysis products.
- The effect of H_2O_2 and O_3 was investigated on degradation of herbicides and intermediates.
- For degradation of herbicides and intermediates the additional experiments were performed in order to optimize conditions for using H_2O_2 and ozonation (H_2O_2 concentration, ozonation time, concentration of dissolve ozone). In the absence and presence of H_2O_2 and O_3 after and before irradiation the amounts of dissolved oxygen and formaldehyde were determined by using oxygen meter and UV-vis spectrometer, respectively.
- The ion chromatograms and retention times of the mixture of aliphatic acids and chloride ionic species standards were recorded for speciation and qualitative and quantitative determination of ionic species by using ion chromatograph.
- The radiation-induced degradation of 2,4-D and 2,4-DP in aqueous solution was studied under various conditions as a function of irradiation dose in the absence and presence of H_2O_2 . The irradiation doses necessary for complete degradation of 50 ppm 2,4-D were 3.0 and 2.0 kGy and for 2,4-DP they are 3.5 and 2.5 kGy in the absence and presence of 1.2 mM H_2O_2 , respectively.
- The amounts of toxic intermediates 2,4-DCP and 4-CP from 2,4-D increased up to approximately 1.0 kGy irradiation dose and completely degradation of 2,4-DCP was realized at 4.5 and 3.0 kGy and for 4-CP 4.5 and 3.5 kGy in the absence and presence of H_2O_2 , respectively. Dechlorination from 2,4-D was increased with the irradiation dose and at 5.0 kGy it was 98.44% and at 3.5

kGy complete dechlorination was observed in the absence and presence of H_2O_2 .

- The amounts of toxic intermediates 2,4-DCP and 4-CP from 2,4-DP increased up to approximately 1.0 kGy irradiation dose and complete degradations of 2,4-DCP and 4-CP were realized at 5.0 and 4.0 kGy in the absence and presence of H_2O_2 , respectively. Dechlorination from 2,4-DP was increased also with the irradiation dose and at 5.0 kGy it was 97.43% and at 4.5 kGy complete dechlorination was observed in the absence and presence of H_2O_2 .
- Since the addition of H_2O_2 to unirradiated 50 ppm 2,4-D and 2,4-DP aqueous solutions, the degradations of 2,4-D and 2,4-DP were 1.6% and 1.2%, respectively. The necessary irradiation doses for complete degradations of 2,4-D and 2,4-DP were decreased from 3.0 to 2.0 and from 3.5 to 2.5 kGy, respectively. These results show the effect of H_2O_2 on degradation of 2,4-D and 2,4-DP herbicides.
- The radiation-induced degradation of unirradiated and 0.2 kGy irradiated 2,4-D and 2,4-DP in aqueous solution was studied under various conditions as a function of ozonation time in the absence and presence of O_3 . The ozonation times necessary for complete degradation of unirradiated and 0.2 kGy irradiated 50 ppm 2,4-D and 2,4-DP were 20.0 and 13.3, respectively.
- From unirradiated and 0.2 kGy irradiated 2,4-D and 2,4-DP solutions, the phenolic intermediate was only 2,4-DCP. The ozonation times necessary for complete degradation of intermediate 2,4-DCP from unirradiated and 0.2 kGy irradiated 50 ppm 2,4-D and 2,4-DP were 13.3 and 8.33, respectively. Intermediate 2,4-DCP was degraded at lower ozonation times than herbicides.
- Dechlorination from unirradiated and 0.2 kGy irradiated 2,4-D and 2,4-DP in aqueous solution was increased continuously with the ozonation time. At 20.0

minute ozonation times for unirradiated 2,4-D and 2,4-DP solutions they were 91.5% and 95.3% but at 16.7 minute ozonation time complete dechlorination was observed for both of herbicides.

- When H_2O_2 /ionizing radiation and O_3 /ionizing radiation processes compared it is clear that O_3 /ionizing radiation process is more effective and has advantages than H_2O_2 /ionizing radiation process on degradation of 2,4-D and 2,4-DP herbicides and intermediates, dechlorination and formation and degradation of ionic species.
- For the degradation of 2,4-D and 2,4-DP and related intermediates, formation of final products, two different degradation pathways were suggested in the presence of H_2O_2 and O_3 .

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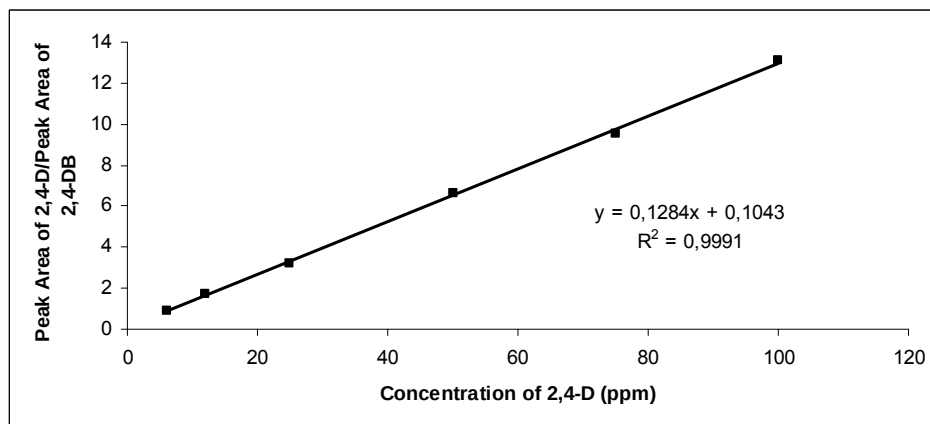
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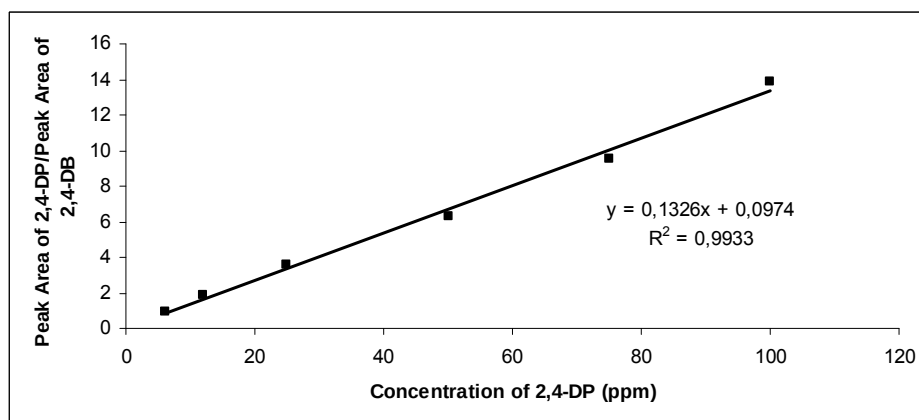
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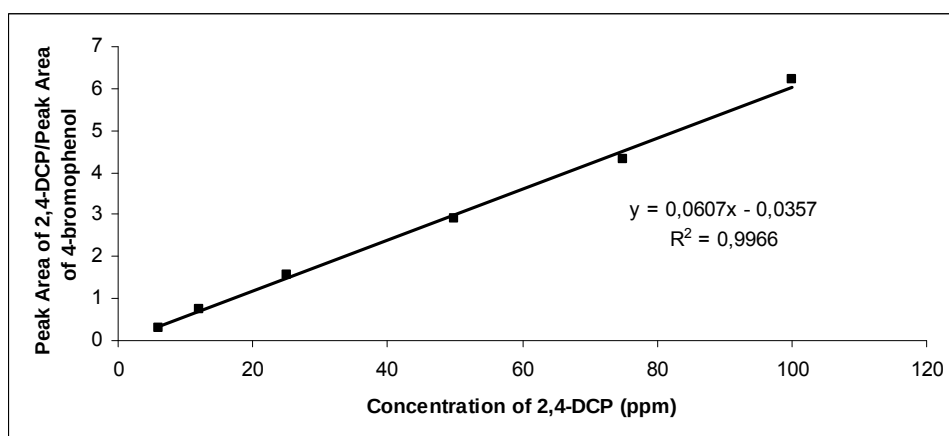
APPENDIXES



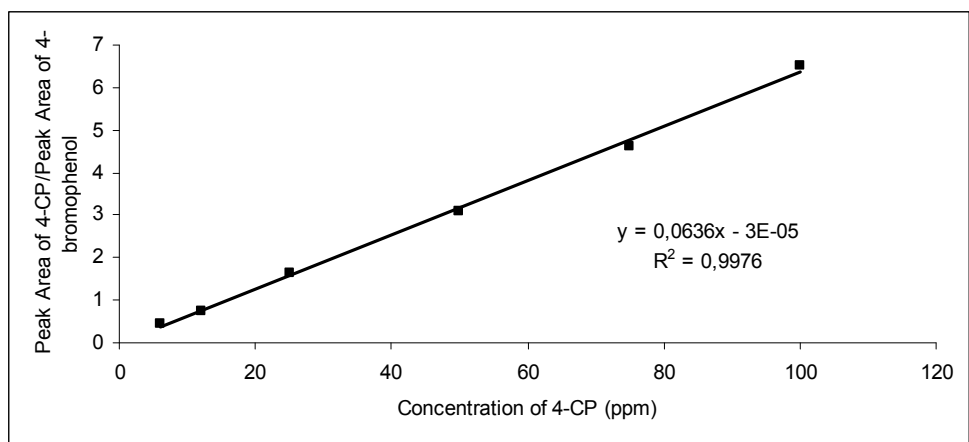
Appendix 1. Calibration graph of 2,4-D (6-100 ppm). 2,4-DB as IS.



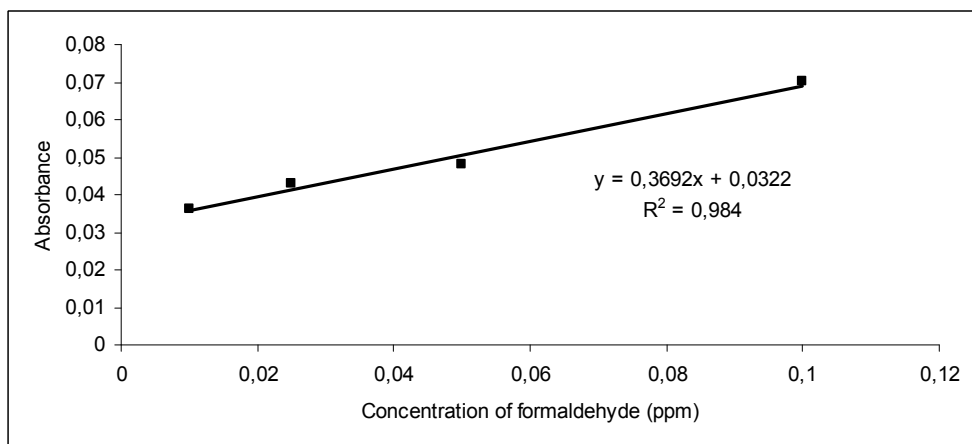
Appendix 2. Calibration graph of 2,4-DP (6-100 ppm). 2,4-DB as IS.



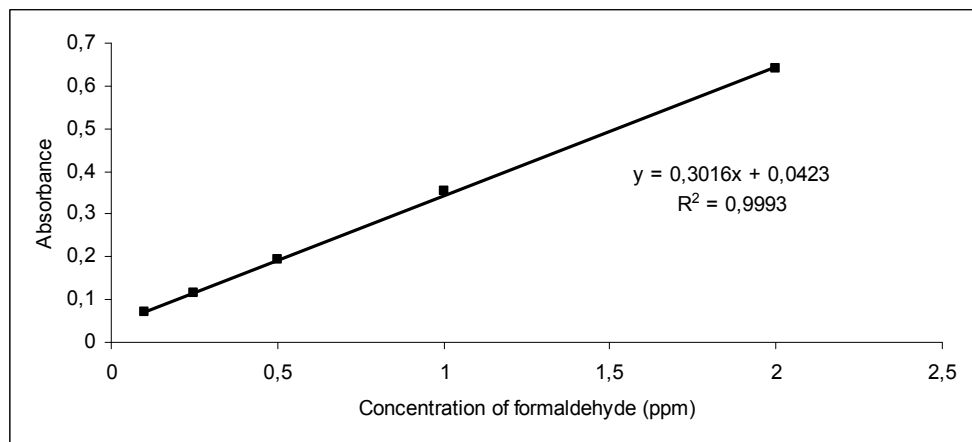
Appendix 3. Calibration graph of 2,4-DCP (6-100 ppm). 4-bromophenol as IS.



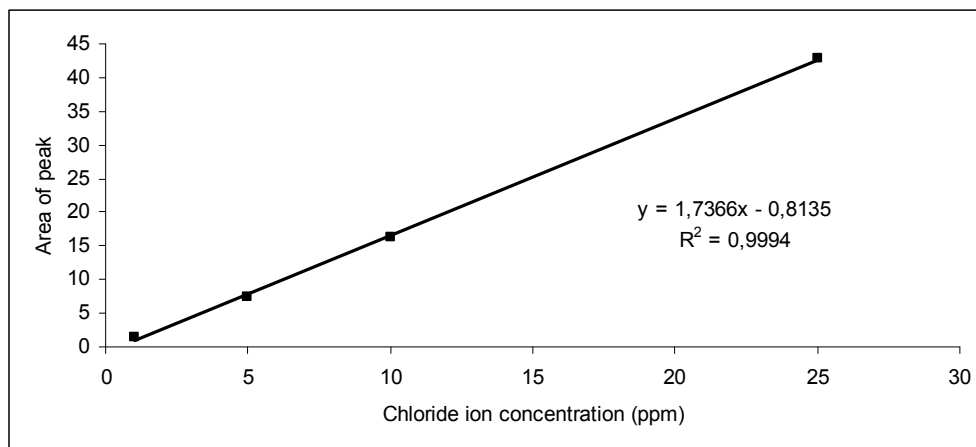
Appendix 4. Calibration graph of 4-CP (6-100 ppm). 4-bromophenol as IS.



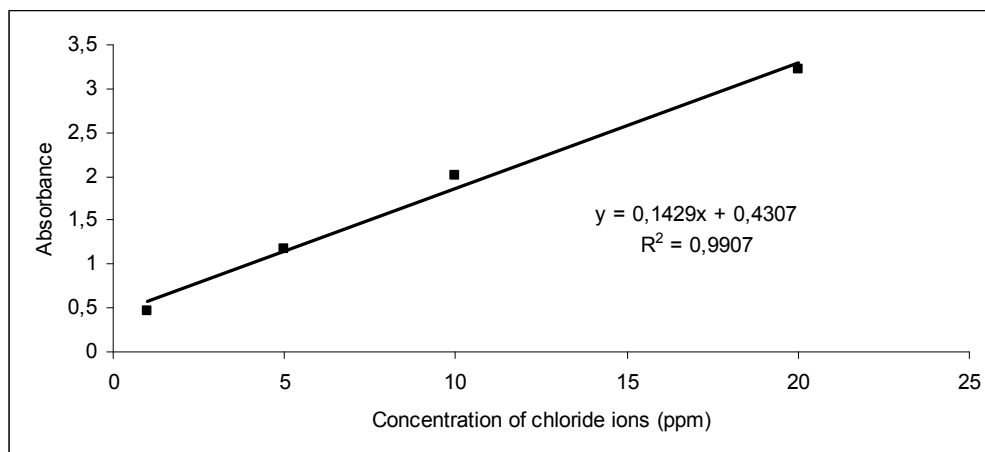
Appendix 5. Calibration graph of formaldehyde (0.01-0.1 ppm).



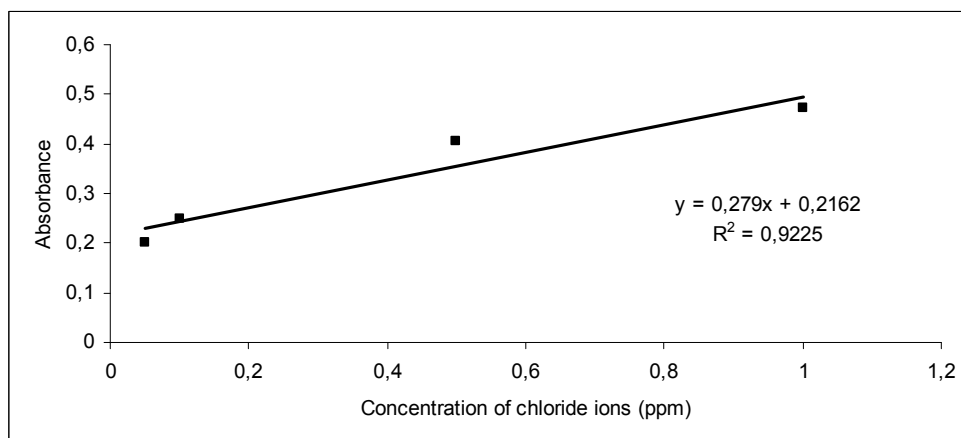
Appendix 6. Calibration graph of formaldehyde (0.1-2 ppm).



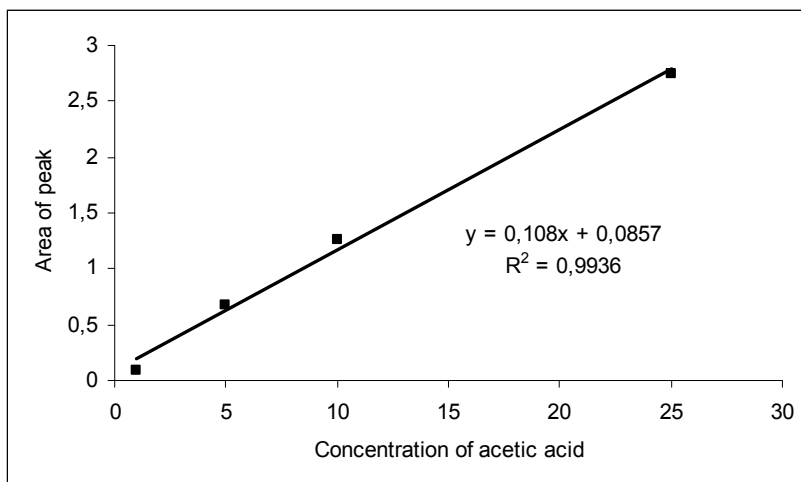
Appendix 7. Calibration graph of chloride ions with ion chromatography (1-25 ppm).



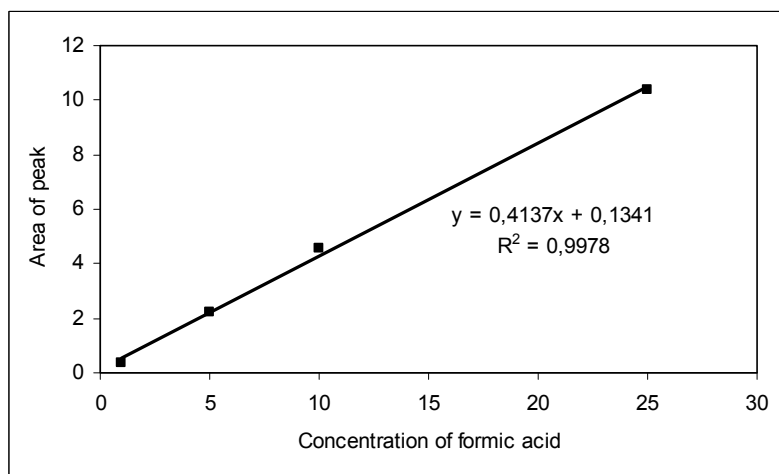
Appendix 8. Calibration graph of chloride ions with uv-vis spectroscopy (1-20 ppm).



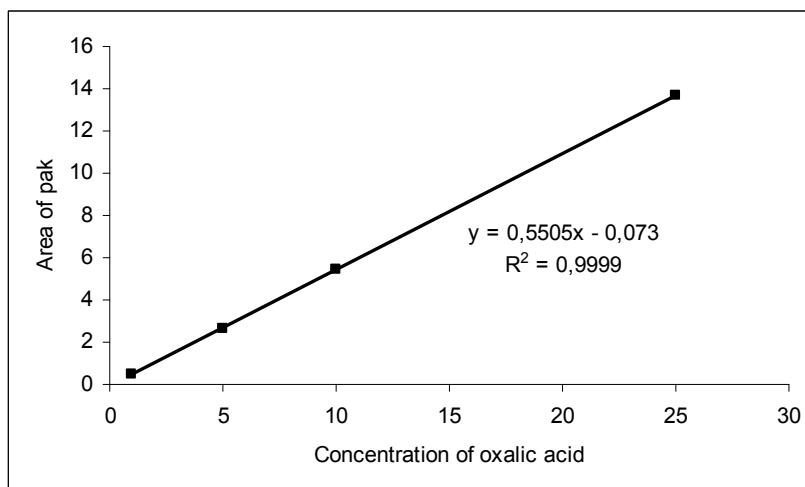
Appendix 9. Calibration graph of chloride ions with uv-vis spectroscopy (0.05-1 ppm).



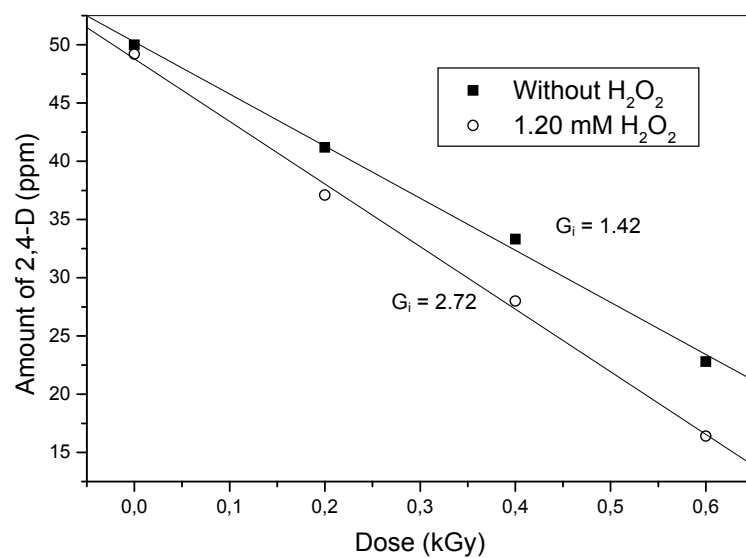
Appendix 10. Calibration graph of acetic acid (1-25 ppm).



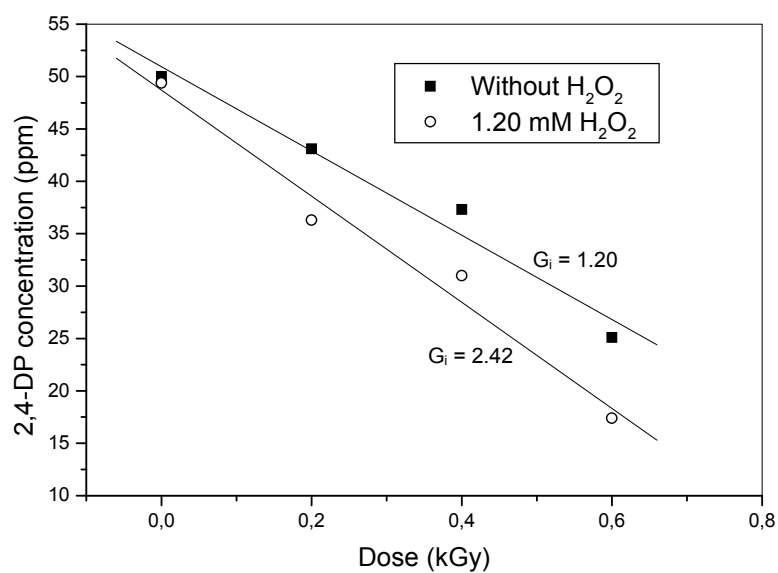
Appendix 11. Calibration graph of formic acid (1-25 ppm).



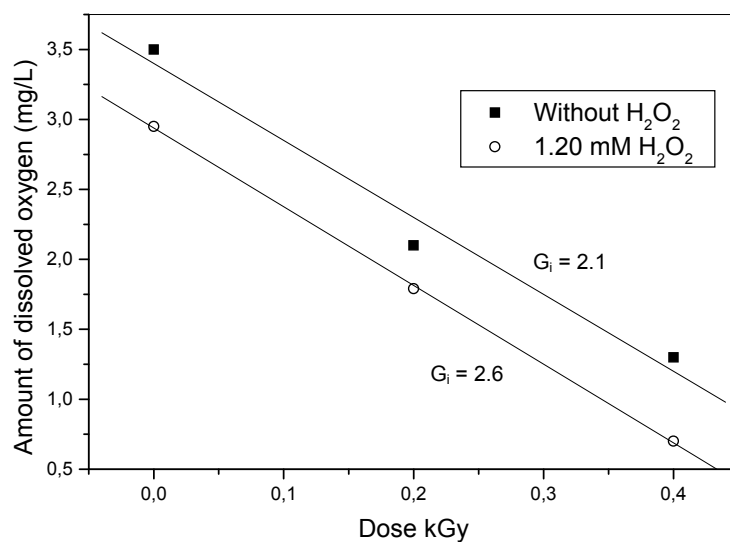
Appendix 12. Calibration graph of oxalic acid (1-25 ppm).



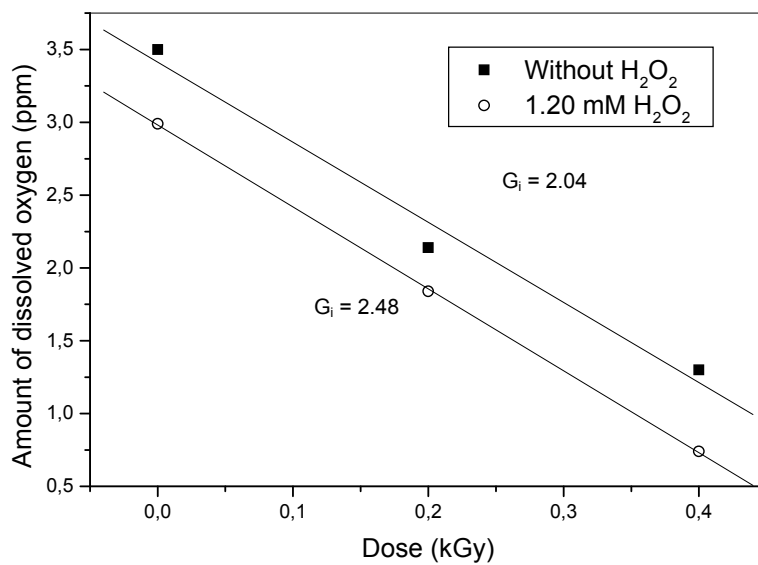
Appendix 13. G_i values of 2,4-D decomposition in the presence and absence of H_2O_2



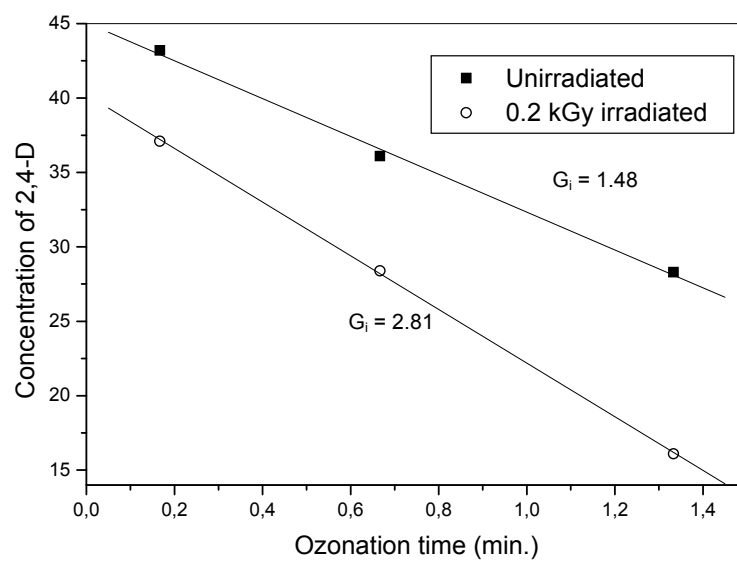
Appendix 14. G_i values of 2,4-DP decomposition in the presence and absence of H_2O_2



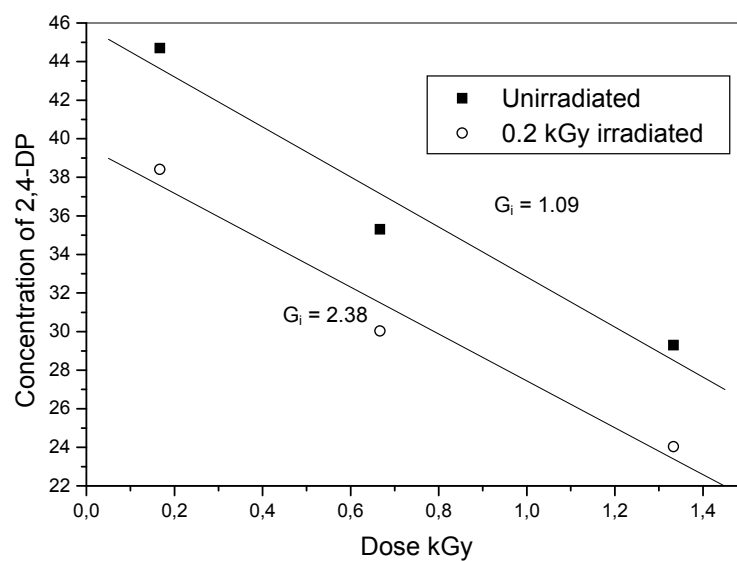
Appendix 15. G_i values of oxygen consumption of 2,4-D decomposition in the presence and absence of H_2O_2



Appendix 16. G_i values of oxygen consumption of 2,4-DP decomposition in the presence and absence of H_2O_2



Appendix 17. G_i values of 2,4-D for ozonized samples.



Appendix 18. G_i values of 2,4-DP for ozonized samples.

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M. Sc.

Synthesis and characterization of (Sodium Alginate/Acrylamide) semi-interpenetrating polymer networks and their usability on removal of lead, cadmium nickel ions.