OUTLINE

Q: What practical means can be developed for removing PCBs from the environment?

-- In U.S.
-- In ex-U.S.

Background:

- No known methods -- except physical removal and incineration.
- Incineration is practical only for highly concentrated PCBs/or mixtures; most PCBs exist in very dilute or diffuse natural environments.
- Therefore logical collections of PCBs that are suspect are --
    - Ponds and river bottoms
    - Pits
    - Landfills -- refuse (even approved landfills)
    - Paper
    - Existing drains/sewers in manufacturing facilities
    - Existing use in transformers, capacitators, and closed systems for heat transformers

Alternate Approaches:

- In house ideas have not been fruitful
- Customer industry ideas no better
- Propose to go to sources of unconventional ideas ~~other~~ e.g., ~~Lasers --- MIT~~
  ~~Enzymes --- Japan~~

Proposal

1. Approach 2-3 research-oriented institutions -- probably MIT and _____.
2. Outline the situation and offer some kind of stepwise financial support for ideas.

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2/15/78
MCT, CFC

less serious threat to the environment.

Since these compounds will be partitioned to various degrees between the organic and aqueous phases of sludge it is important to ascertain the effects of radiation on compounds in these mediums.

Other applications of radiation effects on organics include industrial wastewater treatment and the use of radiation in the sterilization and preservation of food where pesticides residues are highly probable.

C) Experimental Methods

Samples of two herbicides; monuron and 2,4-D, and two PCB's; 3,4,2'-trichlorobiphenyl and 4 chlorobiphenyl were irradiated in various solvents. The solvents used were: water, hexane, water saturated hexane, a mix of 50/50 water and hexane, hexanol, and 6% water in hexanol.

10 milliliter samples were irradiated in petri dishes using the van de Graff electron accelerator at the MIT High Voltage Research Labs. The dishes were transported under the electron beam on a belt at a speed calibrated to the required dose.

All analytical determinations were made using high pressure liquid chromatography and an ultraviolet absorbance detector. Aqueous solutions were analyzed by reverse-phase chromatography and organic solutions by conventional liquid-solid chromatography.

D) Results and Discussion

The results show a striking difference between aqueous and organic systems, in that the organic solutions required two orders of magnitude

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The complete degradation of chlorinated organics in water at low doses is encouraging. If these compounds can be rendered harmless or bio-degradable, then they will not build up in the soil and crops which have been fertilized by irradiated sludge. Industrial waste treatment of these hard to treat compounds could be accomplished by electron-irradiation to make them degradable with a bio-oxidation step as a final treatment.

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TABLE 1-1
Summary of G-Values and Dose
Required for 50% Degradation

Compound	Solvent	Concentration (mg/l)	Dose, Kilorads 50% Degradation	G-Value
3,4,2'-trichlorobiphenyl	H_2O	0.07 - completely degraded down to 1.0 Kilorad		
3,4,2'-trichlorobiphenyl	Hexane	4.0	1,350	0.0086
3,4,2'-trichlorobiphenyl	H_2O Saturated Hexane	3.9	1,700	0.0065
3,4,2'-trichlorobiphenyl	50/50 H_2O/Hexane	3.9	2,000	0.0055
3,4,2'-trichlorobiphenyl	Hexanol	4.3	1,000	0.0099
3,4,2'-trichlorobiphenyl	6% H_2O in Hexanol	4.1	800	0.0122
4-chlorobiphenyl	H_2O	0.8	2.5	0.408
4-chlorobiphenyl	Hexane	4.0	2,450	0.0064
4-chlorobiphenyl	H_2O Saturated Hexane	3.9	2,750	0.0055
4-chlorobiphenyl	50/50 H_2O/Hexane	3.9	3,050	0.0050
Monuron	H_2O	0.40	1.0	0.970
Monuron	H_2O	4.2	6.0	1.698
2,4-D	H_2O	4.9 - completely degraded down to 60 Kilorads		

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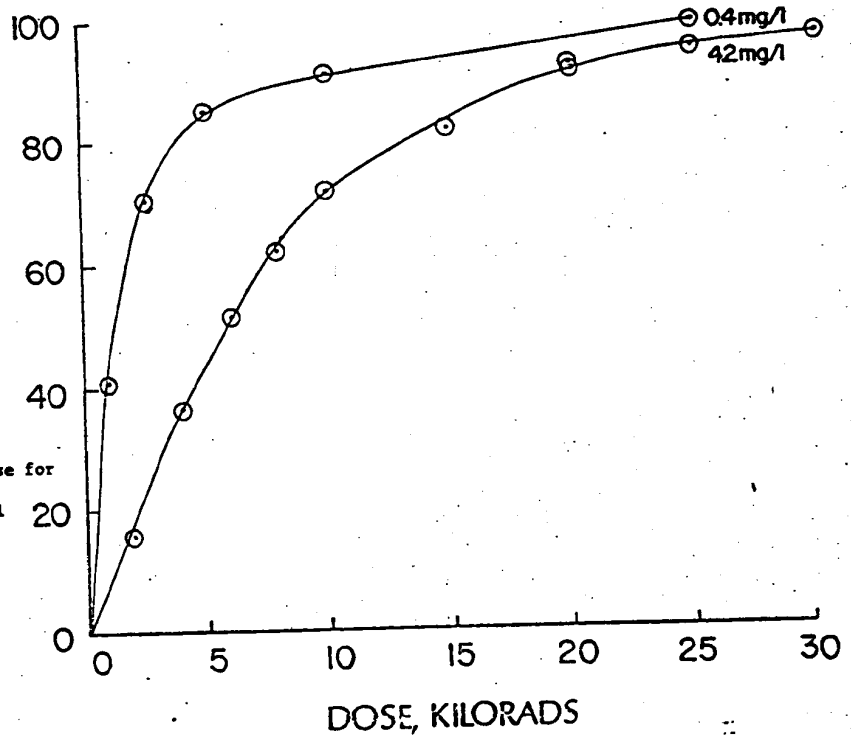


FIGURE 1-1

% Degradation vs. Dose for Monuron in Water, 0.4 mg/l and 4.2 mg/l

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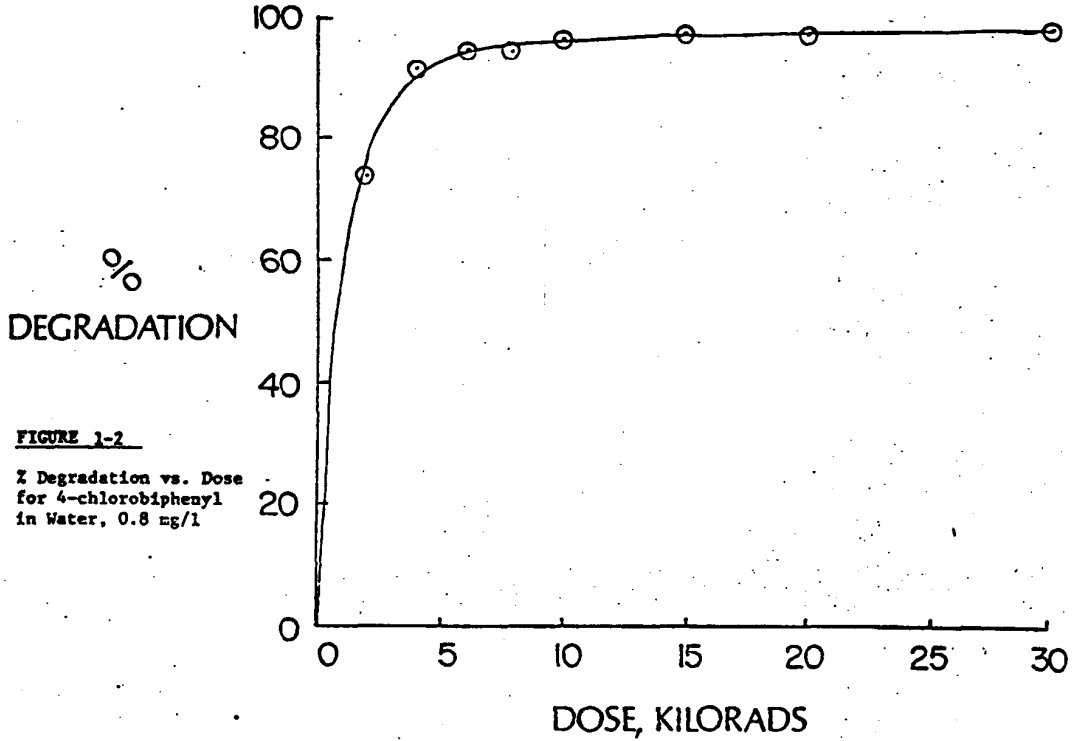


FIGURE 1-2

% Degradation vs. Dose for 4-chlorobiphenyl in Water, 0.8 mg/l

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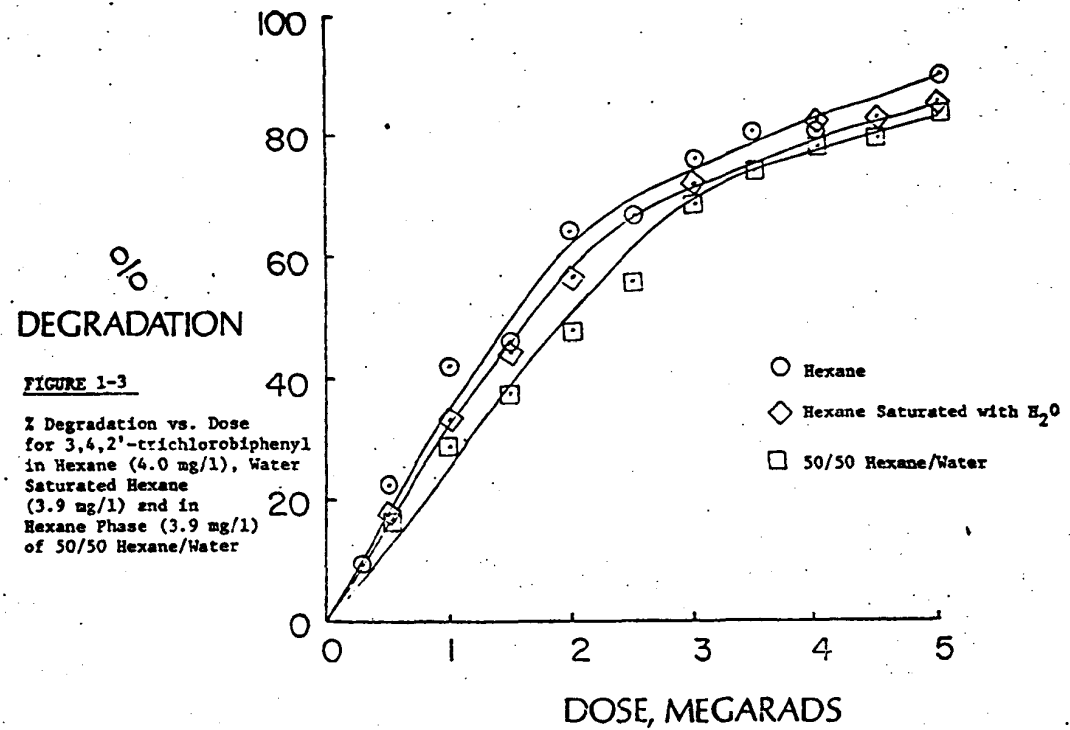


FIGURE 1-3

% Degradation vs. Dose for 3,4,2'-trichlorobiphenyl in Hexane (4.0 mg/l), Water Saturated Hexane (3.9 mg/l) and in Hexane Phase (3.9 mg/l) of 50/50 Hexane/Water

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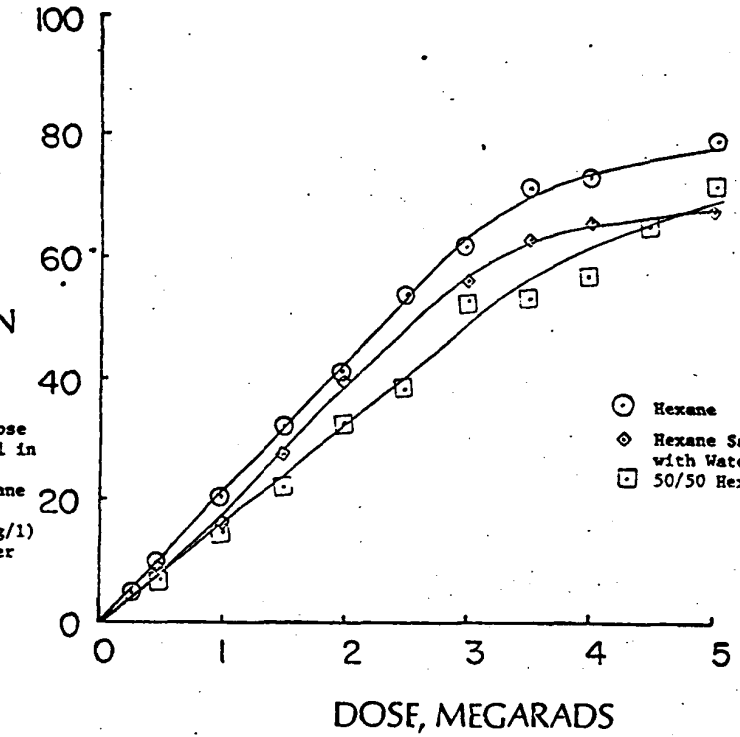


FIGURE 1-4

% Degradation vs. Dose for 4-chlorobiphenyl in Hexane (4.0 mg/l), Water Saturated Hexane (3.9 mg/l) and in Hexane Phase (3.9 mg/l) of 50/50 Hexane/Water

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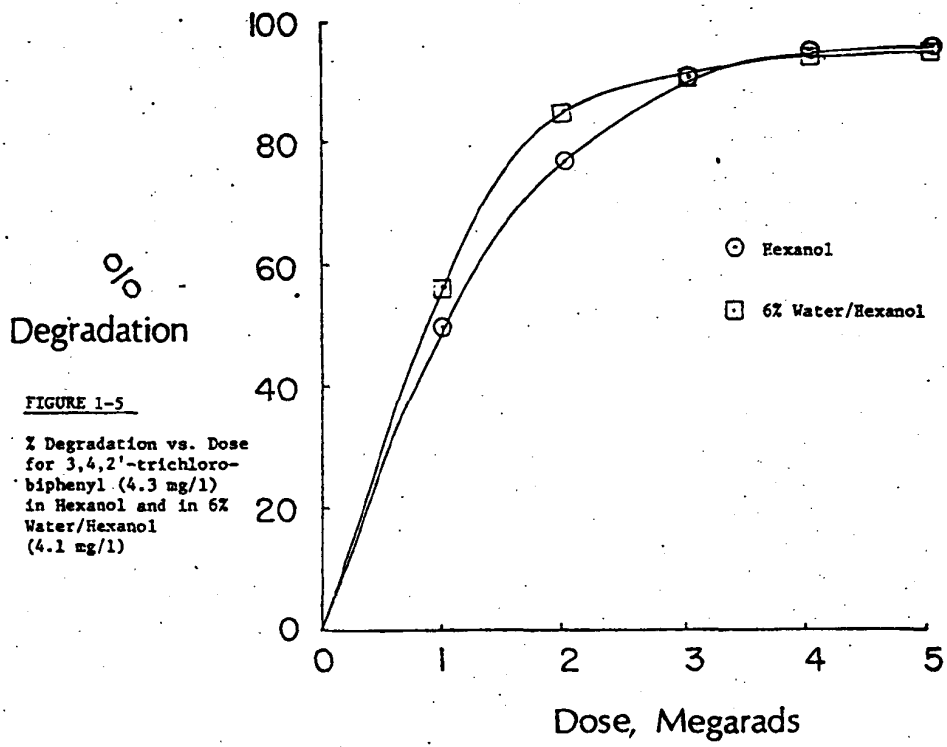


FIGURE 1-5

% Degradation vs. Dose for 3,4,2'-trichloro-biphenyl (4.3 mg/l) in Hexanol and in 6% Water/Hexanol (4.1 mg/l)

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CHAPTER 2: INTRODUCTION

A) The Deer Island Project and Related Applications

In mid 1976, supported by an NSF-Rann grant, MIT completed a 100,000 gallon per day sludge-irradiation facility. This unit takes a stream from the Deer Island wastewater treatment plant operated by Boston's Metropolitan District Commission. It incorporates a 50 kilowatt scanning electron accelerator with a flow system capable of presenting a thin layer of liquid to the beam. Figure 2-1 illustrates the system (Trump et al., 1975). The dose may be varied between 0.1 and 2 megarads with 0.4 megarads being a typical dose. The intent is to produce a sterilized, stable sludge suitable for application as an agricultural nutrient. High energy electrons release their energy rapidly in water (~ 7 Mev/cm) and redistribute this energy to the water molecules. The excited water molecules, through a complicated process, produce H· and OH· free radicals. These highly reactive species are capable of attacking other molecules (pesticides, industrial wastes, etc.) by oxidation, reduction, dissociation and other free radical reactions.

The radicals also have a lethal effect on microorganisms present in the sludge, including bacteria, viruses, protozoa, algae, and parasites. Another interesting effect is a significant increase in the ease of dewatering the sludge. This is not well understood, but could be due to changes in surfactants, in the fibriliar nature of sludge, or by upsetting any colloidal particles present.

Since environmental pollutants are present in sludge and wastewater it is important to know the effects of irradiation on these

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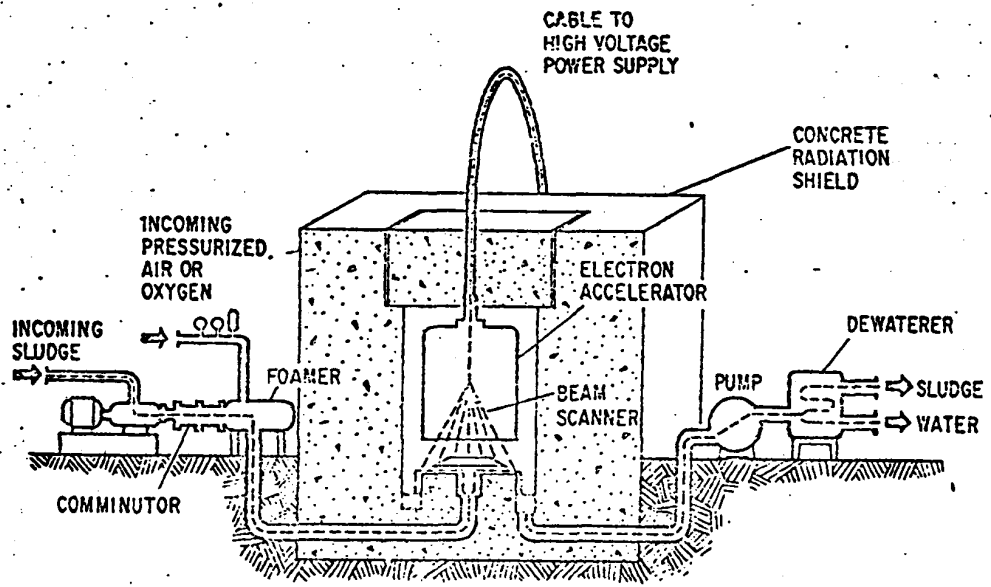


FIGURE 2-1

Electron Irradiation of Sludge
at Deer Island
(Trump et al., 1975)

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components. Past work with chlorinated organic compounds indicate that the general results of irradiation on chlorinated organics in water are: decreased toxicity, increased water solubility, and increased susceptibility to breakdown in the environment, especially by biological action. There is also the possibility that compounds more toxic than the parent will be produced. For example, very hazardous materials, polychlorodibenzofurans, have been identified as UV irradiation products of certain PCB isomers. Sludge is a highly complex mixture of organic matter, living cells, cellulosic fibrous matter, water and other constituents. Because of the complexity, any attempts at analysis of specific compounds is difficult. Therefore model solutions can be studied which offer certain important characteristics of sludge, yet are simple enough that analysis is straightforward. This work uses the simplest models, an organic phase and an aqueous phase in various combinations. Many pollutants of interest, including most pesticides and PCB's are highly lipophilic. Therefore most of these compounds will be partitioned into the organic portion of wastewater. Possible modes include entrapment in soap micelles, solvation in suspended fats, and absorption on particles. Studies of irradiation effects in models which simulate these modes will offer insight into the mechanism and efficiency of wastewater treatment by electron irradiation.

Another important application of wastewater irradiation studies is industrial wastewater treatment. Chlorinated hydrocarbons and other industrial wastes are difficult to treat because of their resistance to biological breakdown and electron irradiation could be an efficient

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means of treating (or pretreating) large volumes of toxic industrial effluents.

It has been proposed in the past that irradiation be used to sterilize foods (Proctor and Goldblith, 1956) to delay spoilage in fresh fish, to control insects in flour and grains (Brownell, 1961), and inhibit sprouting in vegetables such as onions and potatoes (Tripp, 1959). Pesticide residues are highly likely in each of these applications and degradation studies are essential to the safe use of irradiated food stuffs.

B) Radiation Chemistry

Radiation chemistry involves the study of chemical phenomenon caused by radiation absorption and ionization (Spinks and Woods, 1964). High energy radiation has the capability to produce many ionization events whose products in turn can react in many ways with the surrounding medium. The types of radiation used includes: electromagnetic radiation; x-rays (> 50 ev); accelerated particles, such as electrons, protons, etc.; and the emission from radioactive nuclides (α-rays, γ-rays and β-rays). Note that this does not include photochemistry which utilizes the ultraviolet and visible segments of the spectrum. The two differ in that photochemistry involves much less energy and typically a photon produces no ionization, affecting only one molecule in a certain manner.

Radiation chemistry became a science with the observation by Roentgen (1895) that discharge tubes fog photographic plates. Shortly after, Becquerel noted the same phenomena occurred with uranium salts. The earliest chemical reaction noted was that of water being decomposed

MONS 012746

into gas by Curie and Debierne (1901), the gas being later identified as hydrogen and oxygen by Cameron and Ramsay (1907).

Most of the early work in radiation chemistry involved the study of gases utilizing mass spectrometry as a natural method for ion determination. As radiation became adapted to industrial and medical applications, the study of condensed phases, especially aqueous solutions, became important. Fricke and Hart (1936) worked with methanol, formic acid and ferrous sulfate in water. Their work eventually pointed out that irradiated water gave hydroxyl and hydrogen radicals which produced the observed results. Since then many studies have been made on various solvent/solute systems.

1. Electron Interactions with the Bulk Medium

Electrons, depending on their energy, affect matter by three important interactions: elastic collisions, electromagnetic emissions, and inelastic collisions.

Elastic scattering occurs when the electron is deflected by an atomic nucleus. This type of interaction tends to occur more in high atomic number media and with lower electron energies. It is more important in electron interactions than with other charged particles because electrons have a much smaller mass than, for example, protons (9.108×10^{-28} g and 1.672×10^{-24} g, respectively).

Electromagnetic emissions occur when a charged particle decelerates. The emissions are termed *bremsstrahlung*, and depend on the mass of the particle and the charges of the particle and the nucleus involved. *Bremsstrahlung* is maximized with light particles and heavy media. The

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energy of the emissions will be a spectrum from 0 to the energy of the incident electrons. Emissions from electrons with energies below 100 Kev are very small, but for energies above 10 Mev, *bremsstrahlung* is the most important type of interaction. A well known application of this effect is the medical x-ray machine, in which x-rays are emitted by electrons incident on a tungsten target.

Inelastic collision is the primary interaction below *bremsstrahlung* energies. High energy electrons transfer energy to the media's bound electrons, causing ionization and excitation. In the solvents and electron energy (3 Mev) utilized in this investigation, the dominant interaction is inelastic collision.

2. Ionization and Excitation

As a charged particle moves through a medium it leaves a trail of interaction events. For an electron in the inelastic collision range this means that electrons in the media are elevated to higher energy levels, i.e., excitation and ionization. If the incident electron has sufficient energy after a collision it continues on the path to the next collision, until it has slowed down to thermal energy. The thermal electron will then combine with a positive ion, producing a neutral molecule, or with a neutral molecule, to form a negative ion.

The molecules which have been excited or ionized can follow any of numerous and complicated paths, which will be elaborated on in future sections. An immediate result of ionization is secondary ionization. This occurs when a secondary electron (one which was ejected during an ionization event) has sufficient energy to travel into the medium and

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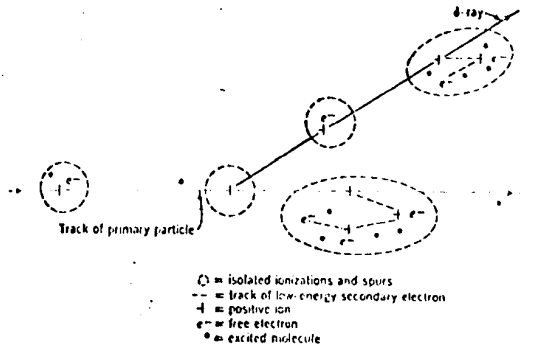


FIGURE 2-2

IONIZATION TRACK OF A FAST ELECTRON
(Spinks and Woods, 1964)

cause further ionization.

These electrons form small clusters or spurs of ionized species close to the original ionization path. It has been estimated that approximately one half of all ionization events caused by a primary particle are caused by secondary electrons with energies greater than 100 EV (Lea, 1946). Samuel and Magee (1953) calculated that fast electrons produce spurs approximately every 10^4 Å and that the spur cluster has a diameter on the order of 20 Å, with the average spur containing 3 to 4 ion pairs. Figure 2-2 illustrates an ionization path.

3. Excited Molecules, Ions, and Free Radicals

The chemical effects seen in irradiated media are generally caused by free radicals, which do not result directly from radiation interactions. Free radicals are formed by the dissociation reactions of excited molecules and by ion reactions, which are radiation produced.

Excited Molecules

Excited molecules are formed when the interaction with a high energy particle does not transfer sufficient energy to the impacted molecule to eject an electron. Instead a loosely bound electron is elevated to a higher orbit in the molecule. The molecule now is in a higher energy level termed an excited state. The level of excitation is governed by the particular interaction and quantum-mechanical principles. The excited molecule can then follow several paths to a lower energy level such as radiative conversion to ground state (flourescence, phosphorescence), various internal conversions, and by reactions.

MONS 012750

Since chemical effects result from the reaction mechanisms, these will be detailed.

The formation of an excited molecule can be represented as:

$$A \sim\!\!\!\!\!\!\rightarrow A^*$$

where the zig-zag represents an interaction with a high energy electron. The energy absorbed by the excited molecule can then be transferred to an adjacent molecule:

$$A^* + B \rightarrow A + B^*$$

after which B* can follow any of the excited molecule pathways. The excited molecule may reach stability by rearrangements within itself, for example, trans 2-butene will rearrange to cis 2-butene. If the absorbed energy is great enough to disrupt a chemical bond the molecule will dissociate:

$$AB^* \rightarrow A\cdot + B\cdot$$

For example, acetone:

$$CH_3\overset{\overset{\cdot\cdot}{O}}{\overset{\|}{C}}CH_3 \sim\!\!\!\!\!\!\rightarrow CH_3\overset{\overset{\cdot\cdot}{O}}{\overset{\|}{C}}CH_3^* \rightarrow CH_3\overset{\overset{\cdot\cdot}{O}}{\overset{\|}{C}}\cdot + CH_3\cdot$$

The molecule may also dissociate into molecular products, although this is uncommon. If there is excess energy the fragments will have enough kinetic energy to disperse into the medium. If there is little left over energy, particularly in condensed phases, the ions may be "caged" by adjacent molecules and recombine.

An excited molecule may also combine with neighboring molecules in different mechanisms. An electron can be transferred between two molecules:

MONS 012751

$$A^* + B \rightarrow A^+ + B^-$$

or an abstraction could occur, particularly hydrogen abstraction:

$$A^* + BH \rightarrow AH\cdot + B\cdot$$

Another possibility is addition; for example, if oxygen is present a peroxide will result:

$$A^* + O_2 \rightarrow AO_2$$

Stern-Volmer reactions can occur between two excited molecules:

$$A^* + A^* \rightarrow B + C$$

An example is:

$$H_2O^* + H_2O^* \rightarrow H_2 + H_2O_2$$

Ions

Ions can result directly from an impact with a high speed electron.

$$A \sim\!\!\!\!\!\!\rightarrow A^+ + e^-$$

The ion produced can then be neutralized, an excited molecule being produced which follows the pathways listed above:

$$A^+ + e^- \rightarrow A^*$$

$$A^+ + A^- \rightarrow A^* + A$$

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Reactions with other molecules may also take place, such as charge transfer:

$$A^+ + B \rightarrow A + B^+$$

and ion/molecule reactions:

$$A^+ + B \rightarrow C^* + D$$

For example:

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH\cdot$$

Ions can also be formed by the capture of thermal, free electrons:

$$A + e^- \rightarrow A^-$$

$$A + e^- \rightarrow B^- + C$$

For instance:

$$H_2O + e^- \rightarrow OH^- + H\cdot$$

This type of formation can only occur with low energy electrons. Higher energy electrons impart enough energy for dissociation.

Free Radicals

Free radicals result when a covalent bond disrupts, leaving each part of the molecule with an unpaired electron:

$$RS \rightarrow R\cdot + S\cdot$$

MONS 012753

This reaction is reversible, giving a stable molecule. Free radicals result from ion reactions and excited molecule dissociation reactions. If the radicals do not recombine immediately, it is possible that they will react with the bulk medium.

Radicals are inherently unstable due to their unpaired electron, but they can range from being extremely reactive (H·) to relatively stable (RO). For organic radicals, stability increases in the order primary < secondary < tertiary radicals. Unsaturated compounds tend to increase stability.

Radical reactions with a substrate can be predicted to a certain extent. The mechanism depends on the reactivity of the particular radical, the bond dissociation energy of the displaced species, and the activation energy of the reaction.

Radicals can rearrange internally to form a more stable state, for instance hydrogen shift, as in butane shifting from a primary to a more stable secondary radical.

$$CH_3CH_2CH_2\dot{C}H_2 \rightarrow CH_3CH_2\dot{C}HCH_3$$

Or dissociation may occur, typically at the bond ß to the radical site:

$$CH_3CH_2CH_2\dot{C}H_2 \rightarrow CH_3\dot{C}H_2 + H_2C{=}CH_2$$

Radicals also combine with the medium in many ways. Addition to unsaturated compounds occurs:

$$A\cdot + H_2C{=}CH_2 \rightarrow ACH_2\dot{C}H_2$$

MONS 012754

Abstraction to form a more stable radical is also frequent:

$$A\cdot + BC \rightarrow AB + C\cdot$$

for example

$$H\cdot + CH_3I \rightarrow HI + CH_3\cdot$$

Radicals can combine with other radicals (the reverse of dissociation):

$$R\cdot + S\cdot \rightarrow RS$$

Recombination reactions are favored because the activation energy is approximately zero, but in the bulk medium the radical concentration is generally low making such reactions improbable. Radicals may also take part in disproportionation reactions such as:

$$2RH\cdot \rightarrow RH_2 + R$$

Perhaps one of the most interesting aspects of radical reactions is the possibility of chain reactions, which are basically as follows:

Initiation	$A \rightarrow R\cdot$
Propagation	$R\cdot + A \rightarrow R\cdot + P$
Termination	$2R\cdot \rightarrow B$

The propagation step can occur many times before the chain is terminated.

4. Aqueous Systems

Radiation effects in a liquid are quite different from that in a gaseous phase. The density of liquids forces the electrons to give up their energy quickly and the species produced are restricted by the

medium. This means that the ions and radicals tend to react with themselves before they can diffuse into the bulk liquid and react with the substrate or a solute. Ions can also become "solvated" affecting reactivity. Solvation involves an orientation of water molecules around the ion forming a cluster of molecules.

Reactions in water subjected to ionizing radiation are complex and not completely understood. There are two predominant models, both of which end up with the same results. The initial ionization reaction is:

$$H_2O \rightsquigarrow H_2O^+ + e^- \qquad (1)$$

although this probably is the result of reactions taking place before any ions become solvated:

$$H_2O + e^- \rightarrow H^+ + OH\cdot + 2e^-$$

$$H^+ + OH\cdot \rightarrow H_2O^+$$

Other possible reactions are:

$$H^+ + e^- \rightarrow H\cdot$$

$$OH^+ + H_2O \rightarrow H^+ + 2OH$$

$$OH^+ + H_2O \rightarrow H_2O + OH\cdot$$

The primary result however is reaction (1). After ionization, the reactions depend on the diffusion of the secondary electron produced in reaction (1). Samuel and Magee (1953) contend that the electron is attracted back to the H_2O^+ and reacts:

MONS 012756

$$H_2O^+ + e^- \rightarrow H_2O^*$$

$$H_2O^* \rightarrow H\cdot + OH\cdot$$

where the radicals produced have enough energy to diffuse before recombination.

Lea (1946) and Gray (1951) theorize that the secondary electrons diffuse sufficiently to escape the H_3O^+ field and react with a water molecule:

$$H_2O + e^- \rightarrow H\cdot + OH^-$$

The result is essentially the same except for the distribution of species around the initial ionization track.

Since the concentration of radicals in the ionization track is high, initial reactions will be radical-radical reactions to give molecular products:

$$2H\cdot \rightarrow H_2$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2$$

The radicals which escape recombination and diffuse into the substrate are termed the radical products. The distribution of radical and molecular products in a given liquid depends on the linear energy transfer (LET) of the radiation. LET is defined as dE/dl, or energy loss per unit traveled (ICRU Report 16, 1970). LET depends on the type of radiation, its energy, and the medium. Figure 2-3 shows the dose distribution of electrons in water as a function of depth. A high LET

MONS 012757

radiation will produce ionization events closer together, giving a higher radical concentration, and producing more molecular products.

A general equation for the radiolysis of water (neutral pH) showing the distribution of molecular and radical products is presented by Hart (1972).

$$4.08\ H_2O \rightarrow 2.63\ e^-_{aq} + 0.56\ H\cdot + 2.72\ OH + 0.68\ H_2O_2 + 0.45\ H_2 + 3.63\ H^+ + 1.0\ OH^-$$

The number of species produced are in terms of G-values. A G-value is defined as the number of molecules produced (or degraded) per 100 ev absorbed. In neutral and alkaline solutions the primary reducing species is the solvated electron, e^-_{aq}. At lower pH this is replaced by hydrogen atoms H·, although their reactions are essentially the same.

pH Effects

As mentioned above, pH affects the distribution of species in irradiated water. This is attributed to certain pH dependent reactions:

$e^-_{aq} + H^+ \rightleftarrows H\cdot$	acid solutions
$H_2^+ \rightleftarrows H\cdot + H^+$	pKa ~ 2.7
$\cdot OH \rightleftarrows H^+ + O^-$	pKa ~ 10
$HO_2\cdot \rightleftarrows H^+ + O_2^-$	pKa ~ 2
$H\cdot + OH^- \rightleftarrows e$	alkaline solutions

Figure 2-4 illustrates the distribution of irradiation products with pH. This distribution can affect solute reactions considerably, especially in the case of the e^-_{aq} and H· distributions. For instance

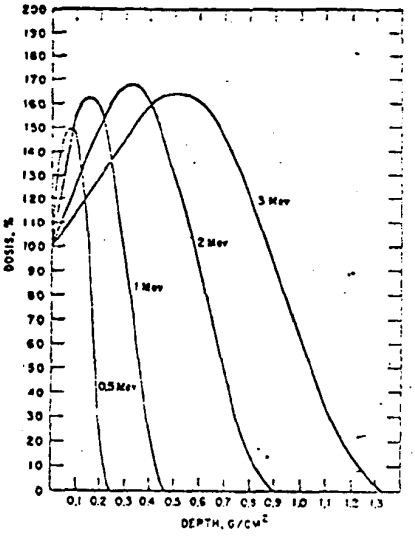


FIGURE 2-3

Dose Distribution as a Function of Depth for Fast Electrons (Dainton and Peterson, 1962)

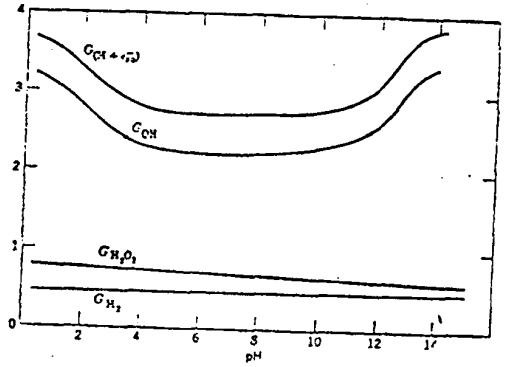


FIGURE 2-4

Variation of Yields with pH in Y-irradiated Water (Dainton and Watt, 1962)

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Jortner and Rabani (1961) studied chloroacetic acid at various degrees of pH. At pH 4 to 10 the primary reaction is:

$$H\cdot + ClCH_2OO^- \rightarrow H_2 + \dot{C}lCHCOO^-$$

and at pH < 11:

$$e^- + ClCH_2COO \rightarrow CL^- + \cdot CH_2OO^-$$

Oxygen Effects

Oxygen, even in air-equilibrated solutions, affects the radiation chemistry of water to a large degree. This occurs mainly as reactions with the reducing radical, e^-_{aq} or H·,

$$H\cdot + O_2 \rightarrow HO_2\cdot$$

$$e^-_{aq} + O_2 \rightarrow O_2^-$$

The $HO_2\cdot$ species is not as reactive as H· and does not abstract hydrogen from organic solutes, but it does act as an oxidizing agent.

Solute Effects

Dilute solutions (< 0.1M) when irradiated, are not affected by direct action of the ionizing radiation. The energy is dispersed in the water, which then acts on any solute by radical reactions. However, as solute concentrations increase the free radicals are increasingly scavenged by the solute rather than being allowed to recombine or act on the solvent, i.e., a concentrated solution transfers energy to the solute more efficiently. Many different systems in water and other solvents have been studied. Systems which give insight to those studied

in this work will be detailed in Chapter 2, part D.

5. Aliphatic Systems

The general pattern of alkane radiolysis is that carbon-carbon and carbon-hydrogen bonds are broken in an apparently random fashion. Organic radiation effects are very different from water in that the organic radicals formed can react with the solvent, whereas hydrogen and hydrogen radicals do not react with water, but do react with themselves and any solute present. The general pattern of reactions is:

$$A \rightsquigarrow A^*$$

$$A^* \rightarrow B\cdot + C\cdot$$

$$A^* \rightarrow D + E$$

$$A \rightsquigarrow A^+ + e^-$$

$$A^+ \rightarrow B\cdot + C\cdot$$

$$A^+ \rightarrow D + E$$

$$A^+ + e^- \rightarrow A^*$$

Alkane irradiation products generally produce compounds with lower molecular weight than the parent, dimers, products with molecular weight intermediate to the parent and the dimer, and a range of unsaturated hydrocarbons. The average effect is an increase in molecular weight.

Hexane

Hexane radiolysis is complex and not completely understood, but it is presumed that all primary ions convert to $C_6H_{13}^+$ which is neutralized to form a hydrogen radical:

MONS 012761

$$C_6H_{13}^+ + e^- \rightarrow C_6H_{13}^*$$

$$C_6H_{13}^* \rightarrow C_6H_{12} + H\cdot$$

Ethyl and propyl radicals have also been identified. By combination, disproportionation and other radical reactions, the initial radicals produce many products (Futrell, 1959):

PRODUCT	G-VALUE	PRODUCT	G-VALUE
H_2	5.0	C_5H_{12}	0.30
CH_4	0.12	t-C_6H_{12}	1.2
C_2H_4	0.30	C_7	0.15
C_2H_6	0.30	C_8	0.53
C_3H_6	0.13	C_9	0.45
C_3H_8	0.42	C_{10}	0.43
C_4H_8	0.03	C_{11}	0.02
C_4H_{10}	0.50	C_{12}	2.0

Hexanol

The radical yield obtained by the irradiation of hexanol can be assumed to be similar to hexane, but modified due to the effects of the hydroxyl group. As shown by the irradiation of ethanol (Spinks and Woods, 1964), the major molecular products can be accounted for by the production of radicals β to the hydroxyl group:

$$CH_3CH_2CH_2CH_2CH_2CH_2OH \rightsquigarrow CH_3CH_2CH_2CH_2CH_2\dot{C}HOH + H\cdot$$

The fact that the β-radical predominates has been supported by the ultraviolet spectra of the transient species and by study of the molecular products of deuterated alcohols.

A large amount of hydrogen in the molecular products (G = 4.87, β-rays) indicates that another primary reaction is:

$$H\cdot + C_6H_{13}OH \rightarrow C_6H_{13}O\cdot + H_2$$

If oxygen is present peroxy radicals can form and react to give hydrogen peroxide and an aldehyde

$$H\cdot + O_2 \rightarrow HO_2\cdot$$

$$C_5H_{11}\dot{C}HOH + O_2 \rightarrow C_5H_{11}(O_2\cdot)OH$$

$$HO_2\cdot + C_5H_{11}\,CH(O_2\cdot)OH \rightarrow H_2O_2 + C_5H_{11}CHO + O_2$$

C. Environmental Pollutants

1. Pesticides

As modern society becomes increasingly dependent on synthetic organic compounds, the environment is being altered by the effect of chemicals it cannot cope with on a short term basis. Pest control and agricultural activities contribute large quantities of various compounds to the environment. To be effective, pesticides must be spread over large areas, making any realistic control efforts impossible. Although

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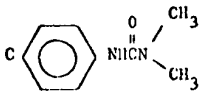
these compounds present hazards which must not be ignored, they are extremely beneficial to modern society. The increase in agricultural crops and the control of human disease are necessary functions which cannot cease. Perhaps the first environmentally suspect and most studied compound is DDT. DDT is an inexpensive and very effective insecticide. However, the characteristics which make it a good insecticide; persistence, toxicity, and lopoid affinity, also make it environmentally hazardous. Chlorinated hydrocarbons, in general, have these properties which causes them to accumulate in the lipid-phase of living organisms at concentrations many times the ambient concentration. This effect is magnified in higher levels of the food chain, causing adverse and lethal effects in higher organisms. The DDT story is long and well studied, so it is beyond the scope of this thesis, but the impact of such a compound is summarized by the fact that the average adipose content of DDT in the U.S. population is 10 ppm (Ray, 1973).

Pesticides are highly varied in use, properties, types of structure and modes of action. Many however, contain one or two phenyl rings with various ring additions typically containing chlorine, nitrogen, and/or phosphorus. Two compounds were investigated: 2,4 dichlorophenoxyacetic acid (2,4-D) and 3(p-chlorophenyl)-N,N-dimethyl urea (Monuron).

Monuron is a member of the urea class of herbicides. Urea herbicides act by entering the roots and being transported to the leaves, where they accumulate and cause damage to the parenchyma vessels. This action is brought about by inhibiting photosynthesis and upsetting the photolysis of water to oxygen (Hill reaction). It is thought that the

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direct chemical action responsible is the formation of hydrogen bonds between the -NH- and C=O groups with protein structure of an enzyme involved in photosynthesis (Overbeek, 1964). In 1973 800,000 lbs of monuron were distributed into the environment (Substitute Chemical program, 1975). Monuron is fairly persistent, taking over a year to degrade in the environment. Mammalian toxicity is low (3400 g/kg LD_{50}, rat) (White-Stevens, 1971). Ureas are widely used as a post and pre-emergent herbicides and monuron is a registered substitute for cancelled and suspended uses of 2,4,5-T, a chlorophenoxyacetic acid herbicide.

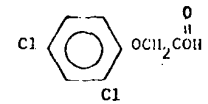


3-(p-chlorophenyl)-N,N-dimethyl urea (Monuron)

2,4-D is a chlorophenoxyacetic acid, a group of herbicides best known for their use as defoliants in Viet Nam. 2,4-D reached peak production in 1968 (9.4×10^7 lb) and has been declining since that time (Ray, 1974). It is environmentally suspect, although slightly persistent (4 weeks), and commonly shows up in environmental sampling.

The chlorophenoxyacetic acids are synthesized auxins (plant growth) hormones). The family of compounds are selective broad-leaf herbicides and were widely used as pre-emergent control in legumes, cereal crops, and other applications. They act by simulating natural auxins and causing abnormal growth in the roots, stem, and leaves of the plant. Physiological systems are reduced and the plants' hormonal balance is

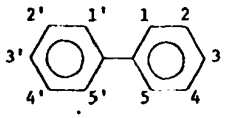
upset. The actual mode of action is not understood but it is suggested that the chlorophenoxyacetic acids raise the permeability of the cell walls causing increased metabolite flow (Wain, 1957). At one time 2,4-D and 2,4,5-T were suspected as carcinogenic, but this has been attributed to extremely toxic chlorodibenzo-p-dioxins which are possible byproducts of the production method (Johnson, 1971). Mammalian toxicity of 2,4-D is moderate (666 mg/kg, LD_{50},rat) (White-Stevens, 1971). It is also produced in many salt and ester forms for different applications and soil conditions.



2,4 dichlorophenoxyacetic acid (2,4-D)

2. PCB's

Polychlorinated biphenyls (PCB's) are a general class of compounds which are produced by chlorinating biphenyl with anhydrous chlorine. They are marketed in the U.S. by the Monsanto Company under the trade name Arochlor. Several grades of Arochlor are made, all being mixtures of isomers. For instance Arochlor 1248 has 48 weight percent chlorine and is a mixture of 38 isomers. Individual isomers are named by the chlorine positions:



PCB Configuration

PCB's have been produced since 1929 with peak production in the U.S. in 1970 (33×10^6 Kg) (Panel on Hazardous Trace Substances, 1972), but have fallen sharply since then with production scheduled to stop as substitute compounds can be phased in. Uses of PCB's include transformer oil, hydraulic fluid, plasticizers, heat transfer fluids, pesticide carriers, and lubricants. Figure 2-5 and 2-6 gives the production and uses of PCB's from 1967 to 1971.

PCB's were not identified in the environment until 1966. Before then they were ignored as interference compounds in pesticide residues. They became suspect in 1968 when more than 1000 people in Japan were affected by cooking oil contaminated with PCB's. Since then, investigation has confirmed widespread environmental effects, persistence, and environmental pathways similar to DDT. It is estimated that an excess of 5×10^4 tons are contained in the U.S. environment. Since PCB's are gradually released from discarded plastics, capacitors, transformers, etc., they will be a serious concern for years to come.

The mammal toxicity of PCB is low (3980 mg/kg, LD_{50}, rats for Arochlor 1221), but it causes chronic problems at lower levels. PCB's like 2,4-D and 2,4,5-T can be contaminated by a highly toxic byproduct, in this case polychlorodibenzofurans (Vos et al., 1970). These compounds could possibly be formed in the environment by UV photolysis (Crosby et al., 1973).

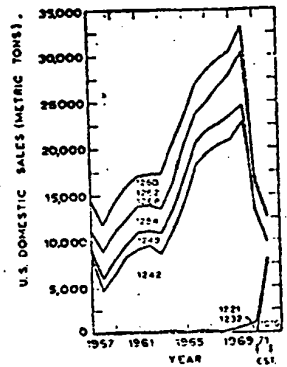


FIGURE 2-5

U.S. Sales of PCB's by Grade
(Panel on Hazardous Trace
Substances, 1972)

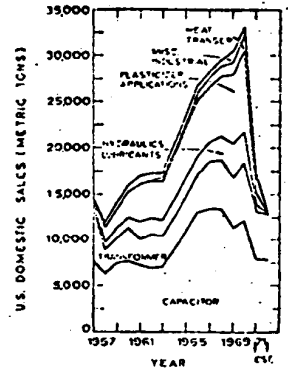


FIGURE 2-6

U.S. Sales of PCB's by
Use Category
(Panel on Hazardous
Trace Substances, 1972)

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PCB's have been identified in sewage sludge by Ahling and Jensen (1970) in Sweden . Holden (1970) sampled sludge entering the Clyde Estuary in Scotland and estimated concentrations ranging from 0.1 to 14 parts per million . Schmidt et al., (1971) identified PCB's in California urban sewage outfalls at concentrations from 0.02 to 97 parts per billion. Daily PCB emissions at one location were estimated to be ~ 100 kilograms/day.

Such compounds as pesticides, PCB's, and industrial wastes which find their way into municipal sewage are a serious detriment to recycling sludge as an agricultural fertilizer. Since these pollutants are lipophilic, they become partitioned into the organic phase of sludge. Any application to food crops would provide a pathway into the general population for concentrated amounts of potentially dangerous chemicals. Repeated applications could cause a buildup in the soil and eventually make the land unfit for further agricultural development.

D. Irradiation of Pollutants

Some irradiation studies have been done with organic compounds in water emphasizing the degradation of environmental pollutants. They differ from this investigation in that γ-ray irradiation is typically used. γ-irradiation is of interest because it can be accomplished with the nuclear wastes from the ever-increasing nuclear power stations. This approach presents problems, however, because neutrons are emitted by certain isotopes present in nuclear wastes. Common elements present in wastewater, such as sodium and chlorine can be neutron activitated

to radioactive isotopes creating a further wastewater problem. Furthermore, such facilities would require heavy shielding and special precautions to insure that no radioactivity escapes.

As compared to radioisotope irradiation, electron facilities are more feasible for design and safety consideration. Electrons can activate certain elements to radioactive nuclides, but at the energies involved, only deuterium and beryllium, which are rare in wastewater, can be activated. Furthermore, the electron beam is extremely localized, can be shielded easily, and can be totally inactivated instantly. Any accidental or intentional misues of the radiation is practically impossible. Although similar results might be expected, the process is not the same since a dose of γ-rays from radioactive nuclides is given over a period of hours, while an equivalent dose of electrons takes seconds. This leads to different rates, chemical effects, and requires a much smaller contact time. Since γ-ray treatment time is large, irradiation facilities must provide for large volume irradiation vessels or use extensive recycle of the wastewater. Electron irradiation requires only a short, once through treatment.

Vollner et al., (1975) studied dieldrin, aldrin, lindane, chlordane, and PCB's in water and mixtures of acetone and water. These compounds were given up to 7 megarads at a dose rate of 0.5 megarad/hour. The radiation utilized was γ-rays from Cobalt-60. They concluded that dechlorinated, hydroxylated and carboxylated compounds were formed. G-values for these compounds in deionized water were on the order of 1×10^{-3}.

Johnson, Stein and Weiss (1951) irradiated aqueous solutions of chlorobenzene and phenol with x-rays, in doses of 1 megarad at a rate of 180 kilorads/hr. The chlorobenzene produced phenolic and diphenyl compounds, while phenol produced quinones, catechol and quinol. They also concluded that oxygen in air equilibrated solutions was exhausted by reactions at a dose of 60 kilorads. Fiti (1975) also irradiated phenol in aqueous solutions, but with electron beams and reported quinonoid-like products. Case (1972) in a U.S. Patent, reports degradation of dieldrin in water under oxygen pressure with G-values of 6.4×10^{-5}. Sherman et al., (1971) studied DDT in 2-propanol under γ-ray irradiation and showed that DDD, a dechlorination product was formed. Carp et al., (1972) investigated aldrin in solutions (17,000 ppm and 10,000 ppm) of hexane, acetone, cyclohexane, corn oil, and lard. They utilized γ-rays up to 6 megarads (0.34 megarads/hour) and found 20%-65% aldrin degradation at 6 megarads, depending on the solvent. They also indicated that dechlorination was occurring. Craft et al., (1975) irradiated various concentrations (400 mg/l to 2.86%) of PCB's, pentachlorophenol, 2,4-D and 2,4,5-T solutions. Doses were up to 20 megarads (1.0 megarad/hr, γ-rays, Cobalt 60) with G-values from 2.1 to 9.0 depending on the compound and increasing with concentration.

E. High Pressure Liquid Chromatography (HPLC)

High pressure liquid chromatography was chosen as the analytical method due to the simplicity of sample preparation, the high resolution attainable, and because it is a somewhat novel approach compared to the

well documented analysis by gas chromatography. By changing the column packing HPLC can be used in one of several modes: liquid-solid, liquid-liquid, reverse phase, ion exchange, and gel permeation chromatography. Further variation is possible by changing the solvent used in the separation.

Aqueous solutions can be analyzed directly without the extraction and concentration techniques commonly necessary in gas chromatography. This is accomplished by reverse phase chromatography on a silica packing which has a C_{18} hydrocarbon bonded to the particles. This effectively forms an immobile organic phase. This type of chromatography can be extended to very low concentration aqueous solutions by solvent gradient techniques. This involves injection of a large volume of sample while water is being used as a chromatographic solvent. The organic compounds being hydrophobic, are quickly partitioned onto the C_{18} packing. When a gradient of solvent, from water to a less polar solvent, is run through the column the compounds are desorbed individually when they have more affinity for the solvent than the packing.

The other technique used in this work was liquid-solid chromatography using a silica column. This involves liquid-solid adsorption/desorption using a non-polar solvent. All organic solvent irradiations were analyzed by liquid-solid chromatography.

The detection method utilized was ultraviolet absorption at a wavelength of 254 nanometers. U.V. detection is an excellent method for many pesticides, especially in the 200-300 nm (Blinn and Gunther, 1963) range. This is primarily due to the predominance of the benzene chromophore (which absorbs at 255 nm) in pesticide structure.

CHAPTER 3: EXPERIMENTAL METHODS

A. Solutions

1. Aqueous Solutions

Clean aqueous solutions are difficult to make because water is hard to purify. The water used throughout this work (for solutions and as a chromatographic solvent) was purified in the following sequence. The water was initially passed through a reverse osmosis filter (Milli-RO15, Millipore Corporation). It was then degassed and filtered by vacuum with a 0.1 micron filter (Millipore VCW 04700, Millipore Corporation). As a final step the water was pumped over a 7 mm x 30 cm column packed with a reverse-phase packing (Bondapak C_{18}/Porasil B, Waters Associates). The column served to remove trace organics remaining in the water. Column regeneration was accomplished by flushing with methanol or acetonitrile. All glassware, filters, etc. were carefully cleaned to prevent any contamination. Plastics were avoided as much as possible to prevent leaching of monomers, plasticizers, and other additives. Purified water was not stored for more than one week to avoid bacteria growth.

Solutions of low concentration (< 0.1 mg/l) were prepared by making concentrated solutions in an appropriate solvent. 3,4,2'-trichlorobiphenyl (Analabs Inc., Lot #002) and 4-chlorobiphenyl (Analabs Inc., Lot #001) were dissolved in hexane (Fisher Scientific Co., Lot #763432). Monuron (Applied Science Laboratories, Lot #876-69) and 2,4-D (Applied Science Laboratories, Lot #876-63) were mixed in methanol (ACS, Matheson, Coleman, and Bell), and purified water respectively. The dilute solutions were

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then prepared by pipetting the desired aliquot of concentrated solution into a 500 ml volumetric flask. The solvent was then removed by vacuum and the residue dissolved in the purified water. Dissolution was insured by shaking for 12 hours on a mechanical shaker.

More concentration solutions were made by directly weighing the desired amount on a microbalance (Model 240S, Sartorious) and transferring the sample to a volumetric flask.

2. Hexane and Hexanol Solutions

Hexane (Fisher Scientific Co., Lot #734784) and 1-hexanol (Aldritch, Lot #030837, #087237) were degassed and filtered through a Flourepore 0.2 micron filter (Millipore Corp., FGLP 04700) prior to use. Solutions were then prepared by the methods described above. Water saturated solutions of hexane were made by shaking the solvent with water for 12 hours and splitting off the remaining water in a separatory funnel. 6% water in hexanol was prepared by pipetting 5 ml of water into a 100 ml flask and adding the hexanol. Solutions were then prepared as described previously.

B. Irradiation

Irradiations were carried out at the MIT High Voltage Laboratory (HVEL), using a compressed gas-insulated Van de Graff electron accelerator. Electron energy was controlled to 3 Mev.

10 milliliter samples were pipetted into 60 mm x 15 mm glass petri dishes, labelled and covered. Split phase irradiations were prepared by pipetting 5 ml of water into the petri dish and then layering 5 ml of

hexane solution on top of the water. Sample size was carefully controlled to 10 milliliters to insure equal depths (1 cm, average). This is important as electrons impart varying amounts of energy to the medium depending on their speed. A different thickness of medium will receive a different dose. (See Figure 2-3).

The petri dishes were then placed on a conveyor belt and transported under the electron beam at a speed calibrated to the required dose. This arrangement has been used successfully in HVRL research for many years.

After irradiation the samples were transferred to 25 mm x 50 mm weigh bottles, stoppered, and stored until analysis. All glassware was carefully cleaned in dichromate cleaning solution, rinsed several times with distilled water, and dried prior to use.

Samples in water and hexanol were handled in batches, while samples in hexane were pipetted, irradiated, and transferred individually because of the high vapor pressure.

C. Analysis

All determinations were made using high pressure liquid chromatography (HPLC). Four techniques of separation were utilized, depending on the media and the sample concentration: 1. Normal phase (polar solid/non-polar solvent) chromatography worked well with hexane solution. 2. Reverse phase (non-polar solid/polar liquid) was used for aqueous solutions of detectable concentrations. 3. Reverse phase with gradient-elution was necessary for low concentration aqueous samples. The

gradient-elution technique effectively concentrated samples in-situ by totally adsorbing all lipophilic compounds on the column. When a gradient in solvent-polarity was passed over the column a compound eluted when the solvent mix was non-polar enough to desorb that particular compound. 4. Hexanol solutions (2 ml) were evaporated under vacuum at room temperature and the residue was dissolved in 2 ml of hexane. These samples were then analyzed similar to the hexane runs. This was necessary as the PCB's could not be separated from their degradation products with hexanol as a chromatographic solvent. All samples were detected by U.V. absorbance at 254 nanometers. The instrument layout is indicated in Figure 3-1.

Analytical parameters varied with the compound, solvent, and concentration, thus the important considerations are shown in Table 3-1.

2,4-D was analyzed by the Wisconsin Alumni Research Foundation (WARF) because 2,4-D does not absorb well at 254 nm. Their equipment and parameters were: Waters Associates Model 202 Liquid Chromatograph equipped with a Schoeffer SF 770 Variable Wavelength U.V. Detector at 272 nm, with a sensitivity of 0.01 AUFS. The column was a 30 cm x 4 mm Bondapak C_{18}/Pl Porasil with 40/60 Methanol/water plus 0.01% H_3PO_4 as a solvent (2.0 ml/min). Sample size was 50 µl.

All solutions and analytical procedures were calibrated by mixing the standard solution with the solvent to make mixes containing 80,60,40, 20 and 0% of the standard solutions. These mixes were analyzed using the proper parameters. In all cases, except 3,4,2'-trichlorobiphenyl, the calibration curve was linear in peak height. 3,4,2'-trichlorobiphenyl was measured by peak area and gave an S-shaped calibration curve.

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A control sample was used for each irradiation. It was handled in the exact same manner as the irradiated samples, except that it received no irradiation. All results are scaled from the control. Samples of the solvents were also irradiated and analyzed so any background caused by solvent irradiation products could be screened out.

D. Material Data

1. 3,4,2'-trichlorobiphenyl

This PCB isomer, of molecular weight 257.6, is a white crystalline material at room temperature and has been identified in Arochlors 1242 and 1248. It has a melting point of 60°C (Bolger, 1973) and a solubility in water of 0.075 mg/l (Wallnofer et al., 1973). Vapor pressure can be deduced from the Arochlor 1242 curve in Figure 3-2.

2. 4-chlorobiphenyl

Another PCB isomer of molecular weight 188.7, 4-chlorobiphenyl is a white crystalline material at room temperature and has been identified as a constituent of Arochlors 1221 and 1223. It has a melting point of 75.5°C (Bolger, 1973) and a solubility in water of 1.2 mg/l (Wallnofer et al., 1973). Vapor pressure can be estimated from Figure 3-2.

PCB's in general are relatively stable, inert chemicals. Solubility is good in most organic solvents and low in water. Water solubility increases with decreasing chlorine content.

3. Monuron (3-(p-chlorophenyl)-N,N-dimethyl urea)

Monuron is a urea herbicide of molecular weight 198.65. It is a white, odorless, crystalline solid at room temperature, with a melting point of 170.5°C (Merck Index, 1965), and decomposing at 185°C.

Solubility in water is .0260 weight percent at 25°C (Zhuravlev, 1969). The vapor pressure is 5×10^{-7} mm Hg at 25°C (Hill, 1971). Monuron is sparingly soluble in petroleum oils and polar organic solvents such as acetone. It is moderately soluble in methanol, ethanol, and acetone and practically insoluble in hydrocarbon solvents (Pesticide Chemicals Official Compendium, 1966).

4. 2,4-D (2,4-dichlorophenoxyacetic acid)

2,4-D is a white crystalline powder with a molecular weight of 221.0 and a melting point of 138°C. It is quite soluble in alcohol, ether, and alkaline solutions, and insoluble in petroleum oils (Pesticide Chemicals Official Compendium, 1966). Solubility in water is 775 parts per million at 25°C (Bailey and White, 1965).

5. Hexane

Hexane is a clear liquid with a molecular weight of 86.2, a normal boiling point of 68.74°C, and a vapor pressure of 151.3 torr at 25°C. Hexane has a density of 0.655 g/cc at 25°C (Riddick and Bunger, 1970), and the U.V. cutoff is 210 nm. (Waters Manual, 1975). The solubility of water in hexane is 0.0111% by weight at 20°C (Black et al., 1948).

6. Hexanol

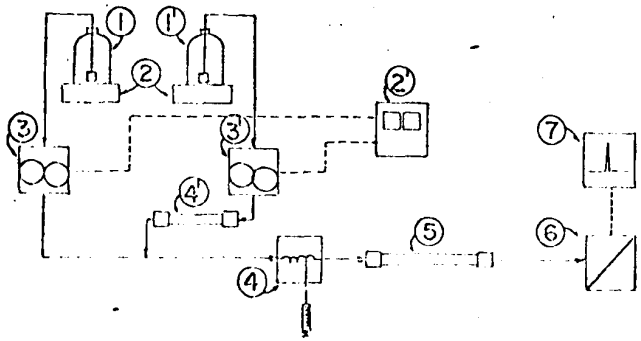
1-hexanol is a clear, relatively viscous liquid with a molecular weight of 102.18. It has a normal boiling point of 157°C and a vapor pressure at 25°C of 0.82 torr. 1-hexanol has a density of 0.8159 g/cc at 25°C (Riddick and Bunger, 1970), and water has a solubility of 7.42% by weight in 1-hexanol (Kirk and Othmer, 1969).

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7. Acetonitrile

Acetonitrile is a clear liquid with a molecular weight of 41.05 and a normal boiling point of 8.160%. It has a vapor pressure of 88.81 torr at 35°C and a density of 0.7766 g/cc at 25°C (Riddick and Bunger, 1970). Acetonitrile and water are completely miscible and the U.V. cutoff is 220 nm. (Waters Manual, 1975).

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1 - One liter solvent supply with filter and teflon line to pump.

2 - Magnetic stirrer.

3 - Pump flow: 0-9.9 ml/min, pressure: 0-408 at.,
Model 6000-A, Waters Associates.

4 - Injector loop: sample size 1 µl to 2ml.
Model U6K, Waters Associates.

5 - Column.

6 - U.V. absorbance detector. Sensitivity to 0.005 AUFS
Model 440, Waters Associates.

7 - Recorder - 10 mv.

1'- Additional solvent supply. Used for gradient elution (see 1).

2'- Gradient programmer. Used for gradient elution
Model 660, Waters Associates.

3'- Additional pump. Used for gradient elution (see 2).

4'- 7mm x 30cm Bondapak C_{18}/Porasil B column. In line only when water was used as a chromatographic solvent.

FIGURE 3-1

List of Chromatographic System

TABLE 3-1
Chromatographic Parameters for all Analyses

Compound	Solvent	Concentration mg/l	Sample Size	Column Packing	Chromatographic Solvent	Flowrate ml/m	UV Sensitivity AUFS*	Chart Speed (in/min)
3,4,2'-tri chlorobiphenyl	Water	0.07	2.0 ml	2 mm x 61 cm Bondapak C_{18}/Corasil	Linear gradient from 50/50 to 0/100 H_2O/CH_3CN in 15 min.	1.0	0.05	0.4
Monuron	Water	0.4	2.0 ml	2mm x 61 cm Bondapak C_{18}/Corasil	Linear gradient from 100/0 to 10/100 H_2O/CH_3CN in 15 min.	1.0	0.50	0.4
Monuron	Water	4.2*	0.4 ml	2 mm x 61 cm Bondapak C_{18}/Corasil	40/60 H_2O/CH_3CN	1.0	0.50	0.4
4-chloro-biphenyl	Water	0.80	0.2 ml	2 mm x 61 cm Bondapak C_{18}/Corasil	40/60 H_2O/CH_3CN	1.0	0.05	0.4
4-chloro-biphenyl	Hexane	4.0	0.4 ml	7 mm x 30 cm u-Porasil	Hexane	1.2	0.50	0.4
3,4,2'-tri-chlorobiphenyl	Hexane	4.1	0.3 ml	7 mm x 30 cm u-Porasil	Hexane	1.2	0.20	0.4
3,4,2'-tri-chlorobiphenyl	Hexanol	4.3	30 µl	7 mm x 30 cm u-Porasil	Hexane	0.5	0.05	0.2

*Absorbance Units, Full Scale

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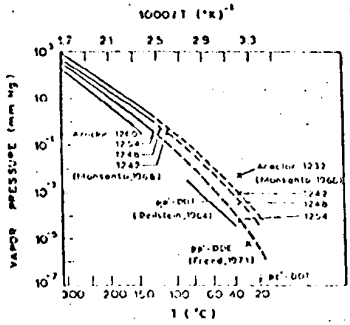


FIGURE 3-2

Vapor Pressures of PCB's,
p,p'-DDE and p,p'-DDT
(Panel on Hazardous Trace Substances, 1972)

CHAPTER 4: RESULTS AND DISCUSSION

A. Aqueous Solutions

3,4,2'-trichlorobiphenyl

3,4,2'-trichlorobiphenyl in water at a concentration of 0.072 mg/l was irradiated with doses ranging from 1 kilorad to 2 megarads. All samples showed no trace of the 3,4,2'-trichlorobiphenyl at 0.05 AUFS (absorbance units full scale) sensitivity. Figures 4-1 and 4-2 illustrate the chromatograms of the standard and a sample irradiated to 2.0 megarads respectively. The diagonal line traces the solvent gradient. At higher sensitivity (0.02 AUFS) a small peak was detected which appeared throughout the dose range (see Figure 4-3). Any irradiation products were difficult to discern because the gradient technique also concentrates and detects impurities in the water being used as a solvent. The gradient was changed from an initial solvent mix of 50/50- H_2O/CH_3CN to 100/0-H_2O/CH_3CN in an attempt to detect any products passing through the column without being picked up by the packing. This revealed a large broad peak eluting early in the gradient program (see figure 4-4). This large peak surely represents many compounds of similar structure which are much more soluble in water than the parent 3,4,2'-trichlorobiphenyl. These findings agree with the general observations of other investigators, i.e., that chlorinated hydrocarbon irradiation products have increased water solubility. The early-eluting products could possibly be hydroxylated compounds similar to those observed in irradiated chlorobenzene (Johnson et al., 1951).

The irradiations were carried out with water solutions of maximum 3,4,2' solubility and at the lower limit of dose available at the HVRL, yet the 3,4,2'-trichlorobiphenyl was completely degraded under these conditions. Because no dose/effect data was obtained, G-values cannot be calculated.

The analysis of 3,4,2'-trichlorobiphenyl is hampered because of the low concentrations, the high sensitivity required, and by the gradient technique which produces a complicated background (see Figure 4-1). Further complications occurred due to the tendency of PCB's to adsorb onto solid surfaces (Nisbet and Sarofim, 1972). This fact meant a loss of concentration due to adsorption on the petri dishes, weigh-bottles, syringes, etc. Adsorption varied from 30 to 80% with the amount of handling and the residence time in glass vessels. Losses were taken into account by a calibration curve before each set of analyses and by scaling all results from the control.

Monuron

Monuron was irradiated at two concentrations, 0.4 mg/l and 4.2 mg/l and with doses from 1 kilorad to 2 megarads. The lower concentration was analyzed using the gradient technique. Figures 4-5, 4-6, and 4-7 illustrate the standard, a 100 kilorad dose, and a 10 kilorad dose. Note the degradation products resulting from the 10 kilorad dose and the lack of these products in the 100 kilorad dose. The change in product distribution indicates that degradation products are themselves broken down into further degradation products. The results for aqueous monuron at 0.4 mg/l are tabulated in Table 4-1 and graphed in Figure 4-8.

MONS 012784

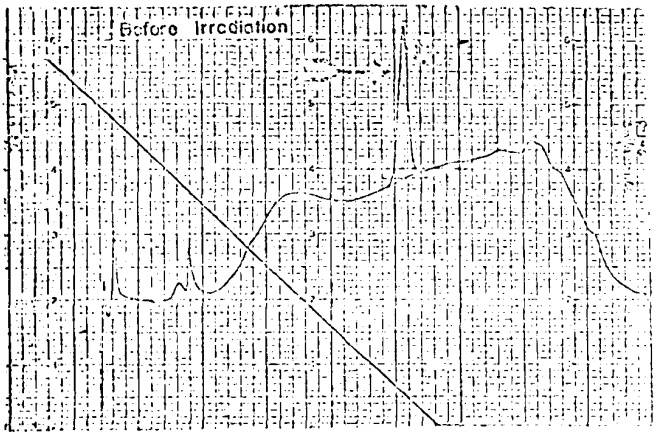


FIGURE 4-1. 3,4,2'-trichlorobiphenyl in Water at 0.07 mg/l, Standard

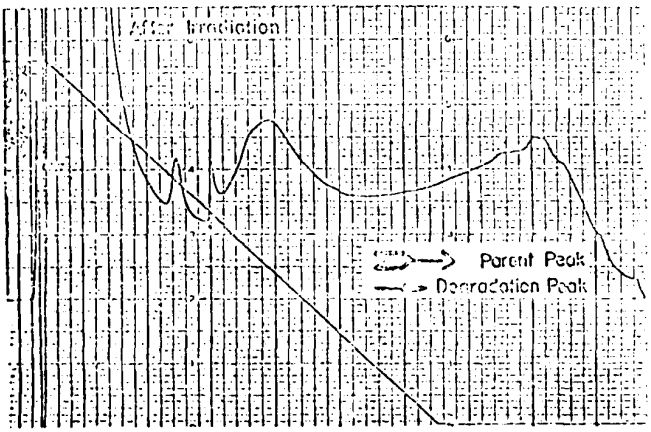


FIGURE 4-2. 3,4,2'-trichlorobiphenyl in Water at 0.07 mg/l Exposed to 2.0 Megarads

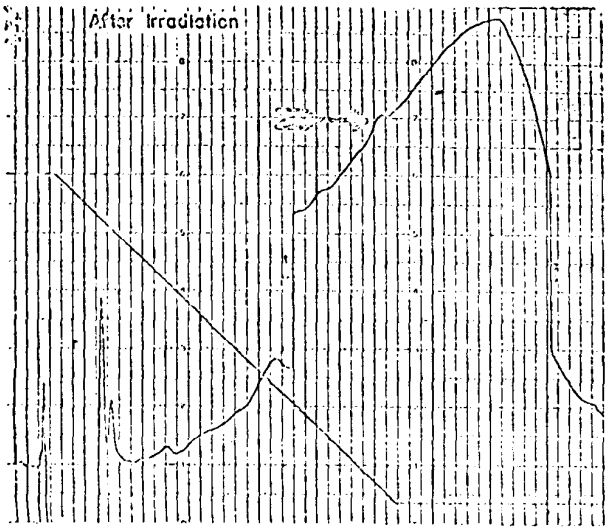


FIGURE 4-3. 3,4,2'-trichlorobiphenyl in Water at 0.07 mg/l, Exposed to 1.0 Kilorads, Sensitivity Increased (x 2.5)

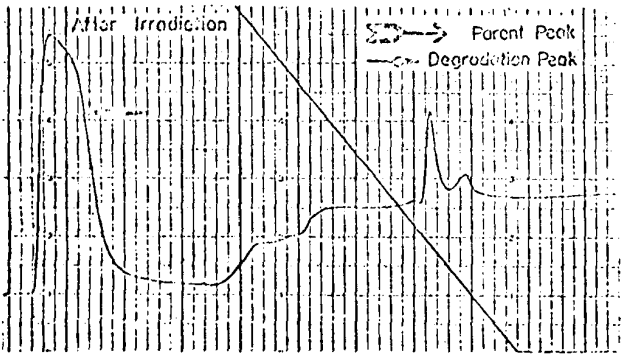


FIGURE 4-4. 3,4,2'-trichlorobiphenyl in Water at 0.07 mg/l, Exposed to 2.0 Megarads, Gradient changed to: 100/0 $H_2O/CH_3CN \rightarrow$ 0/100 H_2O/CH_3CN

MONS 012787

Table 4-1 (continued)
Monuron in Water
0.40 mg/l

Run	Sample	Monuron Peak Height (mm)		Percent Degradation	G(-Monuron)
2	100/0 Standard/Water	115			
	80/20 Standard/Water	92			
	60/40 Standard/Water	71	Calibration		
	40/60 Standard/Water	48			
	20/80 Standard/Water	24			
	100/0 Standard/Water	0			
	Standard x 25 Kilorads	0		100	-
	Standard x 20 Kilorads	0		100	-
	Standard x 15 Kilorads	0		100	-
	Standard x 10 Kilorads	0		100	-
	Standard x 7.5 Kilorads	0		100	-
	Standard x 5.0 Kilorads	1		99.4	0.387
	Standard x 2.5 Kilorads	14		88	0.683
	Standard x 1.0 Kilorads	53		54.7	1.061
	Standard x 0 (Control)	0		0	0

Table 4-1 (continued)
Monuron in Water
0.40 mg/l

Run	Sample	Monuron Peak Height (mm)		Percent Degradation	G(-Monuron)
2	100/0 Standard/Water	115			
	80/20 Standard/Water	92			
	60/40 Standard/Water	71	Calibration		
	40/60 Standard/Water	48			
	20/80 Standard/Water	24			
	100/0 Standard/Water	0			
	Standard x 25 Kilorads	0		100	-
	Standard x 20 Kilorads	0		100	-
	Standard x 15 Kilorads	0		100	-
	Standard x 10 Kilorads	0		100	-
	Standard x 7.5 Kilorads	0		100	-
	Standard x 5.0 Kilorads	1		99.4	0.387
	Standard x 2.5 Kilorads	14		88	0.683
	Standard x 1.0 Kilorads	53		54.7	1.061
	Standard x 0 (Control)	0		0	0

MONS 012788

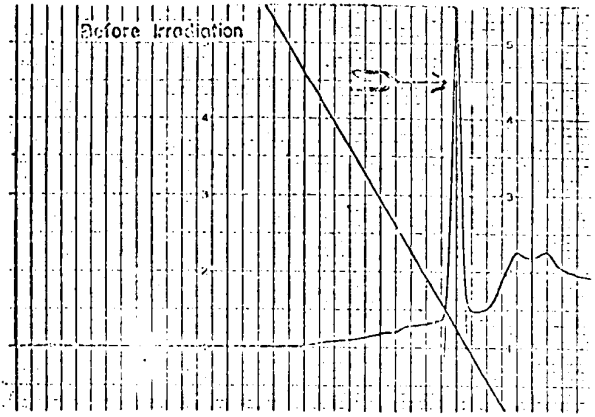


FIGURE 4-5. Monuron in Water at 0.4 mg/l, Standard

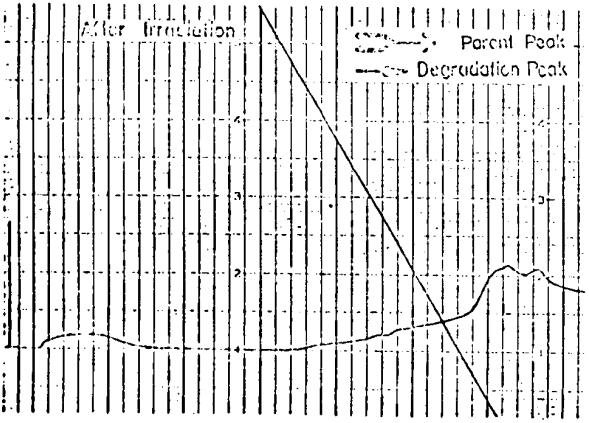


FIGURE 4-6. Monuron in Water at 0.4 mg/l, Exposed to 100 Kilorads

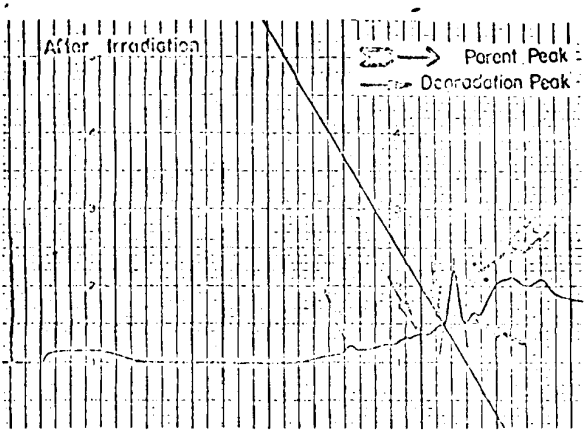


FIGURE 4-7

Monuron in Water at 0.4 mg/l,
Exposed to 10 Kilorads

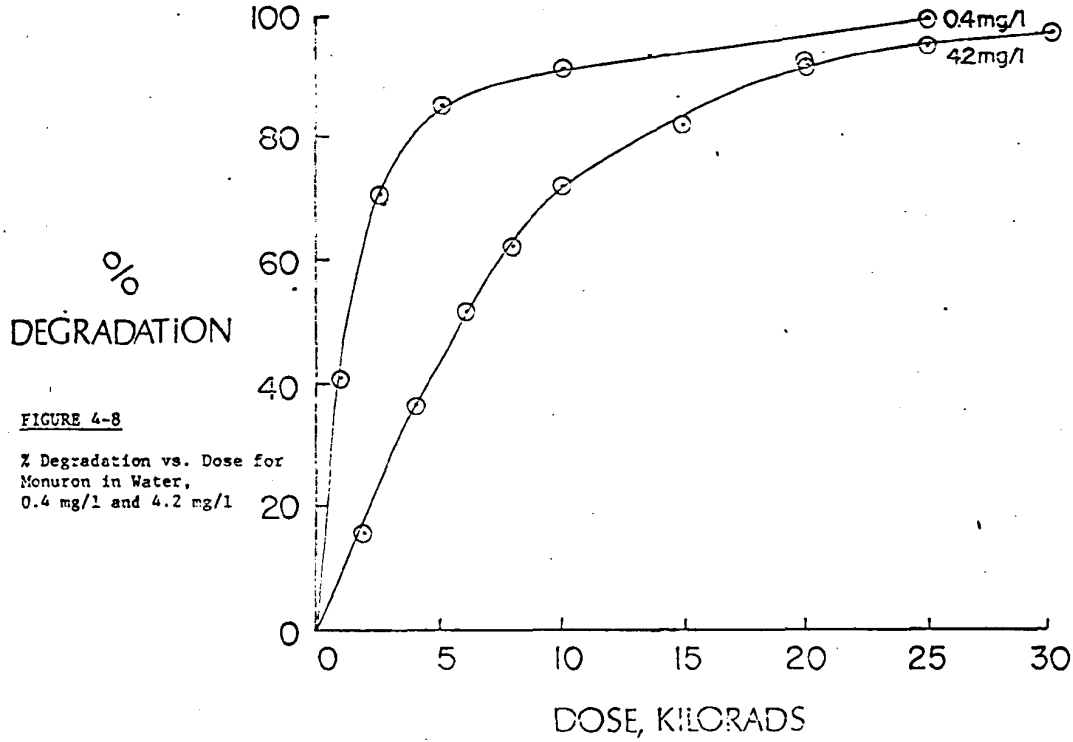


FIGURE 4-8

% Degradation vs. Dose for Monuron in Water, 0.4 mg/l and 4.2 mg/l

MONS 012791

At 4.2 mg/l in water, monuron was irradiated from 2 to 200 kilorads, and analyzed without gradient techniques. Figures 4-9 and 4-10 are chromatograms of the standard, and a 15 kilorad sample respectively. Note the degradation products eluting before the monuron peak. These peaks grew slowly with increasing doses until they reached a maximum at approximately 30 kilorads and then decreased with continued dosing. The results of the irradiation are tabulated in Table 4-2 and graphed with the 0.4 mg/l runs in Figure 4-8. Analysis of identical samples were very reproducible (± 2%) and no monuron was lost in handling. The calibration curves were linear in peak height.

4-chlorobiphenyl

4-chlorobiphenyl was irradiated at a concentration of 0.802 mg/l in aqueous solution with doses ranging from 2 to 200 kilorads. Figures 4-11, 4-12, and 4-13 illustrate analysis of the standard, a 30 kilorad dose and a 2 kilorad dose, respectively. The results are tabulated in Table 4-3 and are plotted in Figure 4-14. As in the 3,4,2'-trichlorobiphenyl analysis there was a small peak which appeared no matter how high the dose (see Figure 4-13). Reproducibility was noticeably less than that obtained with monuron (± 5%) and there was a loss of 10% sample during handling. These anomolies can be explained, once again, by the tendency of PCB's to absorb onto surfaces from aqueous solutions. The calibration curve for 4-chlorobiphenyl was linear in peak height.

2,4-D

2.4-D in water at 4.9 mg/l was irradiated with doses from 60 kilorads to 2 megarads and analyzed by HPLC (as described in Chapter 3) at the WARF Institute. They detected no 2,4-D in any of the irradiated samples.

TABLE 4-2
Monuron in Water
4.2 mg/l

Run	Sample	Monuron Peak Height (mm)	Percent Degradation	G(-Monuron)
1	100/0 Standard/Water	200		
	80/20 Standard/Water	163		
	60/40 Standard/Water	125		
	40/60 Standard/Water	81	Calibration	
	20/80 Standard/Water	43		
	0/100 Standard/Water	0		
	Standard x 30 Kilorads	3	98.0	0.665
	Standard x 25 Kilorads	7	95.8	0.781
	Standard x 20 Kilorads	11	93.4	0.951
	Standard x 15 Kilorads	29	82.6	1.122
	Standard x 10 Kilorads	45	73.1	1.489
	Standard x 8 Kilorads	62	62.8	1.599
	Standard x 6 Kilorads	87	52.1	1.769
	Standard x 4 Kilorads	106	36.5	1.859
	Standard x 2 Kilorads	141	15.6	1.589
	Standard x 0 (control)	167	0	0

MONS 012794

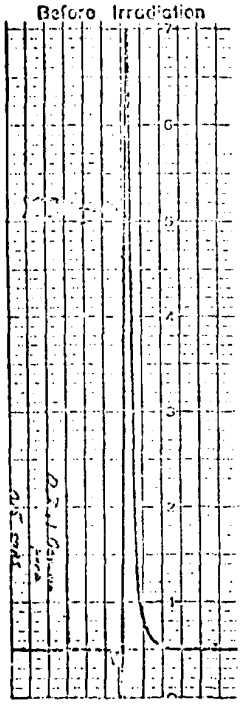


FIGURE 4-9
Monuron in Water
at 4.2 mg/l, Standard

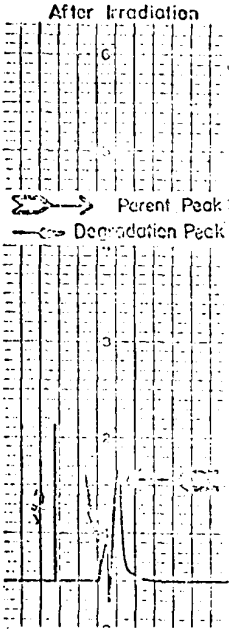


FIGURE 4-10
Monuron in Water
at 4.2 mg/l,
Exposed to 15 Kilorads

TABLE 4-3
4-chlorobiphenyl in Water
0.8 mg/l

Run	Sample	4-chlorobiphenyl Average Peak Height (mm)		Percent Degradation	G(-4-chlorobiphenyl)
1	100/0 Standard/Water	181			
	80/20 Standard/Water	149			
	60/40 Standard/Water	113			
	40/60 Standard/Water	72	Calibration		-
	20/80 Standard/Water	42			
	100/0 Standard/Water	0			
	Standard x 100 Kilorads	4		97.9	0.020
	Standard x 80 Kilorads	6		96.8	0.025
	Standard x 60 Kilorads	7		95.3	0.049
	Standard x 40 Kilorads	8		95.8	0.049
	Standard x 20 Kilorads	15		92.1	0.939
	Standard x 0 Kilorads	184		0	0
2	100/0 Standard/Water	219			
	Standard x 30 Kilorads	4		97.8	0.067
	Standard x 25 Kilorads	4		97.8	0.080
	Standard x 20 Kilorads	4		97.8	0.100
	Standard x 15 Kilorads	3		98.4	0.134
	Standard x 10 Kilorads	5		97.3	0.199
	Standard x 8 Kilorads	9		95.2	0.243
	Standard x 6 Kilorads	9		95.2	0.324
	Standard x 4 Kilorads	14		92.6	0.573
	Standard x 2 Kilorads	47		74.5	0.761
	Standard x 0 Kilorads	207		0	0

MONS 012796

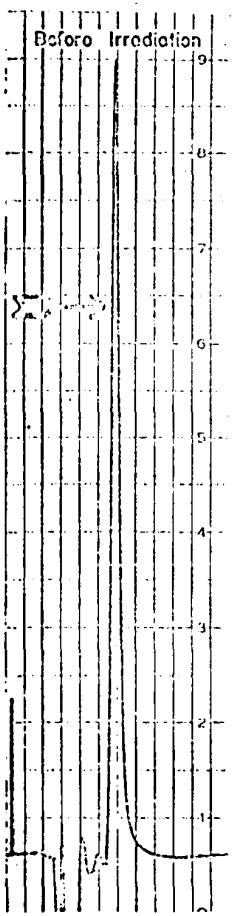


FIGURE 4-11
4-chlorobiphenyl in
Water at 0.8 mg/l
Standard

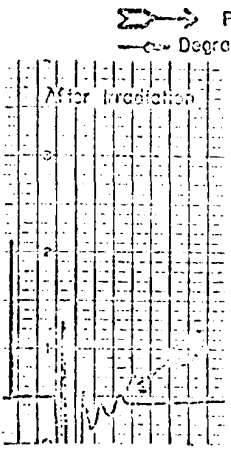


FIGURE 4-12
4-chlorobiphenyl in
Water at 0.8 mg/l
Exposed to 30 Kilorads

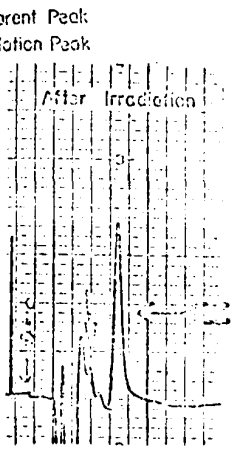


FIGURE 4-13
4-chlorobiphenyl in
Water at 0.8 mg/l
Exposed to 2 Kilorads

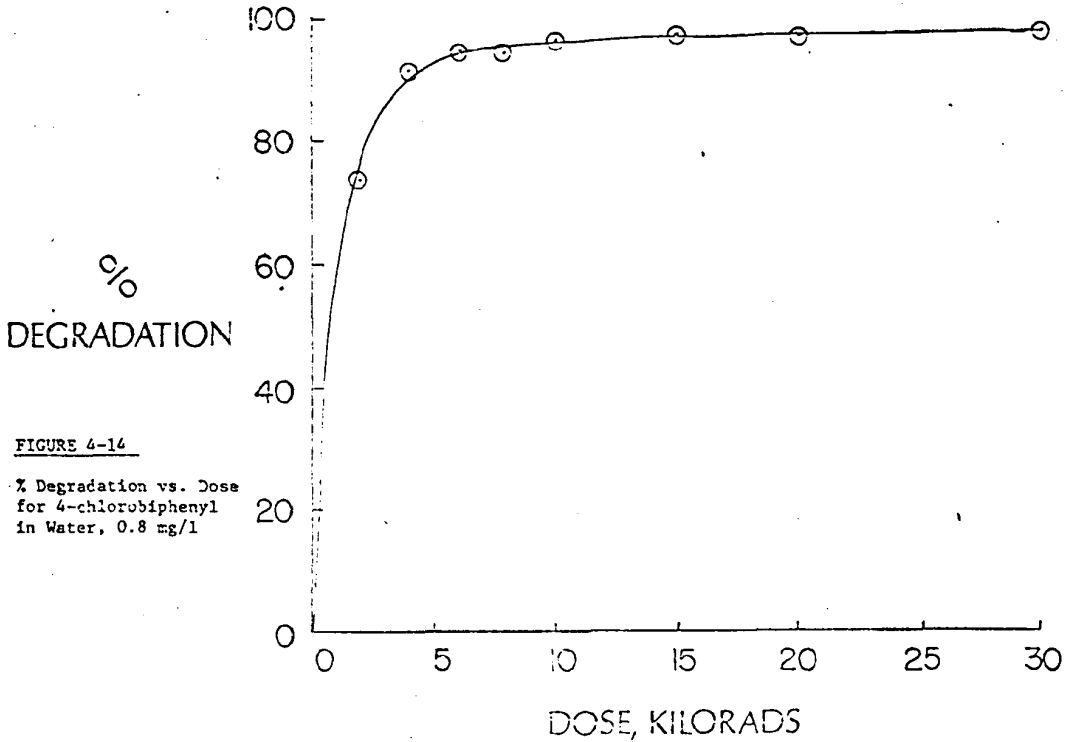


FIGURE 4-14

% Degradation vs. Dose for 4-chlorobiphenyl in Water, 0.8 mg/l

MONS 012798

B. Hexane Solutions

3,4,2'-trichlorobiphenyl

Solutions of 3,4,2'-trichlorobiphenyl in hexane (4 mg/l), in hexane saturated with water (3.9 mg/l), and in split phase samples of hexane and water were irradiated with doses from 250 kilorads to 5 megarads. Typical chromatograms in Figures 4-15 and 4-16 show the standard and 2 megarads. Figure 4-17 shows hexane irradiated to 2 megarads and identifies the early peaks as hexane irradiation products. Chromatograms of the hexane, water saturated hexane, and split phase runs are basically identical. The results are tabulated in Tables 4-4, 4-5, and 4-6 and plotted in Figure 4-18. Note that the water had little effect on the degradation and is in the opposite direction expected, i.e., it should have increased degradation if it took an active part in PCB breakdown. The solubility of water in hexane is small: 0.0111% (110 ppm) by weight at 25°C (Black et al., 1948). The results indicate that the water has too low a concentration to have any effect on a 4 mg/l solute. The water concentration is also too low to be affected directly by the irradiation. Even if the water was directly ionized it would have reacted with the bulk hexane. The decreased radiation effectiveness could be due to the hexane-produced radicals being scavenged by the water molecules rather than being allowed to react with the PCB molecules, which are an order of magnitude less prevalent than the water molecules.

The split-phase irradiation results indicate that the radicals and other active species (produced from water radiolysis) do not diffuse sufficiently over a single interface to have any effect on a solute in

TABLE 4-4
3,4,2'-trichlorobiphenyl
4.0 ug/l in Hexane

Run	Sample	3,4,2'-trichlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Secondary Degradation Peak Height (mm)	Percent Degradation	G(-3,4,2'-trichlorobiphenyl)
1	100/0 Standard/Hexane	193				
	80/20 Standard/Hexane	155				
	60/40 Standard/Hexane	118	Calibration			
	40/60 Standard/Hexane	78				
	20/80 Standard/Hexane	39				
	0/100 Standard/Hexane	0				
	Standard x 1000 Kilorads	117	41	-	39.6	0.0092
	Standard x 500 Kilorads	147	20	-	24.2	0.0112
	Standard x 250 Kilorads	169	-	-	12.9	0.0118
	Standard x 100 Kilorads	185	-	-	4.6	0.0107
	Standard x 50 Kilorads	189	-	-	2.6	0.0121
	Standard x 20 Kilorads	191	-	-	1.5	0.0139
	Standard x 10 Kilorads	192	-	-	1.0	0.0232
	Standard x 0 Kilorads	192	-	-	0	-

MONS 012800

Table 4-4 (continued)
3,4,2'-trichlorobiphenyl
4.0 mg/l in Hexane

Run	Sample	3,4,2'-trichlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Secondary Degradation Peak Height (mm)	Percent Degradation	G(-3,4,2'-Trichlorobiphenyl
2	100/0 Standard/Hexane	195				
	Standard x 5000 Kilorads	20	147	14	89.8	0.0056
	Standard x 4000 Kilorads	40	132	9	79.6	0.0062
	Standard x 3500 Kilorads	38	140	12	80.6	0.0072
	Standard x 3000 Kilorads	47	128	7	76.0	0.0079
	Standard x 2500 Kilorads	65	114	6	66.8	0.0084
	Standard x 2000 Kilorads	79	111	4	64.3	0.0101
	Standard x 1500 Kilorads	106	70	2	45.9	0.0096
	Standard x 1000 Kilorads	112	50	-	42.9	0.0135
	Standard x 500 Kilorads	152	-	-	22.4	0.0141
	Standard x 250 Kilorads	177	-	-	9.7	0.0122
	Standard x 0 (control)	196	0	0	0	0

MONS 012801

TABLE 4-5
3,4,2'-trichlorobiphenyl
3.9 mg/l in Water Saturated Hexane

Rep	Sample	3,4,2'-trichlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Secondary Degradation Peak Height (mm)	Percent Degradation	C(-3,4,2'-trichlorobiphenyl)
1	100/0 Standard/Hexane	100				
	80/20 Standard/Hexane	140				
	60/40 Standard/Hexane	105	Calibration			
	40/60 Standard/Hexane	70				
	20/80 Standard/Hexane	35				
	0/100 Standard/Hexane	0				
	Standard x 5000 Kilorads	28	137	10	84.4	0.0039
	Standard x 4500 Kilorads	32	139	9	82.2	0.0042
	Standard x 4000 Kilorads	32	140	9	82.2	0.0048
	Standard x 3500 Kilorads	47	122	5	73.9	0.0049
	Standard x 3000 Kilorads	51	146	4	71.7	0.0055
	Standard x 2000 Kilorads	78	94	2	56.7	0.0056
	Standard x 1500 Kilorads	100	76	-	44.4	0.0069
	Standard x 1000 Kilorads	120	-	-	33.3	0.0077
	Standard x 500 Kilorads	149	-	-	17.2	0.0080
	Standard x 0 (control)	180	0	0	0	0

MONS 012802

TABLE 4-6
3,4,2'-trichlorobiphenyl
3.9 mg/l in Hexane Phase of 50/50 Hexane/Water

Run	Sample	3,4,2'-trichlorobiphenyl Peak Height (cm)	Primary Degradation Peak Height (cm)	Secondary Degradation Peak Height (cm)	Percent Degradation	G(-3,4,2'-trichlorobiphenyl)
1	100/0 Standard/Hexane	180				
	Standard x 5000 Kilorads	28	140	11	84.6	0.0039
	Standard x 4500 Kilorads	38	128	8	79.1	0.0041
	Standard x 4000 Kilorads	39	125	8	78.6	0.0046
	Standard x 3500 Kilorads	42	126	8	74.2	0.0049
	Standard x 3000 Kilorads	55	121	6	69.8	0.0054
	Standard x 2500 Kilorads	81	82	4	55.5	0.0052
	Standard x 2000 Kilorads	96	75	3	47.3	0.0055
	Standard x 1500 Kilorads	113	-	2	37.9	0.0059
	Standard x 1000 Kilorads	130	-	-	28.6	0.0066
	Standard x 500 Kilorads	152	-	-	16.5	0.0077
	Standard x 0 (control)	152	0	0	0	0

MONS 012803

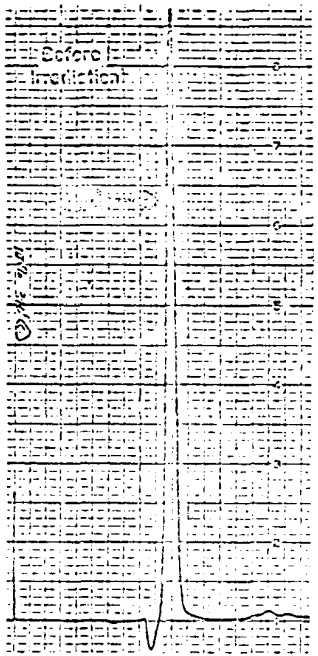


FIGURE 4-15
3,4,2'-trichlorobiphenyl in
Hexane at 4.0 mg/l, Standard

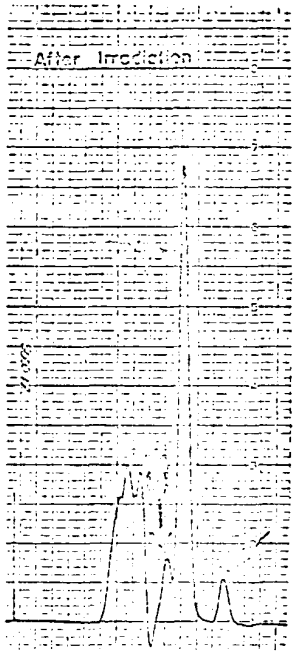


FIGURE 4-16
3,4,2'-trichlorobiphenyl in
Hexane at 4.0 mg/l, Exposed
to 2.0 Megarads

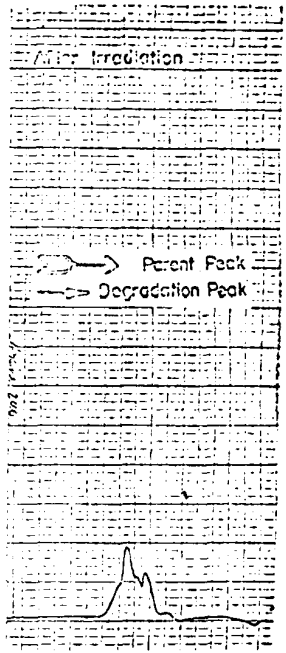


FIGURE 4-17
Hexane, Exposed to
2.0 Megarads

MONS 012804

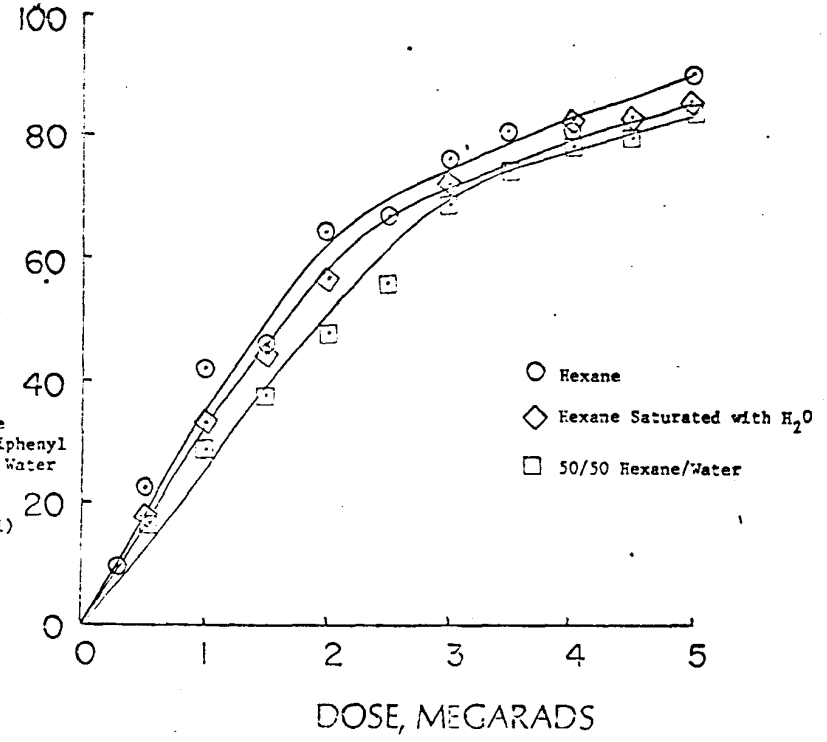


FIGURE 4-18

% Degradation vs. Dose for 3,4,2'-trichlorobiphenyl in Hexane (4.0 mg/l), Water Saturated Hexane (3.9 mg/l) and in Hexane Phase (3.9 mg/l) of 50/50 Hexane/Water

MONS 012805

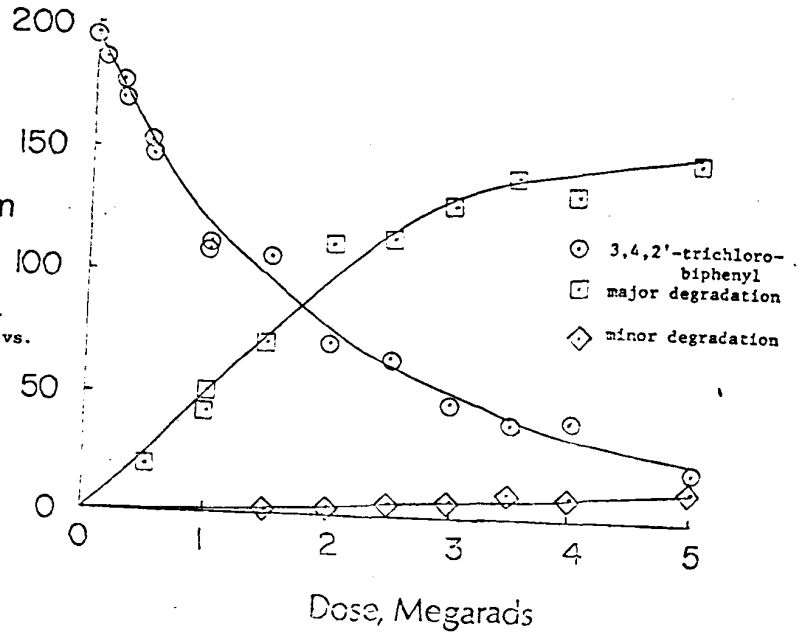


FIGURE 4-19

Peak Heights of Major Degradation Products vs. Dose for 3,4,2'-trichlorobiphenyl in Hexane at 4.0 mg/l

MONS 012809

the organic phase. Note that the two major degradation peaks are evident. The buildup of these with dose is plotted in Figure 4-19.

4 chlorobiphenyl

Hexane, water-saturated hexane, and split phase samples of 4-chlorobiphenyl (4.0 and 3.9 mg/l) were irradiated in the same manner as the 3,4,2'-trichlorobiphenyl. Typical chromatograms show the standard (4-20) and 7 megarad sample (4-21). The data is tabulated in Tables 4-7, 4-8 and 4-9 and plotted in Figure 4-22. Note that there is only one major degradation product compared to the two products evident in 3,4,2'-trichlorobiphenyl irradiation. The buildup of this product is graphed in Figure 4-22. When water is added the same effect (noted above for 3,4,2'-trichlorobiphenyl), a slight decrease in degradation, can be seen for 4-chlorobiphenyl and the same conclusions can be drawn.

In all hexane runs the calibration was linear in peak height and reproducibility was excellent (± 2%). There was some concern that hexane might evaporate and increase the PCB concentrations, especially in the petri dishes. Evaporation, however, was not a problem as the controls agreed well with the standard.

C. Hexanol Solutions

3,4,2-trichlorobiphenyl

Samples of 3,4,2'-trichlorobiphenyl in hexanol (4.3 mg/l) and in hexanol with 6% weight percent water (4.1 mg/l) were irradiated with doses from 1 to 5 megarads. The intent was to ascertain the role of water, dissolved in an aliphatic compound, on the degradation. Hexanol was chosen as an analog to hexane which would dissolve a considerable amount

TABLE 4-7
4-chlorobiphenyl
4.0 mg/l in Hexane

Run	Sample	4-chlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Percent Degradation	G(-4-chloro-biphenyl)
1	100/0 Standard/Hexane	192			
	80/20 Standard/Hexane	151			
	60/40 Standard/Hexane	114			
	40/60 Standard/Hexane	75			
	20/80 Standard/Hexane	35			
	0/100 Standard/Hexane	0			
	Standard x 5000 Kilorads	40	93	79.2	0.0050
	Standard x 4000 Kilorads	52	82	72.9	0.0057
	Standard x 3500 Kilorads	54	84	71.9	0.0065
	Standard x 3000 Kilorads	74	73	61.5	0.0064
	Standard x 2500 Kilorads	88	62	54.2	0.0068
	Standard x 2000 Kilorads	114	45	40.6	0.0064
	Standard x 1500 Kilorads	131	24	31.8	0.0067
	Standard x 1000 Kilorads	153	20	20.3	0.0064
	Standard x 500 Kilorads	173	7	9.9	0.0062
	Standard x 250 Kilorads	183	3	4.7	0.0059
	Standard x 0 (control)	192	0	0	0

MONS 012808

TABLE 4-8
4-chlorobiphenyl
3.9 mg/l in Water Saturated Hexane

Run	Sample	4-chlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Percent Degradation	G(-4-chloro-biphenyl)
1	100/0 Standard/Hexane	163			
	80/20 Standard/Hexane	149			
	60/40 Standard/Hexane	113			
	40/60 Standard/Hexane	74			
	20/80 Standard/Hexane	37			
	0/100 Standard Hexane	0			
	Standard x 5000 Kilorads	63	78	66.7	0.0042
	Standard x 4500 Kilorads	66	77	65.1	0.0045
	Standard x 4000 Kilorads	71	75	62.4	0.0049
	Standard x 3500 Kilorads	86	65	54.5	0.0049
	Standard x 3000 Kilorads	87	12	54.0	0.0057
	Standard x 2000 Kilorads	114	44	39.7	0.0062
	Standard x 1500 Kilorads	138	28	27.0	0.0057
	Standard x 1000 Kilorads	161	13	14.8	0.0046
	Standard x 500 Kilorads	172	7	9.0	0.0057
	Standard x 0 (control)	139	0	0	0

MDNS 012809

TABLE 4-9
4-chlorobiphenyl
3.9 mg/l in 50/50 Hexane Phase of 50/50 Hexane/Water

Run	Sample	4-chlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Percent Degradation	G(-4-chloro-biphenyl)
1	100 Standard/Hexane	189			
	Standard x 5000 Kilorads	54	88	71.6	0.0045
	Standard x 4500 Kilorads	66	83	65.3	0.0046
	Standard x 4000 Kilorads	82	70	56.8	0.0045
	Standard x 3500 Kilorads	91	65	52.1	0.0047
	Standard x 3000 Kilorads	89	64	53.2	0.0056
	Standard x 2500 Kilorads	118	39	37.9	0.0048
	Standard x 2000 Kilorads	129	33	32.1	0.0050
	Standard x 1500 Kilorads	149	20	21.6	0.0045
	Standard x 1000 Kilorads	161	14	15.3	0.0048
	Standard x 500 Kilorads	177	6	6.8	0.0043
	Standard x 0 (control)	190	0	0	0

MONS 012810

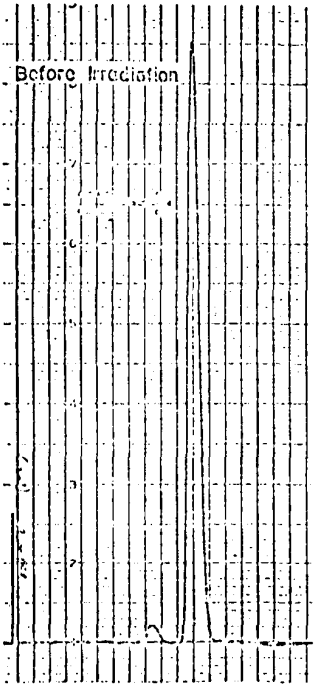


FIGURE 4-20
4-chlorobiphenyl in Hexane at
4.0 mg/l, Standard

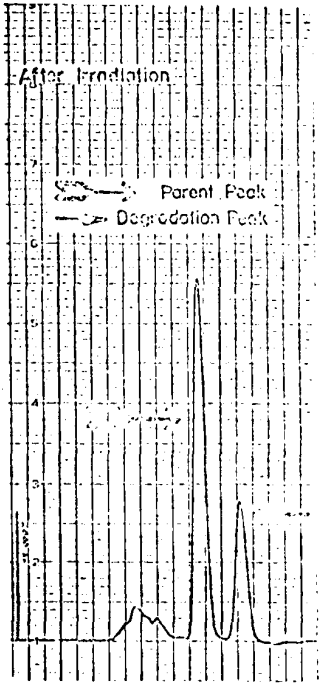


FIGURE 4-21
4-chlorobiphenyl in Hexane at
4.0 mg/l, Exposed to
2.0 Megarads

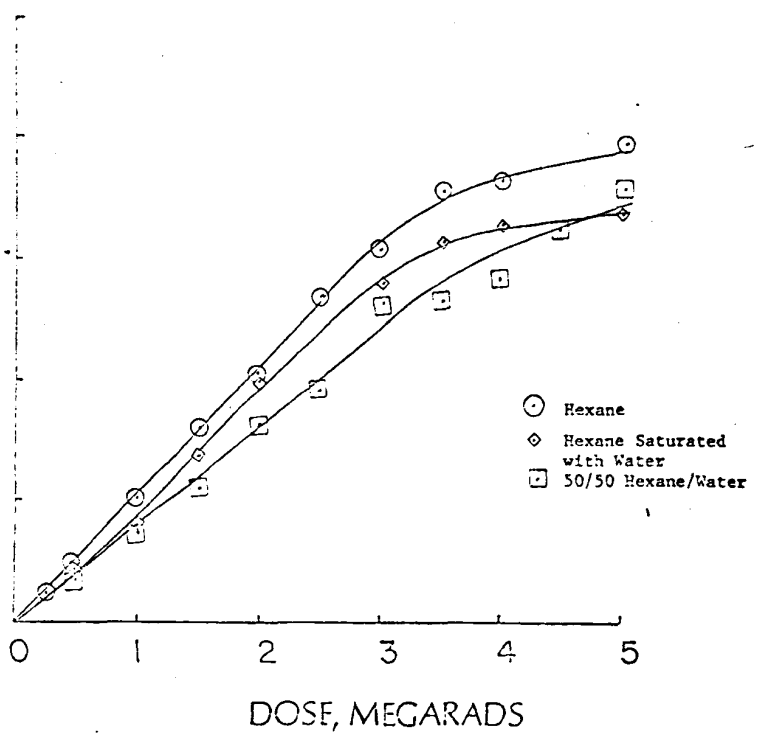


FIGURE 4-22

% Degradation vs. Dose for 4-chlorobiphenyl in Hexane (4.0 mg/l), Water Saturated Hexane (3.9 mg/l) and in Hexane Phase (3.9 mg/l) of 50/50 Hexane/Water

MONS 012812

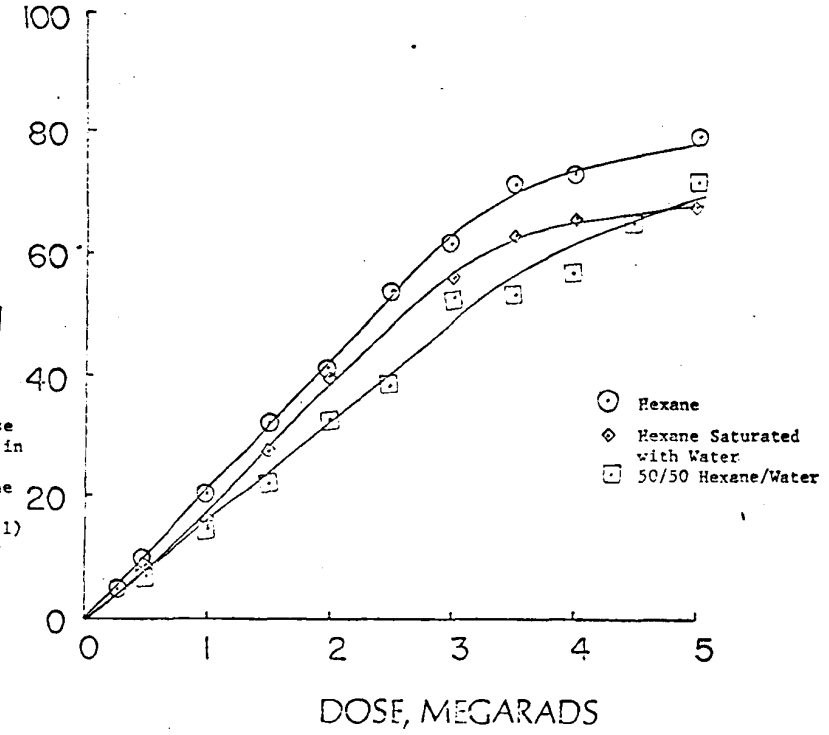


FIGURE 4-22

% Degradation vs. Dose for 4-chlorobiphenyl in Hexane (4.0 mg/l), Water Saturated Hexane (3.9 mg/l) and in Hexane Phase (3.9 mg/l) of 50/50 Hexane/Water

MONS 012813

TABLE 4-10
3,4,2'-trichlorobiphenyl
in Hexanol, 4.3 mg/l

Run	Sample	3,4,2'-trichlorobiphenyl Peak Height (mm)		Degradation Peak Height (mm)	Percent Degradation	G(-3,4,2'-trichlorobiphenyl)
1	100/0 Standard/Hexanol	165				
	80/20 Standard/Hexanol	141				
	60/40 Standard/Hexanol	106	Calibration			
	40/60 Standard/Hexanol	59				
	20/80 Standard/Hexanol	31				
	100/0 Standard/Hexanol	3				
	Standard x 5 Megarads	6		24	50.0	0.0038
	Standard x 4 Megarads	7		16	76.8	0.0047
	Standard x 3 Megarads	13		22	90.6	0.0069
	Standard x 2 Megarads	32		33	94.9	0.0076
	Standard x 1 Megarad	69		19	95.7	0.0099
	Standard x 0 (control)	138		0	0	0

MONS 012814

TABLE 4-11
3,4,2'-trichlorobiphenyl
in Hexanol and 6% Water,
4.1 mg/l

Run	Sample	3,4,2'-trichlorobiphenyl Peak Height (mm)	Primary Degradation Peak Height (mm)	Percent Degradation	G(-3,4,2'-trichlorobiphenyl)
1	Standard x 5 Megarads	7	13	95.1	0.0037
	Standard x 4 Megarads	9	15	93.7	0.0046
	Standard x 3 Megarads	14	14	90.1	0.0059
	Standard x 2 Megarads	21	13	85.2	0.0083
	Standard x 1 Megarad	62	21	56.3	0.0110
	Standard x 0 (control)	142	0	0	0
	Hexanol x 3 Megarads	2	6	-	-
	6% H_2O/Hexanol x 3 Megarads	2	2	-	-
	6% H_2O/Hexanol	2	2	-	-

MONS 012815

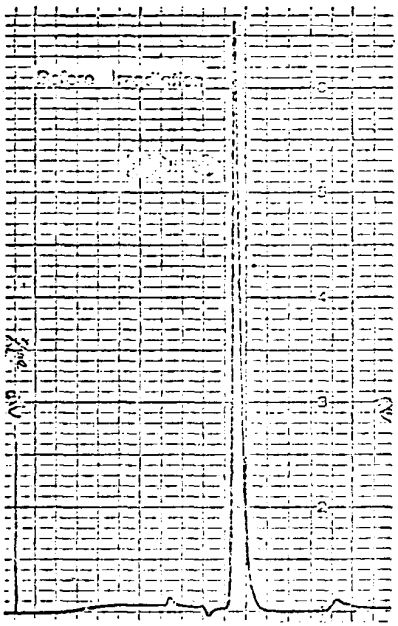


FIGURE 4-23
3,4,2'-trichlorobiphenyl in Hexanol
at 4.3 mg/l, Standard

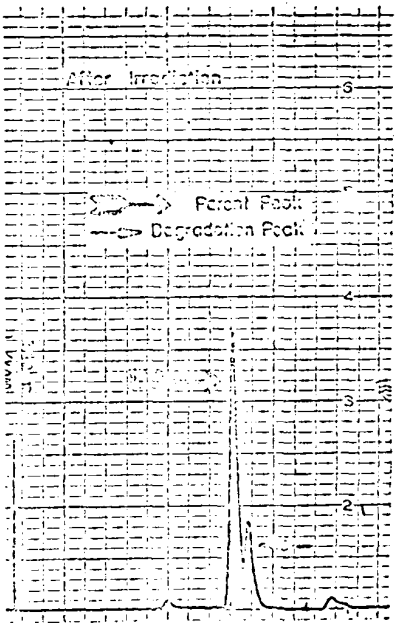


FIGURE 4-24
3,4,2'-trichlorobiphenyl in Hexanol
at 4.3 mg/l, Exposed to
1.0 Megarad

MONS 018816

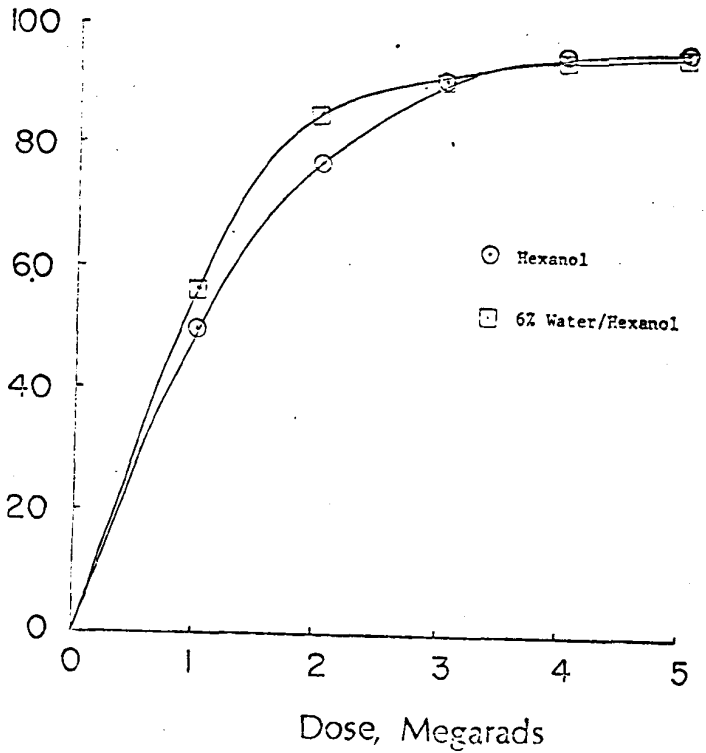


FIGURE 4-25

% Degradation vs. Dose for 3,4,2'-trichlorobiphenyl (4.3 mg/l) in Hexanol and in 6% Water/Hexanol (4.1 mg/l)

MONS 012817

TABLE 4-12
Summary of G-Values and Dose
Required for 50% Degradation

Compound	Solvent	Concentration (mg/l)	Dose, Kilorads 50% Degradation	G-Value
3,4,2'-trichlorobiphenyl	H_2O	0.07 - completely degraded down to 1.0 Kilorad		
3,4,2'-trichlorobiphenyl	Hexane	4.0	1,350	0.0086
3,4,2'-trichlorobiphenyl	H_2O Saturated Hexane	3.9	1,700	0.0065
3,4,2'-trichlorobiphenyl	50/50 H_2O/Hexane	3.9	2,000	0.0055
3,4,2'-trichlorobiphenyl	Hexanol	4.3	1,000	0.0099
3,4,2'-trichlorobiphenyl	6% H_2O in Hexanol	4.1	800	0.0122
4-chlorobiphenyl	H_2O	0.8	2.5	0.408
4-chlorobiphenyl	Hexane	4.0	2,450	0.0064
4-chlorobiphenyl	H_2O Saturated Hexane	3.9	2,750	0.0055
4-chlorobiphenyl	50/50 H_2O/Hexane	3.9	3,050	0.0050
Monuron	H_2O	0.40	1.0	0.970
Monuron	H_2O	4.2	6.0	1.698
2,4-D	H_2O	4.9 - completely degraded down to 60 Kilorads		

MONS 012818

CHAPTER 5. CONCLUSIONS

1. Dissolved organic compounds, such as pesticides, can be degraded by electron irradiation.
2. The degradation of these compounds is not brought about by the direct action of the radiation, but rather by the action of free radicals, ions, and the active molecular species produced by the effect of irradiation on the solvent.
3. Such compounds are degraded much more efficiently in water than in organic solvents. Hexane required ~ 400 times and hexanol ~ 150 times the dose needed for comparable degradation.
4. Water at saturation concentrations (.011%) in hexane increases the required dose for comparable degradation.
5. Water at saturation concentrations (6%) in hexanol decreases the required dose for comparable degradation.
6. Compounds dissolved in hexanol, due to its hydroxyl component, are more efficiently degraded than when dissolved in hexane.
7. The radicals produced in water do not diffuse across a single water/organic interface to increase the degradation of compounds dissolved in the organic phase.
8. Degradation products are produced and increase with dose.
9. Relative degradation tapers off as the parent compound becomes less concentrated, and as degradation products become more concentrated.
10. The degradation products are, in general, more water soluble than the parent compound.

MONS 012819

11. The efficiency of degradation, i.e., the G-value, increases with increasing concentration of the organic compound.

12. 3,4,2'-trichlorobiphenyl is more easily degraded than 4-chlorobiphenyl. This occurs because 3,4,2'-trichlorobiphenyl has 3 chlorines, the most likely spot for hydroxylation.

MONS 012820

CHAPTER 6. RECOMMENDATIONS

As this work is the first of its kind in this department, there are many lines of investigation which could be carried out in future work.

1. Irradiation studies in systems more closely approaching sludge. Different models can indicate the effects imposed by the many components of sludge. For instance, a model consisting of soap solutions is being studied at the time of this writing. Irradiation of organics in soap solutions should indicate what will happen in the micellar element of sludge.
2. Investigations could be extended to other organic compounds. Many pesticides are available, having a wide range of solubilities, persistence in the environment, etc. Compounds such as chlorinated phenols, pthalates and other industrial pollutants would also be candidates for irradiation studies.
3. The irradiation medium, which is very important in the degradation process, should be studied. Two parameters, obviously important and technically feasible to regulate on a large scale, are pH and pO_2.
4. Systems of compounds should be investigated. If a particular compound has a large affinity for radicals, i.e., it is a radical scavenger, it may "protect" the compound which the irradiation is intended to degrade. Some compounds may have a synergetic effect. For instance, barium sulfate has been shown to significantly increase the degradation of 2,4,5-t (a phenoxyacetic acid) (Craft et al., 1975).

MONS 012821

5. Studies in real systems is the ultimate test. Irradiation of sludge or wastewater "spiked" with compounds of interest are necessary before any firm conclusions can be drawn. However, the analytical techniques required for such studies are much more complicated than those used in this work.
6. Cost studies for comparison to present wastewater treatment methods should be done to ascertain the market for electron irradiation of industrial wastes.
7. Investigation of electron-irradiation as a part of waste-treatment systems. For example, a large wastestream containing a non-biodegradable compound could possibly be treated by concentration on carbon, irradiation of the carbon to break the compound into bio-degradable fragments, and then bio-oxidation as a final treatment.

MONS 012822

APPENDIX A

G VALUES

The G value is a means of representing the effectiveness of the radiation by relating the absorbed energy to the desired yield of molecular species. The G-value is defined as the number of molecules formed, or degraded, for every 100 eV of energy absorbed. G(A) refers to the number of A molecules formed, and G(-B) refers to the number of molecules of B which were degraded.

Following is a calculation for a sample of 3,4,2'-trichlorobiphenyl in hexane which was dosed to 1 Megarad. The important parameters are listed below.

3,4,2'-trichlorobiphenyl, Molecular Weight = 257.6

3,4,2'-trichlorobiphenyl, Concentration = 4.08 mg/l

Dose = 10^6 Rads

(100 eV) = 1.602×10^{-12} g Rad

Hexane, Density = 0.66 g/cm^3

Percent Degradation = 39.6%

G(-3,4,2'-trichlorobiphenyl) =

$$\frac{4.08\ \text{mg}_{3,4,2'}}{1_{\text{soln.}}} \cdot \frac{\text{g}_{3,4,2'}}{10^3\text{mg}_{3,4,2'}} \cdot \frac{1_{\text{soln.}}}{10^3\ \text{cm}^3_{\text{soln.}}} \cdot \frac{\text{mole}_{3,4,2'}}{257.6\ \text{g}_{3,4,2'}}$$

$$\cdot \frac{6.023 \times 10^{23}\ \text{molecules}_{3,4,2'}}{\text{mole}_{3,4,2'}} \cdot \frac{\text{cm}^3_{\text{soln.}}}{0.66\text{g}_{\text{soln.}}} \cdot \frac{1.602 \times 10^{-12}\ \text{g rad}}{(100\ \text{eV})} \cdot \frac{1}{10^6\ \text{rads}}$$

$\cdot$ 0.396 Degraded

MONS 012823

$G(-2,4,2'\text{-trichlorobiphenyl}) = 0.0917 \times 10^{-1}$

$= 0.0092 \frac{\text{molecules of 3,4,2'-trichlorobiphenyl degraded}}{100 \text{ eV of energy absorbed}}$

It should be emphasized that the G-value for a particular compound will change when the characteristics of the irradiation are altered. Parameters which will change the G-value include: concentration of the compound of interest, concentration(s) of other specie(s) in the medium, the solvent, type of radiation, and energy of the radiation.

MONS 012824

APPENDIX B

IRRADIATION COSTS

The cost of the MIT Sewage Irradiation System was approximately $500,000 with a capacity of 100,000 gallons/day (378.5 m^3/d). Annual costs are estimated at $100,000. Return on investment from the sale of sludge has not been determined but is estimated at $75,000 - $150,000 per year, depending largely on the solids content of the treated sludge (Trump et al., 1975). This can be compared to a Cobalt-60 Gamma Irradiation Plant in operation at Geiselbullach, Germany, which cost approximately $600,000 and has a capacity of 7500 gallons/day (30 m^3/d) (Trump, 1975). Costs per unit capacity can be expected to decrease with larger installations.

Cost for irradiating organic compounds in water, such as industrial effluent, depend on the G-value and the concentration of the organics in the water. For example, an estimate of treating an effluent similar to the samples irradiated in this work can be made as follows:

$$\frac{\$}{m^3} = \frac{10^2 \text{ eV}}{G \text{ molecules}} \cdot \frac{6.023 \times 10^{23} \text{ molecules}}{\text{mole}} \cdot \frac{\text{mole}}{M \text{ grams}} \cdot \frac{1.602 \times 10^{-19} \text{ watt sec}}{\text{eV}}$$

$$\cdot \frac{\text{hour}}{3.6 \times 10^{-3} \text{sec}} \cdot \frac{\text{Kilowatt}}{10^3 \text{ watts}} \cdot \frac{C\ \$}{\text{Kilowatt hour}} \cdot \frac{\text{gram}}{10^3 \text{ mg}} \cdot \frac{Y \text{ mg}}{1} \cdot \frac{10^3}{m^3}$$

$$= \frac{2.68\ (Y)\ (C)}{(G)\ (M)}$$

where: Y = concentration of organic, mg/l

C = cost of power, $/kilowatt hour

G = G-value of organic

M = molecular weight of organic

MONS 012825

For example, let the organic be 3,4,2'-trichlorobiphenyl with the following specific parameters:

Y = 10 mg/l

C = $.03/kilowatt-hour + $.03 maintenance costs + $.03 capital costs

= $.09/kilowatt-hour

G = 0.5

M = 257.6

$$\$/m^3 = \frac{2.68\ (10)\ (0.09)}{(0.5)\ (257.6)}$$

$= \$.0187/m^3$

$= .2$ cents/m^3

This can be compared to Figure B-1 which shows the costs for 20 industrial plants from 10 different industries.

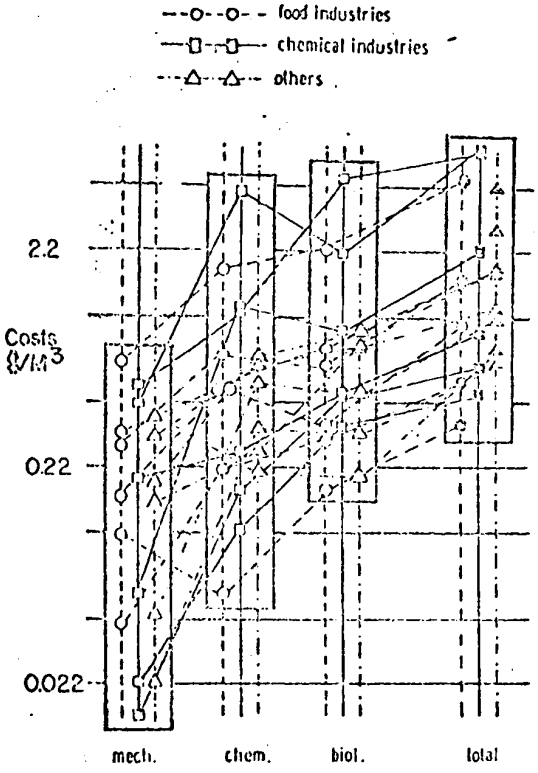


FIGURE B-1

Costs for Waste Water Treatment in 20 Factories from 10 Different Industries (Vollner et al., 1975) (Converted from Deutsche Marks to Dollars)

MONS 012827

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