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**PHOTODEGRADATION OF WASTES IN POLLUTANTS  
IN AQUATIC ENVIRONMENT**

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### EXECUTIVE SUMMARY

Photocatalytic processes have considerable potential to contribute to the degradation of pollutants in the aquatic environment and in wastewater treatment. The sunlight irradiation of humic substances in natural waters has been shown to produce several reactant species including singlet oxygen, superoxide, hydroxyl radical and hydrogen peroxide. These species can react with organic pollutants to cause oxidation and/or dechlorination of these chemicals. Biological components of natural waters such as algae can contain a significant fraction of certain contaminants and studies have shown that algae can photocatalyze the breakdown of several persistent organic compounds. Field studies are required to assess the importance of indirect photochemical processes to the breakdown of persistent organic chemicals such as PCB's, chlorobenzenes and pesticides. Since most of these chemicals do not absorb sunlight, in the past, they were usually considered to be resistant to photochemical breakdown. Heterogeneous photolysis using semiconductors such as titanium dioxide (anatase) has been shown to break down several organic and inorganic pollutants. Some mechanistic considerations as well as practical applications of this method for wastewater treatment are discussed. The process has considerable potential for treating wastewater containing cyanide and/or chlorinated organic chemicals.

## PHOTODÉGRADATION DES DÉCHETS ET DES POLLUANTS EN MILIEU AQUATIQUE

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### RÉSUMÉ ADMINISTRATIF

Les mécanismes de photocatalyse peuvent grandement jouer dans la dégradation des polluants dans le milieu aquatique et dans le traitement des eaux usées. Le rayonnement solaire sur des acides humiques dans des eaux naturelles a produit plusieurs espèces, y compris l'oxygène (singulet), les superoxydes, des radicaux alcoyles et du peroxyde d'hydrogène. Ces espèces peuvent réagir avec des polluants organiques et entraîner l'oxydation ou la déchloruration, ou les deux phénomènes, de ces produits chimiques. Les éléments biologiques des eaux naturelles, comme les algues, peuvent renfermer une fraction importante de ces contaminants et des études ont démontré que les algues peuvent catalyser la photoréduction de bon nombre de ces composés organiques persistants. Des études sur le terrain s'imposent pour évaluer l'importance des mécanismes qui interviennent indirectement dans la photoréduction de produits chimiques persistants comme les BPC, les chlorobenzènes et les pesticides. Comme la plupart de ces produits chimiques n'absorbent pas la lumière, on a eu tendance à croire, par le passé, qu'ils étaient résistants à la photoréduction. En se servant de la photolyse hétérogène avec semiconducteurs comme le bioxyde de titane (anatase), on a pu constater la réduction de plusieurs polluants organiques et inorganiques. On débat certains aspects mécaniques et des applications pratiques de cette méthode pour traiter les eaux usées. Ce mécanisme offre de grandes possibilités pour traiter les eaux usées qui renferment des cyanures ou des produits chimiques organochlorés, ou les deux.

#### MANAGEMENT PERSPECTIVE

Indirect photocatalytic processes may provide an important and, until recently, unrecognized means of detoxification of persistent organic chemicals. Few, if any, studies have been conducted in field situations to assess whether or not chemicals such as PCB's, chlorobenzenes and pesticides are degraded in this fashion so research in this area is necessary. Laboratory studies have shown that heterogeneous photolysis using semiconductor powders such as titanium dioxide can dechlorinate persistent chemicals such as PCB's. This process should be evaluated for treating wastewater and leachates from waste disposal sites which contain a variety of chlorinated chemicals.

## PERSPECTIVE-GESTION

Les mécanismes de photocatalyse indirecte peuvent fournir un important moyen, quoique méconnu jusqu'à présent, de procéder à la détoxification de produits chimiques organiques persistants. Bien peu d'études, s'il en est, ont été menées sur le terrain afin d'évaluer si les produits chimiques comme les BPC, les chlorobenzènes et les pesticides, étaient décomposés de cette façon. Il s'avère donc impérieux de procéder à des recherches dans ce domaine. Des études en laboratoire ont démontré que la photolyse hétérogène avec poudres semiconductrices, tel l'oxyde de titane, peut effectuer la déchloruration de produits chimiques persistants comme les BPC. Ce mécanisme devrait être évalué pour vérifier son applicabilité au traitement des eaux usées et des produits de lexiviation provenant des décharges de déchets qui contiennent une gamme de produits chimiques chlorés.

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**ABSTRACT.** Photocatalytic processes have considerable potential to contribute to the degradation of pollutants in the aquatic environment and in wastewater treatment. The sunlight irradiation of humic substances in natural waters has been shown to produce several reactant species including singlet oxygen, superoxide, hydroxyl radical and hydrogen peroxide. These species can react with organic pollutants to cause oxidation and/or dechlorination of these chemicals. Biological components of natural waters such as algae can contain a significant fraction of certain contaminants and studies have shown that algae can photocatalyze the breakdown of several persistent organic compounds. Heterogeneous photolysis using semiconductors such as titanium dioxide (anatase) has been shown to break down several organic and inorganic pollutants. Some mechanistic considerations as well as practical applications of this method for wastewater treatment are discussed.

### 1. PHOTODEGRADATION IN THE AQUEOUS ENVIRONMENT

The direct and indirect photolysis of environmental contaminants represents an important degradative pathway for certain contaminants in the aqueous environment<sup>1,2</sup>. For example for 3-trifluoromethyl-4-nitrophenol (TFM), a lampricide used in streams flowing into the Great Lakes, direct photolysis is the only known decomposition route<sup>3</sup>. The photochemical half-life of TFM in the aquatic environment is about three days and the photolysis by-products have been shown to be non-toxic to aquatic organisms<sup>3</sup>. Other examples of the importance of direct aquatic photolysis have been demonstrated for the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid)<sup>4</sup>, for the wood preservative pentachlorophenol<sup>5</sup>, and for primary aromatic amines<sup>6</sup>. But these compounds represent only a small fraction of environmental contaminants and are fairly unique since they exhibit significant light absorption in the solar spectral region. Many environmental pollutants are poor absorbers of solar light - either

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exhibiting no absorbance or weak absorbance in the 290-320 nm region. For these chemicals indirect photosensitized and photocatalyzed reactions must be evaluated to assess the importance of photolysis as a degradative pathway.

### 1.1 Mass Balance and Phase Partitioning Considerations

Preliminary mass balance calculations and, where possible, an evaluation of the phases in which the chemicals of interest are found in a particular river/lake system are useful first steps in assessing the potential significance of photolysis and designing appropriate photochemical studies. An illustration of this type of preliminary analysis for several chlorinated contaminants in the Niagara River/Lake Ontario system follows. Figure 1 shows the major potential loss mechanisms for chemicals in the lake. Chemicals could be: 1) absorbed to settling particles and wind up in bottom sediments, 2) discharged via the St. Lawrence River, 3) lost from the water column by volatilization, 4) photolyzed and/or biodegraded. A preliminary mass balance calculation for Lake Ontario for some chlorobenzenes, CB's, polychlorinated biphenyls, PCB's, and mirex for which the Niagara River is thought to be the main source is shown in Table I<sup>7,8</sup>. The bulk (>80%) of the CB's and PCB's

TABLE I Proportion of CB, PCB and Mirex Input to Lake Ontario from the Niagara River Lost by Various Processes

Chemical	% * Sedimenting	% St.** Lawrence River	% Unaccounted For
1,2,4-Trichlorobenzene	1	3	96
1,2,3,4-Tetrachlorobenzene	2	2	96
Pentachlorobenzene	4	3	93
Hexachlorobenzene	15	5	80
2,5,2'-Trichlorobiphenyl	5	5	90
2,5,2',5'-Tetrachlorobiphenyl	10	4	86
2,4,5,2',5'-Pentachlorobiphenyl	9	3	88
2,4,5,2',4',5'-Hexachlorobiphenyl	11	6	83
Mirex	70	18	12

\* From Reference 7.

\*\* From Reference 8.

entering Lake Ontario from the Niagara River are unaccounted for in Table I and are probably lost from the lake by volatilization. Biodegradation for the more highly chlorinated compounds is not likely to be significant<sup>9</sup>. Recent laboratory studies<sup>10,11</sup> have known that CB's and PCB's can be dechlorinated photochemically, so photolysis may provide an alternative loss mechanism to volatilization for these chemicals in the lake. Mass balance calculations for mirex, on the other hand, show that most of this chemical is

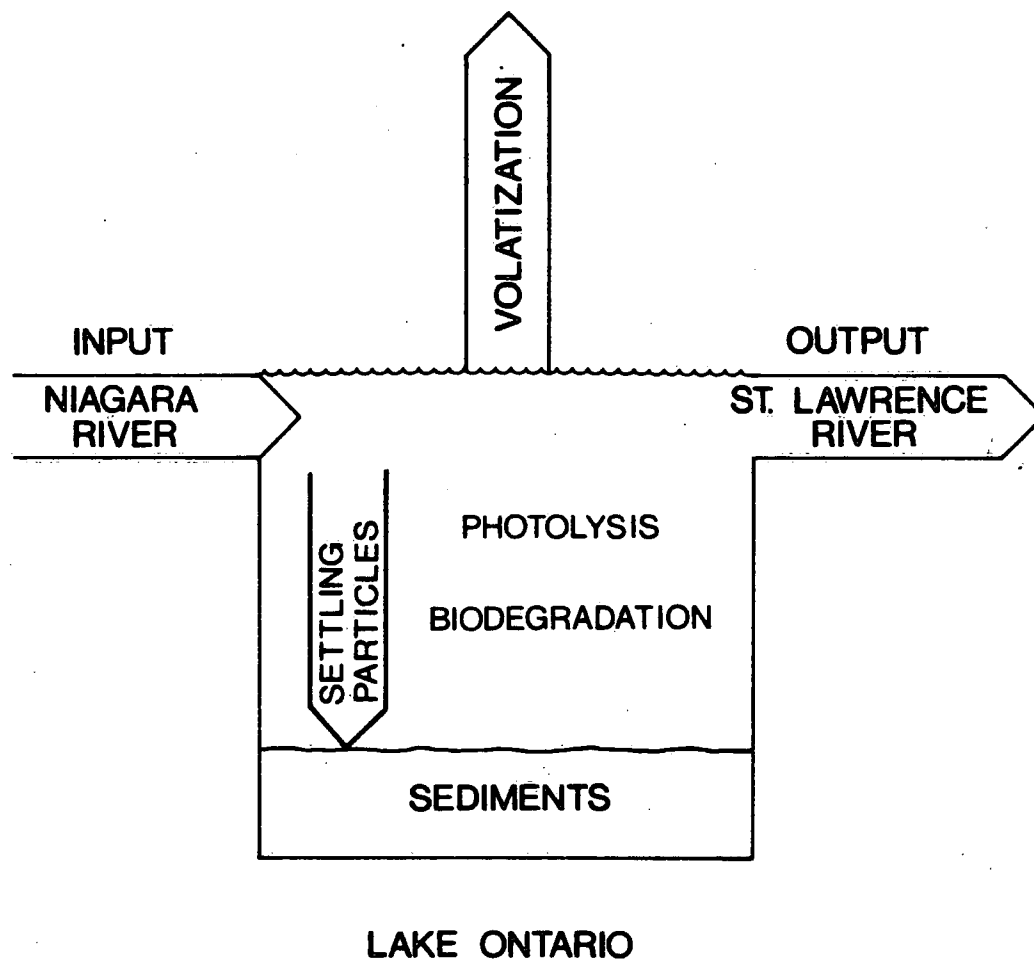


Figure 1 Block diagram of major loss processes for Lake Ontario.



sequestered to settling particulates and likely winds up in bottom sediments. Because Lake Ontario's depth averages 86 meters, photolysis of mirex can largely be ruled out as a significant degradative pathway.

In general, the lower a compound's solubility in water, the greater will be its tendency to partition into the sediment phase. In the absence of field concentration measurements, relationships using physical and chemical properties of the substance such as those developed by Karickhoff<sup>12</sup> can be used to estimate the degree of partitioning into suspended sediments. These relationships should be used with caution, however, since the degree of partitioning is also related to suspended sediment concentration and sediment organic carbon content<sup>12</sup>. In the case of the Niagara River during the course of these measurements, the suspended sediment concentration was about 5 mg/L. In rivers with higher suspended sediment levels, a greater portion of the chemicals will be partitioned into the sediments.

The phases in which chemicals are found in the study area are also an essential element in evaluating degradation pathways. A crude estimate of the partitioning between phases in the Niagara River/Lake Ontario system was accomplished by passing a large volume of water (600 liters) through a series of fine sieves to collect the larger algae and then through a high speed centrifuge to collect the remaining suspended sediment. The centrifuged water was then extracted with a 200 liter stainless steel extraction device<sup>13</sup> and the algae and suspended sediments were soxhlet extracted. The organic extracts were analyzed using capillary gas chromatography<sup>14</sup>. The results of this analysis for several CB's and PCB's are shown in Table II. Most of the lower CB's (up to pentachlorobenzene) are found mainly in the aqueous phase. Significant fractions of HCB and the PCB's are found in the suspended sediment and algae phases. Molar concentrations are extremely low in the

TABLE II Phase Partitioning of CB's and PCB's in the Niagara River Plume (Average of 4 Samples, September, 1984)

Chemical*	% Aqueous	% Suspended Sediment	% Algae
1,2,4-Trichlorobenzene	96	3	1
1,2,3,4-Tetrachlorobenzene	97	2	1
Pentachlorobenzene	90	8	2
Hexachlorobenzene	67	28	5
2,5,2'-Trichlorobiphenyl	86	8	6
2,5,2',5'-Tetrachlorobiphenyl	64	17	19
2,4,5,2',5'-Pentachlorobiphenyl	47	23	30

\* 2,4,5,2',4',5'-Hexachlorobiphenyl and Mirex were not included in this table because they were not detected in every phase.

aqueous phase  $10^{-11}$  to  $10^{-12}$  M/L and four orders of magnitude higher  $10^{-7}$  to  $10^{-8}$  M/kg in the suspended sediment and algae phases. Based on the data in Tables I and II, photolysis could be important for tri-, tetra- and pentachlorobenzenes in the aqueous phase (or in the atmosphere as a result of volatilization). For hexachlorobenzene and the PCB's, photolysis in algae and on suspended sediments should also be considered. In the Lake Ontario system, because of the extreme depth of the water (86 m) and the high settling velocity of the particulates ( $\approx 1$  m/day), association with suspended sediments effectively removes the chemical from the photic zone. However, since photolysis in suspended sediments is possible in shallower water bodies, discussion of photolysis of chemicals on suspended sediments will be included here for completeness.

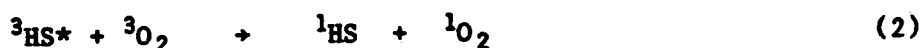
## 1.2 Atmospheric Photolysis

Because of the surprising importance of volatilization of chemicals from certain waterbodies, photolysis in the atmosphere should be examined as a possible major route of decomposition of persistent organics. Direct vapour phase photolysis in pesticide drift during application has been demonstrated to occur<sup>15</sup>. However, very little is known about the atmospheric photolysis of chemicals such as chlorobenzenes and PCB's. PCB's are known to be present globally in air samples<sup>16</sup>, so long range transport is important. PCB's are also found in significant concentrations in precipitation<sup>17</sup>, so some fraction of volatilized material is scavenged by airborne particles and returned to the earth via rain. Hydrogen peroxide and  $\text{OH}^\circ$  and  $\text{HO}_2^\circ$  radicals are known to be photochemically generated in the atmosphere and in clouds<sup>18,19</sup>. Free radicals such as hydroxyl radicals have been shown to produce stepwise dechlorination of PCB's in aqueous solutions<sup>20</sup>, so these reactions may also be important in the atmosphere.

Although there are 209 PCB congeners, most environmental data to date report total PCB concentrations. Improved capillary gas chromatographic methods have made it possible to quantify most individual PCB congeners<sup>21</sup>. A combination approach of (1) laboratory experiments on the sensitized photolysis of major individual PCB congeners present in commercial PCB mixtures (Aroclors) with emphasis on identifying partially dechlorinated products and (2) quantification of atmospheric and precipitation samples for individual PCB congeners should readily show whether or not significant atmospheric photolysis of PCB's is occurring. It is probable that some PCB's will be photochemically dechlorinated to PCB products which are rare or non-existent in the commercial Aroclor mixtures. Finding these rare PCB's in significant quantities in atmospheric and precipitation samples would then indicate that photolysis of PCB's was occurring. Should these initial experiments prove fruitful, detailed work on the photo-degradation of PCB's, CB's and other persistent contaminants in simulated atmospheres containing fog and clouds are recommended to evaluate decomposition rates.

### 1.3 Indirect Photolysis in the Aqueous Phase

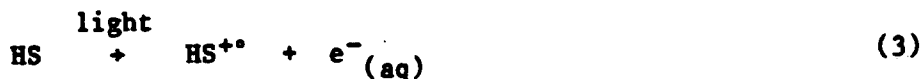
Colored organic material is present in significant concentrations in most natural waters. The major class of materials present is humic substances, HS, of which fulvic acid is the most prevalent<sup>22</sup>. Humic substances, which are yellow/brown in color, have no distinct light absorption bands. They exhibit high light absorption in the ultra-violet region and gradually decreasing absorption throughout the visible. The sunlight irradiation of oxygen-containing colored humic waters has been demonstrated to produce singlet oxygen likely by the following series of reactions<sup>23, 24, 25</sup>.



Singlet oxygen is much more reactive than ground state oxygen. Because it reacts rapidly with 2,5-dimethylfuran (DMF) to produce cis-1,2-diacetylene<sup>26</sup>, the DMF reaction is usually used as a probe to show the presence of  $^1\text{O}_2$ . The irradiation of several natural waters from the United States was shown by Zepp *et al.*<sup>23</sup> to produce between  $10^{-12}$  and  $10^{-13}$  molar singlet oxygen.

A sharp decrease in the DMF reaction rate has been observed after addition of known singlet oxygen quenchers. DABCO (1,4-diazabicyclo [2.2.2] octane)<sup>23</sup> and sodium azide<sup>24</sup>. This provides further evidence for singlet oxygen formation in these irradiations. Singlet oxygen can rapidly oxidize furans, sulfides and electron-rich olefins so pollutants with the required structure may be efficiently degraded by this mechanism. But, singlet oxygen also reacts with biological substrates such as histidine and  $\alpha$ -chymotrypsin<sup>24</sup>. Reactions with biota in natural waters would, therefore, compete with pollutant degradative reactions. Thus the rate of contaminant breakdown by  $^1\text{O}_2$  reactions should be greater in colored oligotrophic as compared with colored eutrophic waterbodies.

Another reactant species produced in sunlight irradiated natural waters is superoxide,  $\text{O}_2^{\cdot -}$ <sup>27</sup>. The presence of superoxide was demonstrated by irradiation of a natural water containing hydroxylamine. The hydroxylamine is converted to nitrite by reaction with superoxide and the reaction was shown to be inhibited by superoxide dismutase (SOD)<sup>27</sup>. Recently, laser flash kinetic spectroscopic measurements have shown that the likely precursor of superoxide is the hydrated electron<sup>28</sup>. This electron is produced either through direct photoionization of the humic substance or from ionization of the excited singlet state<sup>28</sup>.



The hydrated electrons quickly react with oxygen to produce superoxide.



Superoxide has been shown to be capable of dehalogenating some pesticides<sup>29</sup> and undergoes a variety of oxidation and reduction reactions with other organic and inorganic substrates<sup>30</sup>. But its major fate in natural waters is probably disproportionation to hydrogen peroxide.



Hydrogen peroxide has been shown to be produced photochemically in irradiated surface and groundwaters<sup>31,32</sup>. Hydrogen peroxide is a fairly strong oxidant. It is also easily photolized to produce the extremely strong and indiscriminant oxidant hydroxyl radical.



Hydroxyl radicals as well as alkylperoxy radicals have been shown to be present in sunlight irradiated natural waters<sup>33</sup> and have been shown to be capable of breaking down several persistent pesticides<sup>34</sup>.

Zepp *et al.*<sup>35</sup> have recently demonstrated that energy transfer reactions can occur in natural waters. The direct triplet energy transfer from humic substances to cis and trans-1,3-pentadiene resulting in subsequent isomerization of the acceptor has been observed.



Charge transfer reactions between metals, such as iron and copper, and organic ligands such as EDTA and NTA have been shown to occur at solar wavelengths<sup>36-40</sup>. Charge transfer reactions such as these may be involved in the photobleaching observed in humic waters<sup>41</sup> since environmental humics contain large quantities of complexed iron and some copper. Definitive studies should be carried out to estimate the relative importance of charge transfer compared to energy transfer reactions in natural waters.

There is some controversy whether the surface microlayer, a layer about 100 microns thick on the water surface, should be

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treated as bulk water or as a separate entity. The quantity of chemicals in the microlayer can vary dramatically over time<sup>42</sup>. The microlayer is probably important when a pollutant has been discharged to the system in a water-insoluble solvent which has a lower density than water - for example oil. Several studies have shown that photosensitized reactions do occur in oil surface films and that the reaction rates are closer to those observed in hydrocarbon solvents than to water<sup>43,44,45</sup>. Except under special conditions such as those encountered after a large chemical spill to the aquatic environment, photolysis in the microlayer probably does not represent a significant pathway for pollutant degradation.

Zepp and Cline<sup>46</sup> have presented detailed methods, using literature solar flux measurements at various latitudes, for estimating half-lives of direct photolysis for several compounds. Similar techniques are needed for computing half-lives of pollutants degraded by the indirect photolytic processes described above.

#### 1.4 Photolysis on Suspended Sediments

As mentioned earlier, contaminants adsorbed to suspended sediments may be removed from the photic zone by settling. However, in rivers and in shallow lakes where sediment resuspension is an important process, suspended sediments can influence photolysis in several ways. They can reduce photolysis rates by competitively absorbing sunlight<sup>47</sup> or by quenching excited states of absorbed chemicals which normally photolyze<sup>48</sup>. They can enhance photolysis rates by increasing the diffuseness of incoming light<sup>49</sup>. Adsorption to sediments may shift light absorption bands of chemicals into the solar spectral region where photolysis could occur<sup>50</sup>. But the major potential indirect or photocatalytic effect of suspended sediments is probably via the semiconductor-type mechanism which will be discussed in detail later. The decomposition of 1,4-dichlorobenzene in irradiated TiO<sub>2</sub> (anatase phase) slurries has been observed in the laboratory<sup>47</sup>. TiO<sub>2</sub> is found in the environment but mainly in the less photoreactive rutile phase. The decomposition of carboxylic acids has been observed in irradiated slurries of the mineral goethite (iron oxy-hydroxide)<sup>51</sup>. Although there are some instances of the formation of pure metal oxide and sulfide precipitates in natural waters, most suspended sediments in the aqueous environment are coated with an organic film. These films would strongly inhibit semiconductor-like reactions. Since the organic coatings on the particles contain humic substances, indirect photochemical generation of singlet oxygen and/or superoxide may occur with irradiation. However, because oxygen would have to be adsorbed or in close proximity to the particulates for these reactions to occur, the quantum yields would probably be much lower than for solution phase humics. Thus, the importance of indirect and photocatalyzed reactions on suspended sediments in the aqueous environment has yet to be demonstrated.

## 1.5 Photolysis in Algae

Algae may contain an important fraction of persistent organic chemicals in certain water systems. Association with algae would function to keep the contaminant in the photic zone for a longer period and this could enhance direct photolysis rates. Indirect, sensitized, photolysis of several nonionic organic chemicals has been observed by Zepp and Schlottzhauer<sup>52</sup>. For example, methyl parathion and parathion photoreacted 390 times more rapidly when sorbed to algae than in distilled water, and aniline and m-toluidine reacted over 12,000 times faster<sup>52</sup>. The most critical step in algal photolysis seems to be adsorption of the chemical by the algae<sup>53</sup>. Chemicals which had higher octanol-water partition coefficients and partitioned into the algae to a greater extent, showed the greatest reaction rate enhancement<sup>53</sup>. Some preliminary mechanistic studies by Zepp et al.<sup>53</sup> have shown that hydrogen peroxide does not appear involved in algal sensitized photoreactions.

It is of interest to note that the mode of activity of many herbicides, especially the dinitroaniline family, involves scavenging of electrons from the photosynthetic electron transfer system of the target plant. The fate of the resulting herbicide radicals has not been examined. Photochemistry in aquatic biological systems would appear to be an important area for future research.

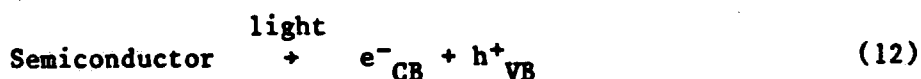
## 2 APPLICATION OF PHOTOLYSIS TO WASTEWATER TREATMENT

### 2.1 Homogeneous Photolysis

Ultraviolet light at 254 nm has excellent germicidal properties so it has been used as a point-of-use water treatment disinfectant device and as an alternative to chlorination for disinfection of treated municipal wastewater<sup>54, 55, 56</sup>. But direct photolysis of organic and inorganic wastes with ultraviolet, U.V. light is not an efficient process so it is usually used in combination with sensitizers for wastewater treatment. The combination U.V. and hydrogen peroxide has been shown to destroy organics in surface<sup>57</sup> and wastewater<sup>58</sup>. The UV/ozone combination has also been used in water and wastewater treatment<sup>59</sup>. There are two main problems with the combination treatment methods above: 1) the high cost of generating 254 nm light and 2) the high cost of continual addition of the photochemical reactants which are consumed in the reaction. These factors make these processes expensive so, except for special applications where no other methods are available, they are not likely to be widely used.

## 2.2 Heterogeneous Photocatalysis

The use of sensitizers which use sunlight and are not consumed during the treatment process should provide a more cost-effective wastewater treatment process. Some work has been done on dyes chemically bonded to porous polymer beads<sup>60,61</sup> but the most promising approach is the use of semiconductors. Photoredox processes can occur at semiconductor interfaces as a result of the absorption of "bandgap" radiation, preferably in the solar spectral region. The immediate products of this excitation are an electron in the conduction band and an electron vacancy or "hole" left in the valence band. Both these reactive species



can migrate to the solid/solution interface and lead to charge transfer across the interface and redox reactions in solution. In order for these reactions to be significant, both the charge separation and the charge transfer processes must be efficient enough to compete with electron-hole recombination.

We tested a group of seven photostable titanium-containing semiconductors to find out which had the highest photoreactivity for organic oxidation<sup>62</sup>. Methanol and isopropanol were chosen as substrates for oxidation since they react with a wide variety of oxygen containing radicals, including those expected to result from the photooxidation of water on the metal oxide surface. In order to suppress chain reactions, ferric perchlorate was included at a concentration large enough to react with all alcohol radicals formed. Alcohol concentrations were chosen from studies of iron photochemistry<sup>63,64</sup> and were large enough to scavenge all hydroxyl and hydroperoxyl radicals in solution. The presence of iron allowed the solutions to be degassed which removed the possible complication of peroxy radical formation by reaction of the alcohol radicals with dissolved oxygen. Thus the degree of alcohol oxidation can be expected to be a true measure of primary photoefficiency for each catalyst. The results of these irradiations are listed in Table III. The quantum efficiency  $\phi$ , also called the quantum yield, is defined as

$$\phi = \frac{\text{number of molecules reacting or formed per unit time}}{\text{number of quanta absorbed per unit time}} \quad (13)$$

The results clearly show anatase to be superior to all semiconductors tested by an order of magnitude, so further studies were limited to this semiconductor. Irradiation of this semiconductor with light of wavelength less than 400 nm produces the electron/hole pair.

Table III Primary Quantum Efficiencies ( $\phi$ ) for Products of the Irradiation of Semiconductor Slurries

Semiconductor	$\phi_{\text{Fe(II)}}$	$\phi_{\text{CH}_2\text{O}}$
TiO <sub>2</sub> (anatase)	.334	.076
TiO <sub>2</sub> (rutile)	.020	.005
ZnTiO <sub>3</sub>	.010	.0001
MgTiO <sub>3</sub>	.034	.0006
CaTiO <sub>3</sub>	.030	.0006
BaTiO <sub>3</sub>	.012	.0001
SrTiO <sub>3</sub>	.020	.0005

Solution composition:

[HClO<sub>4</sub>]=0.5M; [CH<sub>3</sub>OH]=0.494M; [(CH<sub>3</sub>)<sub>2</sub>CHOH]  
= 0.260M; [Fe<sup>3+</sup>] = 0.01M

As mentioned above, for the semiconductor pathway to be important, both electrons and holes must be efficiently separated and both must reach the particle surface and react. This requirement partially explains why many pure mineral substances that absorb visible light are not efficient photocatalysts. In many of these substances, visible light excites electrons from impurity levels located within the bandgap to the conduction band. The holes are not mobile and accumulate in the crystal until recombination. The rate of recombination, which depends on concentrations of both electrons and holes, becomes the predominant process. Even if both charge carriers reach the surface, recombination may still predominate if both species are not consumed in appropriate fast reactions. This kinetic requirement implies that the most effective reaction partners will be already present at the surface when the charge carriers arrive. The thermodynamic factors affecting redox efficiencies across semiconductor-solution interfaces have also been extensively studied and reviewed<sup>65</sup>. Efficient charge transfer may occur only if there is sufficient quantum mechanical overlap between the redox level in solution and the energy level of the charge carrier at the interface. Taken together, these two requirements lead to the conclusion that the most efficient processes will occur for reactions of the solvent or of adsorbed species of appropriate redox potential. Surface states may function as 'storage' traps if their redox potentials permit interfacial electron transfer.

In order for efficient photocatalysis to occur, both oxidation and reduction reactions must occur at the interface. From a practical standpoint, it is useful to consider each process separately. Consider first the conduction band electrons. They will be consumed in reactions resulting in reduction of species on the solution side of the interface. Because it occupies most of the sites at the interface, the first acceptor that must be considered is the solvent itself. The possibility of reducing water to hydrogen has stimulated a great deal of research interest because of



the potential application to convert sunlight to a useable fuel. Unfortunately, water is not that easy to reduce since there are no known naturally occurring substances that can catalyze this reaction without an externally applied potential. A more promising electron acceptor is the oxygen molecule. The generation of superoxide from the one-electron reduction of the oxygen molecule has been shown to occur in humic waters<sup>27</sup>. Superoxide is unstable in aqueous solution, undergoing rapid disproportionation to hydrogen peroxide and oxygen. Many studies of photocatalysis at semiconductor surfaces, including the photolysis of PCBs in anatase slurries, have noted that in the absence of oxygen, no reaction could be observed<sup>20</sup>. Superoxide is a good nucleophile that may become involved in reactions with organic contaminants such as the dechlorination of chlorinated aromatics. In addition to this general route of electron scavenging, if there are electron acceptors present at the surface with the right energy levels, they may also be reduced.

Reactions of valence band holes in  $\text{TiO}_2$  with the solvent water have recently been reported by Carey and Langford<sup>66</sup>. They irradiated 0.5% anatase aqueous slurries which were 0.1 M in perchloric acid, 0.01 M in ferric perchlorate, and 0.2 - 1.7 M in tertiary butanol or 2 to 7 M in methanol. Previous studies<sup>63</sup> have shown that t-butanol reacts only with hydroxyl radicals while methanol reacts with hydroxyl radicals and directly with other free radicals in the system. The primary quantum yields of iron (II) in these systems were 0.17 for t-butanol and 0.33 for methanol. These results show that about half the "holes" produce hydroxyl radicals in the solution while the other half produce weaker oxidants. Comparable scavenging studies with ethylene glycol by the same authors<sup>66</sup>, similar to those conducted by Carey et al.<sup>67</sup>, showed that equal quantities of the products acetaldehyde (the hydrogen abstraction product from hydroxyl radicals) and formaldehyde (the direct reaction product) were produced in yields  $>0.1$ . These results can be rationalized from surface studies of anatase. Two types of OH group exist on an hydroxylated anatase surface - one bound to a single titanium and the other bound to two titanium atoms. Hole migration to the singly bound hydroxyl likely provides the excited state that produces solution hydroxyl radicals. Hole formation at the doubly bound hydroxyl forms an excited state that leads to a weaker oxidizing radical in solution. The two types of hydroxyl groups are about equally abundant on the anatase surface in good agreement with the quantum yield studies.

The irradiation of o, m, and p-chlorobenzoic acids in anatase slurries produced chloride with an average quantum yield of 0.035. The yield of salicylic acid from irradiation of anatase slurries of benzoic acid was 0.017. These results indicate that dechlorination of these aromatics, probably via hydroxyl radical attack, is the preferential process. The photodechlorination of PCB's in anatase slurries has been reported<sup>20</sup>. We irradiated a saturated aqueous solution (30 ppb) of the commercial PCB mixture Aroclor 1254

containing 0.5% anatase with 350 nm light for 1 hour. The effect of the irradiated, unirradiated and distilled water control solutions on algae were measured by monitoring the optical density at 540 nm. The curves in Figure 2 show that the growth of the algae in the irradiated and distilled water control were similar, whereas, the unirradiated Arochlor solution suppressed the algal growth. Recently, Hidaka *et al.*<sup>68</sup> and Barbeni *et al.*<sup>69</sup> have demonstrated partial photodecomposition of sodium dodecylbenzene sulfonate and the total decomposition of 4-chlorophenol in anatase slurries.

These data show that heterogeneous photolysis could be used to detoxify wastewater. It is probably not necessary for the photochemical treatment to completely decompose the organics but it can be used to convert them to biodegradable compounds<sup>62</sup>. The treatment would be combined with a second stage biological reactor, such as the activated sludge process, to provide the final conversion to CO<sub>2</sub>. The most promising types of wastewater for potential heterogeneous photochemical treatment are low volume, fairly concentrated industrial wastewaters containing organics which are not biodegradable. Another potential application is the treatment of leachates from chemical dump sites. In North America there are thousands of dump sites which contain large quantities of chlorinated solvents and chlorinated aromatics such as PCB's. These dump sites are currently polluting groundwater and surface waters throughout the continent. One current method of alleviating this problem is to pump the leachate from below the dump to the surface for treatment. This contaminated water may prove amenable to combined photochemical/biological treatment.

Inorganic pollutants such as cyanide have also been shown to degrade via semiconductor photodegradation processes<sup>70</sup>. Figure 3 shows a plot of CN<sup>-</sup> concentration versus irradiation time at 350 nm for a KCN solution containing 0.5% anatase. The likely reaction mechanism for cyanide disappearance is:



Cyanide is a problem in gold mine effluents since it is used to extract the gold from the ore. The mine wastewater also contains cyanide complexes such as ferricyanide which are difficult to break down with chemical treatment. Wastewater containing these cyanide complexes can be completely nontoxic to biota when first discharged to the aquatic environment. But it can exhibit a phototoxic effect downstream when sunlight photolyzes the complexes and releases free cyanide. Fish kills have been observed several miles downstream of some gold mine discharges. The TiO<sub>2</sub> photolysis process has been shown to be capable of destroying complexed "cyanide" as well as "free" cyanide<sup>62</sup>. Some recent studies explored the economics of this process for treatment of gold mill effluents<sup>71</sup>.

In summary, the treatment of wastewater containing both organic and inorganic pollutants using heterogeneous photocatalysis would seem to have considerable potential. More studies are required to elucidate the reaction mechanisms, to design treatment units and to examine the economics of the process.

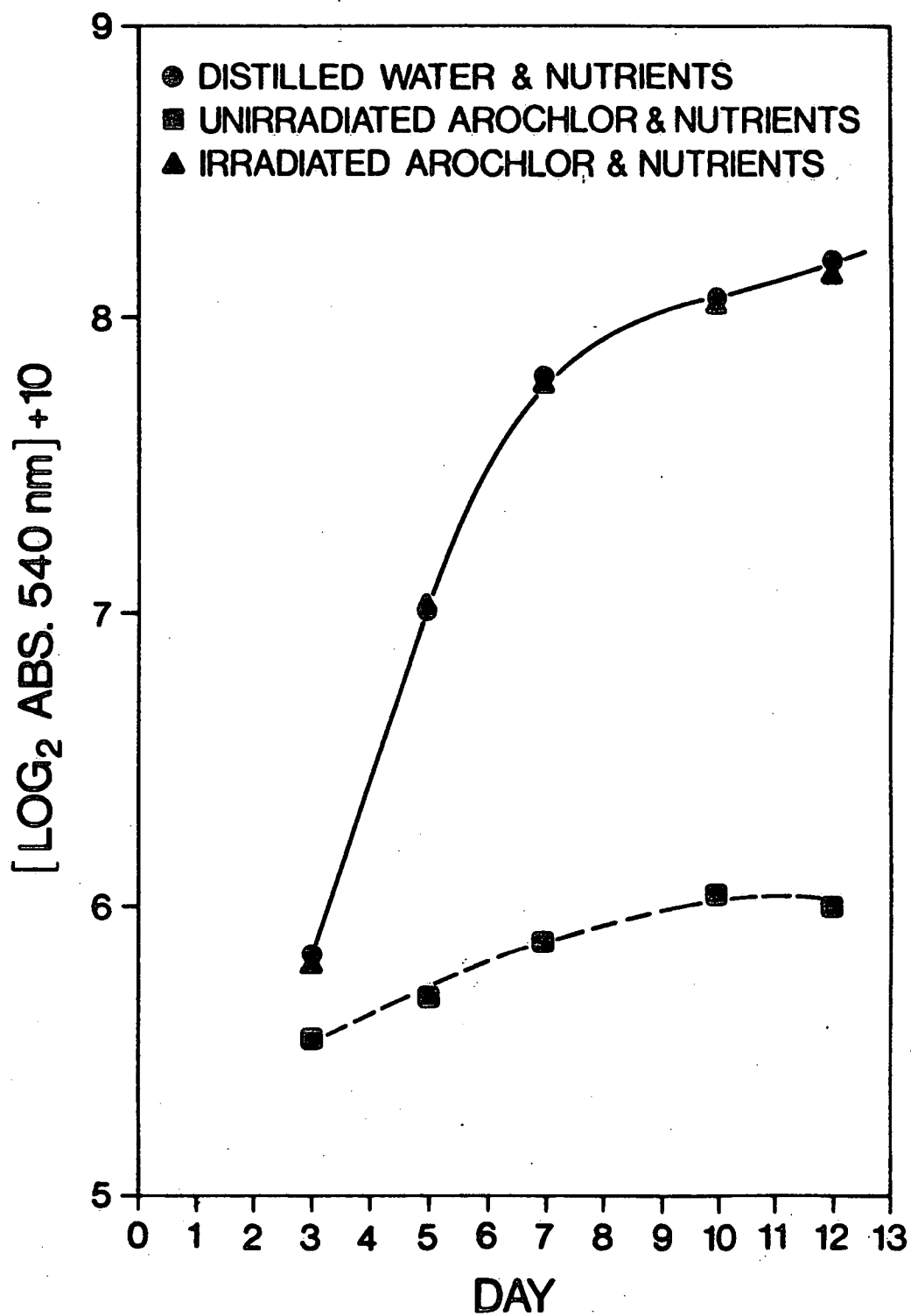


Figure 2 The effect of PCB's and PCB photoproducts on the growth of Scenedesmus quadricauda.

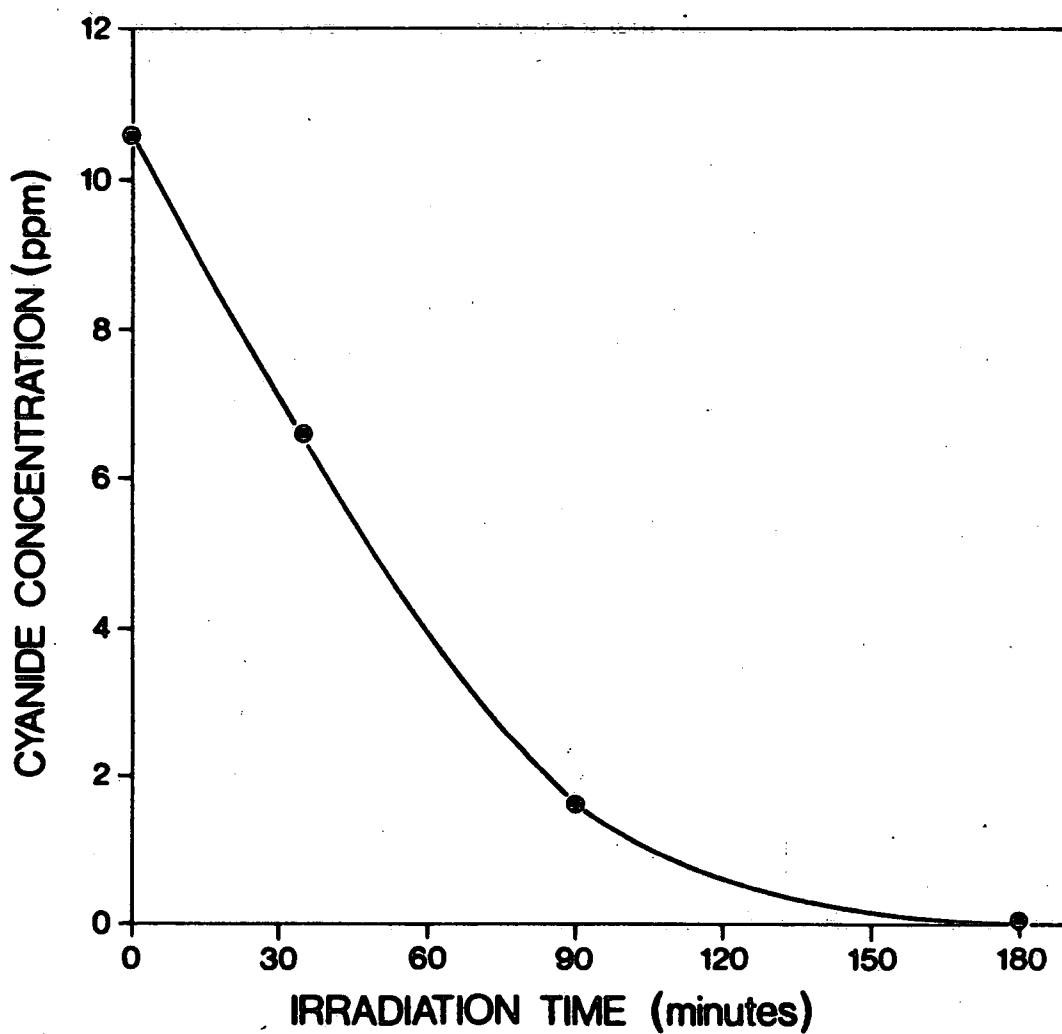


Figure 3 Irradiation of a 0.5%  $\text{TiO}_2$  slurry of a 10.6 ppm KCN, 0.01 M NaOH solution with 350 nm light.

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