Photolysis of Terbufos

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Abstract : This case study considers the rate at which exposure to sunlight can transform a pesticide known as terbufos. Transformation of a contaminant by photolysis will change its behavior in a given situation. In some cases, a product of photolysis is just as toxic or more toxic than the parent compound. In other cases, the products of photolysis are rendered nontoxic and the transformation can be considered beneficial. The experiment described in this case study produced some of the first basic kinetics data available to evaluate the importance of photolysis as a process to remove terbufos from the environment. For more detailed information about this research, see Lee, C. M.; Anderson, B.; and Elzerman, A. W. 1999. Photochemical oxidation of terbufos. Environmental Toxicology and Chemistry. 18(7):1349-1353.

Introduction

Pesticides are used on a regular basis for agricultural, commercial, and domestic protection of plants, woods, and soils, and to control the growth of certain vegetation. Even though there are many positive features associated with pesticides, some can adversely affect the environment and human health (**1**). Many pesticides move from targeted areas to nontargeted areas by volatilization, by transport to surface water and sediment or by penetration through the soil profile. Elevated levels of pesticides in water system can render the quality of water unfit for human consumption (**1**).

The primary transformation processes (e.g., hydrolysis, photolysis, oxidation, and biodegradation) are responsible for reducing persistence and/or diminishing toxicity of pesticides in the environment. For certain pesticides, some processes do not necessarily diminish toxicity but generate products of equal or greater toxicity than parent compounds. Terbufos is an example of several pesticides that undergo **oxidation-reduction reaction** which results in products (e.g./ terbufos sulfoxide and terbufops sulfone) of greater toxicity and more persistence in the environment than the parent compound (**2**).

Terbufos (S- (((1,1-dimethylethyl) thio) methyl) O, O-diethyl-phosphorodithionate) is a widely used, organophosphothionate insecticide that works against a broad range of insects and has been extensively used in the Midwestern United States to control corn rootworms, seedcorn maggots, white grubs, and other pests (**3**). Due to its widespread use, considerable research has focused on the environmental fate of terbufos. The purpose of the research described in this case study was to study the transformation processes, especially photolytic degradation reaction, of terbufos in the aquatic system.

Why is Terbufos a Problem?

Terbufos is of environmental concern because it is extremely toxic to fish and aquatic invertebrates (**4**). The acute **lethal concentration 50** **(LC_{50})** of terbufos to particular species of aquatic organisms ranges from 0.77 to 20 mg/L (**see** **Table 1**). Terbufos is also expected to be toxic to mammals and reptiles (**also see** **Table 1**) (**4**); however, it is nontoxic to bees. Toxicity of this compound in general is based on its ability to inhibit the enzyme **cholinesterase**, a chemical vital to the normal function of the nervous system of living organisms (**5**). **More details of terbufos toxicity are presented elsewhere (6, 7).**

Basic Manufacture and Formulation

Terbufos is manufactured by American Cyanamid of Princeton, NJ, and brought to the market under the trade names of AC 92100, Aragran, Contraven, Counter, and Plydox (3, 8). The most commonly available formulation is granular which consists of 15% active ingredient (terbufos) bound to an inert, clay-like matrix (3). The structures of terbufos and its metabolite products are shown in Figure 1.

Physical and Chemical Properties

Physical and chemical properties of terbufos are shown in Table 2. As can be seen, terbufos is slightly soluble in water with an aqueous solubility of 10 mg/L, and it exhibits a high level of hydrophobicity **($K_{ow} \sim 10^4$)** (8). As a result of its hydrophobicity, terbufos partitions extensively from the aqueous phase into organic fractions of environmental materials. Terbufos is strongly adsorbed by soil and sediment based on its organic carbon partition coefficient **(K_{oc})** of $10^{4.5185}$. Although terbufos has a relatively low vapor pressure (3.55×10^{-7} atm), volatilization has been shown to be a significant mechanism of loss from certain environmental surface (8).

Transport and Transformation of Terbufos

Terbufos is released to the environment through its use as an insecticide and less commonly by accidental spills. If released to soil, terbufos is expected to be only slightly mobile, and therefore very little leaching or transport in soil is expected. In soil environment, terbufos undergoes rapid biological degradation and produces the oxidative by-products (terbufos sulfoxide and sulfone) in a step-wise manner (9). Photolysis in surface waters and in soils would be expected to also produce terbufos sulfoxide and sulfone, however, little published information is available. In aqueous media, terbufos predominately undergoes chemical degradation (hydrolysis) rather than microbial degradation. Formaldehyde was reported as a major hydrolysis product (9). The combined biological and chemical degradation half-lives in various soils plus the hydrolysis half-lives in the aqueous phase are summarized in Table 3. Additionally, terbufos is expected to degrade in the ambient atmosphere quickly by reaction with photochemically produced hydroxyl radicals. Terbufos is reported to have a half-life of 0.004 day in the atmosphere (7). Bioconcentration in aquatic organisms and adsorption to sediments are expected to be other important fate processes for terbufos (11). Numerous studies have been reported on hydrolysis and biological reactions; on the other hand, photolysis reactions have been less examined. Therefore, photolysis was selected as a potentially significant transformation process that should be investigated.

Question 1: If a large quantity of terbufos was accidentally released to the soil would you expect to find high concentrations of terbufos in the ground water? Why or Why not?

Question 2: Why is it important to know the K_{oc} parameter of a potential contaminant?

Question 3: How do the products from hydrolysis, biodegradation, and photolysis differ?

Question 4: Based on Figure 1, would you expect the water solubility and K_{ow} of terbufos sulfoxide and sulfone to be greater or less than the parent compound?

Principles of Photochemistry

A simplified conceptual model of environmental photochemistry would include three components: 1) light source, 2) compound of interest, and 3) other active system components termed photosensitizers (11). Light possesses both a particle and wave characteristic. As a wave, light is a combination of oscillating electric and magnetic fields perpendicular to each other and to the direction of the propagation of the wave. The distance between two consecutive maxima is the wavelength (λ). The wavelength is inversely proportional to the frequency, ν, which is commonly expressed by the number of complete cycles passing a fixed point in 1 second (12):

$$\lambda = C/\nu \qquad 1$$

where C is the speed of light in a vacuum, 3.0×10^8 ms^{-1}. The unit of wavelength is nanometer (nm).

The particle form of light is termed a photon. The photon can be envisioned as a reactant in a chemical reaction (11). The energy (E) of each photon is related to frequency ν and the wavelength λ of the light as expressed by (12):

$$E = h\nu = hc / \lambda \qquad 2$$

where h is the Planck constant, 6.63×10^{-34} J.s.

As can be seen in equation 2, the shorter the wavelength of the light, the greater the energy it transfers to a molecule when absorbed. Note that the energy of photon is dependent on its wavelength. The wavelength of sunlight falls in the range of 280-750 nm, which is in the region of ultraviolet light, visible light, and infrared light. Ultraviolet light is high in energy content, visible light is of intermediate energy, and infrared energy is low in energy (12).

Once molecules absorb the light (usually in the ultraviolet, visible, or infrared region), they immediately undergo a change in the organization of their electrons. The electrons can move from a ground state (most stable level) to an excited state (less stable), where bond-breaking or bond-making process occurs. However, molecules do not generally remain in the excited state, and therefore do not retain the excess energy provided by the photon for very long (12). Within a tiny fraction of a second, they must either use the energy to react photochemically or return to their ground state either by emitting a photon or by converting the excess energy into heat that is quickly shared among several neighboring molecule as a result of collisions. Thus, molecules normally cannot accumulate energy from several photons until they receive sufficient energy to react (12). All the excess energy required to drive a reaction usually must come from a single photon. Therefore, for a chemical reaction to occur energy from the light source must have high enough energy to initiate the reaction. The phenomenon in which energy from the light source initiates the reaction is called a photochemical reaction (14). The photochemical reaction may take place either directly or indirectly. In direct photolysis, the organic molecule itself can absorb sufficient light energy to initiate the transformation. Indirect photolysis, on the other hand, involves light energy transfer through an intermediate, the photosensitizer (13).

Kinetic of Photochemistry

Both direct and indirect photochemistry processes can be defined as a first-order reaction with respect to the disappearance of the compound. On this basis, the overall photolysis rate for a given compounds is expressed as a summation of direct and indirect photolysis rates (14):

$$-d[C]/d_t = k_p[C] = \{k_d + k_s\} [C] \qquad 3$$

where $[C]$ is the molar concentration of compound of interest,
k_p is the overall photolysis rate constant ($time^{-1}$),
k_d is the direct photolysis rate constant($time^{-1}$), and
k_s is the indirect photolysis rate constant($time^{-1}$).

The rate of direct photolysis can further be expressed in terms of the rate of light absorption by the compound and the efficiency of the chemical transformation process (14):

$$k_d = \phi k_a \qquad 4$$

where ϕ is the efficiency of the chemical transformation (commonly called the quantum yield) (unitless), and
k_a represents the light absorption rate of the compound ($time^{-1}$).

The quantum yield (ϕ) estimates can be determined through measurements using a reference compound. The quantum yield can be calculated from the results of the experiment by:

$$\phi = (k_p/k_r) \times [(\Sigma\varepsilon_{\lambda r}L_{\lambda r})/(\Sigma\varepsilon_\lambda L_\lambda)] \times \phi_r \qquad 5$$

where k_p is the overall photolysis rate constant ($time^{-1}$),
k_r is the reference photolysis rate constant ($time^{-1}$),
ε_r is the reference molar absorption coefficient,
ε is the molar absorption coefficient,
ϕ_r is the reference quantum yield, and
L_λ is the solar irradiance applicable to shallow depths in a water body (millieinsteins/cm^2d).

The light absorption rate (k_a) is a function of both the absorbance of the compound and the intensity of the incident light. The k_a is generally defined as:

$$k_a = \Sigma\, k_{a\lambda} = 2.3\, \Sigma\, (\varepsilon_\lambda Eo_\lambda) \qquad 6$$

where Eo_λ is irradiance (photon/cm^2s),
ε_λ is scalar molar absorptivity (L/mole cm).

The rate of indirect photolysis is more complicated than that of direct photolysis, since it involves the presence of photosensitizer. However, Zepp (14) expressed the rate of indirect photolysis at low concentration of compound and near surface conditions as below:

$$k_s = 2.3\, \Sigma\, (Q_\lambda \varepsilon_\lambda Eo_\lambda)[S] \qquad 7$$

where Q_λ is the proportionality constant between photosensitizer quantum yield and compound concentration $[C]$,
$[S]$ is the photosensitizer concentration (mole/L).

The corresponding half-life, t 1/2 ($time^{-1}$) for the first-order photolysis reaction (either direct or indirect) can be presented as:

$$t_{1/2} = 0.693/k_p \qquad 8$$

Research Objective

This research measured the specific rate constant for the disappearance of terbufos in the absence and presence of sunlight, and then evaluated the significance of the photolysis rates in relation to other environmental transformation processes for terbufos.

Experimental Approach and Method

The photolysis studies of terbufos were conducted in both unbuffered and buffer deionized-distilled water (DDI) matrices at three pH values (5, 7, and 9). The buffer solutions employed in this experiment consisted of a 0.05 M potassium acid phthalate ($KHC_8H_4O_4$) and 0.023 M sodium hydroxide (NaOH) solution;- a 0.05 M potassium dihydrogen phosphate (KH_2PO_4) and 0.03 M NaOH solution;- and a 0.013 M borax ($Na_2B_4O_7$) and 0.005 M hydrochloric acid (HCL) solution for adjusting the pH to 5, 7, and 9, respectively. Sample solutions of terbufos were freshly prepared at concentration of 1.91×10^{-3} mol/L by diluting the appropriate amount of stock solution (terbufos in acetone) with DDI water or buffer solution. All sample solutions contained less than 2 % (v/v) acetone. Sample solutions were transferred into 11 x 100-mm quartz vials, and then sealed with polyethylene caps. The vials were irradiated by natural sunlight. Irradiation of samples was conducted at approximately 35^o north latitude and 83^o west longitude near Clemson, South Carolina, USA. Sample vials were locked in painted non-reflective black racks that held them at an angle of 30 degree from the horizontal oriented in a north-south manner, with the tops of each vials pointing north. Temperature and pH of the sample solutions were monitored throughout the studies. Duplicate samples were removed and extracted by a liquid-liquid extraction method. Extract samples were refrigerated for later analysis by gas chromatography.

Dark control studies were run to determine the transformation rate of aqueous terbufos in the absence of sunlight energy. Identical samples were prepared and placed in quartz vials wrapped in aluminum foil. The vials were then stored in a dark cabinet at room temperature and sampled at selected time intervals. At subsequent time intervals, duplicates of the terbufos solution were removed and extracted by a liquid-liquid extraction method. Extract samples (in hexane) were analyzed by gas chromatography (GC). The buffer solutions, quartz vials, and necessary glassware employed in this experiment were autoclaved prior to each study to minimize biodegradation. Temperature and pH were measured throughout the studies.

The absorption spectrum of terbufos was quantified by a ultraviolet-visible spectrophotometer**.** Double beam mode was used as a standard for all spectra measurement. Both a deuterium and a tungsten lamp were employed as light sources. The deuterium source provided light energy in the 200-370 nm wavelength ranges, whereas the tungsten source provided for 350-800 nm wavelength ranges. Quartz sample cells of either 1 cm or 5 cm light path length were utilized to accumulate ultraviolet (< 400 nm wavelength) light transmission. The absorbance accuracy of the instrument was verified according to the U.S. Environmental Protection Agency procedures (15 USEPA, 1985). Aqueous concentrations of terbufos were 0.24, 1.18, and 0.25 ppm in buffer solutions prepared at pH 5, 7, and 9, respectively.

Results

The disappearance rate constants calculated from the experimental data under dark and light studies are summarized in Table 4. The absorption data of terbufos at pH 5, 7, and 9 are reported in Table 5.

Question 5. Use data from Table 4 calculate the half-life of terbufos under dark and light conditions. How does the photolysis half-life compare to the half-lives for other transformation reactions such as hydrolysis and biological degradation?

Question 6. Use data from Table 5 to plot the absorption profile (molar absorptivity versus wavelength (nm) in distilled water and in solutions buffered at pH 5, 7, and 9.

Question 7. Explain how the pH affects the absorbence of terbufos.

Quiz

1. Transformation of organic contaminants will always result in less toxic products.
True or false

2. The wavelength of light is defined by
a. the distance between minima
b. the distance between maxima
c. the distance between atoms in a bond

3. The organisms most acutely affected by the toxicity of terbufos are
a. bees
b. fish
c. reptiles
d. mammals

4. The mathematical expression describing the kinetics of photolysis includes
a. indirect photolysis
b. direct photolysis
c. both
d. neither

5. Which of the following transformation processes can lead to a wide variety of products?
a. hydrolysis
b. oxidation
c. biodegradation
d. reduction

6. Terbufos is not likely to be found in groundwater because of its
a. use as a pesticide
b. molecular weight
c. hydrophobicity
d. small K_{ow}

7. Photolysis is not a significant transformation process for terbufos because it has a slow photolysis rate.
True or false.

8. Direct photolysis requires the compound to
a. interact with an intermediate
b. absorb radiation
c. react with a photosensitizer
d. react in the dark

9. Quantum yield provides information about
a. molar absorptivity
b. wavelength
c. frequency
d. efficiency

10. Which instrument is used to measure the absorption spectrum?
a. gas chromatograph
b. UV-visible spectrophotometer

c. atomic absorption spectrometer
d. mass spectrometer

Answers for Questions

Question 1 If a large quantity of terbufos was accidentally released to the soil would you expect to find high concentrations of terbufos in the ground water? Why or Why not?:
The concentration of terbufos in ground water would be expected to be low because terbufos is hydrophobic (high K_{oc}) and only slightly soluble in water. Its chemical-physical properties would indicate that it binds tightly to soil particles rather than leaching into ground water.

Question 2 Why is it important to know the K_{oc} parameter of a potential contaminant?:
The importance of the K_{oc} parameter is that

1). K_{oc} can help us to predict which phase or environmental compartment a contaminant might be found and how it might be transported through the environment. For instance, will the compound sorb by organic matter in the soil or will it easily dissolve water?
2). K_{oc} also helps us to predict the physical and chemical properties of compounds. For example, the compound that possesses high K_{oc} will be less soluble in water.
3). K_{oc} is used as an important parameter in environmental modeling. Mathematical models have been developed that use information about the chemical-physical properties of contaminants to predict their behavior under different environmental conditions.

Question 3 How do the products from hydrolysis, biodegradation, and photolysis differ?:
Hydrolysis is the reaction of compound with water. The products of hydrolysis are usually more polar than the parent compound. Hydrolysis products are usually less toxic than the parent compound. Biological degradation is the biochemical decomposition of organic molecules by microorganisms. The products from biological degradation can be very diverse depending on the biochemical pathway used by the microorganism. If the biodegradation is complete, then basic inorganic compounds such as CO_2 and H_2O are formed. These products are considered harmless. If the biodegradation is incomplete, the products may be just as toxic than the parent compound or even more toxic. On the other hand, the products of incomplete biodegradation may be nontoxic. Photolysis is the chemical reaction initiated by absorption of light. Photolysis is similar to biodegradation in that the products created can be quite diverse in their properties. Photolysis may result in products with toxicities similar to the parent compound or in products that are benign.

Question 4. Based on Figure 1, would you expect the water solubility and K_{ow} of terbufos sulfoxide and sulfone to be greater or less than the parent compound?:
According to **Figure 1**, terbufos sulfoxide and sulfone should have higher water solubility than the parent compound because the oxygen atoms attached to the S atom decrease the hydrophobicity of terbufos sulfoxide and sulfone and make the compounds more polar. We would expect the K_{ow} of these two products to be lower and their solubility in water to be higher than terbufos.

Question 5. Use data from Table 4 to calculate the half-life of terbufos under dark and light conditions. How does the photolysis half-life compare to the half-lives for other transformation reactions such as hydrolysis and biological degradation?:

See Table 6. The half-lives can be calculated by assuming the rate constants are for first-order reactions and dividing 0.693 (or ln 2) by the rate constant (see equation 8). Note that the half-lives for photolysis (light conditions) are shorter than the half-lives for hydrolysis (dark conditions). Half-lives from the literature shown in Table 3 for hydrolysis and for biological degradation are also longer. Under the right conditions, terbufos could be transformed much more rapidly by photolysis than either hydrolysis or biodegradation. The right conditions would be a bright sunny day with terbufos dissolved in the surface waters of a shallow pond or lake that does not contain any particles.

Question 6. Use data from Table 5 to plot the absorption profile (molar absorptivity versus wavelength (nm) in distilled water and in solutions buffered at pH 5, 7, and 9.
See Figure 2. An absorption profile is a graphical way to visualize data. Trends become obvious that might be overlooked when considering tabular data.

Question 7. **Explain how the pH affects the absorbence of terbufos.**
As can be seen in Figure 2, neutral (pH 7) and basic (pH 9) conditions do not appear to have significant effects on the magnitude of light absorption. At pH 5, however, the magnitude of light absorption decreases at wavelengths less than 305 nm. The decrease at the acidic pH may be due to the semipolar nature of the phosphorus-sulfur bond.

Glossary

Bioconcentration is the increase in concentration of a chemical in an organism resulting from tissue absorption levels exceeding the rates of metabolism and excretion.

Biological degradation is the biochemical transformation of organic molecules by microorganisms. Biological degradation may be complete, that is inorganic products such as CO_2 and H_2O are the final products or incomplete. Incomplete biological degradation can lead to products that are of equal or more concern than the parent compound. Generally, materials are considered biodegradable if they degrade in the particular test system after 28 days by more than 70 %.

Cholinesterase is an enzyme found at nerve terminals that inactivates **acetylcholine** by hydrolyzing it to form acetic acid and **choline.** Certain pesticides act as cholinesterase inhibitors and prevent the formation of the enzyme. Without cholinesterase, acetylcholine is not inactivated and the nerve keep firing or transmitting electrical pulses without relief.

Acetylcholine is a chemical in the body that functions as a neurotransmitter. It sends electrical impulses across junctions between nerve cells, and from motor neurons to muscle cells, causing the muscle cells to contract. As an electric impulse reaches the nerve ending, the nerve cell releases acetylcholine, which passes across the junction and bonds chemically with a receptor molecule in the membrane of the neighboring nerve cell. The bonding of acetylcholine to the receptor molecule alters the polarity and permeability of the membrane so that the nerve impulse can be transmitted. The effect of acetylcholine can be neutralized by an enzyme, such as cholinesterase, which decomposes acetylcholine through the process of hydrolysis. When acetylcholine is decomposed, the muscle relaxes.

Choline is a natural amine, often classed in the vitamin B complex and a constituent of many other biologically important molecules, such as acetylcholine and lecithin. It's a natural substance from foods, and needed by the body to make acetylcholine.

Direct photolysis is a photochemical reaction in which a molecule absorbs the light energy necessary to cause a transformation to the molecule. Compare to indirect photolysis.

An excited state is a higher energy level (unstable) where a bond-breaking or bond-making process has more probability of occurring.

Gas chromatography (GC) is a separation technique that uses gas as a mobile phase and a liquid or solid as a stationary phase coated on a column. Organic compounds are separated because of their different interactions with the stationary phase. Different devices are available for the detection of the compounds as they exit the column. **ECD** is an electron capture detector. **FID** is a flame ionization detector.

A ground state is the lowest-energy (most stable) arrangement of electrons.

Half-life is the time required for 50 percent of the compound to disappear.

Hydrolysis is a bond breaking and bond forming reaction in which a molecule R-X, where X is a leaving group, reacts with water (H_2O) or hydroxide ion (OH^-) to form a new R-O bond and cleave a R-X bond in the original molecule. The products of hydrolysis reactions are usually less of an environmental concern than the parent compounds because they are usually more polar compounds which are less hydrophobic than the original molecules and therefore their behavior in the environment is less problematic. To learn more about hydrolysis, see the case studies on endosulfan and carbaryl.

Hydrophobicity is a characteristic of an organic molecule that causes the molecule to seek surroundings that are less polar than water. Hydrophobic molecules are described as molecules with a log K_{ow} greater than 2 (log $K_{ow}>2$).

Indirect photolysis is a photochemical reaction in which an intermediate known as a photosensitizer is energized and then transfers energy to the organic contaminant. Compare to direct photolysis.

Infrared energy is electromagnetic radiation with wavelengths greater than 750 nm which is low in energy compared to ultraviolet radiation.

Irradiance is the radiant flux of all incident light on an infinitesimal element of surface containing the point of interest divided by the area of that element. The SI unit is the watt per square meter.

LC_{50} or lethal concentration is the concentration of a toxic substance in the environment [water or air] that causes the death of 50% of the exposed group of organisms within a specified period of time. The duration of the exposure time should be indicated (eg. 7-d LC_{50} = LC_{50} after an exposure time of 7 days). LC_{50} is usually reported as parts per million [ppm] - volume/volume or weight/volume or as cubic centimeters [cm^3] or milligrams [mg] per cubic meter [m^3].

Liquid- Liquid Extraction is a separation process that takes advantage of the relative solubilities of solutes in immiscible solvents. The solute dissolves more readily and becomes more concentrated in the solvent in which it has a higher solubility. A partial separation occurs when a number of solutes have different relative solubilities in the two solvents used.

Millieinstein is one millimole of photons. The einstein is the equivalent of 1 mole of photons or 6.02×10^{23} photons. The einstein is not sanctioned by the IUPAC (International Union of Pure and Applied Chemistry).

Molar absorbance coefficient is related to the absorption of electromagnetic radiation by a substance. It indicates the probability of an electronic transition in a chromophore. The molar absorbance coefficient is the absorbance divided by the absorption pathlength and the concentration. The SI units are square meters per mole ($m^2\ mol^{-1}$). Also known as the molar extinction coefficient.

Octanol/water partition coefficient (K_{ow}) is the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water at equilibrium system. Chemists use the K_{ow} of a compound as an indication of its hydrophobicity. The K_{ow} can be expressed as below:

$$K_{ow} = \frac{\text{concentration in octanol phase}}{\text{concentration in aqueous phase}} = \frac{C_o}{C_w}$$

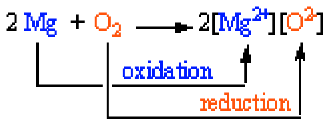
The values of K_{ow} are unitless. The concept was developed by chemists studying the partitioning of pharmaceuticals in the body. Octanol serves as a good model or surrogate for fatty tissue.

An organic carbon partition coefficient (Koc) is the ratio of a chemical's concentration in the organic carbon phase to its concentration in the aqueous phase at equilibrium. The organic carbon phase represents the natural organic matter that is found in sediments and soils. There is a positive correlation between the K_{ow} of a compound and its K_{oc}. The K_{oc} can be expressed as below:

$$K_{oc} = \frac{\text{concentration in organic carbon}}{\text{concentration in aqueous phase}} = \frac{C_{oc}\,(\text{mol/kg})}{C_w\,(\text{mol/L})}$$

An oxidation-reduction reaction is a reaction in which electrons are transferred between two reactants. Whenever a substance is oxidized, another substance must be reduced. Similarly, when a substance is reduced, another substance must be oxidized. The substance that is oxidized is called the reducing agent. The substance that is reduced is called the oxidizing agent.

An oxidation is defined as the loss of an electron or electrons and reduction is the gain of an electron or electrons. A simple scheme of an oxidation-reduction reaction is shown below.



Further information about oxidation-reduction reactions can be found at:
http://chem.boisestate.edu/~rcbanks/inorganic/oxidation-reduction/redox.htm
http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch9/redox.html
http://www.ilpi.com/msds/ref/oxidation.html

A photochemical reaction is a chemical reaction initiated by absorption of light.

Photosensitizer is a light-absorbing molecule that mediates an indirect photolysis reaction.

Ultraviolet light is electromagnetic radiation with wavelengths between 50 and 400 nm. which is high in energy content compared to infrared radiation.

An ultraviolet/visible spectrophotometer is an analytical instrument that is designed to measure the amount of light absorbed at wavelengths characteristic of ultraviolet and visible region. Further information about UV/visible spectroscopy can be found at **http://www.onu.edu/A+S/chemistry/ultra.html** and http://www.imp.mtu.edu/matchar/uv.html.

Visible light is electromagnetic with wavelengths between 400(violet light) to 750 (red light) nm which is of intermediate energy.

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Table 1: Terbufos Toxicity Data (3,6)

Test Subject	Lethal Concentration (96 hr-LC_{50}), mg/L	Type of organisms
Daphnia Magna	0.00031	Aquatic invertebrate
Gammarus psendogomnaens	0.0002	Aquatic invertebrate
Bulegill	0.0017-0.0024	Aquatic invertebrate
Rainbow trout	0.008-0.013	Aquatic invertebrate
Fathead minnow	0.390	Aquatic invertebrate
Bobwhite quail	143-157	Terrestrial
Japanese quail	194-265	Terrestrial

Table 2: Physical and Chemical Properties of Terbufos (6)

Parameters	Value
Molecular weight	288.43
Vapor pressure (mP_a, 25°C)	34.6
Solubility (mg/L)	10
K_{ow}	51400
Henry law constant, K_H ($atm\ m^3 mol^{-1}$)	2.3×10^{-5}
K_{oc}	$10^{4.5185}$

Table 3: The Half-Life of Terbufos and Its Metabolite Products

Compound	Breakdown processes			
	Water (hydrolysis)	Half-life (day)	Soil biodegradation	Half-life (day)
terbufos	**pH 5** **pH 7** **pH 9**	**4.5** **5.5** **8.5**	**silt loam (0.43-16.8%OC)** **muck (47.2 %OC)** **sandy loam (2.6%OC)**	**8 to 18** **7** **7**
terbufos sulfoxide		**32**		**116**
terbufos sulfone		**68**		**96**

Table 4: Summary of Disappearance Rate Constant of Aqueous Terbufos in Buffered and DDI Water Under Dark and Light Conditions.

pH	Average rate constant, k_p (h^{-1})	
	light study	Dark study
DDI	0.776	N/A
5	0.51	0.0206
7	0.654	0.021
9	0.679	0.0168

Table 5: Absorption Data of Terbufos in Deionized-Distilled Water (DDI) and Buffered Solution (pH 5, 7, 9)

Wavelength (nm)	Molar absorptivity (L/mol-cm)			
	DDI	pH 5	pH 7	pH 9
370	769	N/A	N/A	N/A
360	2190	N/A	N/A	N/A
350	3610	N/A	155	N/A
340	5110	288	577	404
330	6340	346	923	577
323.1	7280	613	1240	923
320	8050	2130	2130	1730
317.5	9140	3890	3350	2940
315	10800	5980	5310	4790
312.5	13600	9830	9230	8190
310	18300	15600	15600	14000
307.5	25900	24500	25700	23200
305	37200	32200	40500	36600
302.5	55300	40400	62100	5610
300	80700	43600	92100	82000
297.5	115000	54600	131000	116000
295	154000	64500	177000	157000
292.5	201000	72800	231000	204000
290	253000	63700	290000	259000
287.5	308000	47100	349000	316000
285	357000	31600	399000	370000
282.5	402000	20200	441000	423000
280	422000	16100	474000	465000

Table 6: The Calculated Half-Life of Terbufos in Buffered and DDI Water under Light and Dark Conditions

pH	Average rate constant, k_p (h^{-1})			
	light study	**half-life (h)**	Dark study	**half-life (h)**
DDI	0.776	**0.8932**	N/A	**N/A**
5	0.51	**1.3591**	0.0206	**33.6479**
7	0.654	**1.0599**	0.021	**33.0070**
9	0.679	**1.0208**	0.0168	**41.2588**

Figure 1: Chemical Structures of (a) Terbufos, (b) Terbufos Sulfoxide, and (c) Terbufos Sulfone

Figure 2: Absorption Spectra for Aqueous Terbufos in Buffered and Distilled Water Matrices