Hydrolysis of Endosulfan

Authors: Sarunya Hengpraprom and Cindy Lee, Environmental Engineering and Science, Clemson University.

Introduction

Extensive use of pesticides in the United State has raised concerns among many researchers since the behavior and some characteristic of pesticides present in the environment are responsible for ecological risks. Pesticides applied to soil may undergo microbial decomposition, photodecomposition, chemical degradation, volatilization, plant uptake, or adsorption, and may be transported in surface runoff, sediment or leached through the soil profile. The greatest potential for adverse effects of pesticides is through contamination of the hydrologic system. Water is one of the primary media by which pesticides are transported from the site of application to other compartments in the environment. Surface waters are particularly vulnerable to contamination by pesticides because most urban and agricultural areas drain pesticides into the waterways. Subsequently they can be transported downstream and widely dispersed into rivers, lakes, reservoirs, and eventually the ocean. Losses from volatilization, aerial spraying, and agricultural runoff are also considered to be important in the transport of pesticides to the aquatic environment.

Use of Pesticide

Pesticides employed in South Carolina agriculture likely present one of the greatest risks to the quality of water owing to the intense degree of farming and cultivation of crops that require large quantities of pesticides. One of the most used-pesticide in South Carolina is "endosulfan".

Endosulfan is heavily used, especially, in tomato fields in Charleston County, SC. The amounts of endosulfan applied in South Carolina accounts for 25% of the total used in the U.S. (1). More than 89% of endosulfan from all coastal agricultural areas drain into estuarine receiving water causing serious impacts to aquatic organisms (1). Examples of pesticides use in the state of South Carolina are shown in Figure 1.

Why is endosulfan a problem?

Endosulfan is of environmental concern because it is highly toxic to aquatic organisms (2). The lethal concentration 50 (LC_{50}) of endosulfan to particular specie of aquatic organisms is relatively high as compared with other pesticides such as DDT (See Figure 2). The U.S Fish and Wildlife Service (1984) (3) labeled endosulfan as supertoxic particularly to rainbow trout (0.001 mg/L LC_{50} at 96 hr). The toxicity classification is shown in Table 1. The EPA and State of Florida water quality criteria for endosulfan is 0.0085 m g/L in surface waters and 0.1 to 0.2 mg/L in agricultural products (4). To learn more about aquatic toxicity testing, click here. Concentrations of endosulfan in a tidal creek water column following agricultural runoff events were found to exceed the LC_{50} (>0.50 m g/L) for many aquatic habitats and predictably caused large fish-kills (1). The major degradation product of endosulfan, endosulfan sulfate, has been shown to be as toxic or more toxic than the parent compounds to some aquatic species (5). In addition, endosulfan is a suspected endocrine-disruptor compound (6). The effects of such compound on human and wildlife as well as ecosystems are discussed elsewhere (6).

Chemical and Physical Properties of Endosulfan

Endosulfan (1,2,3,4,7,7-hexachlorobicyclo- (2,2,1)-hepten-2-3-bisixymethylene 5, 6-sulfite) is a broad-spectrum cyclodiene insecticide that is markedly different than other cyclodienes, for example, chlordane, dieldrin, and heptachlor, in its physical, chemical, and physiological properties and behavior in organisms (9) (See Table 2). Endosulfan is an unsaturated cyclic organic sulfite (10). This insecticide was synthesized by Frensch and Goebel (11) and brought to the market under the trade name "Thiodan". This pesticide is synthesized by the action of thionylchloride on the addition product from hexachlorocyclopentadiene and cis-butene-1,4-diol (11). Technical endosulfan consists of two isomers, a - and b -endosulfan,

in the ratio of 70:30. Both of these isomers have quite different physical properties such as melting point, aqueous solubility, and vapor pressure. The structural formula of endosulfan and its metabolites are shown in Figure 3.
Question 1: Why does technical endosulfan contain both isomers? Check your answer.
Question 2: According to the Table 2, which isomer would you expect to be more mobile in the environment, why? (Hint: check vapor pressure and water solubility). Check your answer.
Question 3: Based on Figure 3, would you expect the water solubility of endosulfan diol to be greater or less than the parent compounds? Check your answer.

Transport and Partition of Endosulfan
Endosulfan is a moderately hydrophobic (log Kow ~3.98) compound. Therefore, sorption is considered to be the major route of disappearance from a water body, with volatilization, hydrolysis and biodegradation as minor routes by comparison (11). The two isomers of endosulfan express different degradation times in a soil system. The different values of half-life of each isomer under different laboratory conditions were demonstrated by many researchers. For example, Miles and Moy (13) reported the half-life under neutral pH condition (pH 7) of the a-isomer as 88 days, and as 40 days for the b -isomer. These two isomers will persist longer under more acidic conditions. Endosulfan sulfate, a metabolite of endosulfan, will also be associated with colloids or particulates, leaving very little freely dissolved in the water. Because endosulfan and its metabolite are hydrophobic, they will partition to adipose (fatty) tissues of organisms. Subsequently, endosulfan will bioaccumulate and be transported in the environment by the organism itself and through the food chain from organism to organism. The bioaccumulation of endosulfan has been observed in animals as well as humans (14).

Transformation of Endosulfan
Degradation of endosulfan can occur through both abiotic and biotic processes. The two primary reactions though which degradation occurs include oxidation by microorganisms to endosulfan sulfate, which is as toxic or more toxic than the parent compounds, and by hydrolysis (abiotic and biotic) to endosulfan diol, which is much less toxic. Hydrolysis is the dominant pathway for the degradation of endosulfan in water and is greatly dependent on the pH and temperature. Both isomers of endosulfan are susceptible to alkaline hydrolysis (15). The b-isomer hydrolyzes faster, as compared to the a-isomer. This has been attributed to less steric hindrance from the S=O bond of the b-isomer structure, leading to more susceptibility for nucleophilic (OH^-) to attack at the S atom (15). Endosulfan is reported to degrade faster in the aqueous phase than in the solid phase. Under strongly alkaline conditions the half-life of the endosulfan in the aqueous phase is approximately 1 day.
Question 4: Why do you think the endosulfan diol is less toxic? Check your answer.

Hydrolysis
Hydrolysis is a bond breaking and bond forming process in which a molecule R-X, where X is a leaving group, reacts with water (H_2O) or hydroxide ion (OH^-) forming a new R-O bond and cleaving a R-X bond in the original molecule. The products of hydrolysis reaction are usually less of an environmental concern than the parent compounds because they are usually transformed into more polar compounds which are less hydrophobic than the original molecules and therefore behave differently in the environment (16).

Hydrolysis can be usually defined by a simple pseudo-first order reaction:

$$\frac{-d[C]}{dt} = k_{obs}[C] \qquad (1)$$

where
[C] is the molar concentration of the chemical,

k_{obs} is the observed pseudo-first order rate constant for hydrolysis at a given pH.
The rate constant may contain contributions from acid-catalyzed hydrolysis, alkaline hydrolysis, and neutral hydrolysis.

Consequently, $k_{obs} = k_a[H^+] + k_b[HO^-] + k_n$ (2)

where

k_a, k_b, and k_n are the specific rate constants for acid-catalyzed, alkaline-hydrolysis, and neutral hydrolysis, respectively (17).

When a reaction follows first-order kinetics, the concentration decreases exponentially with time. According to equation 1, a plot of $\ln[C]_t$ against time will vary linearly with a slope of $-k_{obs}$. This slope and the rate are dependent on the concentration.

The hydrolysis half-life, the time required for 50% of the compound to disappear, will be determined for first-order and pseudo-first order reactions by:

$$t_{1/2} = \frac{\ln(2)}{k_{obs}} \quad (3)$$

In aquatic environments endosulfan can be expected to hydrolyze rapidly in alkaline conditions, but not in acidic conditions. In addition, each of these reaction routes is sensitive to temperature. Chemical reaction rates generally increase with increasing temperature. The temperature dependence of the rate constant is expressed by the Arrhenius equation.

Arrhenius Equation

This Arrhenius equation can be written as:

$$k = Ae^{\frac{-E_a}{RT}} \quad (4)$$

where

A is the probability that a given collision involving sufficient energy will be successful,
e is the case of the natural logarithm system,
R is the gas constant,
E_a is the activation energy, which is the energy the molecules must have in order to react,
T is the absolute temperature.

Another form of the Arrhenius equation, which is obtained by taking the logarithms of both sides of equation (4), is

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

A plot of lnk versus $\frac{1}{T}$ will provide a straight line with a slope of $\frac{-E_a}{RT}$ and an intercept of ln A. The rate (k) is typically dependent on temperature.

Question 5: Express the relationship of the kinetic rate (k) versus temperature. Is it inversely or directly proportional?

The activation energy, E_a, is generally stated in units of joules or calories per mole (SI unit). Calculating the activation energy of a reaction can be important in predicting the rate of a reaction at any temperature and in identifying individual reaction steps that control overall rates in a complex reaction process. The magnitude of the activation energy for a complex reaction involving several steps or stages is controlled by the slowest or rate-limiting step (18). Hence an experimental evaluation of E_a for a multiple process can indicate the rate-limiting step of the natural reaction by comparing E_a for the overall reaction with E_as for simple steps. In addition, the activation energy is a direct determinant of reaction rate. The larger the value of E_a, the slower the reaction will be (18).

Objective and Hypotheses

This research measured the rate of hydrolysis of both isomers of endosulfan in water at two pH values (5 and 8) and at three temperatures (25, 30, and 40°C) under both sterile and non-sterile conditions in order to test the following hypotheses:
1). Increasing temperature under sterile and non-sterile conditions increases the hydrolysis rate of endosulfan, and
2). b-endosulfan hydrolyzes faster than a-endosulfan under non-sterile condition.

Experimental Approach and Methods

The rates of hydrolysis of a-and b-endosulfan were measured in autoclaved distilled/deionized water at pH 5 and 8 and temperatures of 25, 30, and 40° C. During the experiment, 1000 mL of distilled/deionized water were placed in each of two 1500-mL beakers covered with foil and autoclaved at 121° C and 15 psi for 15 min. The beakers were allowed to cool to room temperature in a purifier clean bench hood, then were adjusted to pH 5 and 8 by addition of 0.1 M HCl and 0.1 M $Na_2HPO_4.12H_2O$. The pH-adjusted water was pipetted into each of 48 20-mL vials and the pH was again measured. The 48 vials were then divided and spiked with 10 m L of a commercial stock solution (1000 m g/mL in methanol) of either a-endosulfan (24 vials) or b-endosulfan (24 vials). The resulting concentration of each isomer in the vials was 0.5 m g/mL. The pH of the solution was measured before and after each round of sampling to ensure that the pH remained constant during the experiment. The vials were capped with Teflon-faced septum and incubated in a water bath, which was covered with a stainless steel lid to minimize exposure to light, at three temperatures (25, 30, and 40° C) for 8 days. Sampling was carried out on day 0, 1, 2, 3, 4, 5, 6, and 8. Ten mL of duplicated-aliquots were taken from each vial at time zero (approximately 1 hour after incubation) and subsequent time intervals, and extracted with 1 mL of isooctane in a 12-mL vial. The extraction was performed by shaking the vial vigorously for 2 min using a shaker table. After allowing the sample to separate at room temperature, 1 mL of isooctane layer was transferred to 1 mL autosampling vial with further addition of 1 m L (20mg/mL) of internal standard aldrin. Finally, 1 m L of sample in isooctane layer was manually injected directly on the GC-ECD.

Results

The rate constants calculated from the experimental data are summarized in Table 3
Question 6- Use data from Table 3 calculate the half-life of both isomers under a given condition. Check your answer.
Question 7 - Use data from Table 3 plot the Arrhenius curve of each isomer at pH 8 under autoclave and non-autoclaved conditions. Check your answer.
Question 8 - Calculate the activation energy (Ea) of each isomer based on the results obtained from question 4 and also report the frequency factor (ln A). Check your answer.
Question 9 – Would the hypotheses been accepted or ejected based on your results? Check your answer.
For further information, check out these links to additional resources.

Answers for the questions

Question 1: The technical endosulfan consists of two isomers (α-and β-isomer) because synthesis and purification of a single isomer is expensive and both isomers are effective for the target organisms. Other examples of pesticides containing several isomers are lindane and chlordane.
Question 2: The α -endosulfan is expected to be more volatile and less water-soluble than β -endosulfan. The higher volatilization rate of the α -isomer is due to its low water solubility and relatively high vapor pressure and Henry's Law constant. The α -endosulfan has a Henry's Law constant approximately 27 times that of β -endosulfan, which correlates well with the greater rate of disappearance. The slightly higher water solubility of β -endosulfan

as compared to that of α -endosulfan is a consequence of the difference in the polarity of compounds. The dipole moment is 1.02 and 3.18 Debye unit for α -and β -endosulfan, respectively.

Question 3 – According to Figure 3, endosulfan diol should have higher water solubility than the parent isomers because the two hydroxyl groups attached to C-H bond allow endosulfan diol to form hydrogen bonds. In addition, the molecular weight of endosulfan diol is lower than the parent compounds, leading it to have the higher water solubility. We would expect the K_{ow} of endosulfan diol to be lower as well.

Question 4: Endosulfan diol is less toxic than the parent compounds because of its higher water solubility, leading it to favor the aqueous phase rather than organic phases.

Question 5: The kinetic rate is inversely proportional to the negative value of temperature: $k \propto (-1/T)$

Question 6 –See Table 4

Question 7 – **See** Figure 4 **and** Figure 5

Question 8 – **See** Table 5

Question 9– See Hengpraprom S, Lee, CM, Coates JT, Elzerman AW. 1998. The Hydrolysis of endosulfan

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21. http://pmac.net/data.html

Glossary

Abiotic transformation is the degradation process of organic chemicals via chemical (hydrolysis) or physical (photolysis, volatilization) reactions.

Bioaccumulation of a substance is its capacity to accumulate in the tissues of organisms either through direct exposure to water, air or soil or through consumption of food. It is calculated as the ratio, in a steady-state situation, of its concentration in the organism to the concentration in the medium to which this organism is exposed (Bioaccumulation Factor, BAF). When the intake in the organism is only due to the substance dissolved in the medium, generally water, the ratio is called the Bioconcentration Factor (BCF). Generally, fish are the preferred test organisms. As the tendency of organic substances to bioconcentrate in tissue has often been related to their hydrophobicity or lipophilicity, it is suggested, when BAF or BCF values are not available, the logarithm of the substance's octanol-water partition coefficient (log K_{ow}) be used to estimate the bioconcentration potential. The use of this coefficient does not consider the metabolism and implies biological stability, i.e. the absence of metabolic pathways for biodegradation.Consequently, criteria recommended for bioaccumulation are preferably based on the BAF or BCF values. If they are not available, the log K_{ow}, used with scientific judgment, may be a useful screening criterion. To be considered as liable to bioaccumulate through the food chain a substance must be characterized by either a BAF or BCF value higher than 5000 , or in the absence of available BAF or BCF data, an octanol-water partition coefficient, log Kow, higher than 5.0. Remarks: Substances which have molecular weights higher than 600, or which are characterized by a log K_{ow} higher than 7, typically have molecular structures too large to cross biological membranes and bioaccumulate. In these cases, log K_{ow} data must be interpreted very cautiously.

Biodegradation is the complete biochemical decomposition of organic molecules by microorganisms.Biodegradability reduces a substance being emitted into the environment or a substance being retained by it. The more complete the biodegradation of a product within a given time, the less important other ecological protection aspects become. Generally, materials are considered biodegradable if they degrade in the particular test system after 28 days by more than 70%.

Biotic transformation is the degradation process of organic chemicals via metabolism of microorganisms.
Daphnia magna, Daphnia pulex, and Ceriodaphnia dubia are freshwater microcrustaceans, commonly refered to as water fleas, belonging to the class of Crustacea.The selection of Daphias for routine use in toxicity tests is appropriate for a number of reasons:

-They are broadly distributed in freshwater bodies and are present throughout a wide range of habitats.
-They are important links in many important food chains and a significant source of food for small fish.
-They have a relative short life cycle and are relatively easy to culture in the laboratory.
-They are sensitive to a broad range of aquatic contaminants and widely used as test organisms for evaluating acute and chronic toxicity of chemicals, and,
-Their small sizes require only small volumes of test and dilution water.

The reasons for selecting fathead minnow and rainbow trout for routine toxicity tests are:

-Extensive toxicological database
-Proven sensitivity to aquatic toxicants -Widespread availability.

EPA is the United State Environmental Protection Agency.
Endosulfan sulfate is an oxidation by-product of endosulfan mediated by microorganism.It seems to be the dominant product detected in the soil and/or sediment samples.
Endocrine-disruptor is a chemical that mimics or inhibits the effects of hormones. **GC-ECD** is a gas chromatograph with an electron capture detector.
Henry's Law constant - the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution.The following formula can be applied for Henry's Law 1.CaP 2.C=kP Where c is the molar concentration (mol/L) of the dissolved gas and P is the pressure (in atm) of the gas over the solution. k for a given gas is the Henry's Law constant dependent only on temperature.
Hydrophobic compound is an organic molecule that has a log K_{ow} greater than 2 (log $K_{ow}>2$).
Lethal Concentration 50 (LC_{50}) 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].
96 hr LC_{50} is the concentration at which 50 percent of the test organisms die within 96 hours of exposure
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. 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.
Organic Sulfite is an organic molecule containing a S atom with an oxidation state equal one.
Pesticide is a substance or material used to kill any undesirable or unwanted fungi, plants, insects, or any organisms.This generic term is used to describe fungicides, algicides, herbicides, insecticides, rodenticides, and other substances
pH is a measure of acid or base, as determined by negative log of the hydrogen ion concentration.

Pseudo first order is a reaction in which the concentrations of all but one of the reactants are so large that they change a little over the course of the reaction; or in other words, these concentrations are constant at a given system.
For example, the rate of cometabolic biotransformation of some halogenated organic compounds or biological transformation can be expressed as:
-dC/dt=kCX
whereC is the concentration of organic compound transformed
X is the concentration of bacteria
Minus sign (-) represents the disappearance of organic compounds
During biotransformation process, X might be so large that would not affect the reaction; subsequently, X can be considered as a constant and the rate of statement becomes:
-dC/dt=k'C
wherek' is equal to kX and the reaction in this form is typically termed a pseudo-first-order reaction with k' being the pseudo-first-order rate constant.
Toxicant is an agent that can produce an adverse effect in a biological system, seriously damaging its structure or function or producing death.

Additional Information or WWW links of Interest

Pesticides
http://entweb.clemson.edu/pesticide/index.htm
http://psei.ext.vt.edu/pesticidering/pring.shtml
http://nav.webring/yahoo.com/hub?ring=pesticide&list
http://www.atsdr.cdc.gov/99list.html
http://www.epa.gov/pesticides/
http://www.cdpr.ca.gov/
http://www.pesticideinfo.org/
http://water.wr.usgs.gov/pnsp/
http://picol.cahe.wsu.edu/
http://www.pesticide.org/default.htm
http://www.pestlaw.com/
http://www.rsc.org/is/journals/current/pest/pohome.htm
http://www.pesticidewatch.org/
http://vm.cfsan.fda.gov/~frf/pestglos.html
http://ipmwww.ncsu.edu/opmppiap/
http://www.pestfacts.org/
http://www.ianr.unl.edu/pubs/pesticides/ec2505.htm
http://www3.extension.umn.edu/projects/mpiap/napiap/nindex.htm
http://ace.orst.edu/info/extoxnet/
http://pmep.cce.cornell.edu/
http://ipmwww.ncsu.edu/ncpiap/homepage.htm
http://spo.nos.noaa.gov/projects/agchemuse/ag_chem_use.html
Aquatic toxicity
http://www.ensr.com/services/water/aquatox_assess.htm
http://www.ectesting.com/biomon.html
http://www.epa.gov/opptsfrs/home/opptsim.htm
http://www.mich.com/~glec/gl03000.htm
http://www.ecpi.org/health-and-environment/environmental-effects/aquatic.htm
http://www.science.mcmaster.ca/Biology/4S03/at2.html
http://rredc.nrel.gov/biomass/doe/rbep/hs_diesel/ten.html
http://www.cerc.cr.usgs.gov/data/acute/acute.html
Endocrine-disruptor

http://www.agius.com/hew/resource/endodis.htm
http://www.awwa.org/endocrine/
http://www.riskworld.com/NEWS/99q1/nw9aa081.htm

Figure 1: **Examples of Pesticide Use in South Carolina (21)**

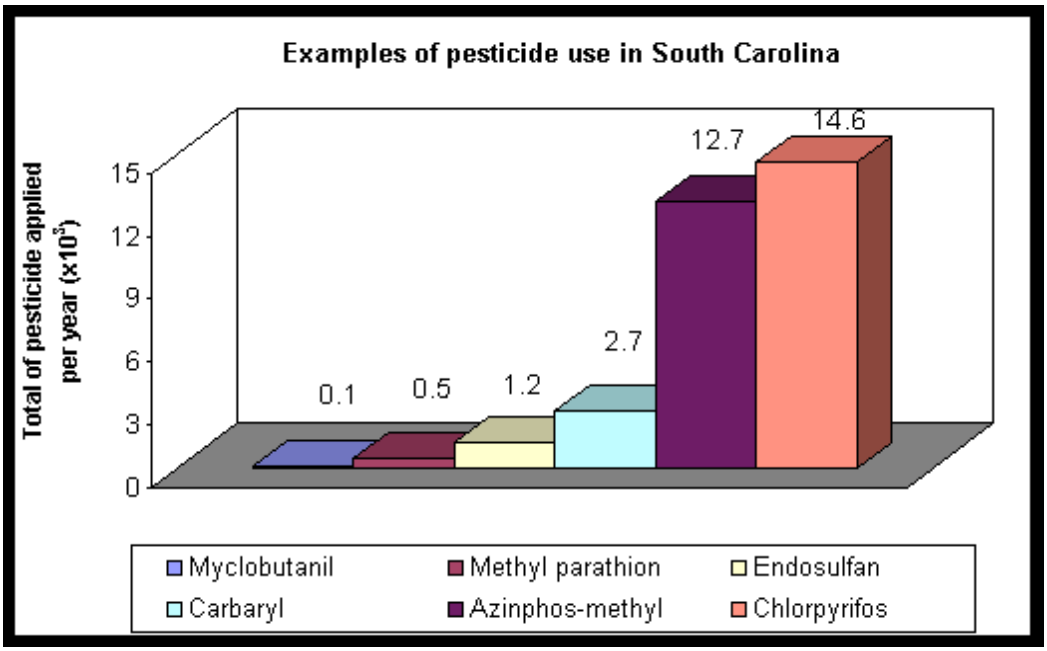


Figure 2: **The Comparison on LC_{50} of Endosulfan with Other Pesticides (21)**

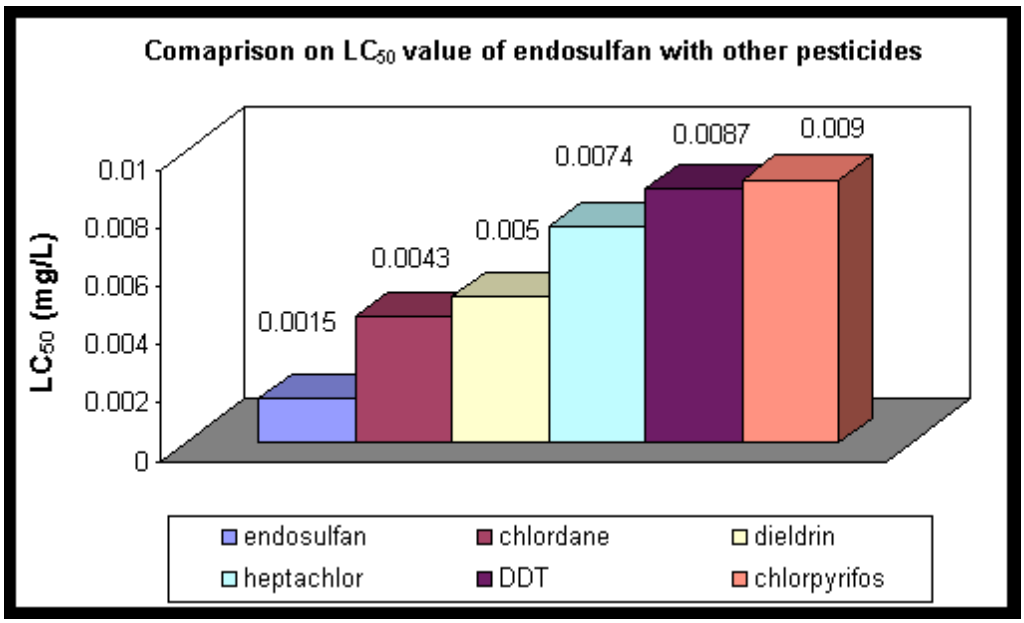
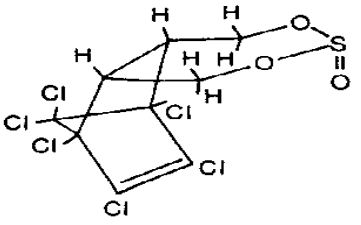
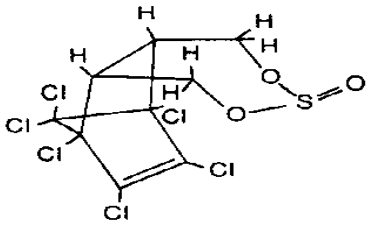


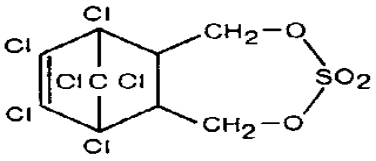
Figure 3: **The Structural Formula of Endosulfan and its metabolites**



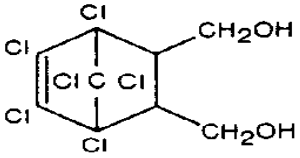
α – endosulfan



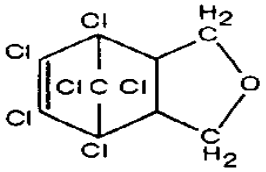
β – endosulfan



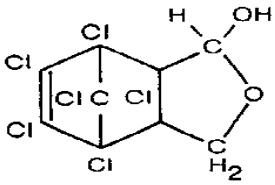
endosulfan sulfate



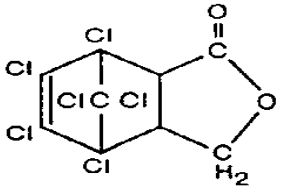
endosulfan diol



endosulfan ether



endosulfan α-hydroxy ether



endosulfan lactone

Figure 4: **The Activation Energy Curve of α-Endosulfan at pH 8 Under Autoclaved and Non-autoclaved Conditions**

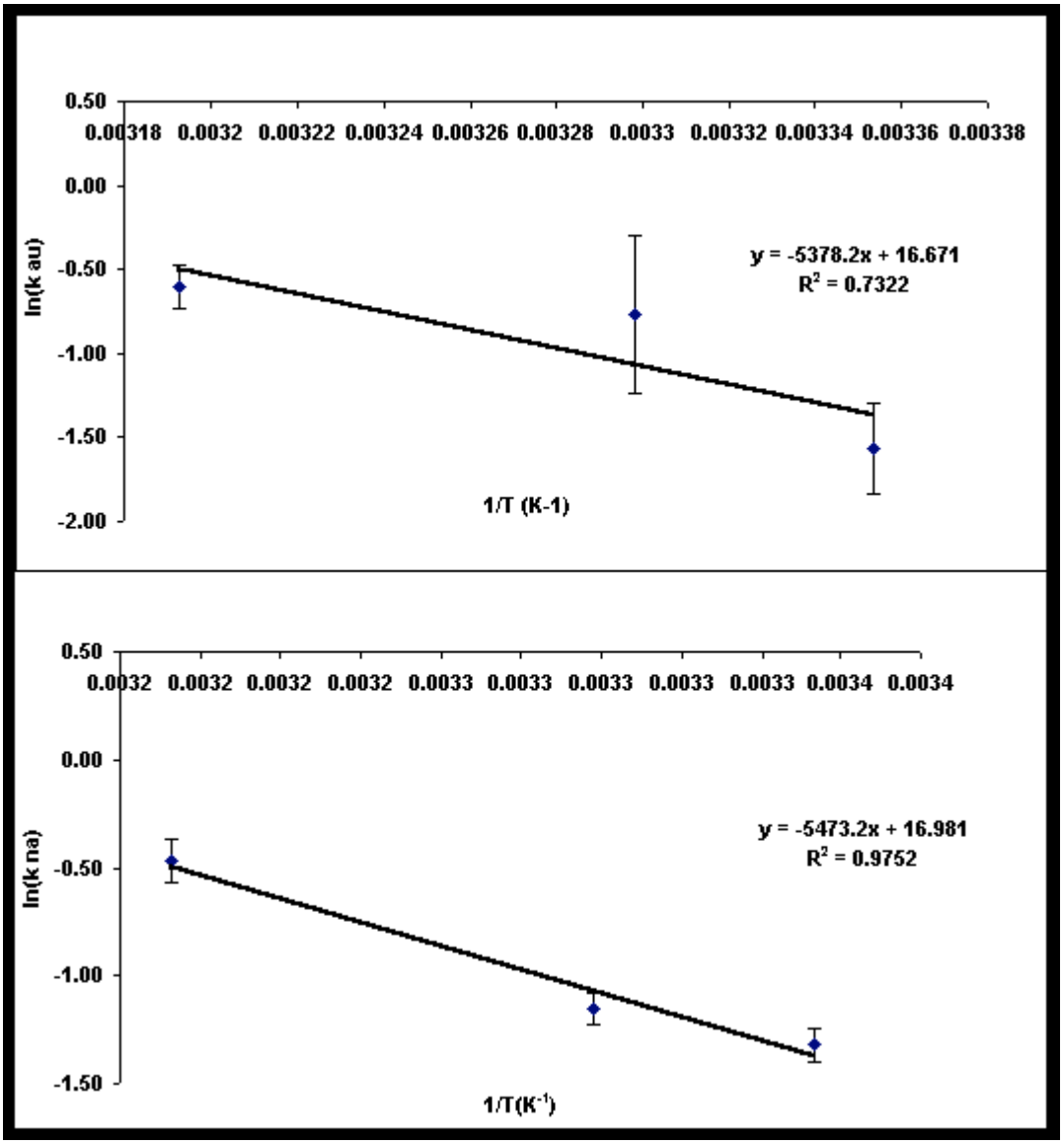


Figure 5: **The Activation Energy Curve of β-Endosulfan at pH 8 Under Autoclaved and Non-autoclaved Conditions**

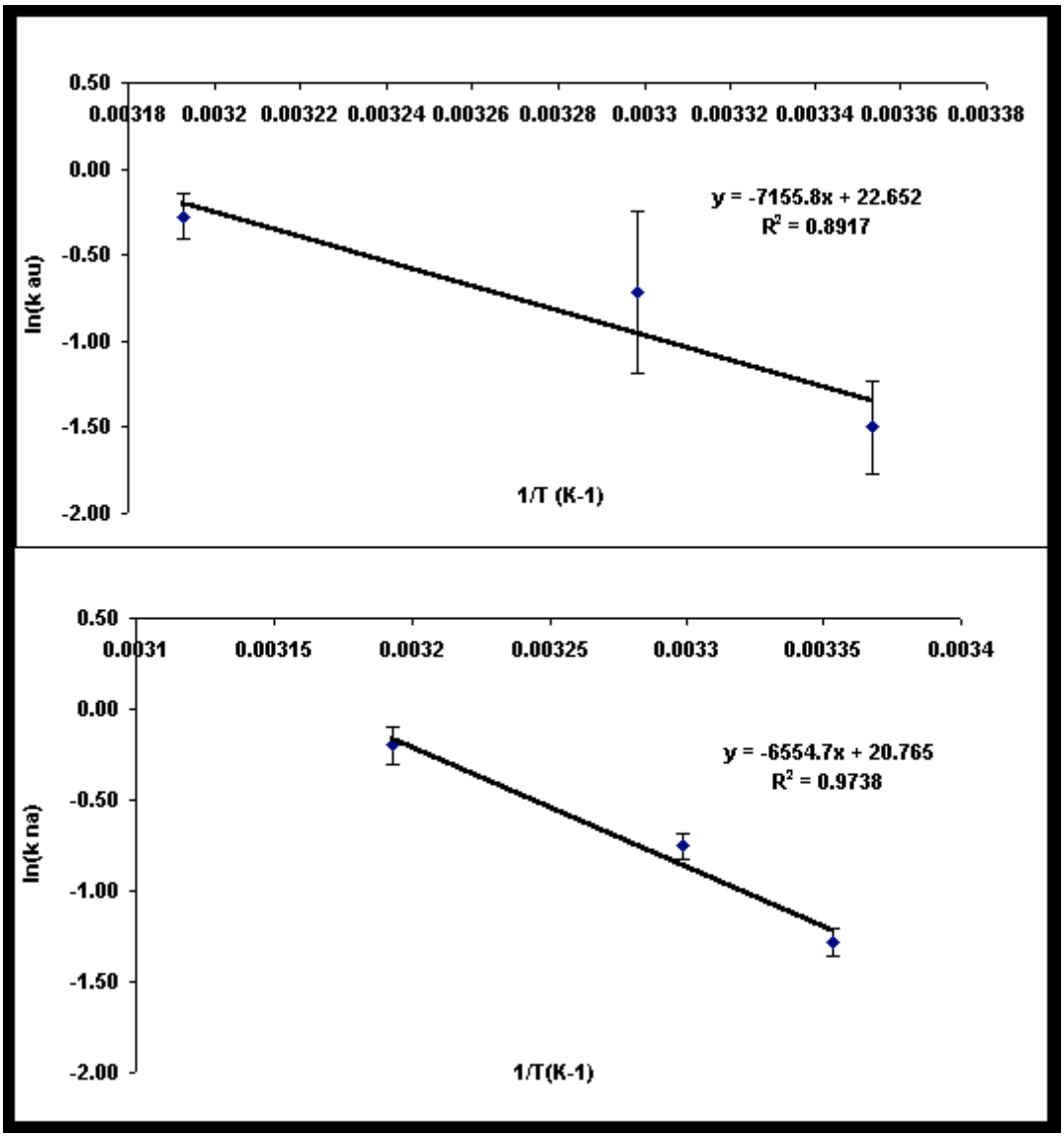
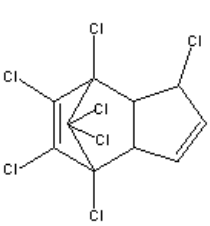
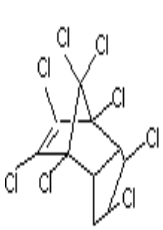
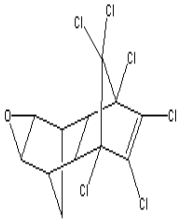
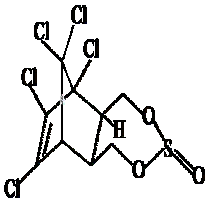
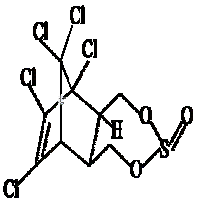


Table 1: **Toxicity Classification** (19)

Toxicity Classification	LC_{50} (mg/L)
super	< 0.01
extreme	0.01-0.10
high	0.11-1.0
moderate	1.1-10
Slight	11-100
Minimal	>100
nontoxic	-

Table 2: **Physical and Chemical Properties of Endosulfan and Related Compounds**

	Endosulfan		Dieldrin [a]	Chlordane [a]	Heptachlor [a]
	α-endosulfan [a]	β-endosulfan [a]			
Structure					
Moleculra wight (MW)	406.95	406.95	380.93	409.83	373.34
Molecular Formula	$C_9H_9Cl_6O_3S$	$C_9H_9Cl_6O_3S$	$C_{12}H_8Cl_6O$	$C_{10}H_6Cl_8$	$C_{10}H_5Cl_7$
Vapor pressure (V_p) P_a at 25°C	$6.0x10^{-3}$	$3.0x10^{-3}$	$3.6x10^{-4}$	$1.3x10^{-3}$	$5.3x10^{-2}$
Henry's Law constant (H), $P_a\ m^3mol^{-1}$	10.23	1.94	5.84	9.02	$1.12x10^{2}$
Water Solubility (S_w) mg/L at 25°C	0.32	0.33	0.19	$5.6x10^{-2}$	$5.6x10^{-2}$
Partition coefficient (log K_{ow})	3.83	3.62	3.69	3.32	5.44
Sorption coefficient (log K_{oc})	3.46	3.83	4.08	4.33	4.38
Melting point (M_p) °C	108-110	210-215	175-176	104-107	95-96 (pure)
Density (g/cm^3 at 20°C)	N/A	N/A	1.75	1.59	1.65

[a] MacKay et al. (20)

Table 3: **Summary of Rate Constants for Each pH, Temperature, and Condition Tested**

Compound	Temperature (° C)	pH	Rate Constants (Observed)	
			Autoclaved (k_a, day^{-1})	Non-autoclaved (k_{na}, day^{-1})
α -endosulfan	25	5	0.0470	0.0067
β -Endosulfan	25	5	0.0076	0.0523
α -endosulfan	30	5	0.0404	0.0680
β -Endosulfan	30	5	0.0025	0.0308
α -endosulfan	40	5	0.0070	0.0124
β -Endosulfan	40	5	0.0103	0.0290
α -endosulfan	25	8	0.2097	0.2670
β -Endosulfan	25	8	0.2240	0.2776
α -endosulfan	30	8	0.4652	0.3161
β -Endosulfan	30	8	0.4880	0.4704
α -endosulfan	40	8	0.5464	0.6271
β -Endosulfan	40	8	0.7597	0.8205

Table 4: Summary of Half-Lives for Each Temperature, pH, and Condition Tested

Compound	Temperature (° C)	pH	Half-lives (Observed)	
			Autoclaved (day)	Non-autoclaved (day)
α -endosulfan	25	5	14.7478	103.4548
β -Endosulfan	25	5	91.2036	13.2533
α -endosulfan	30	5	17.1571	18.8355
β -Endosulfan	30	5	277.2589	22.5048
α -endosulfan	40	5	99.0210	55.8990
β -Endosulfan	40	5	67.2958	23.9016
α -endosulfan	25	8	3.3054	2.5961
β -Endosulfan	25	8	3.0944	2.4969
α -endosulfan	30	8	1.4900	2.1928
β -Endosulfan	30	8	1.4204	1.4735
α -endosulfan	40	8	1.2686	1.1053
β -Endosulfan	40	8	0.9124	0.8448

Table 5: **Summary of Arrhenius Parameters**

Compound	Observed rate constant (day^{-1})			Arrhenius Parameters	
	25° C	30° C	40° C	Activation Energy, E_a (kJ/mol)	Frequency factor ln(A)
α -endosulfan	0.210 (0.267)	0.465 (0.316)	0.546 (0.627)	44.71±0.513 (45.50±0.452)	16.671 (16.981)
β -Endosulfan	0.224 (0.278)	0.488 (0.470)	0.760 (0.821)	59.49±0.618 (54.49±0.5420)	22.652 (20.765)

Note: The numbers in parentheses represent the observed data under non-autoclaved condition.

Aquatic toxicity test

The toxicity tests of endosulfan on aquatic organisms have been conducted by numerous toxicologists. The tests have been performed for acute and chronic effects. Chronic effects occur when the chemical produces deleterious effects as a consequence of repeated or long-term exposures (several weeks to year) to low levels of persistent compounds, alone, or combination with other toxicants. Chronic toxicity test is a use of full life cycle tests (i.e., embryos, larvae, early juveniles, and adults). The duration time of chronic test is several days to months. For instance, the duration time for full life cycle tests on algae is 72 to 96 h (7), 7 d to 21 d on Daphia (8), and 30 d to 110 d for fish (7). Acute effects are those that occur rapidly as a consequence of short-term exposure (usually 2 to 4 days) to chemicals. Acute toxicity test is usually defined by their short duration and simple experimental designs. The end points used most commonly in acute and chronic tests are lethality or mortality of tested-organisms (7). Sub-lethal effects are becoming more important as researchers consider the effects of endocrine disruptors.

The selection of the organism employed in toxicity tests is of particular concern since the most ecologically appropriate organism differs from ecosystem to ecosystem and under various site-specific conditions. Under certain conditions, approval can be obtained to use indigenous organisms in toxicity tests to better model the instream effects on local biota. Only a few species that represent the various trophic levels (e.g., producer, primary

consumer, and secondary consumer) are recommended for use in toxicity testing. Three invertebrate species (Daphnia magna, Daphnia pulex, and Ceriodaphnia dubia) and two vertebrate species (fathead minnow and rainbow trout) are the most common organisms used in acute toxicity tests. For chronic toxicity tests, *Ceriodaphnia dubia* and fathead minnow are the recommended species (7).
