ABIOTIC REACTIONS OF ACETANILIDE
HERBICIDES WITH
BISULFIDE

By

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ABIOTIC REACTIONS OF ACETANILIDE HERBICIDES WITH BISULFIDE

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CHAPTER I

INTRODUCTION

In recent years, the contamination of groundwater due to excessive on-farm use of pesticides has become a growing concern to the public and to government agencies. Pesticide ingestion is a potential threat to human health (Bouwer, 1989). Once contaminated by pesticides, which may persist for years, groundwater is thus unsuitable for human and animal consumption. Treating drinking water to remove pesticides or restore groundwater quality can be difficult and expensive. Since 90% of rural households and three-quarters of U. S. cities use groundwater as their major drinking water source, these concerns have inspired extensive investigations to determine the fate and transformations of pesticides in groundwater (Williams et al., 1988; Ventullo and Larson, 1985; McAllister and Chiang, 1994). It is hoped that this information can be used to avoid further damage and provide the data needed for remediation.

When the pesticides are applied to soil, they may eventually leach to groundwater. Their behavior in such an environment is decided by the site's hydrogeology, sorption to subsurface materials, and by biological and nonbiological transformations (Wilson et al., 1985). Mechanisms governing the degradation of pesticides at or near the soil surface have been extensively studied (Beestman and Deming, 1974; Zimdahl and Clark, 1982). Progress has also been made in studies of biotransformation in the subsurface systems

(Cavalier et al., 1991). However, only recently have abiotic reactions received much attention. Research has shown that abiotic transformations, either reductive reactions or nucleophilic substitutions, of halogenated compounds may result in dehalogenation, which frequently results in products less toxic, less likely to bioaccumulate, and more susceptible to further degradation.

To date, little research has been conducted to characterize the rate and pathways of the abiotic reactions of pesticides, particularly under anoxic or hypoxic conditions. Hypoxic conditions, with oxygen levels between aerobic and anaerobic condition that commonly occurr in groundwater, create a suitable reductive reaction environment. Furthermore, bisulfide, a chemical which has been found in wells and groundwater under anoxic conditions, plays a significant role because it can act as either a nucleophile or electron donor in the course of transformations of halogenated compounds in the subsurface system. When pesticides are exposed to groundwater with a high concentration of sulfides, the reaction between them (for instance, either reductive or nucleophilic substitution reaction) may be significant. It may reduce contamination levels of pesticides in the groundwater or it may pose a greater threat to groundwater quality due to harmful products formed (Schwarzenbach et al., 1985).

Four commonly used herbicides investigated in this study are the acetanilide herbicides (including alachlor, butachlor, metolachlor, and propachlor). These herbicides exhibit excellent pre- and post- emergence selectivity for grassy weeds control in corn and other crops (WSSA, 1989). About 37 million Kg of alachlor and 22 million Kg of metolachlor are used annually in the United States (Chesters et al., 1989). Alachlor and metolachlor have also frequently been detected in groundwater by nation-wide monitoring programs (Pontius, 1992). All four of these herbicides are listed as contaminants to be monitored under the Safe Drinking Water Act (Pontius, 1992).

In light of the information known, a research project was initiated to investigate the fates of alachlor, propachlor, butachlor, and metolachlor under conditions similar to those in groundwaters with low oxygen levels and sulfide concentrations within the range of $7 \times 10^{-5} - 2 \times 10^{-3}$ M.

It was further intended that the results of this study, in combination with similar studies, would be useful to elucidate mechanisms and pathways of pesticide degradation in similar groundwaters. The specific primary objectives of this research include :

1) To investigate the kinetics of abiotic reaction between acetanilide herbicides (including alachlor, butachlor, metolachlor, and propachlor) and bisulfide present at different concentrations and characterize their relative persistence in groundwater.
2) To examine the impact of temperature on the rates of abiotic reaction between pesticides and bisulfide.
3) To determine the effect of pH on kinetics of the abiotic reaction.

Following this introduction, Chapter II includes a review of published literature related to this research. The methodology and materials used in this research are detailed in Chapter III. The results of the experiments and a discussion of their significance are found in Chapter IV. Chapter V concludes the research with a summary, conclusions and recommendations for further study.

CHAPTER II

LITERATURE REVIEW

Pesticides in Ground Water

As mentioned, the growing evidence of groundwater contamination by agriculturally applied pesticides can be found in many reports and nation wide surveys. Each year over 382 million kilograms of pesticide active ingredient are directly applied on farms (Varshney et al., 1993). Nearly 60% of private rural drinking water and 30% of community wells have been found to contain measurable levels of pesticides (Hallberg, 1989). According to an EPA survey, 101 pesticides and 25 pesticide metabolites were detected in samples from nation-wide community water supply wells and rural domestic wells (EPA, 1990). A number of other surveys report similar findings (Cohen et al., 1984; Williams et al., 1988).

As the members of the chloroacetanilide herbicide family, alachlor, metolachlor, propachlor, and butachlor represent four of the most widely used herbicides in the United States, as well as southeast Asia and South America. An 1987 Iowa state-wide rural well water survey ranked atrazine, metolachlor, alachlor, and propachlor as the most commonly detected pesticides (Hallberg, 1989). The shallow groundwater in the Del-Marva Peninsula has been regularly identified as containing alachlor and metolachlor

(Koterba et al., 1993). A study by Pereia and Hostettler (1993) indicated that there were 56 tons metolachlor and 18 tons alachlor being transported into the Gulf of Mexico through surface waters in 1991, contaminating the entire navigable reach of the Mississippi river. In Wisconsin, alachlor was found in 47 of 377 groundwater samples with 21 samples exceeding the health advisory limit of 2 ppb (Holden, 1986). The concentration of alachlor measured up to 16 ppb in groundwater in northeastern Iowa (Hallberg, 1985).

Studies have shown that pesticide ingestion may cause health problems including cancer, nervous system disorders, birth defects and male sterility (Bouwer, 1989). A study issued by EPA (1985) indicated that at least one chemical in the acetanilide herbicide family is oncogenic in laboratory animals. Alachlor and metolachlor are found to cause tumors at a number of sites in rats. Other family members of this class await further investigations. Since contaminated sites occur across the country, and due to their potentially insidious effects on the human health, the EPA has taken actions to regulate these pesticides. The drinking water MCL for alachlor is 2 μg/L (ppb) (Holden and Graham, 1992). The other acetanilide family members like propachlor, butachlor and metolachlor are listed as contaminants to be monitored (Pontius, 1992).

Sources of Ground Water Contamination

Groundwater contamination may originate from both non-point and point sources. The primary non-point source is the result of the prolonged and massive use of pesticides on farmland, especially throughout 1960s and 1970s, when pesticide usage increased greatly. The improvement of pesticides at that time (making them generally more soluble, and less persistent) caused a larger potential threat to groundwater contamination (Goodrich et al., 1991). Point sources of groundwater contamination at high levels may be the result of improper handling, spills and leaks (Huang and Frink, 1989). A report issued by EPA indicated that 32 pesticide detections in 12 states were suspected to be point sources and 46 pesticides detected in 26 states were suspected to be non-point sources of agricultural contamination (Williams et al., 1988).

Ground Water Contaminant Transformations

When halogenated compounds, including pesticides, enter the environment, either from non-point or point sources, they transport gradually into underlying groundwater by percolation through the topsoil and the unsaturated zone or by infiltration from contaminated surface waters. The routes of these and other halogenated compounds transferring to groundwater have been widely investigated. According to Mackay (1985), Wilson (1985) and coworkers, the potential of groundwater contamination by compounds applied to soil is a function of the following factors: 1.) the pesticides' hydrophobicity, 2.) the physicochemical properties of the soil, and 3.) degradation due to biotic or abiotic processes. In general, low organic carbon or clay content of soil results in low pesticide detention (Pionke and Glotfelty, 1989). A pesticide with solubility greater than 30 mg/L is considered to pose a risk to groundwater (Creeger, 1986). Most pesticides, including the acetanilide herbicides, have solubility over 30 mg/L. Lamoreaux (1994) and Pionke and Glotfelty (1989) related pesticides' application rates, soil half-lives, and climates with leachbility of pesticides to groundwater contamination. If the mobility of a pesticide is faster than its rates of transformation, the pesticide will likely leach into groundwater. Because of the complexity of the transport of groundwater contaminants, uncertainties remain about how to quantify the combined effects of the above processes on the fate of the contaminants. These complexities will be summarized briefly below.

Dynamic processes such as advection and hydrodynamic dispersion can dilute contaminant concentrations by increasing the flow of groundwater. Adsorption is also an important process to remove contaminants by bonding chemicals to sites on soil mineral or organic matter. Many studies have shown that the hydrophobicity of contaminants and the higher organic content of aquifer matter result in the retardation of the movement of contaminants (Mackay et al., 1985). Meanwhile, in many instances, biotic processes are believed to play a predominant role, resulting in the metabolism or mineralization of these organic compounds by microbial mediation. The success or failure of biotransformation largely depends on environmental conditions including electron acceptor conditions, nutrients, pH, temperature, inherent reactivity of chemicals, and the microbial population itself (Agertved et al., 1992). Many studies have shown that subsurface biotransformation of halogenated compounds is due to reductive dehalogenation reactions which usually result in lower toxicity, less bioaccumulation, and more easily degraded metabolites (Peijnenburg et al., 1992). The reductive dehalogenation of many different halogenated compounds, including chloroacetanilide herbicides, has been found in many field and laboratory studies. However, biotic processes which can completely degrade these chemicals are still largely unidentified.

Residues of these compounds and their unidentified metabolites are also environmental concerns. Several factors may contribute to the failure of biotic processes, including a low proportion of active cells in the subsurface environment, low nutrient or low temperatures, which may prevail in the subsurface system, inhibiting the activities of microbial populations (Bouwer and McCarty, 1984; Ventullo and Larson, 1985), and the structure of these organic compounds attached to halides and alkyl functional groups intrinsically resisting microbial attack (Alexander, 1973).

Since biotransformation and other aforementioned processes are not enough to account for the fate of halogenated compound, it is reasonable to turn attention to abiotic reactions which may be significant in the subsurface system. As stated by Vogel and coworkers (1987): "Most abiotic transformations are slow, but they can still be significant within the time scales commonly associated with groundwater."

Abiotic Reaction of Halogenated Compounds in Ground Water

In reviewing abiotic reductions of anthropogenic organic chemicals in anaerobic systems, Macalady and coworkers (1986) defined abiotic reactions as "all processes not directly involving the participation of metabolically active microorganisms". Bouwer and McCarty (1984) further stated that abiotic processes in the subsurface environment generally originate with the transformations of biotic processes which "with existence of reductants, oxidants, acids and bases around their living environments, microorganisms can obtain energy for cell growth and maintenance through a series of oxidation-reductive reactions, by utilizing or producing these reactants, which may result in environmental changes of the system, for instance, changes of pH and electrochemical potential. Such environmental changes can finally result in abiotic degradation reactions such as hydrolysis and/ or chemical oxidation or reduction of compounds".

The abiotic reactions of organic compounds and sulfide species are among the abiotic processes considered environmentally relevant, and studies of haloaliphatics compounds have proven the importance of abiotic transformations by bisulfide (Schwarzenbach et al., 1985; Barbash and Reinhard, 1989). For example, laboratory studies have showed that the abiotic debromination of halogenated aliphatic compounds exists in sterile controls (Barbash and Reinhard, 1989). To date, no field or laboratory studies have been conducted to investigate the acetanilide herbicides. Furthermore, organic aliphatic sulfur compounds like ethanethiol, thioether or cyclic sulfides, disulfides have been detected in groundwater samples by several field investigations (Schwarzenbach et al., 1985; Weintraub, 1989). These compounds were found to be the reaction products of aliphatic compounds and bisulfide (Barbash and Reinhard, 1989; Weintraub, 1989). Aromatic herbicides may encounter similar abiotic transformations in groundwater (Wilber and Garrett, 1994).

The following section will briefly review the roles of sulfide, abiotic reductions and nucleophilic substitution in groundwater.

• The Role of Bisulfide

Hydrogen sulfide is recognized as a significant environment pollutant itself. It is obnoxious due to its "rotten egg" odor, toxicity at higher concentrations, and low odor threshold concentrations. Concentrations as low as 0.0001 mg/L (2.9×10^{-6} M) in drinking water can produce significantly disagreeable odors and tastes (Pomeroy and Cruse, 1969). Total reduced sulfur concentrations as high as 10^{-4} M can commonly originate from the bottom sediments of lakes, wells, and groundwater or from industrial wastes (Dohnalek and Fizpatrick, 1983; Chen and Morris, 1972; O'Brien and Birkner, 1977). The formation of hydrogen sulfide results from the reduction of sulfate by the microbial action of the two genera, *Desulfovibrio* and *Desulfotomaculcum*, in anaerobic conditions (Dohnalek and Fizpatrick, 1983). In natural waters (pH 6-9), bisulfide is the primary species of interest since the first acidity constant (pK_a) of hydrogen sulfide is about 7 at temperature 25 ^{o}C (Barbash and Reinhard, 1989). Bisulfide plays a special role here because it can act as a reductant as well as a nucleophile during abiotic transformation processes (for instance, reductive reaction and nucleophilic substitution reaction) of halogenated compounds in groundwater (Barbash and Reinhard, 1989; Schwarzenbach et al., 1990).

- Reductive Reaction of Halogenated Compounds

Reductive processes in subsurface systems include dehalogenation of halogenated compounds, reduction of nitroaromatic compounds, and reduction of aromatic azo compounds (Schwarzenbach et al., 1990). The reduction of organic contaminants involves electron transfer between an electron acceptor and an electron donor. Halogenated compounds in a subsurface system can act as electron acceptors because they contain highly electronegative substituents like chlorine (Vogel et al., 1987; Sims et al., 1991). The main abiotic bulk electron donors in anaerobic environments are reduced Fe(II) and sulfides species. Studies conducted on the reduction of nitroaromatic compounds in anaerobic soils, aquifers, and sediments by either reductant suggested that such reactions are surface-mediated processes or catalyzed by organic electron mediators (Heijman et al., 1993; Schwarzenbach et al., 1990; Yu and Bailey, 1992). Schwarzenbach and coworkers (1990) conducted experiments on reductive reactions of nitrobenzene in homogeneous sulfide solution containing quinone and iron porphrin. It was found that quinone and iron porphyrin mediated the reduction of nitrocompounds by transferring electrons from sulfide to pollutants which were reduced rapidly. Yu and Bailey (1992) reported that aniline was a reductive reaction product from a nitrobenzene solution containing sodium sulfide, which appeared to take a "bridging role" to carry or transfer electrons during the reduction of nitrobenzene. In an investigation of the reduction of halogenated compounds, Kriegman-King and Reinhard (1994) suggested that the abiotic dehalogenation of CCl_4 occurs via radical substitution. CCl_4 undergoes reduction to form a trichloromethyl radical which then reacts with HS^- to form CS_2, which is then hydrolyzed to CO_2. The presence of mineral material further catalyzed this reaction (Kriegman-King and Reinhard, 1994).

• Nucleophilic Substitution Reaction of Halogenated Compounds

In an investigation of the abiotic dehalogenation of 1,2-DCA (1,2-dichloroethane) and 1,2-DBE (1,2-dibromoethane) in 0.67 mM homogenous sulfide solution (with 50 mM phosphate buffer at pH 7), Barbash and Reinhard (1989) concluded that nucleophilic substitution predominated the overall reaction under hypoxic conditions. For 1,2-DCA, its reaction rates with HS^- were substantially higher than those with H_2O and HPO_4^{2-}, by factors of 17000, and 7200, respectively. 1,2-DBE encountered abiotic dehalogenation similar to 1,2-DCA. Bisulfide was proven a rather "soft" nucleophile because it contained a more loosely held and more polarizable electron cloud which was more available for attacking a positive center. This would be expected to react more rapidly with a soft electrophile, such as halogenated compounds, than with the "harder" nucleophiles such as H_2O or HPO_4^{2-}. The product of the reaction with either 1,2-DCA or 1,2-DBE was 1,2-dithioethane. Studies regarding the nucleophilic substitution reactions of haloaliphatic compounds have been widely conducted and documented (Schwarzenbach et al., 1985; Hagg and Mill, 1988; Weintraub, 1989).

Most of these studies, whether under laboratory or field conditions, were undertaken to investigate the fate of a class of halogenated compounds, i.e. halogen elements in alkyl groups of aliphatic compounds or linked with the benzene ring of aromatic compounds. The transformation processes of these compounds vary greatly as a function of the reaction conditions. These transformations are further complicated by the varying role of sulfide. Quantitative descriptions of the environmental fate of acetanilide herbicides (i.e. in which the halogen element is on a side chain of the benzene ring) are rarely found. An approach to better understanding such reductive processes has been proposed by Wolfe and Macalady (1992), who state that, at first, it is essential to determine functional groups which have the potential to be transformed in anaerobic aquatic systems. Secondarily, it is necessary to determine factors which can affect the rates of reductive transformation of these functional groups. Finally, structural characteristics of chemicals should be selected to investigate reactivity of related compounds. These rules might be also useful to better understanding nucleophilic substitution in the environment.

Transformations of Pesticides

Alachlor, metolachlor, propachlor, and butachlor are structurally-related chlorinated acetanilides. These compounds contain aniline linked to a carbonyl group via an amide bond and are in the category of halogenated compounds because one hydrogen in the carbonyl group is replaced by a chlorine. Their main differences exist in the kinds and number of alkyl groups on both the benzene ring and the side chain substitution. These structurally-related chemicals are therefore expected to have similar modes of action, basis of selectivity, physical properties and transformation processes. The proposed mode of action of these herbicides is the inhibition of protein synthesis in the target plants (Sharp, 1988). These are selective, pre-emergence and early post-emergence herbicides used to control crops or non-crop plants. These pesticides exhibit low volatility, resistance to photodecomposition and are degraded primarily by biotransformations in the environment. The variances in their structures and physico-chemical properties determine their dissipation rate, which, in general, follows this order: propachlor > alachlor >butachlor ≅ metolachlor (Beestman and Deming, 1974; Zimdahl and Clark, 1982). The structure and physico-chemical properties of alachlor, butachlor, metolachlor and propachlor are shown in Figures 1, 2, 3, and 4, respectively.

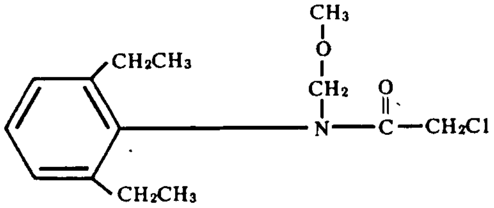
Previous studies have shown these herbicides to be capable of leaching to groundwater. Cohen et al. (1984) and Lamoreaux (1994) suggest that pesticides are most likely to leach when their soil half-lives are greater than 2-3 weeks, solubilities are greater than 30 ppm, and high application rates are greater than >1 Kg/ha. The parameters of alachlor and metolachlor, seen in Figures 1 and 3, are close to the values suggested. The primary structural difference of the methoxyalkyl side chain attached to the nitrogen atom gives metolachlor a higher solubility and K_{ow} (octanol/water partition coefficient) values, which means that metolachlor is slightly more mobile than alachlor in the environment. According to parameters in Figure 4 and the above criteria, propachlor is less likely to leach to groundwater. There is some discrepancy in the parameters of butachlor, making it more difficult to evaluate. However, both of them have been detected in various groundwater samples.

The following literature review focuses on the individual properties and transformations of alachlor, propachlor, metolachlor and butachlor in nature.

Alachlor

Alachlor (2-chlor-2',6'-diethyl-N-(methoxymethyl) acetanilide) was registered with the USEPA for use in 1969. It is mainly used on corn, soybeans, peanuts and the row crops. As specified previously, alachlor has been frequently detected in a number of

Alachlor

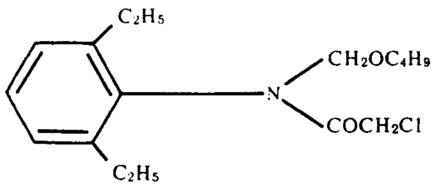


Properties

CAS Number	15972-6080
Chemical Formula	$C_{14}H_{20}NO_2Cl$
Molecular Weight	269.77
Physical State	White, odorless, crystalline solid
Density (20 °C)	1.113
Boiling Point (°C)	100 (at 0.003 mmHg)
Vapor Pressure (25 °C)	1.65×10^{-5} (mmHg)
Water Solubility (22 °C)	240 (mg/L)
Log Octanol/water Partition Coeff.	2.3
Half-life in Soil	14 (days)
Application Rate	1.68-8.96 (Kg/ha)
Leaching Potential	Medium

Figure.1 Alachlor (WSSA, 1989; Spalding et al., 1989).

Butachlor

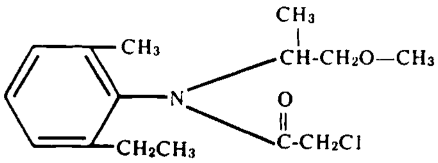


Properties

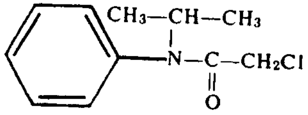
CAS Number	
Chemical Formula	$C_{17}H_{26}ClNO_2$
Molecular Weight	311.9 (g/mol)
Physical State	Slightly sweet aromatic amber liquid
Density (25 °C)	1.07 (g/mL)
Boiling Point (°C)	156 (at 0.5 mmHg)
Melting Point (°C)	Less than -10 °C
Vapor Pressure (25 °C)	$4.5*10^{-6}$ (mmHg)
Water Solubility (22 °C)	23 (mg/L)
Log Octanol/water Partition Coeff.	
Half-life in Soil	9.4-14.4 (days)
Application Rate	0.75-2 (kg/ha)

Figure 2. Butachlor (WSSA, 1989; Beestman and Deming, 1974).

Metolachlor



Propachlor



	Properties	Properties
CAS Number	51218-45-2	1918-16-7
Chemical Formula	$C_{15}H_{22}ClNO_2$	$C_{11}H_{14}ClNO$
Molecular Weight	283.8 (g/mol)	211.7 (g/mol)
Physical State	Liquid, white to tan, ordorless	Light tan solid
Density (25 °C)	1.085±0.005 (g/mL)	1.134 (g/mL)
Boiling Point (°C)	100 (at 0.001 mmHg)	100 (at 0.03 mmHg)
Melting Point (°C)		77
Vapor Pressure (25 °C)	1.3×10^{-5} (mmHg)	103 (mPa)
Water Solubility (22 °C)	530 (mg/L)	580 (mg/L)
Log Octanol/water Partition Coeff.	3.45	1.62-2.3
Half-life in Soil	15-50 (days)	1.9-7 (days)
Application Rate	1.8-3.36 (kg/ha)	3.36-6.72 (Kg/ha)
Leaching Potential	Medium	Small

Figure 3. Metolachlor (WSSA, 1989; Beestman and Deming, 1974; Chesters et al., 1989; Spalding et al., 1989)

Figure 4. Propachlor (WSSA, 1989; Beestman and Deming, 1974; Spalding et al., 1989)

shallow and deep groundwaters in the U.S. The U.S. EPA has promulgated an MCL of 2 ppb and classified it as a potential carcinogen (Ware, 1988).

Previous studies regarding the fate of alachlor in the environment have demonstrated that alachlor transformation is primarily controlled by volatilization, adsorption and biotransformation. Other processes such as abiotic reactions await further investigation.

The volatilization of alachlor from soil is associated with soil temperature and humidity. Hargrove and Merkle (1971) reported that high temperature and low relative humidity resulted in significant losses of alachlor in sandy loam soil because of chemical degradation and volatilization processes. Agricultural applications which spray alachlor solutions on soil can result in the volatilization of alachlor on moist soil and elevated temperature due to solar energy (Chesters et al., 1989). Beestman and Deming (1974) ranked the volatility of three acetanilide herbicides in the order: propachlor > alachlor > butachlor.

Microbial degradation is believed to be a primary pathway for dissipation of alachlor in soil. Zimdahl and Clark (1982) reported that ninety percent of all chloroacetanilide loss was from microbial decomposition. Beestman and Deming (1974) found that degradation of alachlor in unsterilized soil was 50 times faster than in sterilized soils. Many studies have shown that degradation of alachlor and other chloroacetanilide herbicides at low concentrations is a cometabolic process (Novick et al., 1986; Kaufman and Blake, 1973). Novick et al. (1986) reported that less than 8% of alachlor in soil was mineralized in 30 days. Kaufman and Blake (1973) concluded that the growth of a soil fungus *Rhizoctonia solani* and the degradation of alachlor depended on supplemented carbon sources. 28% and 90% of alachlor were degraded within 10 days by this organism in the presence of sucrose at 0 and 17.6 mM.

Few studies have focused on the reaction mechanisms of alachlor and other chloroacetanilide herbicides in the subsurface system. In a study of degradation of alachlor and propachlor in aquifer material, Novick et al. (1986) found that less than 1% of alachlor could be mineralized within one month. This result was consistent with the previous finding regarding the frequent detection of alachlor in groundwater.

Some laboratory column studies have been performed to study the effects of electron acceptors on degradation of alachlor. Wilber (1991) reported that alachlor was degraded to some extent under aerobic, nitrate-reducing, sulfate-reducing and methanogenic conditions. The sulfate-reducing condition was found to have the greatest degree of alachlor removal. Evidence of cometabolism processes were also proven in the laboratory studies. The abiotic reaction of alachlor with bisulfide was also observed, as will be discussed below.

Metolachlor

Metolachlor (2-chloro-N-(2-ethyl-6-methylphyl)-N (2-methoxy-1-methylethyl) acetamide) has been frequently detected in various groundwater surveys (Koterba et al., 1993; Spalding et al., 1989). Its product names include DUAL®, BICEP®, and MILOCEP®. In 1976, metolachlor was registered for use on the same crops as those of alachlor, as well as for potatoes, and for weed control near highway and railroad rights-of-way.

Many studies have demonstrated that adsorption and microbial decomposition primarily affect the fate of metolachlor in soils (Zimdahl and Clark, 1982, Obrigawitch et al., 1981, Beestman and Deming, 1974). The adsorption of metolachlor onto soils is correlated with increasing organic and clay contents of the soil (Bouchard et al., 1982). Obrigawitch et al. (1981) concluded that less than 1% of organic matter in soil resulted in metolachlor easily leaching to groundwater.

Higher temperature and moisture were found to quicken the biological degradation of metolachlor (Zimdahl and Clark, 1982; Braverman, 1986; Bouchard et al., 1982). In the investigation of metolachlor cometabolism in soil, Krause (1985) showed that incubation of *Actinomycete* in batch culture completely degraded metolachlor within 16 days in the presence of sucrose and yeast extract. Little information was found concerning transformation of metolachlor under anaerobic conditions. McGahen (1982) reported the reductive dechlorination of metolachlor in sediments from a eutrophic lake. Two nonpolar metabolites identified were dechlorinated metolachlors on which the chlorine in the chroloacetyl group was replaced by either one proton or a thiomethyl group.

Propachlor

Propachlor (2-chloro-N-isopropylacetanilide) was registered in 1965 for a wide variety of crops including corn, sorghum, soybean and other legume crops and onions. Trade names for products containing propachlor include RAMROD® and BEXTON®.

It is known that the loss of propachlor in soil by photodecomposition is negligible (WHO, 1993). Its volatilization mainly occurs under windy conditions and exposure on the surface of wet soil (WHO, 1993). Adsorption and biotransformation largely retard its transport to groundwater. However, abnormal cases of low temperature or dry soil conditions may result in propachlor persisting in soil (WHO, 1993).

Novick et al. (1986) studied the fate of propachlor in contaminated soil suspensions and ground water aquifer materials. The microorganisms in the soil suspension mineralized 16-61% of ring-labeled propachlor within 30 days at a concentration of 0.025 and 10 mg/L. Two bacterial strains together were shown to be capable of mineralizing 57.6 % of ring-labeled propachlor in 52.5 hour. Under identical conditions, less than 8% of ^{14}C-ring-labeled alachlor was converted to CO_2 at concentrations of 10 and 0.073 mg/L. It was concluded that the structural characteristics of alachlor, including the presence of alkyl substituents at the 2,6 position of the aniline ring sterically hinder the mineralization of alachlor compared to propachlor. In the investigation of the degradation of several chloroacetanilide herbicides in soils, Beestman and Deming (1974) and Zimdahl and Clark (1982) ranked the degradation rates of the four herbicides in following order, propachlor >alachlor>butachlor ≅ metolachlor.

Butachlor

Butachlor (2-chloro-2',6'-diethyl-N- (butoxymethyl) acetanilide is widely used in South East Asia and South America for controls of annual grasses, certain broadleaf weeds, aquatic weeds, and transplanted and seeded rice. Butachlor is also used in some areas of the U.S.A. for post-emergence application with propanil, another herbicide. Because butachlor is mainly applied in other countries, studies concerning its fate in the environment are rarely reported in U.S. However, it may still be rationalized that the fate of butachlor in the environment may follow similar pathways of its family members. Chakraborty and Bhattacharyya (1991) demonstrated that two soil fungi could effectively degrade over 50% of the total butachlor applied after 3 days in 0.02 M KH_2PO_4 buffer solution. No report was found regarding its abiotic transformation in subsurface systems.

Kinetics of Abiotic Transformation

To quantitatively understand the pathways and relative significance of abiotic reactions in the environment, kinetic experiments under laboratory conditions have often been employed to determine the rates of those reactions, as well as the factors that influence the rates and the reaction mechanisms. It is essential to consider both what kind of kinetic expression is used and what type of experiment (or reactor) is employed. Many different approaches have been used to address these problems.

Many studies have reported that a second-order model has been successfully employed to describe a reductive reaction with a reductant, or a nucleophilic substitution with a nucleophile, for both halogenated aliphatic and aromatic compounds in simulated aqueous environments (Kriegman-King and Reinhard, 1992; Schwarzenbach et al., 1990; Barbash and Reinhard, 1989; Hagg and Mill, 1988; Weintraub, 1989). The second-order equation predicts first-order behavior for both the halogenated compounds and the reductant or nucleophile in the solution.

Batch reactor methods are extensively used in laboratory studies to investigate such abiotic processes. The initial concentrations of reactants in the batch reactor are assayed, and depletion of these reactants or appearance of products are monitored over time. If concentration of the reductant can be held relatively constant throughout the reaction period, pseudo-first-order rate constants are obtained from least-square regression plots of log "remaining halogenated compound concentration" versus time. Second-order rate constants are obtained by dividing the pseudo-first-order constants by bisulfide concentration. These methods have been successfully employed to elucidate kinetics of a number of halogenated compounds, including herbicides (Yu and Bailey, 1992; Peijnenburg, et al., 1992; Wilber and Garrett, 1994). Studies by Wilber and Garrett (1994) also employed batch reactors dosed with 300 μg/L of alachlor and 17 mg/L total sulfide to examine the similar abiotic transformation of alachlor over a period of 300 hours. With a bisulfide concentration at least two hundreds times larger than that of alachor, the degradation of alachlor followed pseudo-first-order kinetics with respect to alachlor concentration. A good linear relationship is observed with correlation coefficients ranging from 0.97-0.99. Second-order constants for the above reactions were obtained for alachlor and propachlor, with values of 0.0011 and 0.0016 (1/hour/[HS^-]/L), respectively (Wilber and Garrett, 1994).

Batch reactor methods have also been used to investigate other factors affecting abiotic transformations of halogenated compounds. The disappearance of halogenated compounds versus time can be observed after changing a reaction parameter and keeping other parameters constant over a selected reaction time period. Some studies have reported that both reductive and nucleophilic substitution rates are related to the concentration of reductant or nucleophile (Yu and Bailey, 1992; Wolfe and Macalady, 1992; Hagg and Mill, 1988; Weintraub, 1989). Yu and Bailey (1992) investigated the reductive reaction of nitrobenzene with several sulfide minerals in batch systems. The reaction with sodium sulfide was found to be most rapid because sodium sulfide has a high water solubility, resulting in higher sulfide concentrations than other salts like MnS, ZnS, MoS_2. This result was consistent with studies by Wolfe and Macalady (1992).

In the investigation of the nucleophilic substitution reaction of 1, 2-DBE with sulfide, Weintraub (1989) found that degradation rates of the chemical in a phosphate buffer solution at 25 °C, 40 °C and 60 °C doubled correspondingly when sulfide concentration was increased by a factor of 2 at each temperature. Barbash and Reinhard (1989) conducted experiments with regard to the nucleophilic substitution reaction between 1,2-DCA and 1,2-DBE and bisulfide. It was found that phosphate buffer catalyzed the hydrolysis of the above chemicals. March (1985) also related various nucleophiles to their apparent reaction rate. Nucleophilicity in aprotic solvents displayed the following decreasing order: $SH^- > CN^- > I^- > OH^- >> H_2O$. Kriegman-King and Reinhard (1992) concluded that the CCl_4 transformation rate in the presence of sulfide is at least 1 order of magnitude greater than K_{H_2O} even though H_2O is 50 times more concentrated than bisulfide. The role of bisulfide as a strong nucleophile could be found in other similar studies (Barbash and Reinhard, 1989; Hagg and Mill, 1988; Weintraub, 1989).

Effect of Temperature

It is well known that the rates of both non-biological reactions and biological processes are , in general, increased by increasing temperature. Therefore, the degradation rates of halogenated compounds, including herbicides, should follow this rule of thumb (Morrill et al., 1982). The dependence of the rate constant of a chemical reaction on temperature can be expressed by the Arrhenius equation (Snoeyink and Jenkins, 1980).

$$K = A\, e^{(\frac{Ea}{RT})} \tag{2.1}$$

in which K is the first-order rate constant (1/days); A, the Arrhenius constant (1/days), is a measure of the molecule collision frequency; Ea, the activation energy (J/mol), is the minimum energy required for a reaction to take place; R is the universal gas constant (8.314 J/mol-K), and T is the temperature (K). Barbash and Reinhard (1989) investigated the rate of EDB reacting with 0.67 mM bisulfide over a temperature range of 25 °C to 87.5 °C. The degradation rate of EDB at 87.5 °C was 2 orders of magnitude greater than that at 37.5 °C. Furthermore, the activation energy for the reaction with bisulfide was smaller than those with both H_2O and $HPO^{2-}{}_4$. This means that bisulfide is a stronger nucleophile than H_2O and $HPO^{2-}{}_4$. Similar results were found in the study by Weintraub

(1989). No information was found on the temperature effects on the degradation of herbicides.

Effects of pH

In general, pH is the controlling variable in nucleophilic substitution reactions in which water is the dominant nucleophile. Several studies have demonstrated that the degradation of haloaliphatic compounds could be proceeded faster in the nucleophilic substitution reaction at higher pH values. However, below pH 11, a pH dependence for substitution reactions is generally not observed (Mabey and Mill, 1978; Vogel et al, 1987). In other cases, pH effects on the specific reaction rates are often a reflection of positions of acid-base equilibria for reactants. When sulfide species are involved in a reaction, the concentrations of sulfide species, H_2S, HS^-, and S^{2-} in water are determined by two equilibria. When the weak acid H_2S or any of its salts is added to water, the equilibria are described as follows :

$$H_2S \Leftrightarrow H^+ + HS^- ; \qquad K_{a_1} = \frac{(H^+)(HS^-)}{(H_2S)} \tag{2.2}$$

$$HS^- \Leftrightarrow H^+ + S^{2-} ; \qquad K_{a_2} = \frac{(H^+)(S^{2-})}{(HS^-)} \tag{2.3}$$

Chen and Morris (1972) reported that the pK_{a1} value at 25 °C is 7.02 while pK_{a2} varies from 12.35 to 15. Therefore, when the values of pH range from 7 to 12.5 , a sulfide solution is dominated by bisulfide ion, HS^-. It will therefore play an important role in natural waters with pH values of 6-9 (Dohnalek and FitzPatrick, 1983; Chen and Morris, 1972). Hagg and Mill (1988) examined the abiotic reaction of haloaliphatic compounds with bisulfide over a pH range from 4 to 12. The pseudo-first-order rate constants of 1-bromohexane reached a maximum at pH above 8, in which over 90 % of total sulfide is in the bisulfide form. H_2S and S^{2-} were proven to be unimportant reactants at pH = 4 and pH = 12. No information is publicly reported regarding the effect of pH on the abiotic reaction of herbicides with sulfide at high pH.

Quantitative Structure-Activity Relationships

Quantitative structure-activity relationships (QSARs) are widely used by regulatory agencies and industry to make rapid and cost-effective predictions of the biological activity and environmental reactivity of compounds, based on data from related compounds of known activity. They can provide insight into breakdown mechanisms and pathways in the environment and identify reaction metabolites. Much research work has focused on molecular structure and physical properties (Isaacs, 1987; Hansch and Leo, 1979; Peijnenburg et al., 1992).

For example, Alexander (1973) related slight modifications in the structure of organic molecules (including highly branched groups, the type, number, and position of substituents) with their remarkable resistance to biodegradation. These modifications include substitution of methyl groups in aliphatic alcohols instead of hydrogen, chlorine in triazines instead of methoxyl groups, benzoic acids with *meta*-methoxy groups instead of the corresponding isomers with the substituent in *ortho*-or *para*-positions.

In a study on biodegradation of propachlor and propanil, the propachlor biodegraded more quickly than propanil due to the hindrance posed by substitutions at the amide linkage on propanil, which inhibits attack by hydrolase enzymes of the suspended bacterial populations (Steen and Collette, 1989). Similar results, in which non-mineralization of propachlor in soil was attributed to the resistance to the alkyl substitution at the acetanilide nitrogen, were obtained by Bartha (1968). Other researchers (Villarreal et al., 1991) suggested that the presence of the 2',6'-dialkyl substituents on the aniline ring may sterically hinder the cleavage of bonds to the N-atom. In the investigation of biodegradation of aniline and the related compounds in sewage, Novick and Alexander (1985) demonstrated that aniline was mineralized, while only 81% and 21% of the added propachlor and alachlor, respectively, were metabolized in sewage. These differences were attributed to the increasing complexity of substituents on the two pesticides. Though QSAR techniques are often employed to explain the biodegradation of halogenated compounds and the chloroacetanilide herbicides, they may also provide insight regarding the abiotic transformations for chloroacetanilide herbicides. Relatively little information is currently available regarding to the effects of chemical structure on the rate of reactions with sulfide compounds.

Summary

Recently progress has been made concerning biotransformations of alachlor, butachlor, metolachlor, and propachlor in environments. However, limited information was found regarding the abiotic transformation of alachlor and propachlor by bisulfide under conditions considered environmentally relevant. Little information has been reported concerning the fate of metolachlor and butachlor. Thus, the current literature can provide the basis for selecting the objectives of this study and also serve as the basis for the experimental and analytical techniques used to achieve them. The research described in this thesis has as its aim a better understanding of the abiotic transformations of these herbicides by bisulfide, which may be significant in ground water. It will provide useful information for answers to the following questions: What is the best way to describe the kinetics of abiotic reaction of these herbicides with bisulfide? What effect does the different sulfide concentrations have on the kinetic constant of the reaction? How do the environmental factors such as temperature and pH affect the kinetics of the reaction?

CHAPTER III

METHODS AND MATERIALS

Experimental Approach

This study focused on evaluating the abiotic reaction of four acetanilide herbicides with bisulfide. These reactions may be significant in certain groundwaters. A series of batch reactor experiments were employed in this investigation. Effects of different parameters, such as the concentrations of pesticides and bisulfide, temperature and pH, on the rate and extent of pesticide removal were investigated. The chemicals used, analytical methods for both pesticides and sulfide, the experimental procedures, and the methods of data analysis of rate constants are described below.

Reagents, Pesticides and Laboratory Protocols

The water ($\geq$18 MΩ·cm purity) used in all the experiments was produced by a Milli-Q purification system (Millipore corp., CA) via deionization and reverse osmosis. All chemicals used in this study were commercially available and were used as received. They include potassium phosphate monobasic (KH_2PO_4), potassium phosphate dibasic (K_2HPO_4), sodium thiosulfate ($Na_2S_2O_3 \cdot 5\ H_2O$), iodine (I_2), sodium sulfide ($Na_2S \cdot 9$

H_2O), potassium bi-iodate ($KHIO_3$), and potassium iodine (KI). These chemicals were obtained either from HACH (Loveland, Co.), or Fisher Scientific, Inc. Methanol and ethyl acetate used for extraction were pesticide-grade solvents from Fisher Scientific, Inc. Each pesticide in aqueous stock solution was prepared from pure, analytical grade chemicals obtained from ChemService (West Chester, PA).

All glassware was washed with detergent, followed by rinsing with 10% nitric acid, tap water, Milli-Q water, and dried for 4 hours at 110 °C before use.

Analytical Methods

Pesticide Extraction Procedures

Extraction of aqueous samples containing pesticides was performed by the solid-phase extraction (SPE) method described by Thurman and coworkers (1990). PrepSep C-18 cartridges (Fisher Scientific, Inc.) were used as extraction columns, which contained 360 mg of 40 μm bonded silica. The C-18 cartridges were prepared by sequentially washing with 3 mL of methanol, 3 mL of ethyl acetate, 3 mL of methanol, and 2 mL of distilled water. The samples (50 mL) from batch reactors was passed through the PrepSep cartridges using a Prep Torr Vacuum Box (Fisher Scientific, Inc.). The cartridges were then dried with air to remove residual water and then eluted with exactly 2 mL of ethyl acetate. The extracts were stored in the dark at 4 °C until analysis by gas chromatograph (GC).

Pesticide Analysis

Extracted Pesticides were analyzed on an HP 5890 Gas Chromatograph (GC) (Hewlett-Packard Company) equipped with an electron capture detector (ECD). 1 μL of extracts were injected onto a DB-5 fused silica capillary column, with film thickness 0.25 μm; inner diameter 0.25 mm; length 30 m (J & W Scientific, Folsom, CA). Quantification was achieved by injecting herbicide standards as well as samples, and comparing relative areas under separated peaks recorded by a model 3396 Hewlett Packard Series II integrator. The minimum detectable concentration for each of four pesticides was 5 μg/L. Injections were made in the split mode (ratio 1:45) at an injector temperature of 200 °C and a column temperature of 175 °C. Helium gas was employed as the carrier gas, with a flow rate of 45 mL/min and a column head pressure of 25 psi. A combination of 95% argon and 5% methane mixture was used as the ECD make-up gas. The column temperature was held at 175 °C for 1 minute and then ramped at a rate of 5 °C/min to a final temperature of 185 °C. The gas chromatograph was calibrated with a minimum of five calibration standards for each experiment, and duplicate measurements were made for each sample or standard. The average of the two measures was used.

Sulfide Analysis

The analysis of dissolved sulfide was determined by the Iodometric Method (Method 4500E, APHA, 1989), which is performed as follows. An aliquot of 0.025 N standard iodine solution, which exceeded the equivalent amount of sulfide present in sample, was put into a 500 mL flask. To this, 2 mL 6 N HCl were added, followed by 50 mL of the sample containing sulfide, quickly discharging the sample under the solution surface to minimize volatilization. The unreacted iodine remaining in solution was back-titrated with 0.025 N $Na_2S_2O_3$ solution. When titration was close to the end point, three or four drops of starch indicating solution were added. Titration continued until blue color disappeared. The titration method, accurate for sulfide concentration above 1 mg/L, can be accurate only if a great care is taken in the following ways: 1) keep solution in acid condition to avoid sulfide oxidation to sulfur; 2) titrate quickly to minimize the volatilization of hydrogen sulfide; and 3) minimize interferences from impurities such as those produced from the oxidized surface layer of sodium sulfide. The last point is particularly important when making solutions with Na_2S solid, and will be discussed in more detail in Chapter IV.

Batch Reactor Studies

Wheaton 120 mL serum bottles were used as batch reactors. For each batch study, a solution in a 4 L glass container containing 50 mM phosphate buffer was stripped of oxygen by bubbling vigorously with nitrogen gas, dosed with a known concentration of bisulfide and pesticide, and mixed completely. The solution was then quickly distributed among a series of batch reactors, which then were covered without headspace with 1-cm thick PTFE-faced silicone septa (Supelco) to avoid adsorption and sealed with aluminum crimp seals to avoid volatilization of hydrogen sulfide. This step was always finished within several minutes. The reactors were then moved into an incubator (range 5 °C to 50 °C, Precision Scientific Co.) to provide a constant-temperature environment in the dark. Samples were collected periodically by opening one bottle, and sampling each time for pesticide and sulfide analysis. Rate constants were then calculated from these data, as discussed below.

Stock sulfide solutions were prepared before each experiment. Individual crystals of $Na_2S\cdot 9\ H_2O$ (Baker Chemical Co., Baker Analyzed Reagent Grade) were rinsed with deoxygenated Milli-Q water inside a nitrogen-filled atomsbag (Aldrich) to dissolve and remove oxidized surface crystals and then wiped dry with Kimwipes. These crystals were then dissolved in a volumetric flask with deoxygenated water. This stock sulfide solution was standardized by the Iodometric Method (APHA, 1989)

In these batch studies, the effects of different parameters, such as the concentrations of bisulfide, temperature, pH and concentrations of pesticides on the extent of pesticide removal were investigated. For each of above parameters, only one was varied at a time to observe its effect on the rate constants of the abiotic reaction. The descriptions of the procedures to evaluate the effects of these parameters on the abiotic reaction are found in following sections.

Effect of Sulfide Concentrations

The sulfide concentrations for each set of batch reactors were produced from a stock solution of known concentration. The diluted solutions were standardized twice before using. The aforementioned batch reactor study procedures were followed to investigate the effects of sulfide concentration on the reaction orders of pesticide reaction.

Sulfide in these experiments was present in considerable excess compared to the pesticides. It was varied over range of 3 mg/L to 100 mg/L, which were concentrations considered environmentally relevant (Barbash and Reinhard, 1989). Most of experiments in this study focused on the sulfide concentrations between 20 to 60 mg/L. For most of the experiments, the initial pesticide concentrations were approximately 300 µg/L. Other experiments were conducted to investigate the effect of 3 mg/L pesticide concentration on the reaction orders.

Effect of pH

As mentioned above, hydrogen sulfide, a weak diprotic acid, exists in three chemical forms in solution, H_2S (aq), HS^- and S^{2-}. The pH in solution determines the distribution of these reduced sulfur species ($pK_{a1} = 7.01$ and $pK_{a2} = 12.9$ at 25 °C). When pH is lower than 6 or higher than 12, hydrogen sulfide (H_2S) and sulfide (S^{2-}), respectively, may be present at significant levels. In the pH range of most natural waters (pH = 6-9), bisulfide is the primary species of interest. In the investigation of abiotic reaction of haloaliphatic compounds with sulfide, Barbash and Reinhard (1989) and Weintraub (1989) used phosphate salts (KH_2PO_4/Na_2HPO_4) to buffer solutions at pH 7.1 to simulate natural water conditions. Given the similar objectives of this study, phosphate salts were also employed.

This study investigated the effect of pH, at 4, 7 and 12 respectively, on the abiotic reaction by using different phosphate buffers. Table I shows the different buffer formulas used for pH 4, 7 and 12. Measurements of pH were made before and after each experiment with an Accumet 900 pH meter, which was standardized at pH 4.0, 7.0 and 10.0 individually. The effect of these buffer phosphate salts at 0 mM, 5 mM and 50 mM was also examined as minor part of this study to investigate the reactivity of the phosphate salts with the pesticides (Barbash and Reinhard, 1989).

Table I

FORMULA OF BUFFER SOLUTIONS AT DIFFERENT pH VALUES

pH	Buffer ingredients	Ratio of buffer solution (g/L : g/L)
pH=12	K_2HPO_4/K_3PO_4	6.125 : 3.7312
pH=7	KH_2PO_4/K_2HPO_4	6.69 : 6.75
pH=4	KH_2PO_4/H_3PO_4	217.6 : 1.97

Effect of Temperature

Changes of temperature can greatly affect the kinetics of abiotic reactions. As such, a series of experiments were conducted in which temperature was varied. An incubator (Model 850, Precision Scientific Co.) was employed to keep constant temperature for each experiment. Three temperatures, 8 °C, 21 °C, and 35 °C were investigated in this study. The middle range of sulfide concentration (40 - 50 mg/L) and a pesticide concentrations near 0.3 mg/L were employed in this study to find the effects of temperature on the rate of the abiotic reactions.

Results from these experiments also allowed investigation of activation energies of these reactions. Activation energies were obtained by plotting log first-order rate constants at different temperatures (as described below) vs 1/T (K).

Data Analysis of Rate Constants

As mentioned in Chapter II, the second-order kinetic model can be employed to predict first-order behavior for both the halogenated compounds and the reductant or a nucleophile in solution. For instance, the rate law for the disappearance of herbicides reacting with the reductant bisulfide has been hypothesized as follows:

$$-\frac{dC}{dt} = K_{HS^-} \times [C] \times [HS^-] \qquad (3.1)$$

where C (mole/L) is the herbicide, HS^- (mole/L) is either a reductant or a nucleophile, depending on the kind of reaction involved, and K_{HS^-} (1/days/[HS^-]mole/L) is the second-order rate constant for reaction between the herbicide and bisulfide (Barbash and Reinhard, 1989). Degradation of halogenated compounds present at trace levels may proceed in the presence of excess sulfide species, in which case the second-order expression can be simplified to pseudo-first-order kinetics:

$$-\frac{dC}{dt} = K_{obs}\,[C] \qquad (3.2)$$

K_{obs} is the observed pseudo-first-order rate constant, which equals $K[HS^-]$. When integrated, yield

$$\ln[C]_t/\ln[C]_o = -K_{obs} \times t \qquad (3.3)$$

$[C]_t$ is the amount of herbicide left at a given time t, related to the amount present $[C]_o$ at time $t = 0$. By plotting $\ln([C]_t / [C_o])$ as a function of the reaction time, the pseudo-first-order reaction rate constant K_{obs}, equal to the slope of this line, can be obtained. The second-order rate constant K therefore equals the pseudo-first-order rate constant divided by the bisulfide concentration over all ranges.

CHAPTER IV

RESULTS AND DISCUSSION

Preview

The results of the experiments described in Chapter III are presented and discussed in the following section. It includes the experimental data analyses, determination of reaction order, pH dependence, phosphate buffer effects, and temperature effect on the abiotic reaction of acetanilide herbicides with sulfide species. A kinetic equation which is suitable for simulating the disappearance of these herbicides in the groundwater is presented, followed with a brief discussion of steric effects of the structures of the herbicides on the relative reactivities of the abiotic reaction of the four herbicides.

Before reviewing the experimental results, it is worth mentioning some observations from experiments performed at early stages of this study. It was found that sodium sulfide used to prepare the stock solution must be washed to remove the oxidized layer of its surface. Otherwise, polysulfides would be formed, and compete with bisulfide for the decay of herbicides, causing increased variability in reaction rate. Reports found in the literature (Hagg, 1988) also described this phenomenon. As will be shown in Table II, a higher reaction rate constant (at bisulfide concentration of 19 mg/L) for propachlor was found by using unwashed sodium sulfide. Therefore, all of experiments at later stage of this study used washed sodium sulfide.

Obtaining reaction rates for the herbicide degradation is the main object of this study. As will be discussed later, some reactors exhibited a rapid initial reaction rate, followed by a much slower one (see Figure 5). In these cases, the rapid initial reaction rate will be employed in this study to determine the reaction rate of interest. The slower, second phase of the reaction (as seen in the tail of the data for the 19.5 mg/L HS^- experiment in Figure 5) will be discussed, but will not be included in the calculations of the rate constants. Causes and results of this will be discussed below.

Experimental Data Analyses

As stated previously in Chapter III, the second-order kinetic model was assumed in this study to predict the disappearance of herbicides under simulated groundwater conditions. However, in many cases, pseudo-first-order conditions were created. The apparent first-order degradation rate constant, K_{obs}, can be obtained by plotting the natural log of the percent herbicides remaining ($\ln(C/C_o)$) as a function of time. The uncertainty of this rate constant is reflected by the standard deviation of the slope. Based on the "student's t" distribution table given by Johnson (1976), the 95% C. I. (confidence interval) for K_{obs} was equal to:

$$\{ K_{obs} - t\,(n-2, \alpha/2)\, S_{b1}, K_{obs} + t\,(n-2, \alpha/2)\, S_{b1}) \}$$

where n is the number of data points obtained, α (0.05) represents the 95% confidence level, and S_{b1} is the calculated standard error. Illustrated as an example in Figure 5

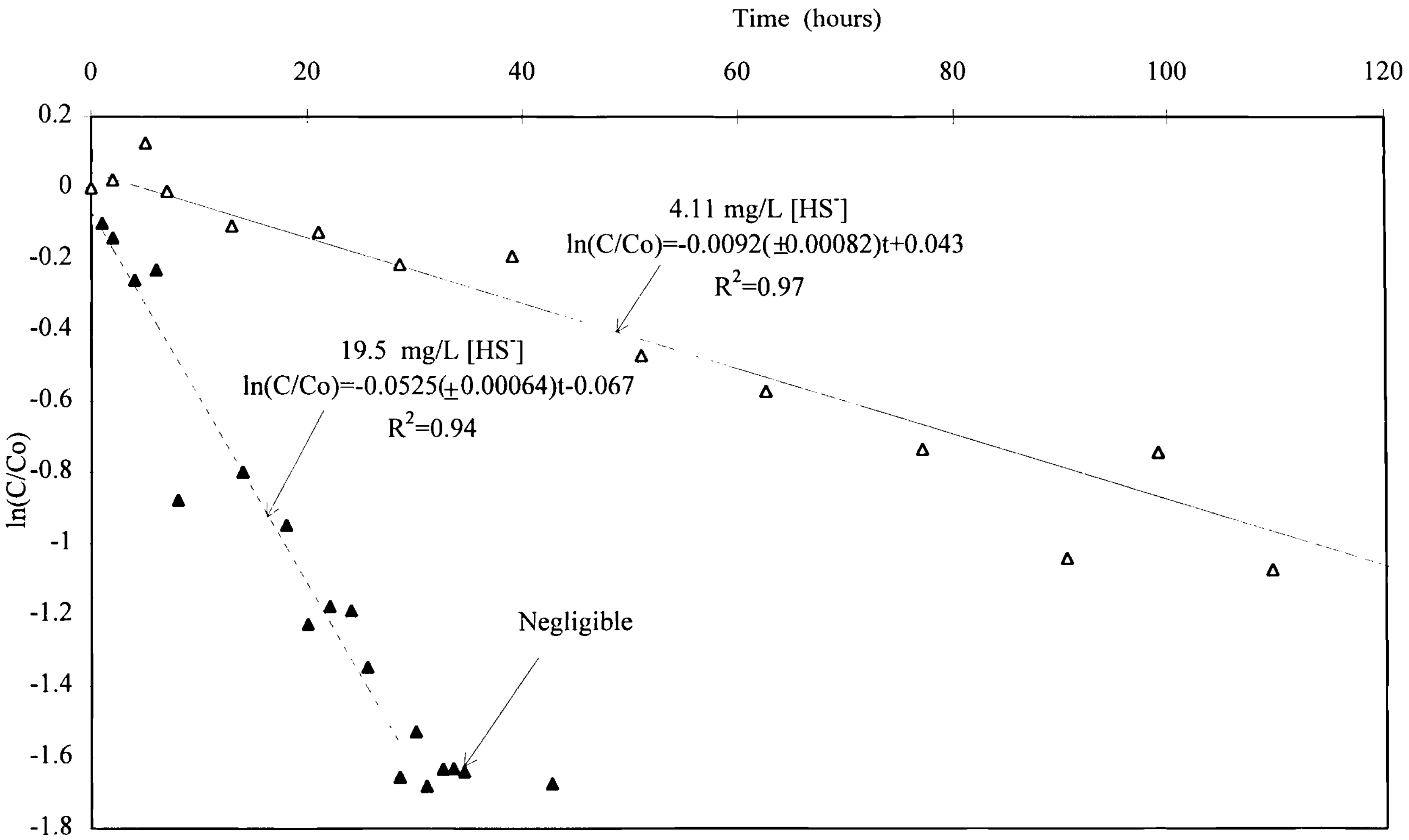


Figure 5. Determination of kinetic constants of propachlor at bisulfide concentration of 4.11 and 19.5 mg/L, respectively.

(Appendix A) is a plot of disappearance of propachlor against time with bisulfide concentrations of 4.11 mg/L and 19.5 mg/L. K_{obs} were calculated by using the statistical method described above (for instance, K_{obs} being 0.0525 ±0.00064 (1/h) at 19.5 mg/L [HS^-] and 0.0092 ±0.00082 (1/h) at 4.11 mg/L [HS^-]).

In some cases of higher bisulfide concentration (for instance, 19.5 mg/L bisulfide), the herbicides degraded very quickly initially, and then virtually stopped transforming. This is also true for the other three herbicides of interest. Therefore, the statistical analyses were used to calculate the initial degradation rates for reactions at higher bisulfide concentrations. The disappearance of herbicides at latter stages was considered separately. The second-order reaction rate constant K_{HS^-} is obtained by dividing by the bisulfide concentration, while the characteristic half-life of disappearance is calculated by using the following equation:

$$t_{\frac{1}{2}} = \frac{\ln 2}{K_{obs}} \tag{4.1}$$

The experimental values for K_{obs}, K_{HS^-} and $t_{1/2}$ will then be used to draw conclusions about the effect of various reaction conditions on the rate at which these reactions occur.

Determination of Rate Law

Since the concentrations of sulfide in the reactors were generally kept at great excess in comparison with herbicides, the pseudo-first-order model was proposed in this study to express the disappearance of herbicides under conditions that resemble groundwater environments as closely as possible. The disappearance of herbicides was assumed to have the following overall form (Barbash and Reinhard, 1989):

$$-\frac{d[C]}{dt} = K_{obs} \times [C] = K_{HS^-} \times [C] \times [HS^-] \tag{4.2}$$

where

$\frac{d[C]}{dt}$ = change in herbicide concentration with respect to time (µg/L/h)

[C] = herbicide concentration at time t (µg/L)

$[HS^-]$ = bisulfide concentration (mg/L)

K_{obs} = observed rate constant when considering the effect of pH, phosphate buffer, and bisulfide concentration on the reaction (1/h)

$K_{obs} = \{K_{H_2O} \times [H^+] + K_{H_2PO_4^-/HPO_4^{2-}} \times [HPO_4] + K_{H_2S}\}$,

K_{H_2O} (1/h), $K_{H_2PO_4^-/HPO_4^{2-}}$ (1/h) and K_{H_2S} represent rate constants of the effect of pH, phosphate buffer and hydrogen sulfide for the reaction with the herbicides.

K_{HS^-} = second-order rate constants (1/h/mg $[HS^-]$/L), obtained from the observed rate constant divided by bisulfide concentration $[HS^-]$.

The following sections will focus on the determination of reaction order. Included are the correlation between concentration and time, reaction order with respect to both herbicides and bisulfide, and correlation between pseudo-first-order rate constants and bisulfide concentration.

Correlation between Concentration and Time

The effect of HS^- concentration was studied over a range of 1.24 mg/L to 41.43 mg/L (0.0376 - 1.06 mM) at constant initial pesticide concentration of 0.3 mg/L for each herbicide (0.0011 mM for alachlor and 0.0014 mM for propachlor), room temperature and neutral pH, as described previously. Alachlor and propachlor were the primary subjects of these studies.

Figures 6 and 7 show the correlation between concentrations vs. time typically observed for the disappearance of alachlor and propachlor under three different bisulfide concentrations (1.24, 8.8 and 41.43 mg/L for alachlor and 1.24, 9.23 and 31.8 mg/L for propachlor). At the highest sulfide concentration of 41.43 mg/L (1.06 mM), alachlor disappearance was very fast, with a half-life less than 1.5 hours and the degradation completed within 20 hours. At the lowest bisulfide concentration of 1.24 mg/L (0.0376 mM), more than 50% of alachlor remained after 12 days. In the case of bisulfide concentration less than 10 mg/L, the disappearance of alachlor was initially very rapid followed by slower decay over a period of approximately 50 to 100 hours. This clearly illustrated that the decay of alachlor strongly depends on bisulfide concentration. The degradation of propachlor was similar to that of alachlor under the same reaction conditions, with somewhat faster degradation rates. Resulting rate constants will be discussed below.

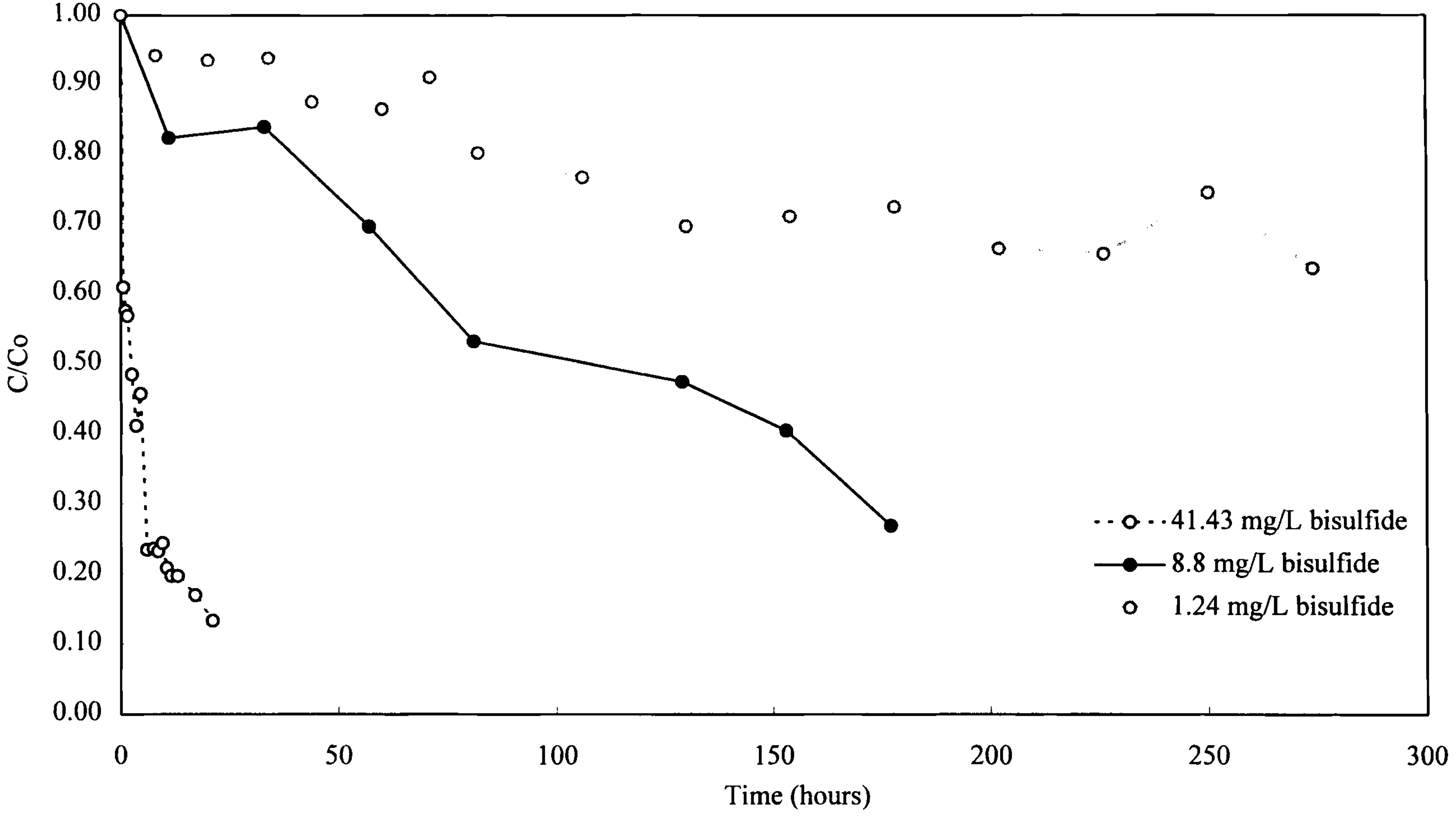


Figure 6. The removal of alachlor at the bisulfide concentrations of 1.24, 8.8, and 41.43 mg/L.

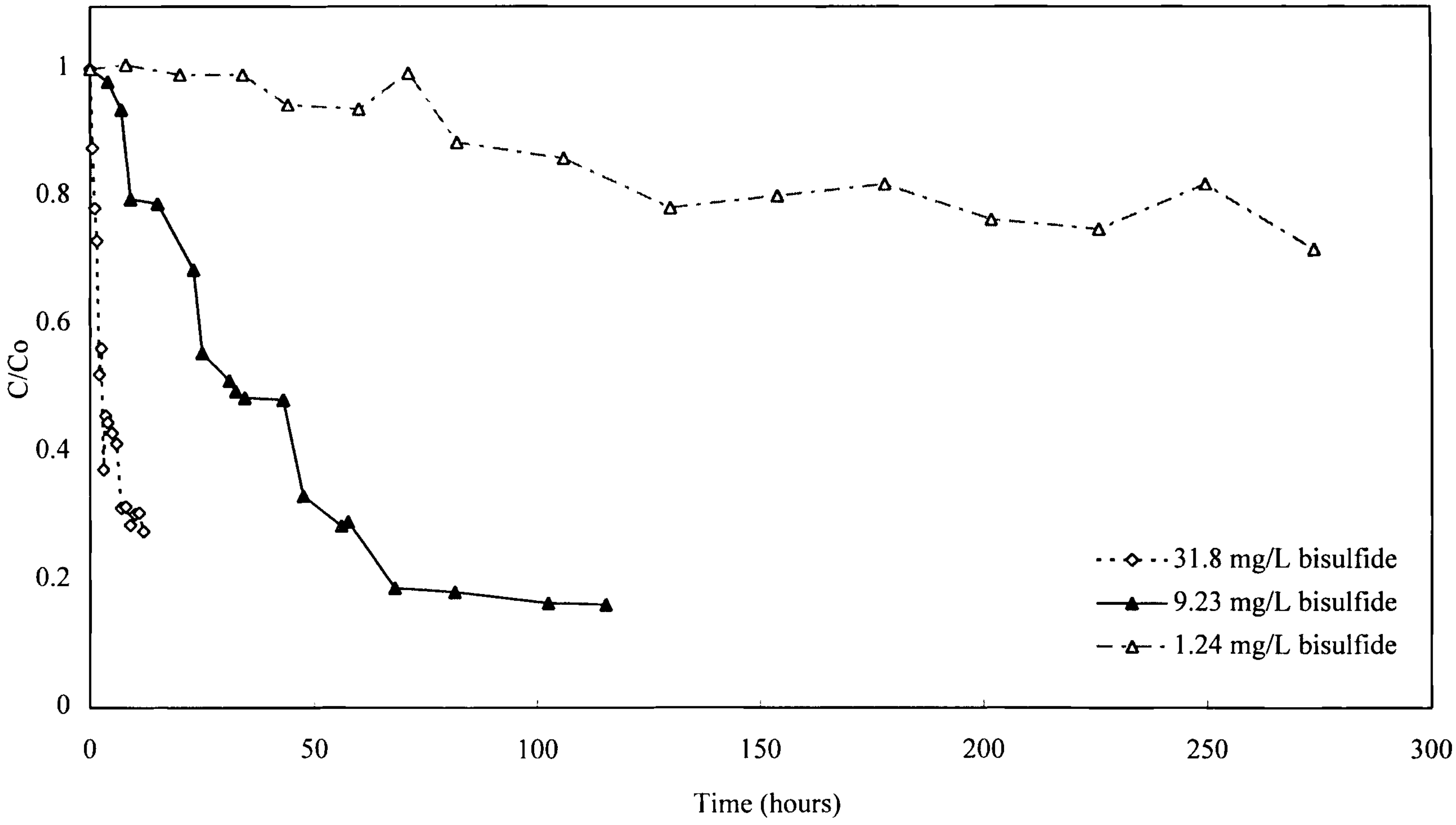


Figure 7. The removal of propachlor at the bisulfide concentrations of 1.24, 9.23 and 31.8 mg/L.

Reaction Order with Respect to Herbicides

The experiments for determination of the reaction order of herbicide decay were run under room temperature, with a 50 mM phosphate buffered solution containing different sulfide concentrations at near neutral pH. Figures 8 and 9 illustrated the linear relationships (correlation coefficients above 0.9) of "ln percent remaining" for propachlor (Appendix B) and alachlor (Appendix C) as function of time at bisulfide concentrations of 4.28, 9.23 and 20.67 mg/L for propachlor, and 1.24, 9.23 and 19.5 mg/L for alachlor. This indicates that the degradation of propachlor and alachlor are first-order reactions with respect to herbicide concentration. Linear relationships were also found for butachlor and metolachlor, which are shown in Figures 10 and 11 (Appendix D), respectively. At the higher concentrations of bisulfide, the degradation of herbicides (alachlor and propachlor) also exhibit such first-order behavior, as shown in Figure 12 (Appendix E). Figure 12 indicates that the degradation of alachlor showed a rapid initial reaction rate followed by a much slower one. This was the case in other reactors for the reaction of herbicides with higher bisulfide concentrations. It is possible that sulfide reacted with herbicides most quickly at the beginning of reaction period when there was little accumulation of reaction intermediates , and later began reacting actively with the intermediates instead of the parent compounds. The gas chromatography output revealed that the concentrations of unknown intermediates increased with reaction time while the herbicides degradation slowed down when intermediates accumulated.

The complicated distribution of sulfide species in solution may be another cause.

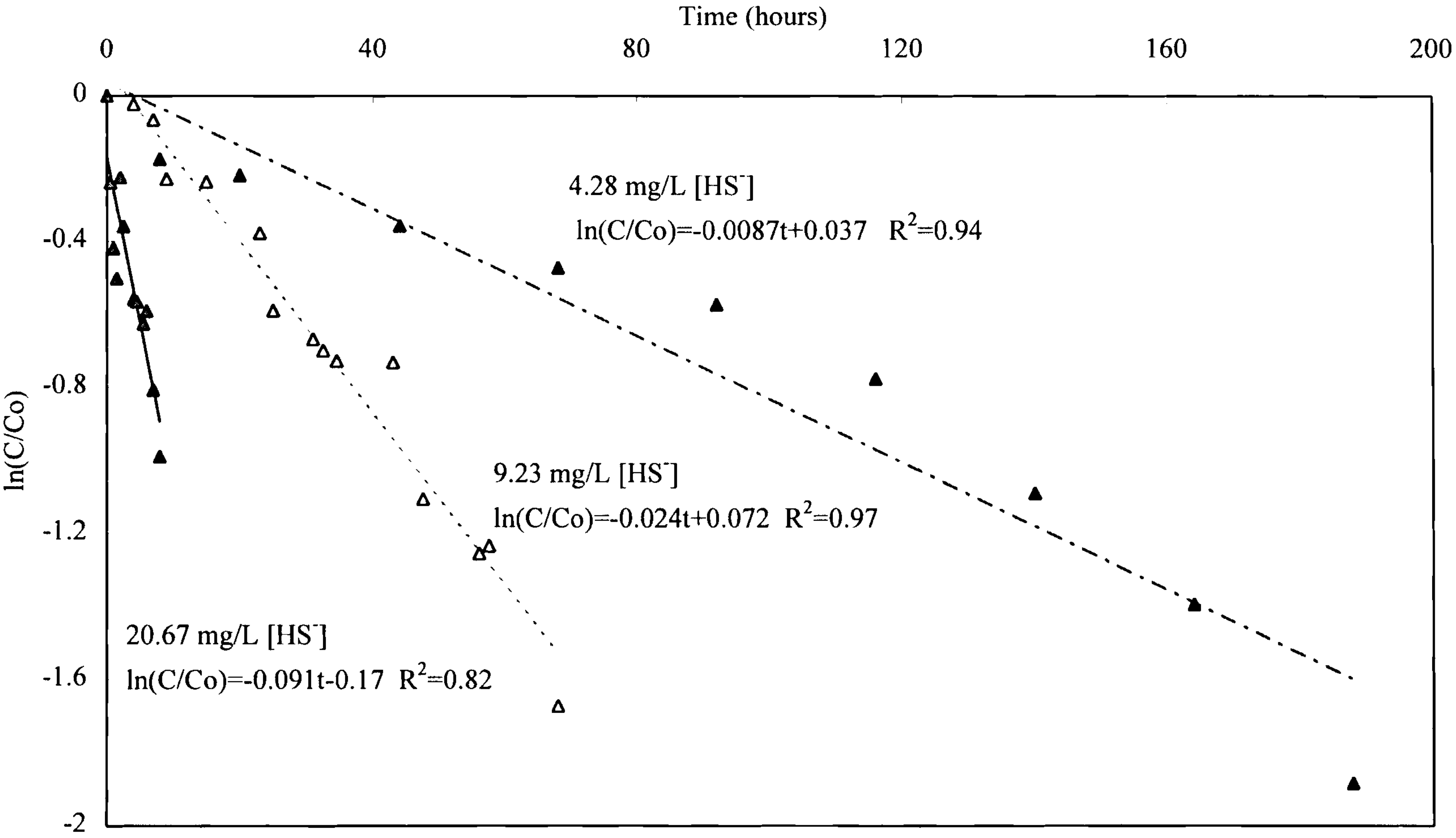


Figure 8. The first-order plot of 0.3 mg/L propachlor at different bisulfide concentrations.

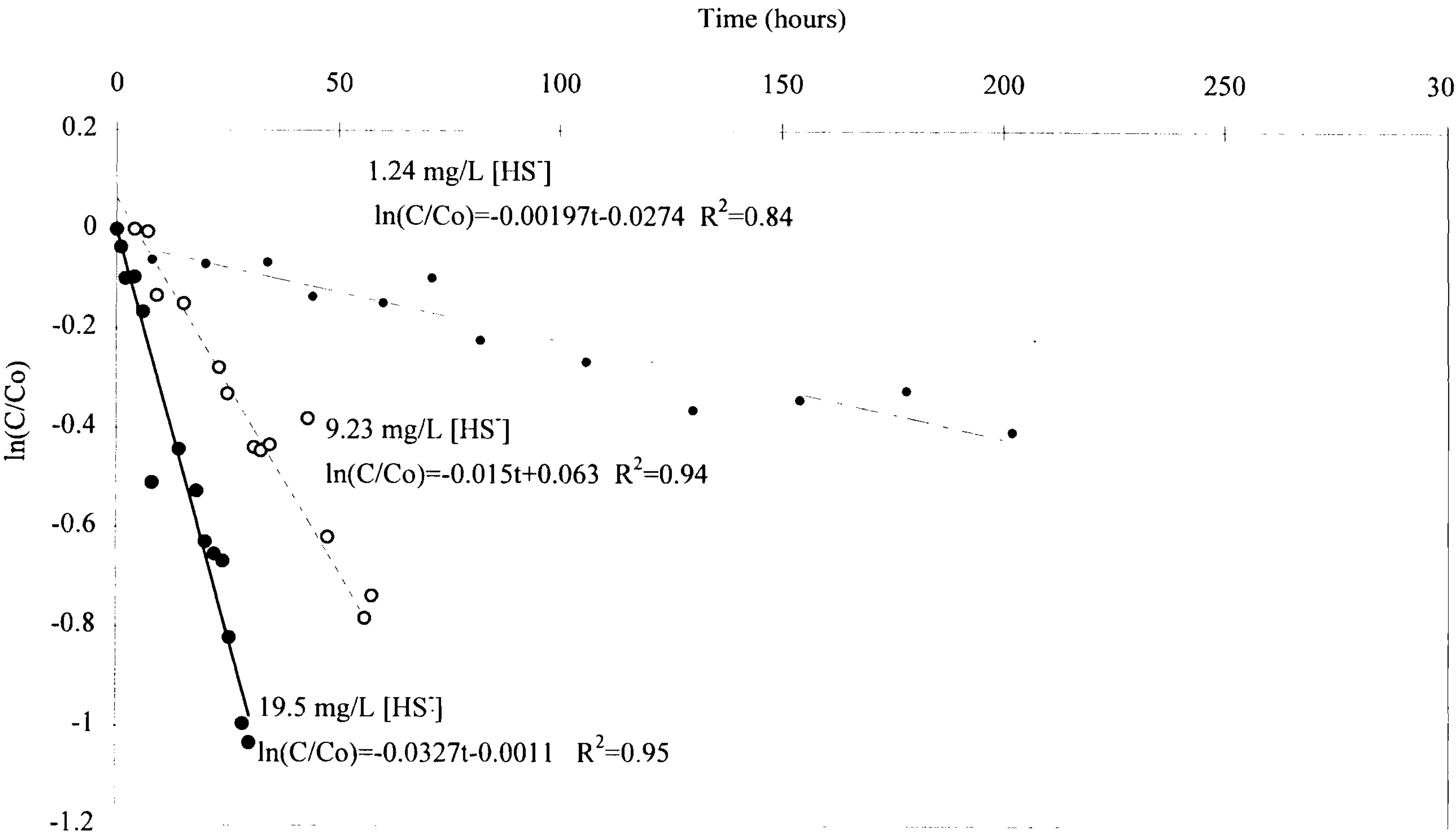


Figure 9. The first-order plot of 0.3 mg/L alachlor at different bisulfide concentrations.

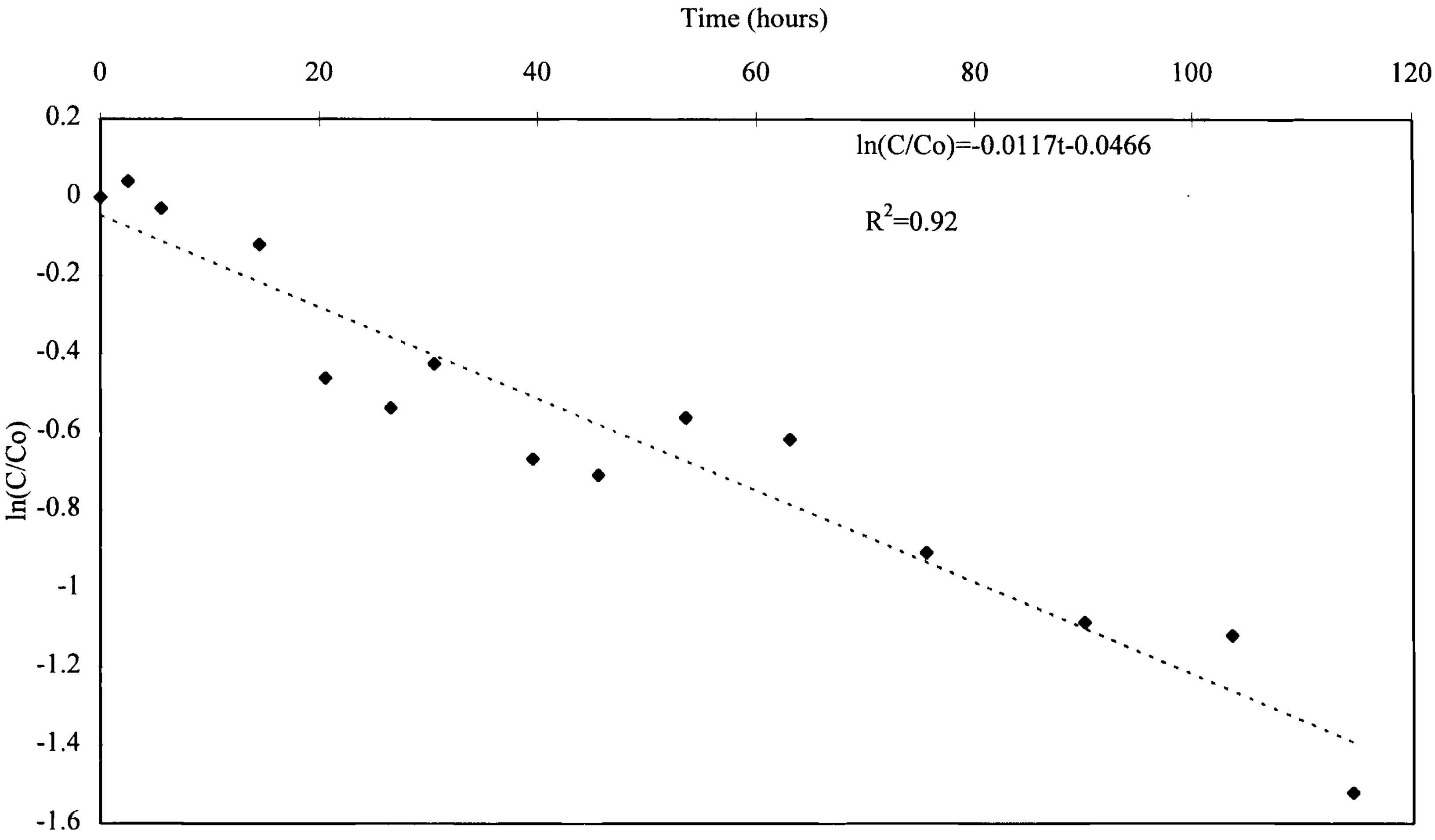


Figure 10. The first-order plot for 0.3 mg/L butachlor and 15.3 mg/L bisulfide concentration.

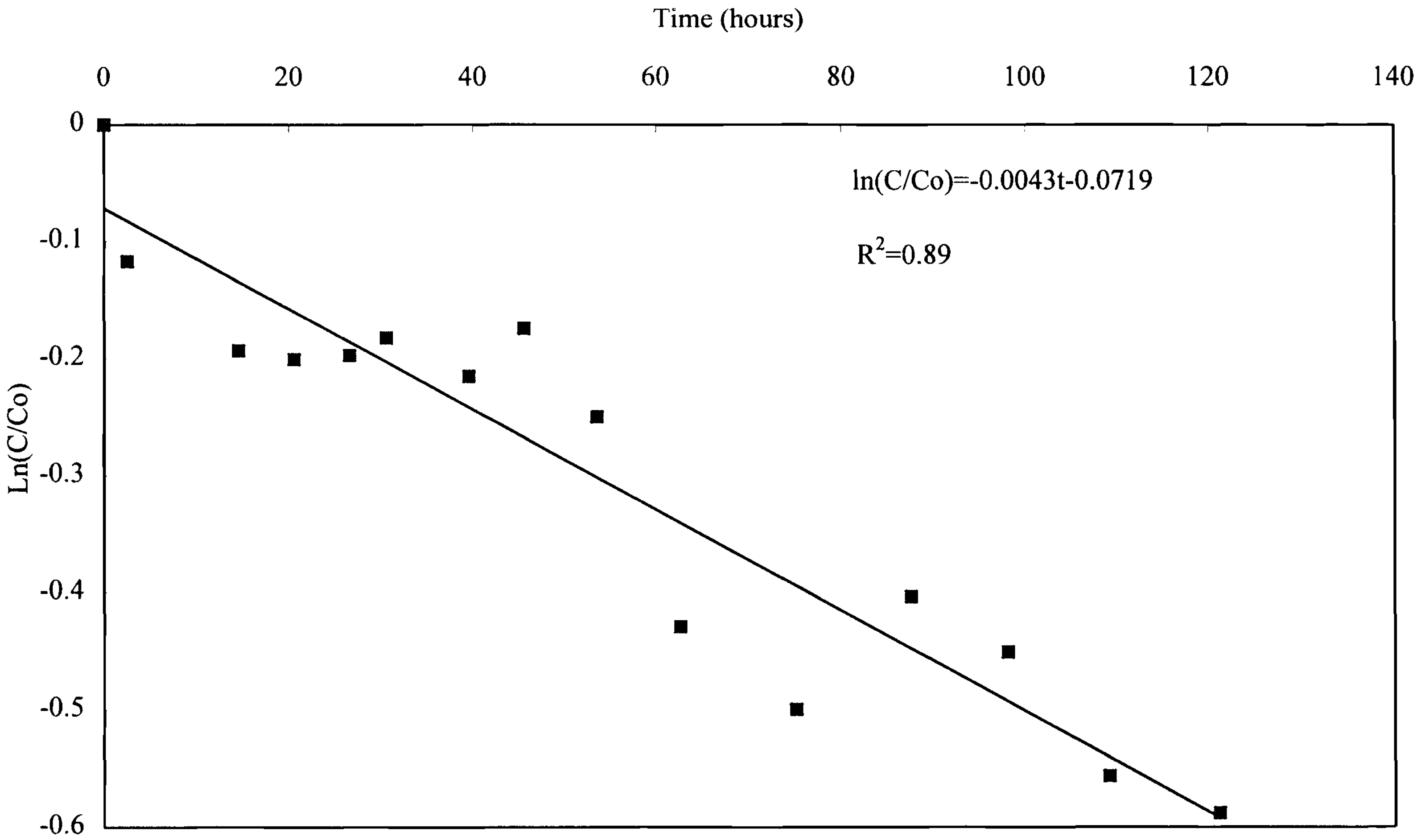


Figure 11. The first-order plot for 0.3 mg/L metolachlor and 11.6 mg/L bisulfide concentration.

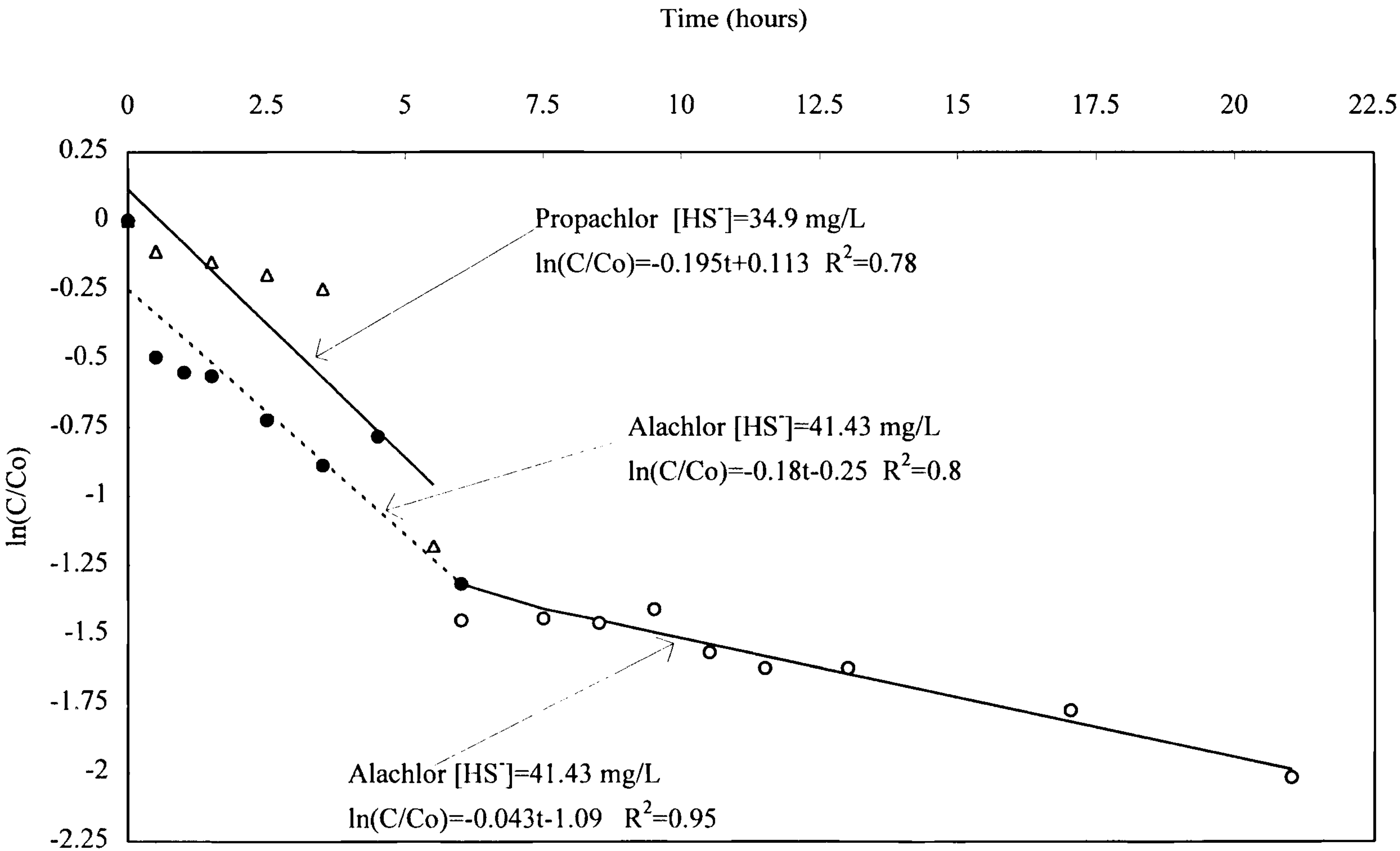


Figure 12. The first-order plot for propachlor and alachlor at higher bisulfide concentrations.

The bisulfide, may be transformed to other less reactive but unknown sulfide species, gradually losing its reactivity with herbicides. The sulfide titration revealed a stable concentration of total sulfide in solution, however.

Table II summarizes the results of all rate experiments of alachlor, butachlor, metolachlor, and propachlor in the presence of bisulfide concentrations over the range of 1.24 mg/L to 41.43 mg/L. Included are the K_{obs} and calculated K_{HS^-} values. The correlation coefficients for propachlor at bisulfide concentrations less than 20 mg/L were over 0.93 (with one exception). All were above 0.78 at bisulfide concentrations higher than 20 mg/L. All correlation coefficients for the first-order plots of alachlor were above 0.91, with two exceptions, as shown in the table. The correlation coefficients for the degradation of butachlor and metolachlor were also found to be above 0.85. The interpretation of this table leads to the conclusion that the rates of degradation of all four herbicides are first order in the herbicide concentrations investigated in this study.

Table II also gives 95% confidence interval of the K_{obs} values of the four herbicides under the various bisulfide concentrations. It was found that the half-lives of propachlor and alachlor were 3.1 and 5.7 days at the low bisulfide concentration of 4.11 mg/L (0.037mM) while reduced to less than 0.1 and 0.3 days at 34.9 and 41.43 mg/L individually. The half-lives of butachlor and metolachlor at bisulfide concentration of 13.4 and 11.6 mg/L were 2.6 and 6.7 days, respectively. All of these half lives are still significant on the time scale of groundwater transport. The second-order rate constants ranged from a low of 0.00037 (1/h/mg [HS^-] /L) for metolachlor to a high of 0.0055 (1/h/mg [HS^-]/L) for propachlor.

Table II. Kinetics summary of the abiotic reaction of alachlor, butachlor, metolachlor and propachlor with bisulfide at 21 °C and pH 7

	$[HS^-]$ (mg/L)	Kobs (1/hours)	95 % C.I. (±)	K_{HS^-} (1/hours/mg$[HS^-]$/L)	Half-lives (days)	R^2
Propachlor	1.24	0.0012	0.00028	0.000968	24.1	0.85
	2.95	0.0042	0.0014	0.00142	6.9	0.98
	4.11	0.0092	0.00082	0.00224	3.1	0.97
	4.28	0.0087	0.00185	0.00203	3.3	0.94
	6.44	0.0084	0.00155	0.00130	3.5	0.98
	8.8	0.0145	0.00340	0.00165	2.0	0.94
	19	0.0875	0.00713	0.00461	6.3	0.97
	20.6	0.0762	0.0171	0.00370	0.4	0.82
	24.7	0.0909	0.0202	0.00368	0.3	0.84
	31.78	0.0983	0.0285	0.00309	0.3	0.81
	34.9	0.1947	0.1437	0.00558	0.1	0.78
Average				0.00255		
Standard deviation				0.00132		
Alachlor	1.24	0.0020	0.00038	0.00159	14.7	0.91
	2.95	0.0041	0.00213	0.00140	7.0	0.84
	4.11	0.0051	0.0005	0.00123	5.7	0.96
	4.28	0.0041	0.00113	0.00096	7.0	0.84
	6.44	0.0038	0.00112	0.00059	7.5	0.94
	8.8	0.0064	0.00145	0.00073	4.5	0.95
	9.23	0.0123	0.0018	0.00133	2.3	0.93
	15.27	0.0446	0.0098	0.00292	0.6	0.96
	19.5	0.0346	0.004	0.00177	0.8	0.94
	20.6	0.0578	0.0106	0.00281	0.5	0.91
	33.1	0.0496	0.0127	0.00150	0.6	0.95
	34.9	0.0671	0.0095	0.00192	0.4	0.93
	41.43	0.0857	0.0211	0.00207	0.3	0.91
Average				0.00160		
Standard deviation				0.00071		
Butachlor						
	15.3	0.0118	0.002	0.000771	2.4	0.92
	13.4	0.0111	0.0033	0.000828	2.6	0.92
	15.3	0.0137	0.0078	0.000895	2.1	0.86
Average				0.00083		
Standard deviation				0.000062		
Metolachlor	11.58	0.0043	0.0009	0.000370	6.7	0.89

Note: The rate constant of propachlor at bisulfide concentration of 19 mg/L was not included in the calculation of averaged second-order rate constant of propachlor, resulting from using unwashed sodium sulfide.

Table III shows some different reaction rates obtained by Garrett (1993) as well as by this study. At the bisulfide concentration of 8.8 mg/L (0.27 mM), the rate constant of propachlor 0.0028 (1/h) obtained by Garrett was almost twice as high as that of this study 0.0016 (1/h). The rate constant of alachlor obtained in this study, 0.00079 (1/h), was lower than that reported by Garrett's (0.0011). A possible explanation for the differences of rate constants among these studies may lie in the procedures of preparing sulfide solution, that is, whether or not the oxidized surface layer of sodium sulfide was washed off.

Table III also shows the results of Barbash and Reinhard (1989). The same pseudo-first-order model was employed in their study to investigate the reaction of haloaliphatic compounds such as dibromoethane (DBE) with bisulfide. In a solution of 9.9 mg/L bisulfide, the observed rate constant of DBE decay was 0.00042 (1/h). The plot of ln (C/C_0) versus time yielded the correlation coefficient of 0.92, which showed a first-order dependence of reaction rate on the DBE concentration.

The pseudo-first-order model employed by Barbash and Reinhard (1989), as well as in this study, clearly fits the abiotic transformation by bisulfide of both haloaliphatic compounds such as DBE and haloaromatic compounds such as the herbicides of our interest here.

Correlation between Pseudo-First-Order Rate Constants and Bisulfide Concentrations

Referring to the model equation (4.2), the following equation $K_{obs} = K_{HS^-}\ [HS^-]$ is established. The observed rate constant is proportional to the bisulfide concentration if a

Table III. Comparison of kinetics of different studies at 21 °C and pH 7

	$[HS^-]$ (mg/L)	K_{obs} (1/hours)	K_{HS^-} (1/hours/mg$[HS^-]$/L)	Half-lives (days)	R^2
			Alachlor		
This study	8.8	0.00695	0.00079	4.2	0.95
Garrett (1993)	8.5	0.00935	0.0011	3.1	0.99
Wilber (1991)	8.5	0.01275	0.0015	2.3	0.99
			Propachlor		
This study	8.8	0.0145	0.0017	2.0	0.94
Garrett (1993)	8.5	0.0238	0.0028	1.2	0.99
			1,2-Dibromoethane (DBE)		
Barbash (1989)	9.9	0.00042	4.29E-05	69.31	0.92

plot of K_{obs} vs. [HS^-] passes through the origin. A plot of observed rate constants vs. concentration of bisulfide for the degradation of propachlor and alachlor is shown in Figure 13. It was found that an increase in bisulfide concentration from 0.0376 mM to 1.06 mM caused a corresponding increase in K_{obs} from 0.0012 (1/h) to 0.195 (1/h) for propachlor, and from 0.00197 (1/h) to 0.0857 (1/h) for alachlor respectively. A least-square analysis on the linear regression for propachlor, yields a correlation coefficient of 0.91. This indicates that the pseudo-first-order model of propachlor, $K_{obs} = K_{HS^-} [HS^-]$, at different bisulfide concentrations is valid. The correlation for alachlor is also shown in the same plot. Its correlation coefficient is above 0.80.

In order to verify the linear correlation described by the above method, the correlation between halogenated compounds and sulfide can also be tested in another way (Hagg and Hill, 1988). For the reaction of halogenated compounds with the bisulfide, taking logarithm of both sides of the equation, $K_{obs} = K_{HS^-} [HS^-]$ and plotting log K_{obs} vs. log [HS^-], a linear relation should be obtained if it is a first-order reaction. As shown in Figure 14, very good linear relationships were obtained as the correlation coefficients for both herbicides were above 0.91. The slopes of the plot, i.e., the reaction orders in bisulfide concentration were 1.3 for alachlor, and 1.5 for propachlor. This value should be 1 for a true first-order relationship. Given the variability of the data, these values are reasonably close.

If the abiotic reaction between herbicides and bisulfide follows the second-order model, when present in great excess, the bisulfide will not be significantly consumed, as indicated in Table IV. At the bisulfide concentration of 41.3 mg/L (1.25 mM),

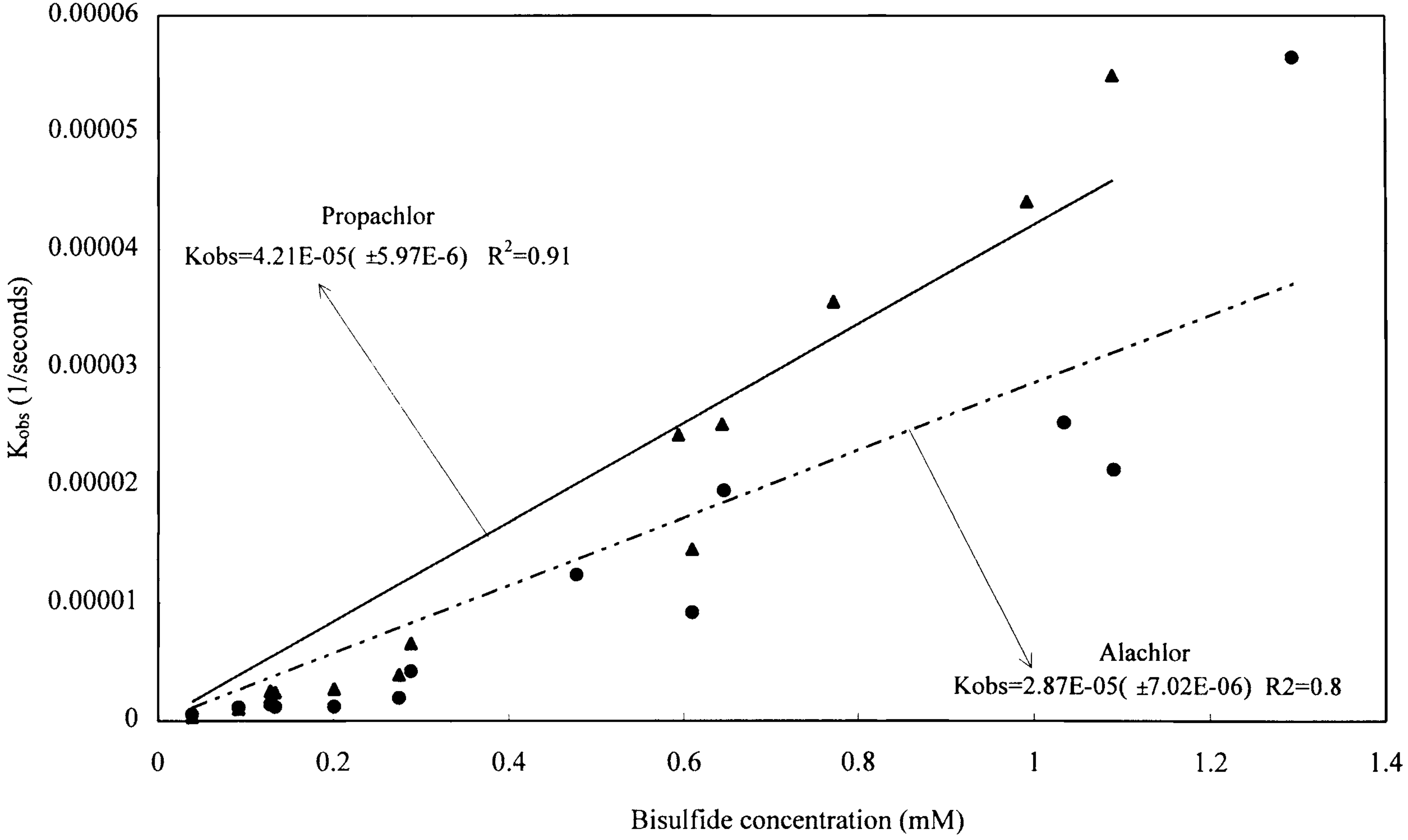


Figure 13. The correlation between K_{obs} and bisulfide concentration for propachlor and alachlor.

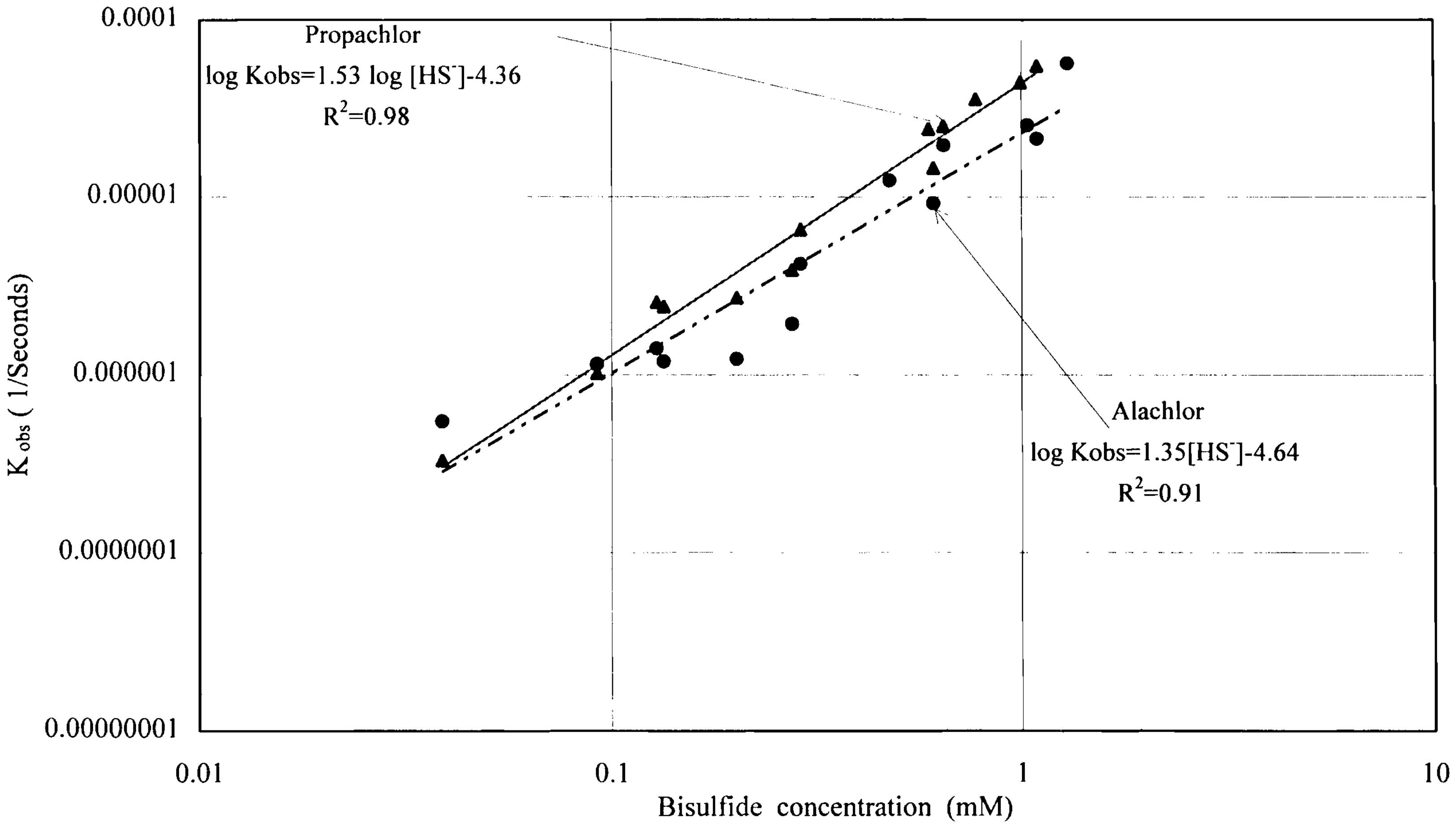


Figure 14. The first-order plot of log K_{obs} vs bisulfide concentration for alachlor and propachlor.

Table IV. Consumption of sulfide when reacting with alachlor

	2.95 mg/L			41.43 mg/L	
Time (hours)	[HS$^-$] (mg/L)	Pest. conc. (10E-03 mg/L)	Time (hours)	[HS$^-$] (mg/L)	Pest. conc. (10E-03 mg/L)
0	3.65	359	0	41.90	278
8	2.40	312	0.5	41.90	169
20	2.60	347	1	42.06	160
34	3.60	343	1.5	41.06	158
44	3.60	241	2.5	42.75	135
60	2.60	302	3.5	41.89	114
71	3.05	249	4.5	41.89	127
82	3.05	281	6	41.90	65
106	3.05	269	7.5	41.89	66
130	2.95	205	8.5	41.71	65
154	2.95	244	9.5	41.89	68
178	2.80	149	10.5	41.04	58
			11.5	38.80	55
			13	40.42	55
			17	41.04	47
			21	40.69	37

completely degradation of 0.3 mg/L (0.0014 mM) alachlor only decreased the bisulfide concentration from 41.90 mg/L to 40.69 mg/L over the period of 21 hours. At the low bisulfide concentration of 2.95 mg/L (0.12 mM), the decay of 0.0014 mM alachlor, which lasted eight days, decreased the bisulfide concentration by less than 20%. This low bisulfide consumption also was apparent during reaction with the other three herbicides, shown in Appendix A and D, for propachlor, and butachlor and metolachlor, respectively.

Reaction Order with Respect to Bisulfide

An additional experiment investigating the reaction order with respect to bisulfide was conducted with both herbicides and sulfide concentrations of 3 mg/L, room temperature and neutral pH. Here, the sulfide concentration could not be considered in "great excess". A first-order plot of "ln percent remaining herbicides" as a function of time for propachlor and alachlor is shown in Appendix F. In summary, it was found that the degradation of these two herbicides by sulfide did not appear to follow the first-order kinetic model very well, as shown by the correlation coefficients of alachlor and propachlor of 0.8 and 0.5, respectively. The second-order rate constants K_{HS^-} of propachlor and alachlor were 0.0012 and 0.0013 (1/h/mg [HS^-]/L) which were similar to those found at a herbicide concentration of 0.3 mg/L (as shown in Table II). It implied that loss of sulfide does not fit the model as expected. Bisulfide concentrations remained fairly constant throughout the reaction time. Therefore, it was not possible to test the model equation with both sulfide and herbicide changing over time. Ideally, this experiment should be run with herbicide present at an order-of-magnitude (or more) greater concentration than bisulfide. However, the lower limits of the sulfide titration method (approximately 3 mg/L) make this difficult.

Correlation between Second-Order Constants and Bisulfide Concentrations

As indicated in Figure 9, pseudo-first-order kinetics were observed in the systems in which the concentration of alachlor at 287 μg/L (0.00107 mM) was relatively low compared with the initial concentration of bisulfide of 1.24 mg/L (0.0376 mM); i.e., the bisulfide concentration was almost 35 times as high as that of the herbicides. At a concentration of bisulfide as high as 1.25 mM, the sulfide concentration is 1210 times higher. This indicates that the reaction was, indeed, under pseudo-first-order reaction conditions. Figure 15 shows the correlation between the second-order rate constant and [HS$^-$] for alachlor. After averaging all second-order rate constants, K_{HS^-}, listed in Table II, an average value of 0.0016 (1/h/mg [HS$^-$]/L) for alachlor was obtained, which is shown in the figure by the dashed line. It was found that at least five data points are close to the averaged value, even while other data show significant variances. This indicates that the degradation of alachlor may follow the second-order model in which the rate constants remain unchanged no matter what the bisulfide concentration. Illustrated in Figure 16 is the correlation between the second-order rate constant K_{HS^-} and bisulfide concentration for propachlor. The correlation was similar to that of alachlor, though with rate constants more scattered away from their averaged value of 0.0026 (1/h/[HS$^-$] mg/L).

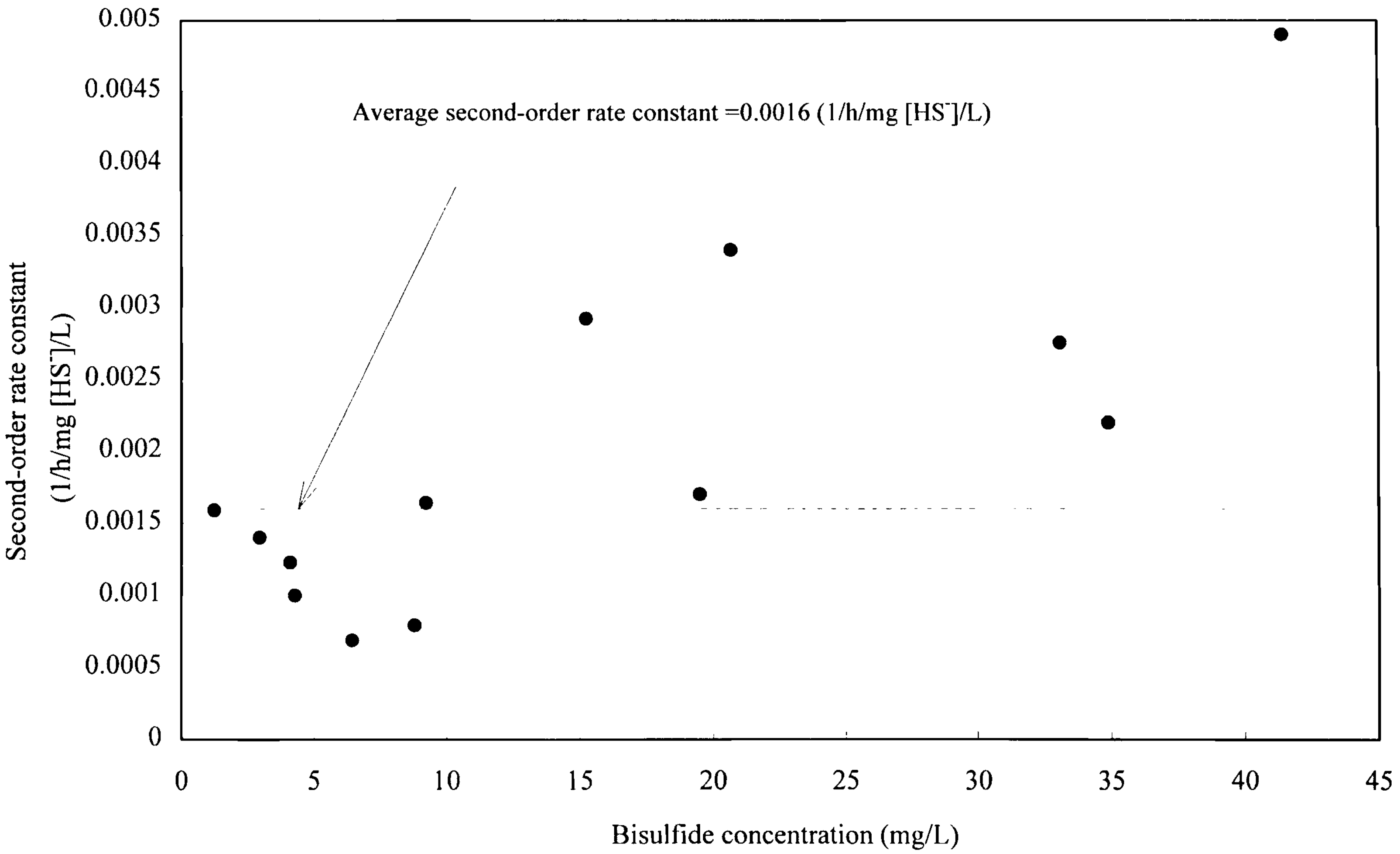


Figure 15. The correlation between second-order constant and bisulfide concentration for alachlor.

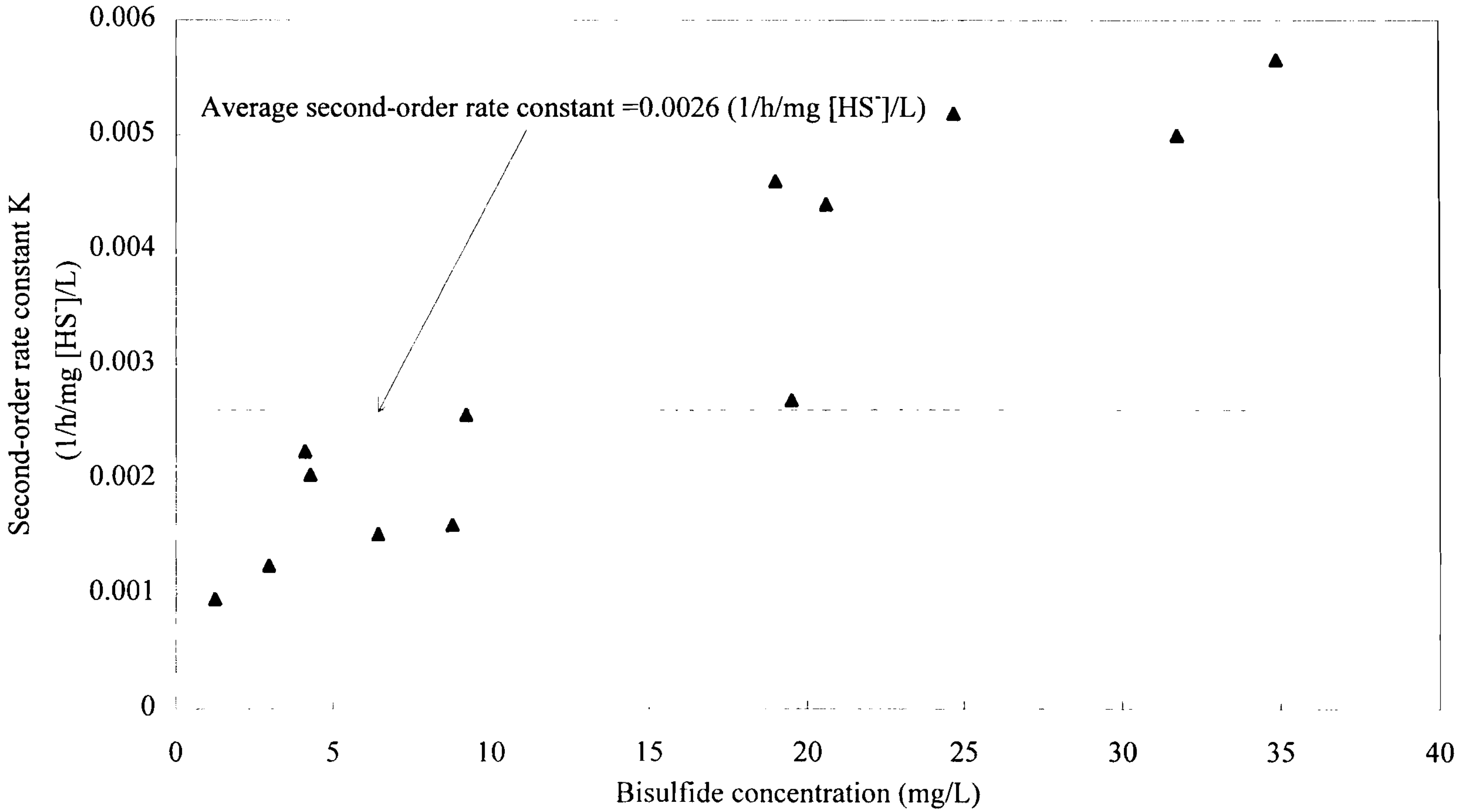


Figure 16. The correlation between second-order constant and bisulfide concentration for propachlor.

The deviation from the second-order model may be attributed to several factors. First, the volatile nature of sulfide makes the accurate titration of high sulfide concentrations extremely difficult, resulting in lower than actual HS^- concentrations measured, which then yield falsely high second-order rate constants. This would result in lower bisulfide concentrations, yielding lower second-order rate constants. Secondly, since the complex speciation of sulfides in solution is not well defined, it may cause other unknown reactions that compete for bisulfide (for instance, polysulfides), resulting in variance of rate constants. These would become much more prevalent at high sulfide concentrations.

Effect of Temperature

The effect of temperature on the pesticide transformation rates was studied over the temperature range of 8 °C to 35 °C. All experiments were performed with constant initial concentrations of 0.3 mg/L herbicides and 20 mg/L of bisulfide, buffered at pH7. The corresponding phosphate control experiments were also conducted at the same time.

It was found in these control experiments that no loss of herbicides kept overall reaction period. A plot of "ln alachlor remaining vs. time" at three temperatures, 8 °C, 21 °C and 35 °C, is shown in Figure 17 (Appendix G). The plot indicates that temperature had considerable effects on the reaction rate of alachlor. When the temperature was increased by a factor of 2.6, i.e., from 8 °C to 21 °C, the degradation rate of alachlor increased from 0.0102 (1/hour/[HS^-]mM) to 0.0586 (1/hour/[HS^-]mM) (i.e. +474.5 %). The reaction rate at 35 °C was 17 times higher than that at 8 °C. The temperature effects on the degradation of the other three herbicides under the same

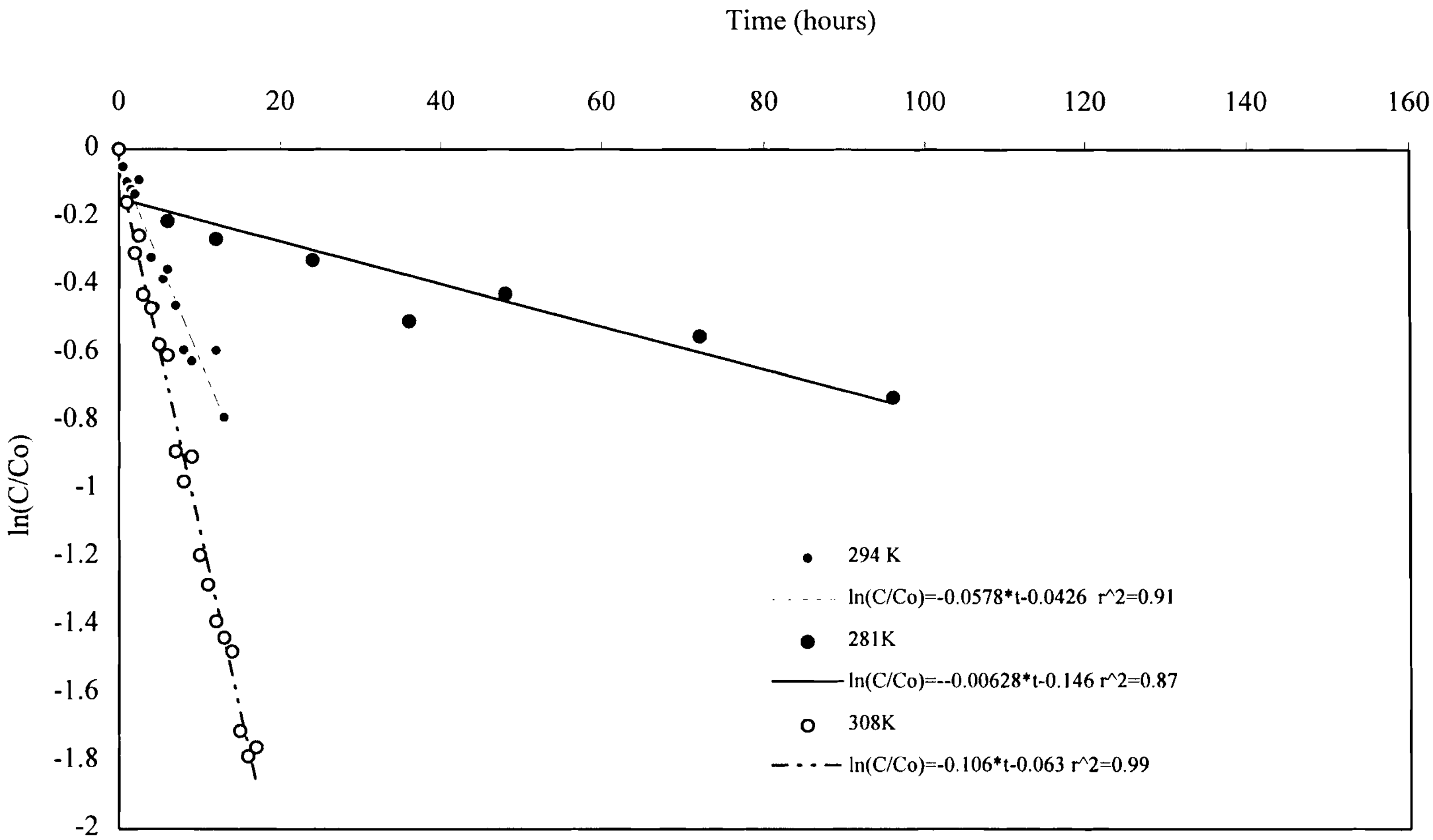


Figure 17. The effect of temperature on the degradation of alachlor at bisulfide concentration of 20 mg/L.

conditions are summarized in Table V. For propachlor, the most simple herbicide in structure among the four acetanilides, when temperature was increased by a factor of 2.6, i.e. from 8 °C to 21 °C, the degradation rate was increased by 7 times, while the reaction rate at 35 °C was 33 times faster than that at 8 °C. Whether at 35 °C or 8 °C, the degradation rates of herbicides were in the same order as those at room temperature. i.e. propachlor >alachlor>butachlor>metolachlor.

Arrhenius Plot

The Arrhenius equation was employed in this study to investigate the energetics of the reaction of bisulfide and the herbicide, assuming that this is the dominant reaction. The dependence of the K_{HS^-} on temperature was found by fitting the rate constants of four herbicides at three different temperatures to the Arrhenius equation:

$$K_{HS^-} = A \times e^{(\frac{Ea}{RT})} \qquad (4.3)$$

A plot of log K_{HS^-} vs. 1/T is shown in Figure 18, which indicates that the temperature dependence of pesticide degradation rates in the presence of sulfide has a linear relationship. The correlation coefficients (R^2) for all four herbicides were greater than 0.92.

The activation energies (E_a) for the abiotic reaction of the four herbicides with bisulfide, and the Arrhenius pre-exponential factors, A, for each herbicide are listed in Table V. These results show that the activation energy for propachlor is the highest among the four herbicides, followed by alachlor, metolachlor, and butachlor,

Table V. Temperature effect on degradation of herbicides at pH7 and bisulfide concentration of 20 mg/L

Temperature (K)	Alachlor K (1/h/mM)	Butachlor K (1/h/mM)	Metolachlor K (1/h/mM)	Propachlor K (1/h/mM)
281	0.0102	0.0044	0.00208	0.0154
294	0.0980	0.0255	0.01223	0.0960
308	0.1740	0.0563	0.03119	0.5024

Parameters of Arrhenius plot

Ea:(Kcal/mol)	18.1	16.3	17.3	22.2
A:(1/hours/mM)	1.60E+12	2.40E+10	6.50E+10	2.88E+15

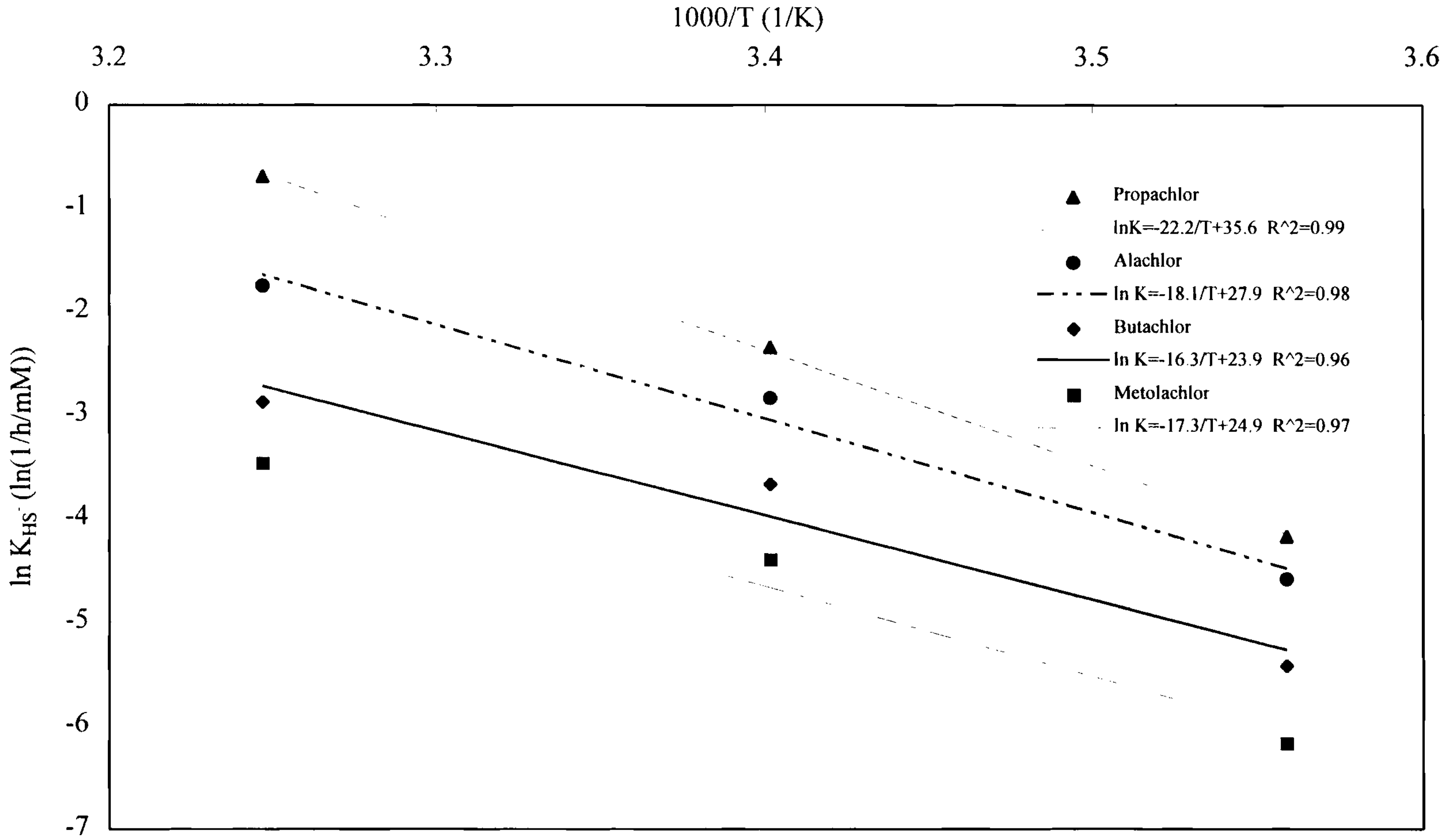


Figure 18. The Arrhenius plot for the degradation of herbicides at pH7 and [HS^-]=20 mg/L.

respectively. These results conflict somewhat with the general rule that the reaction rate is inversely related to activation energy, i.e., a faster reaction implies a lower activation energy. Given the variation in the K_{HS^-} values found, the activation energies for each herbicide are still in the same order of magnitude. This is not surprising, given the relative similarities in their structure among the herbicides. The Arrhenius plot of the data yields activation energies from 16.3 KJ/mol for butachlor to 22.2 KJ/mol for propachlor. The differences among the rates of degradation for the four herbicides may be explained by using the relative magnitude of the frequency or entropy factor, A. The larger the value of A of a chemical, the faster the reaction. A (1/mM/hours) values of the four herbicides ranged from 2.6×10^{15} for propachlor, 1.3×10^{12} for alachlor, 2.4×10^{10} for butachlor, and 6.5×10^{10} for metolachlor. Based on these A values, propachlor should have the fastest degradation rate among the four herbicides, followed by alachlor. Because the entropy factors of metolachlor and butachlor are within one order of magnitude, the difference of the A values was not enough to predict that the metolachlor will be degraded faster than butachlor even though the A value of metolachlor was somewhat higher than that of butachlor.

Testing Reaction with Phosphate Buffer

In order to investigate the reaction between phosphate salts and halogenated compounds as has been found in other studies (Barbash and Reinhard, 1989), three sets of experiments were conducted to investigate the effect of buffer on the degradation of the herbicides (alachlor and propachlor) at pH 7. Phosphate buffer capacities of 0, 5 and 50 mM were employed respectively, and the results are shown in Figure 19 (Appendix H). No rate enhancement-effect of the phosphate buffer on the disappearance of two herbicides, unlike that observed by Barbash and Reinhard (1989) for EDB and DCA, was found in this study. Under different phosphate buffer capacities, the concentrations of the two target herbicides fluctuated irregularly about an average of 326 μg/l over a duration of 132 hours at room temperature, with a standard deviation of 6.4%. There is no evidence that any significant reaction was occurred during the reaction period. This result is somewhat contradictory to the prediction of Perdue and Wolfe (1983) who reported that phosphate buffer at the concentration above 0.001 mM may play a potential buffer catalysis in laboratory studies. It is also different from the result of kinetic studies for the abiotic reaction of halogenated aliphatic compounds by Barbash and Reinhard (1989). In their study, the phosphate buffer at 50 °C and 87.5 °C was found to accelerate the nucleophilic substitution reaction of EDB and 1,2-DCA. However, it is consistent with the study of Weintraub (1989) who investigated the reaction of EDB with bisulfide under environmental conditions. 5 mM of several buffer solutions (including carbonate, phosphate, boric acid), with pH range from 4 to 9, were used as controls. No buffers (including phosphate buffer) showed buffer-catalysis abilities on the disappearance of EDB except boric acid buffer at pH 7.8 to 8.3.

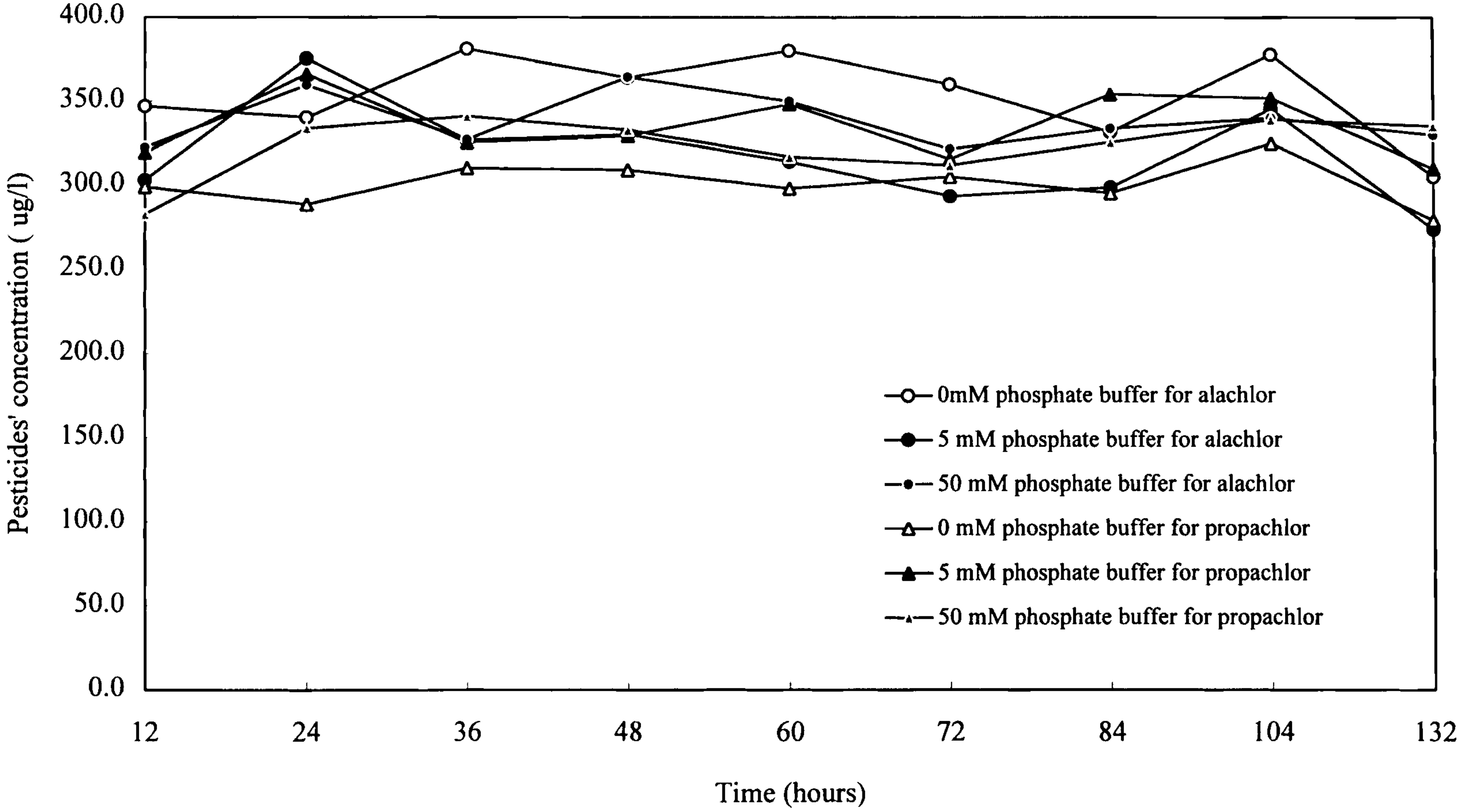


Figure 19. The effect of buffer capacities on the abiotic reaction of alachlor and propachlor at pH 7 and 21 °C.

pH Dependence

Since either low pH or high pH are known to catalyze abiotic reactions (such as hydrolysis), four sets of experiments were set up to investigate the effect of pH on the abiotic reactions. Experiments were conducted at pH 4 and 12 with phosphate buffer solutions alone, and at pH 4 and 12 with phosphate buffer solution containing 40 mg/L sulfide, all at room temperature.

Because bisulfide is thought to be the reactive species among the sulfide species, it is helpful to identify the fraction of bisulfide among sulfide species. A distribution curve (as shown in Appendix I), with regard to the distribution of H_2S, HS^- and S^{2-} among sulfide species as function of pH, can be determined. At pH 4, H_2S predominates the sulfide species with a concentration of 98%, while S^{2-} predominates at pH 14. Between pH 7 and 12, bisulfide plays a dominant role and has a maximum at pH 10. The effects of these species on the reaction will be discussed in following section.

Based on the different bisulfide fractions in solution over the pH range of interest, the observed rate constants, K_{obs} can be used to predict the decay of herbicides at pH 4 and 12. The second-order rate constant, K_{HS^-} and K_{H_2S} can be used to predict the correlation between rate constants and pH.

Effect of pH 4 on Sulfide Reaction

As described by Snoeyink and Jenkins (1980), at pH 4, all sulfide is hydrogen sulfide. Two sets of experiments were performed to investigate the effect of pH 4 on the abiotic reaction of the four herbicides. One was conducted in pH 4 buffer solution alone and another was conducted at the same pH with 40 mg/L sulfide. As shown in Figure 20 (Appendix J), over a duration of 250 hours, there was little difference between the initial and final concentrations of all four herbicides in the pH 4 phosphate buffer solution alone, indicating that acid-hydrolysis is insignificant.

Figure 21 (Appendix K) shows that the low pH does not significantly stimulate the degradation of herbicides, since only 0.098% of the sulfide is present as bisulfide (HS^-). The average K_{obs} values are 0.0006, 0.00056, 0.00044, and 0.00091 (1/hours) for alachlor, butachlor, metolachlor and propachlor, respectively, which can be considered much slower reaction rates when compared with the results obtained at pH 7 under the same conditions. The correlation coefficients of the least-square regression line for the herbicides are 0.43,0.8,0.76, and 0.53 respectively.

Effect of pH 12 on Sulfide Reaction

At pH 12, 88% of sulfide is in the form of bisulfide. Two sets of experiments were performed to investigate the effect of pH 12 on the abiotic reaction of the four herbicides. One was conducted in pH 12 buffer solution alone and another was conducted at the same pH with 40 mg/L sulfide. As shown in Figure 22 (Appendix L), little difference is observed between the initial and final concentrations of alachlor, butachlor and metolachlor in the pH 12 phosphate buffer solution, indicating that base-hydrolysis was insignificant over a duration of 30 hours. The behavior of propachlor is an exception. It appeared to hydrolyze quickly in the first 13 hours and then suddenly

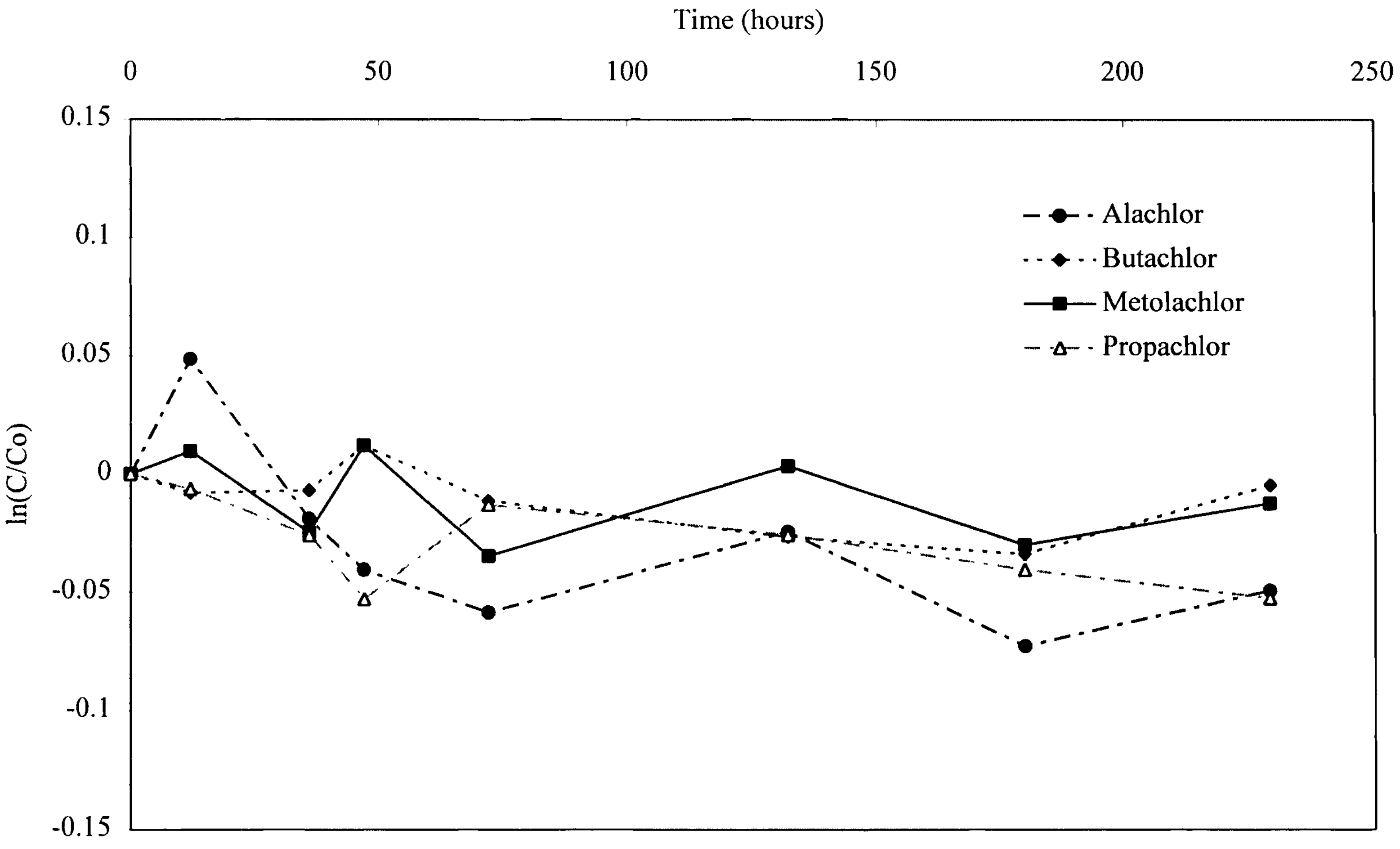


Figure 20. The effect of pH 4 on the degradation of four herbicides at 21 °C and 50 mM buffer only.

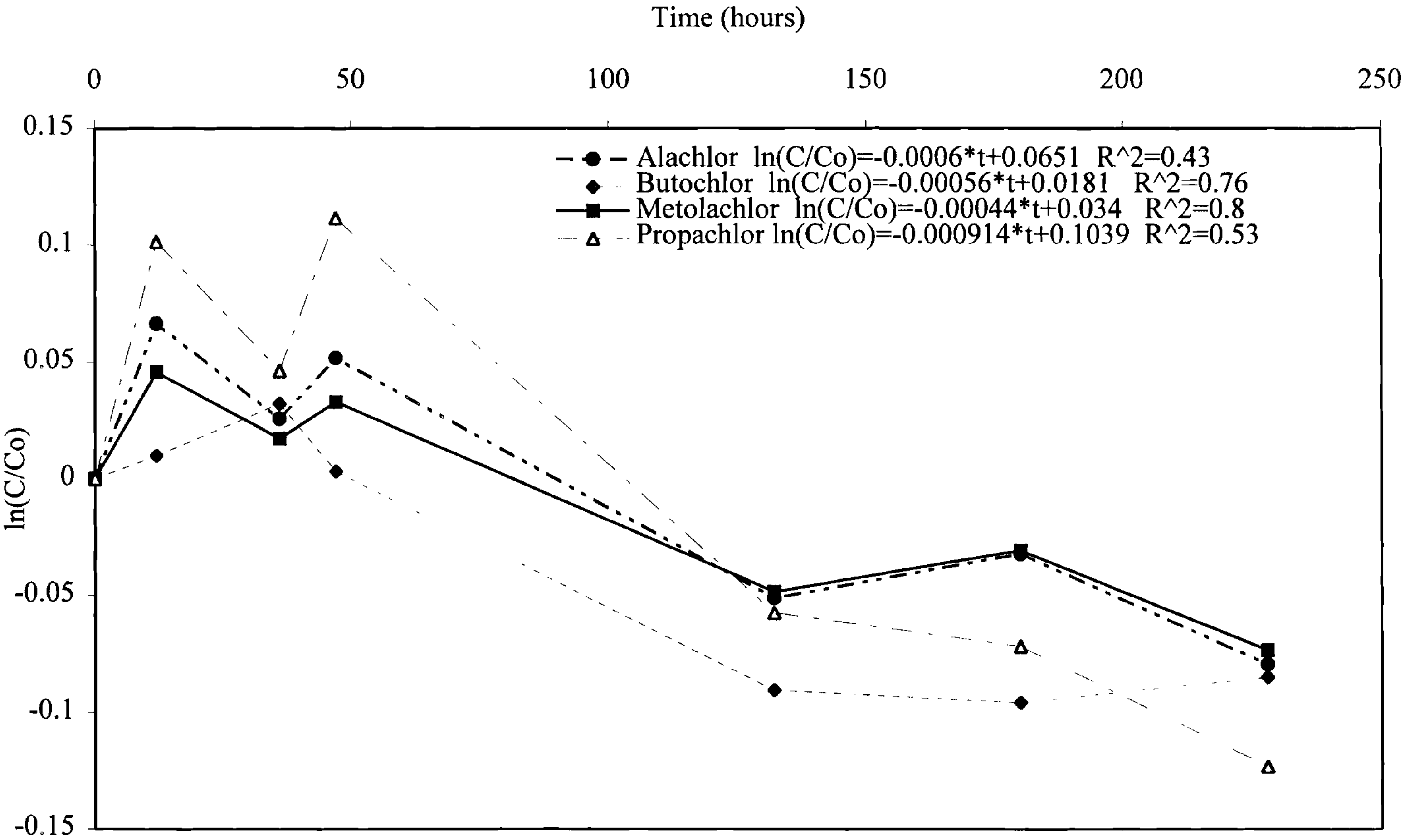


Figure 21. The effect of pH 4 on the degradation of four herbicides at total sulfide concentration of 40 mg/L.

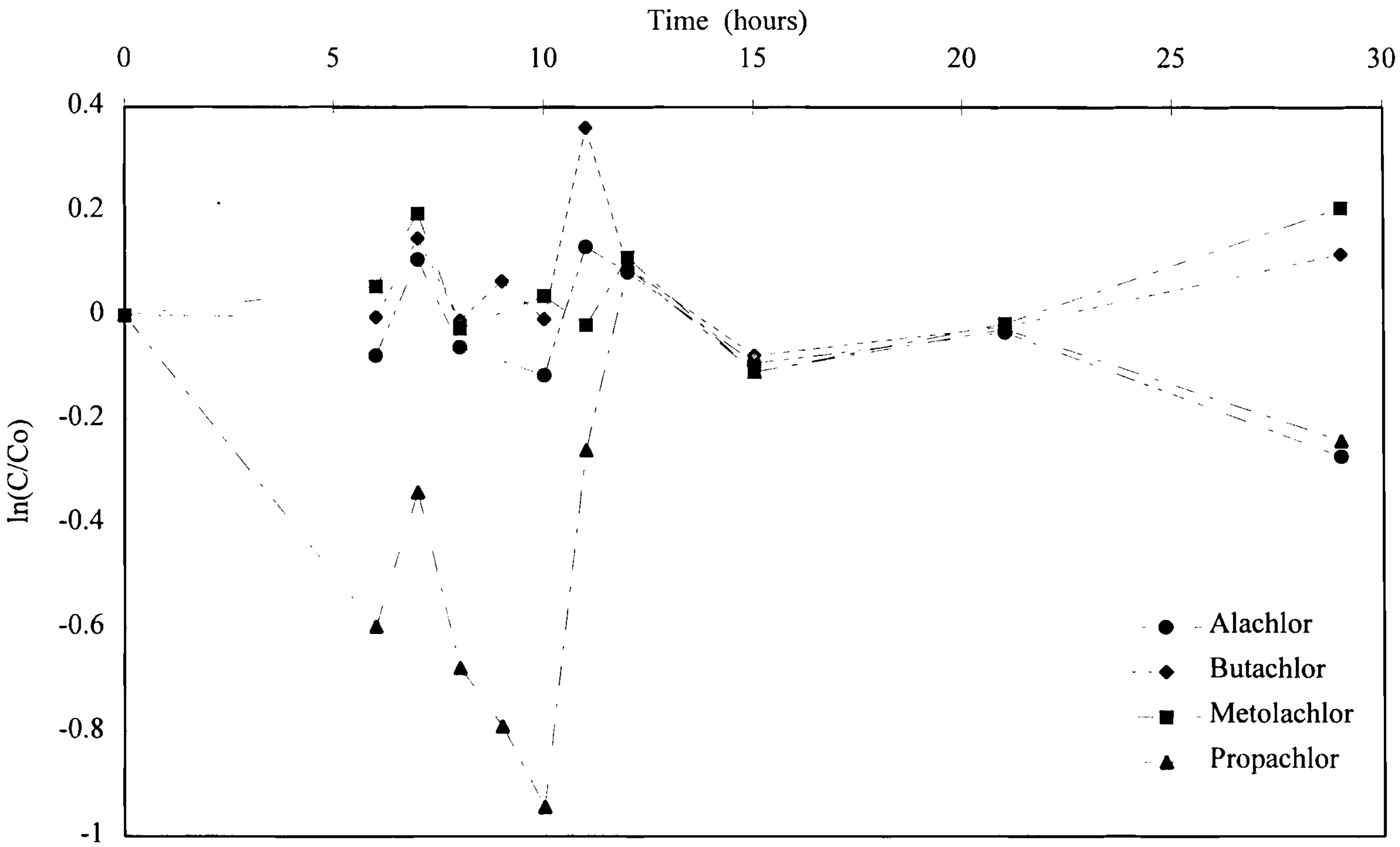


Figure 22. pH12 effect on the degradation of four herbicides at 21 °C and 50 mM buffer only.

returned to the original concentration. Clearly, this must be the result of an experimental error. This experiment ought to be repeated to verify that this was strictly an anomalous result.

Figure 23 (Appendix M) shows the degradation of four herbicides (at the concentration of 0.3 mg/L) at pH 12 with 40 mg/L sulfide concentration. The rate constants for all four herbicides at pH 12 are somewhat larger than those at pH 7. The K_{obs} increases with the increase of pH value because the fraction of bisulfide, considered as either a strong nucleophilic or strong reductive agent, increases with pH. At pH = 12, at least 88% of sulfide species are bisulfide (HS^-) while only 50% bisulfide exists in solution at pH7. The correlation coefficients of three herbicides, alachlor, butachlor and propachlor are above 0.85, though that of metolachlor is only 0.43. Metolachlor clearly reacts more slowly than the other three herbicides even under this relatively high pH and sulfide concentration.

Correlation between Second-Order Constants and pH

The second-order rate constants for the reaction of herbicides with sulfide can be expressed in terms of either total sulfide (K_{H_2S}) or bisulfide only (K_{HS^-}), calculated as follows:

$$K_{H_2S} = \frac{K_{obs}}{[H_2S]_T} \qquad (4.4)$$

$$K_{HS^-} = \frac{K_{obs}}{[HS^-]} \qquad (4.5)$$

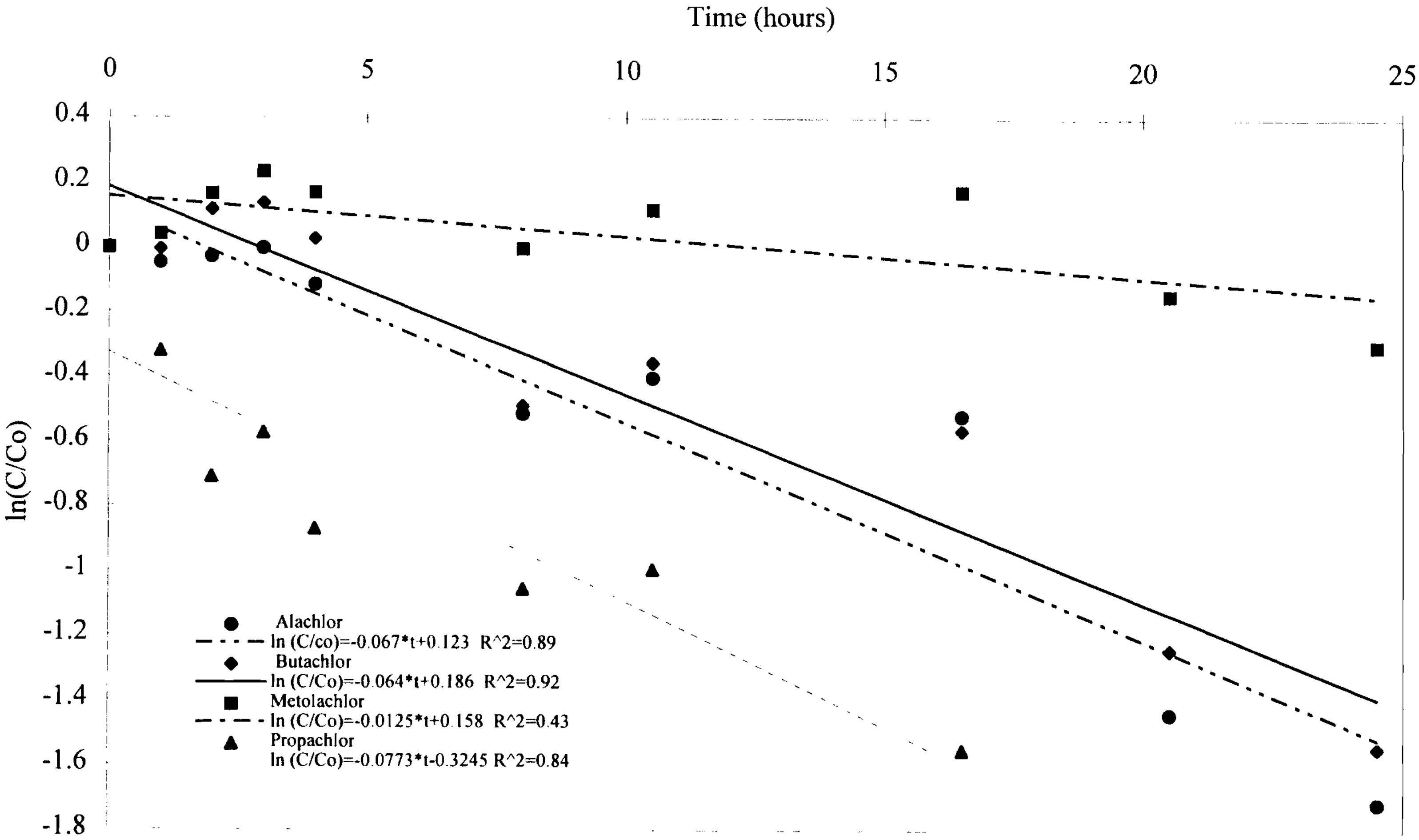


Figure 23. pH12 effect on the degradation of four herbicides at total sulfide concentration of 40 mg/L.

where $[H_2S]_T$ is the total initial molar concentration of sulfide as H_2S (aq), and $[HS^-]$ is the initial molar concentration of bisulfide(i.e. only the fraction in the HS^-).

The experiments at pH 4 and pH 12 demonstrated that the degradation of herbicides were not acid or base catalyzed reactions. However, the changes of pH govern the distribution of sulfide species in solution. Figure 24 (and the data summarized in Table VI) illustrates the pH dependence of the sulfide species distribution over the pH range 4 - 12. This plot roughly follows a distribution diagram for HS^- in the pH region 4-12 (Snoeyink and Jenkins, 1980). In the pH range 4 - 7, the slope of K_{H_2S} vs. pH increases with the increase in pH, just as fraction of bisulfide also increases with the change of pH. Almost 50 % of initial sulfide was found in the form of bisulfide at pH 7. Above that pH, bisulfide replaces hydrogen sulfide as the predominant reactive species. Hence, the resulting total sulfide concentration-corrected second-order rate constants should remain constant above pH 8. In the region below pH 4, the decrease in K_{obs} tapers off and gives a slope which approaches zero because 99% of initial sulfide remains its H_2S form, which reacts slowly with herbicides. This result is in agreement with that obtained by Hagg (1988). Figure 25 (summarized in Table VII) shows the correlation between K_{HS^-} and pH after correcting for the bisulfide concentration. K_{HS^-} should therefore be independent of pH. However, the K_{HS^-} at pH 4 is almost 2 orders of magnitude larger than that at pH 7 through pH 12. Hydrogen sulfide or other unknown sulfide species may take part in a reaction with herbicides or the acidic conditions may be catalyzing the reaction with the small amount of HS^- present.

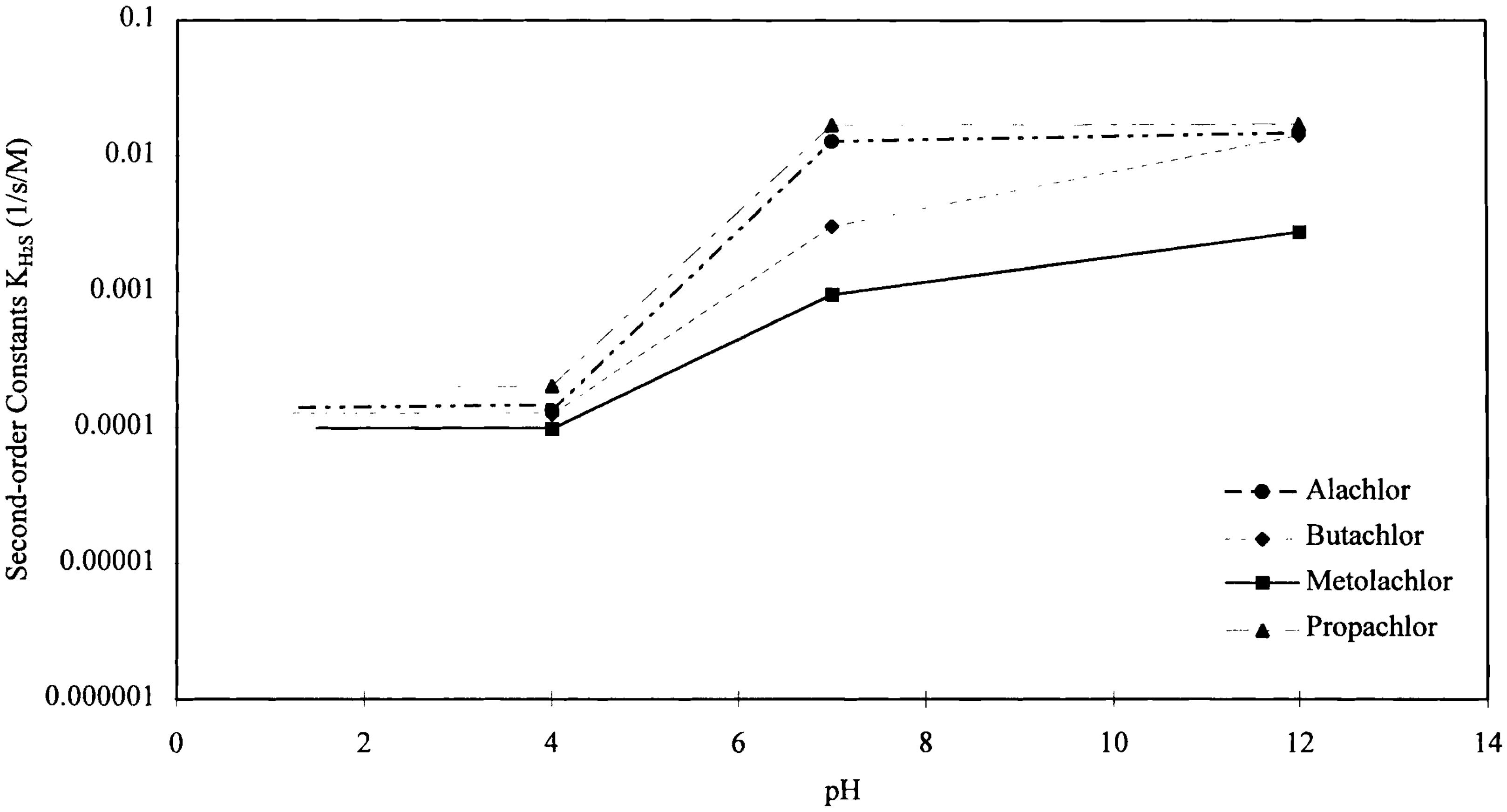


Figure 24. pH effect on the second-order constants of four herbicides at total sulfide concentration of 40 mg/L.

Table VI. The correlation between pH and the second-order rate constant at the total sulfide concentration of 40 mg/L

pH	Alachlor K_{H_2S} (1/s/ M)	Butachlor K_{H_2S} (1/s/ M)	Metolachlor K_{H_2S} (1/s/ M)	Propachlor K_{H_2S} (1/s/ M)
4	133.3E-6	124.4E-6	97.8E-6	203.1E-6
7	12.8E-3	3.0E-3	955.6E-6	16.9E-3
12	14.9E-3	14.2E-3	2.8E-3	17.2E-3

Table VII. The correlation between pH and the second-order rate constant at the bisulfide concentration of 20 mg/L

pH	Alachlor K_{HS^-} (1/s/ M)	Butachlor K_{HS^-} (1/s/ M)	Metolachlor K_{HS^-} (1/s/ M)	Propachlor K_{HS^-} (1/s/ M)
4	140.9E-3	131.5E-3	103.3E-3	214.6E-3
7	26.5E-3	6.3E-3	2.0E-3	34.9E-3
12	17.4E-3	16.7E-3	3.2E-3	19.9E-3

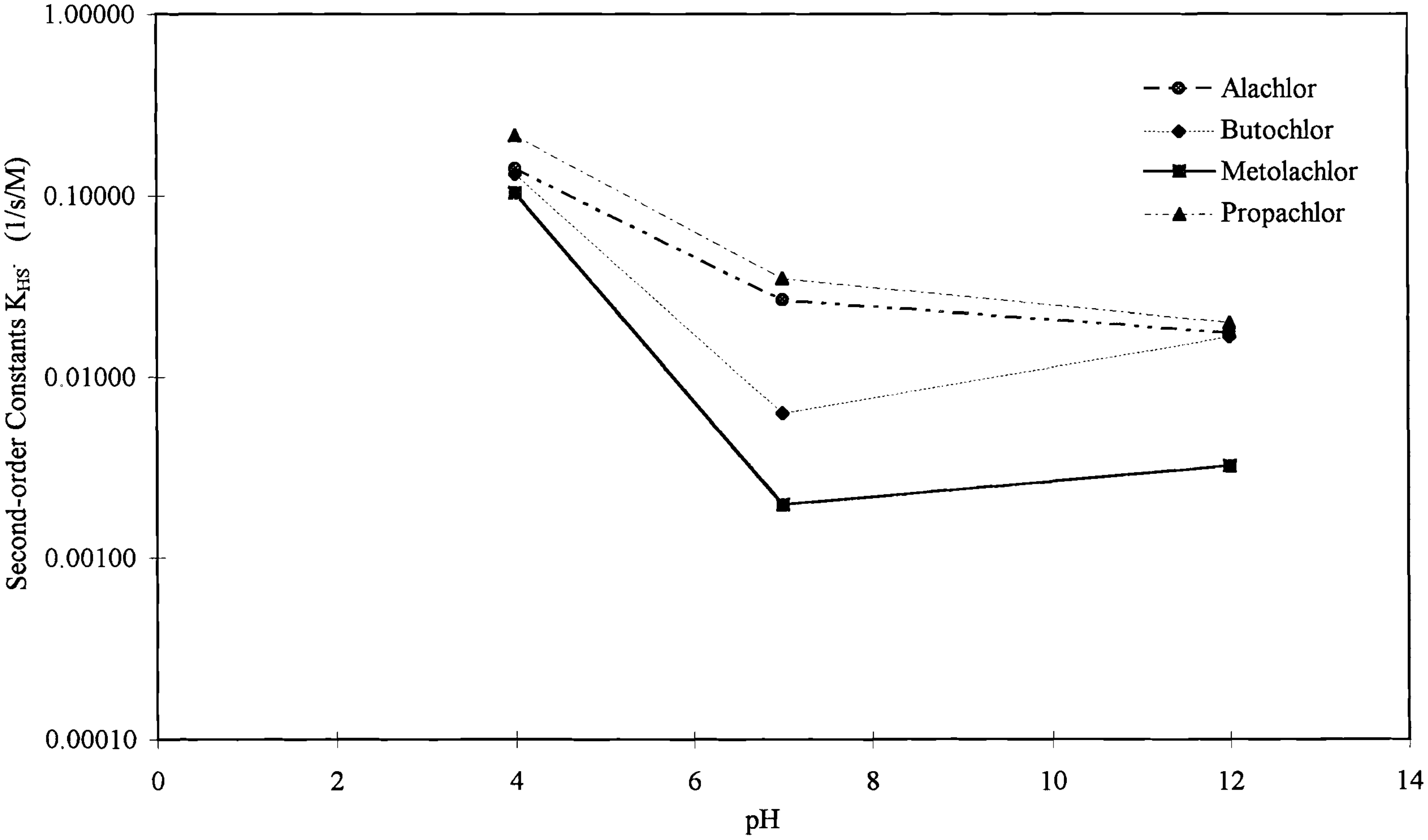


Figure 25. pH effect on the second-order constants of four herbicides at bisulfide concentration of 20 mg/L.

In summary, under the experimental conditions of this study, the reactions between these herbicides and bisulfide are first order with respect to herbicide concentration and approximately second order overall. Earlier studies on similar reactions inferred this (Wilber and Parkin, 1991; Garrett 1993) but did not thoroughly test it. Data in Figures 19, 20 and 23 indicate that phosphate buffers do not have a significant effect on these reactions. Furthermore, pH 4 and pH 12 do not appear to contribute acid- or base-catalysis for the reaction. As such, the following kinetic equation can be adapted to predict the disappearance of the four herbicides under conditions similar to groundwater.

$$-\frac{d[C]}{dt} = K_{HS^-} \times [C] \times [HS^-] \qquad (4.6)$$

Summary of the Relative Reactivities of the Four Acetanilide Herbicides

The comparison of the abiotic reaction rates among the four herbicides at 21 °C, pH = 7, is shown in Figure 26 (Appendix N). The second order rate constants of metolachlor, butachlor, alachlor, and propachlor were 0.00037, 0.00083, 0.00145, 0.0016 (1/h/ mg [HS^-] /L), respectively. Hence, the rate preference of the abiotic degradation for the four herbicides is in the order of propachlor > alachlor > butachlor > metolachlor. The temperature dependence of the degradation of four herbicides, as shown in Table IV, is in the same order. Tables VI and VII, in conjunction with Figures 23, 24 and 25 demonstrate that the pH dependence on the decay of four herbicides also follows the same order: propachlor>alachlor>butachlor>metolachlor.

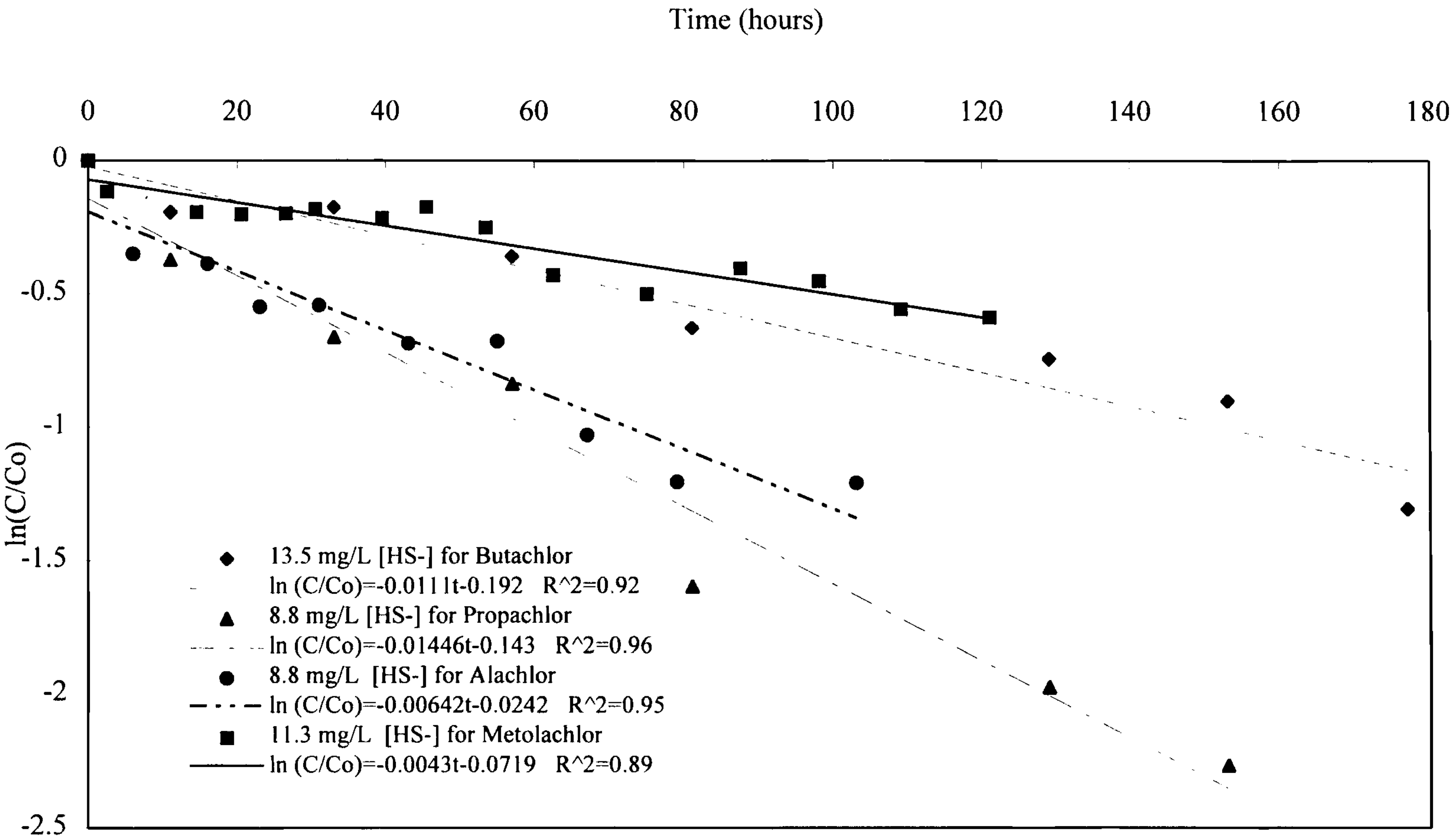


Figure 26. Comparison among the abiotic reaction of four herbicides at 21°C, pH 7, and similar bisulfide concentrations.

Based on the rate constants of four herbicides obtained above, an attempt can be made to explain why one rate constant is larger than another by simply comparing the differences in their molecule structures. The lower rate constant of alachlor than that of propachlor may be caused by steric hindrances imposed by the substitutions of two ethyl groups in alachlor's aromatic ring. The attacks toward the compound's most active site (i.e. the chlorine) by bisulfide may be inhibited. However, this explanation is not enough to account for the rate differences among alachlor, butachlor and metolachlor. The structural difference of butachlor from alachlor is that the butoxy group is substituted for the side chain methoxy group of alachlor. This substitution may also gave rise to steric influences that somewhat reduced the abiotic transformation of butachlor. The presence of a tertiary structure linked with the amide in metolachlor may adversely affect its reactivity. Metolachlor was found to be degraded two times more slowly than butachlor in this study. Their main structural difference is the ethyl groups on the benzene and groups in the link of amide. However, as is apparent from the discussion above, any effort to predict the abiotic rate constants from intuitive structural inferences is very difficult, particularly for compounds structurally very close to each other. Due to the limits of this study, it is not possible to perform definitive product identification using GC-MS or to do further in-depth structure/activity evaluation by quantifying steric properties, Taft constants, van der waals radii, etc. to make quantitative prediction for these herbicides.

Previous studies have demonstrated that bisulfide is a strong nucleophile which may attack the halogen elements of halogenated alkanes through nucleophilic substitution reactions (Barbash and Reinhard, 1989; Schwarzenbach et al., 1985; Hagg, 1988; Weintraub,1989). Though the four herbicides of interest here are aromatic compounds, nucleophilic substitution reaction by bisulfide attack on the halogen may still occur, since the chlorine is located on the alkyl groups linked to the benzene ring. Furthermore, it was also concluded from these various studies that a variety of sulfur-containing products can be formed even from a single halogenated alkyl compound. This is due to the very complicated mechanisms involved in addition to the nucleophilic substitution reaction. For example, for similar abiotic reaction conditions using DBE reacting with bisulfide, 1,2-ethanedithiol was produced, as expected (Hagg, 1988; Barbash and Reinhard, 1989), while a series of cyclic sulfides, disulfides and trisulfides was found in the Weintraub's similar study (1989). These sulfur-containing compounds may also cause concern because they may be very persistent in the subsurface (Barbash and Reinhard. 1989; Weintraub, 1989). Therefore, the products from this study, that is, the end products or the intermediates of abiotic reaction of herbicides with bisulfide, may cause similar concerns associated with potential health risks. This is true despite the fact that it is not clear whether those herbicides undergo direct nucleophilic substitution by the attack of bisulfide or whether they proceed through other unknown reactions.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

This study has provided a look into the abiotic transformation of alachlor, butachlor, metolachlor, and propachlor under reductive conditions in the presence of hydrogen sulfide. The effects of several specific environmental parameters, including sulfide concentration, temperature and pH, on the abiotic transformation of the four herbicides of interest were also investigated.

The main findings of this study are as follows:

- The overall abiotic reaction between these herbicides and bisulfide follows pseudo first-order kinetics with regard to herbicide concentration, when bisulfide concentration is present in excess.
- After bisulfide concentration was divided into the pseudo-first-order rate of herbicide disappearance, second-order rate constants were obtained. The average second-order rate constants and standard deviation at 21 °C and pH 7 for propachlor, alachlor, butachlor, and metolachlor were 0.0026 (±0.0013), 0.0016 (±0.00071), 0.00083 (±0.000062), and 0.00037 (1/hours/[HS^-] mg/L), respectively.

- The abiotic reaction of herbicides with sulfide in this study is significant on the time scale of groundwater transport. At 21°C, pH 7, and bisulfide concentration of 20 mg/L, the half-lives of four herbicides were ranged from 0.1 day for propachlor to 6.7 days for metolachlor.
- The changes of temperature have a considerable effect on the degradation of herbicides reacting with bisulfide. An increase in temperature by 13 °C increased the degradation rate of butachlor and metolachlor by a factor of six; alachlor and propachlor rates increased by a factor of ten.
- The temperature dependence of the degradation rate of herbicides in the presence of bisulfide follows the Arrhenius kinetics. Over the temperature range of 8 °C to 35 °C, activation energies of four herbicides were 22.2, 18.1, 17.3, and 16.3 (Kcal/mole) for propachlor, alachlor, metolachlor, and butachlor, respectively.
- The phosphate buffers did not enhance the abiotic reaction.
- Neither acid-catalysis nor base-catalysis was found in either the pH 4 and the pH 12 control experiments in the absence of sulfide.
- At 21°C, the observed disappearance rate of herbicide was increased with pH, resulting from an increase in bisulfide concentration among sulfide species. Hydrogen sulfide appeared to have a slow reaction with heribicides at pH 4. The observed rate constants of herbicide disappearance were considerablely increased from pH 7 to pH 12 since only half of bisulfide is present in pH 7 and 88% bisulfide is present in pH 12.

- Propachlor was most susceptible to abiotic transformation in all experiments tested. The rate preferences of the abiotic transformation of the four herbicides were in the following order: propachlor> alachlor> butachlor> metolachlor.

Recommendations for Further Research

Based on the results obtained in this study, the following further studies are recommended.

- The first-order kinetics in herbicide concentration was successfully applied in this study to characterize the disappearance of herbicides in presence of sulfide. However, it is still unclear whether the abiotic reaction follows second-order kinetics overall with different bisufide concentrations. Further studies are needed to confirm the reaction order of the abiotic transformation.
- All experiments conducted in this study used deionized water as solvent. To understand the actual transformation process in real subsurface environment, studies are needed to find how the results obtained in the lab are applicable at different environmental conditions.
- Since the complicated speciations of sulfide might result in several concurrent reactions, continuous research to further understand sulfur chemistry is necessary, in particularly, with respect to reactions with chlorinated organics.
- Sulfide species are relatively unsteady in both solid state or in solution and accurately determining their concentrations is difficult, resulting in some ambiguous experimental

results. The analytical techniques used to determine sulfide concentrations in water solutions need improvement.

- The intermediates of the abiotic transformation in this study were not identified and the pathways of the reaction are still not clear. Therefore, it is recommended that the pathways and intermediates of the abiotic transformation of these herbicides be further investigated to find whether their transformation products are of similar or even greater environmental concern than their parent compounds. If so, more research is necessary to focus on their transformations, both abiotic and biological, to ultimately find the pathways which render these chemicals harmless.

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APPENDICES

APPENDIX A

RAW DATA, THE REMOVAL OF PROPACHLOR AT BISULFIDE CONCENTRATIONS OF 4.11, AND 19.5 mg/L

4.11 mg/L Bisulfide				19.5 mg/L Bisulfide			
Time (hours)	$[HS^-]$ (mg/L)	Herbi. Conc. (1E-03 mg/L)	ln(C/Co)	Time (hours)	$[HS^-]$ (mg/L)	Herbi. Conc. (1E-03 mg/L)	ln(C/Co)
0	4.47	338	0.000	0	19.80	281	0.000
2	4.64	346	0.023	1	19.25	254	-0.099
5	4.64	383	0.127	2	19.95	244	-0.140
7	4.47	335	-0.010	4	19.60	217	-0.258
13	4.64	304	-0.107	6	20.30	223	-0.230
21	4.30	298	-0.125	8	19.95	117	-0.878
28.5	3.96	272	-0.216	14	20.30	126	-0.799
39	3.96	279	-0.192	18	19.95	109	-0.948
51	4.13	211	-0.472	20	19.95	82	-1.226
62.5	3.96	191	-0.572	22	19.80	87	-1.177
77	4.13	162	-0.737	24	19.45	86	-1.187
90.5	4.30	119	-1.043	25.5	19.25	73	-1.346
99	3.96	161	-0.744	28.5	18.90	54	-1.656
109.5	3.78	115	-1.074	30	18.75	61	-1.527
122.5	3.96	114	-1.084	31	18.90	52	-1.681
				32.5	18.90	55	-1.632
				33.5	18.75	55	-1.632
				34.5	19.60	54	-1.642
				42.65	19.25	53	-1.673

APPENDIX B

RAW DATA, THE REACTION OF 0.3 mg/L PROPACHLOR WITH DIFFERENT BISULFIDE CONCENTRATIONS AT pH 7 AND 21 °C

4.3 mg/L Bisulfide			9.2 mg/L Bisulfide			20.7 mg/L Bisulfide		
Time (hours)	Concentration (micrograms/L)	ln(C/Co)	Time (hours)	Concentration (micrograms/L)	ln(C/Co)	Time (hours)	Concentration (micrograms/L)	ln(C/Co)
0	250	0.000	0	299	0.000	0	269	0.000
8	210	-0.174	4	293	-0.023	0.5	212	-0.238
20	201	-0.218	7	280	-0.066	1	177	-0.419
44	175	-0.357	9	238	-0.228	1.5	163	-0.501
68	156	-0.472	15	236	-0.236	2	215	-0.224
92	141	-0.573	23	205	-0.377	2.5	188	-0.358
116	115	-0.777	25	166	-0.589	4	154	-0.558
140	84	-1.091	31	154	-0.667	4.5	153	-0.564
164	62	-1.394	32.5	149	-0.698	5.5	144	-0.625
188	38	-1.884	34.5	145	-0.727	6	149	-0.591
			43	144	-0.731	7	120	-0.807
			47.5	99	-1.106	8	100	-0.990
			56	85	-1.255			
			57.5	87	-1.234			
			68	56	-1.674			

APPENDIX C

RAW DATA, THE DEGRADATION OF 0.3 mg/L ALACHLOR BY DIFFERENT BISULFIDE CONCENTRATIONS AT pH 7 AND 21 °C

1.2 mg/L Bisulfide			9.2 mg/L Bisulfide			19.5 mg/L Bisulfide		
Time (Hours)	Pest. Conc. (micrograms/L)	ln(C/Co)	Time (Hours)	Pest. Conc. (micrograms/L)	ln(C/Co)	Time (Hours)	Pest. Conc. (micrograms/L)	ln(C/Co)
0	287	0.000	0	320	0.000	0	371	0.000
8	270	-0.061	4	321	0.001	1	358	-0.036
20	268	-0.069	7	319	-0.005	2	336	-0.099
34	269	-0.066	9	280	-0.133	4	337	-0.096
44	251	-0.135	15	276	-0.150	6	314	-0.166
60	248	-0.148	23	243	-0.278	8	223	-0.510
71	261	-0.097	25	230	-0.331	14	238	-0.443
82	230	-0.223	31	207	-0.439	18	219	-0.527
106	220	-0.266	32.5	205	-0.446	20	198	-0.630
130	200	-0.364	34.5	208	-0.434	22	193	-0.654
154	204	-0.342	43	219	-0.381	24	190	-0.668
178	208	-0.324	47.5	172	-0.620	25.5	163	-0.822
202	191	-0.407	56	147	-0.782	28.5	137	-0.996
			57.5	153	-0.737	30	132	-1.034

APPENDIX D

RAW DATA, THE REACTION OF BUTACHLOR AND METOLACHLOR WITH BISULFIDE CONCENTRATIONS OF 15.3, 11.6 mg/L, RESPECTIVELY

		15.3 mg/L Bisulfide				11.6 mg/L Bisulfide	
		Butachlor				Metolachlor	
Time (hours)	$[HS^-]$ (mg/L)	Herbi. Conc. (1E-03 mg/L)	ln(C/Co)	Time (hours)	$[HS^-]$ (mg/L)	Herbi. Conc. (1E-03 mg/L)	ln(C/Co)
0	16.07	226	0.000	0	12.19	316	0.000
2.5	15.9	235	0.041	2.5	11.85	281	-0.117
5.5	15.22	220	-0.028	14.5	12.02	261	-0.193
14.5	15.56	200	-0.121	20.5	11.68	259	-0.201
20.5	15.22	142	-0.463	26.5	11.85	259	-0.197
26.5	15.39	132	-0.540	30.5	11.68	263	-0.182
30.5	15.06	147	-0.427	39.5	11.85	255	-0.215
39.5	15.22	116	-0.669	45.5	11.51	266	-0.174
45.5	15.06	111	-0.711	53.5	11	246	-0.250
53.5	15.39	128	-0.564	62.5	11.68	206	-0.429
63	14.89	122	-0.619	75	11.68	192	-0.500
75.5	15.06	91	-0.909	87.5	11.51	211	-0.403
90	15.39	76	-1.088	98	11	201	-0.451
103.5	15.06	74	-1.121	109	11	181	-0.556
114.5	15.06	49	-1.523	121	11.17	176	-0.588

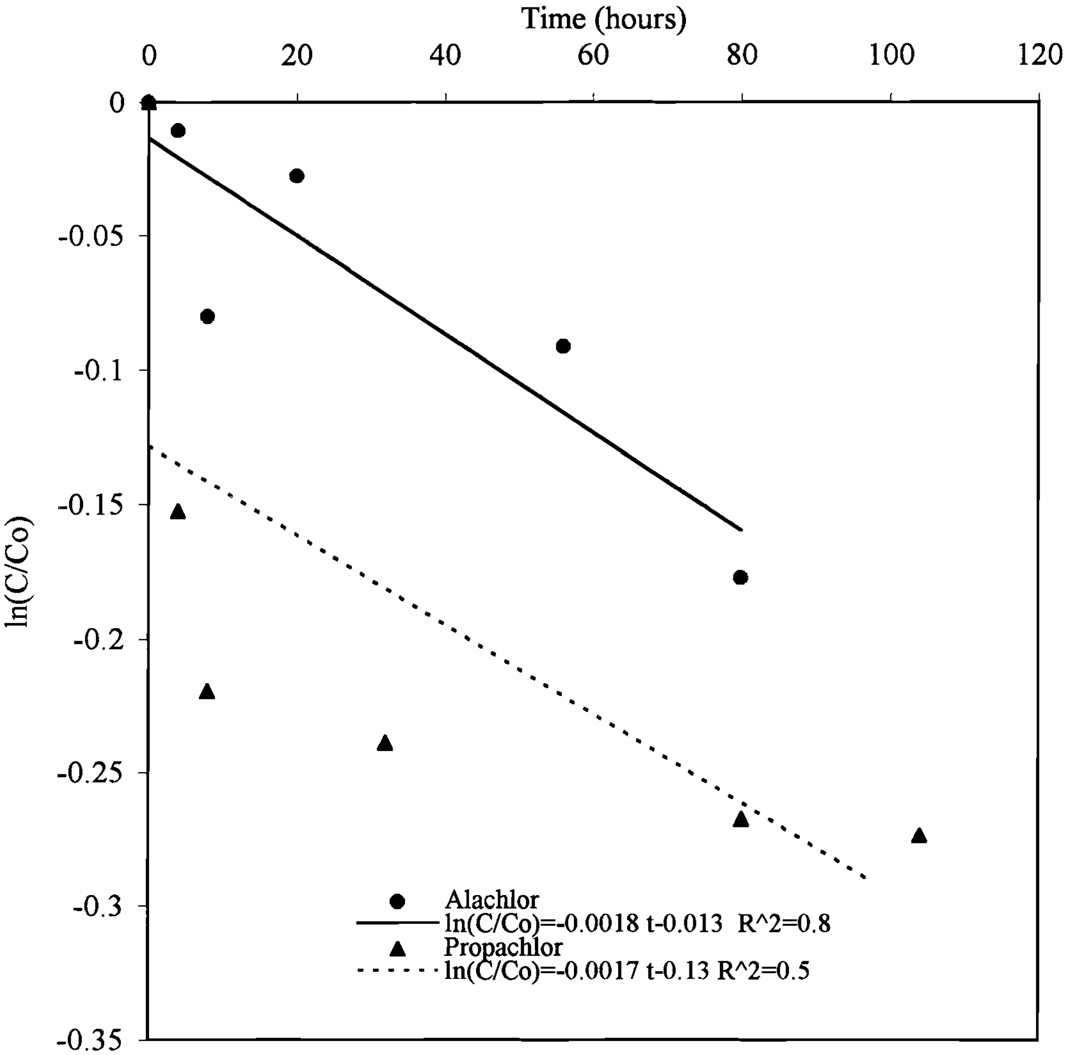
APPENDIX E

RAW DATA, THE REACTION OF PROPACHLOR AND ALACHLOR WITH HIGHER BISULFIDE CONCENTRATIONS AT 21 °C AND pH 7

	41.43 mg/L Bisulfide			34.9 mg/L Bisulfide	
	Alachlor			Propachlor	
Time (hours)	Concentration (micrograms/L)	ln(C/Co)	Time (hours)	Concentration (micrograms/L)	ln(C/Co)
0	278	0.000	0	306	0.000
0.5	169	-0.496	0.5	273	-0.111
1	160	-0.552	1.5	263	-0.149
1.5	158	-0.565	2.5	251	-0.196
2.5	135	-0.725	3.5	239	-0.248
3.5	114	-0.889	5.5	94	-1.181
4.5	127	-0.783			
6	65	-1.451			

APPENDIX F

THE FIRST-ORDER PLOT FOR THE DEGRADATION OF 3 mg/L HERBICIDES AT SULFIDE CONCENTRATION OF 3 mg/L



APPENDIX G

RAW DATA, TEMPERATURE EFFECTS ON THE DEGRADATION OF ALACHLOR AT pH 7 AND BISULFIDE CONCENTRATION OF 20 mg/L

	8 °C			21 °C			35° C	
Time (hours)	Herbi. Conc. (micrograms/L)	ln(C/Co)	Time (hours)	Herbi. Conc. (micrograms/L)	ln(C/Co)	Time (hours)	Herbi. Conc. (micrograms/L)	ln(C/Co)
0	339	0.000	0	368	0.000	0	384	0.000
6	275	-0.211	0.5	350	-0.051	1	328	-0.158
12	261	-0.264	1	334	-0.097	2	283	-0.306
24	245	-0.327	1.5	327	-0.119	2.5	298	-0.255
36	205	-0.506	2	322	-0.132	3	250	-0.428
48	222	-0.426	2.5	336	-0.091	4	240	-0.468
72	196	-0.550	4	267	-0.319	5	216	-0.575
96	163	-0.731	4.5	232	-0.463	6	209	-0.606
			5.5	251	-0.383	7	158	-0.890
			6	258	-0.354	8	144	-0.979
			7	232	-0.460	9	155	-0.905
			8	204	-0.591	10	116	-1.195
			9	197	-0.624	11	107	-1.282
			12	203	-0.593	12	96	-1.389
			13	167	-0.790	13	91	-1.438
						14	88	-1.478
						15	69	-1.713

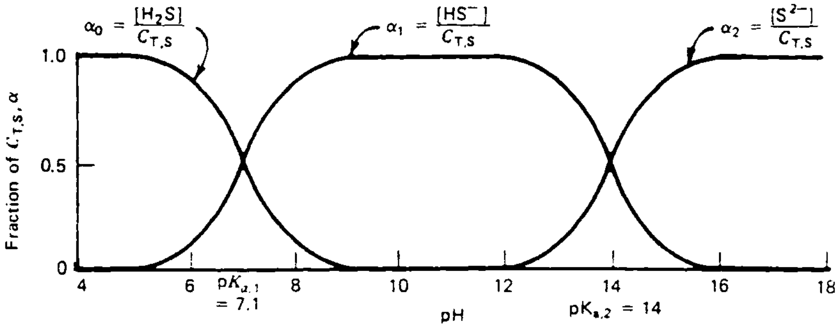
APPENDIX H

RAW DATA, THE EFFECT OF BUFFER ON THE DEGRADATION OF ALACHLOR AND PROPACHLOR AT pH 7 AND 21 °C

Time	Alachlor Buffer Capacities			Propachlor Buffer Capacities		
(hours)	0 (mM)	5 (mM)	50 (mM)	0 (mM)	5 (mM)	50 (mM)
0	307.5	310.4	314.2	274.1	330.6	307.1
12	347.1	303.2	322.7	299.1	319.5	282.8
24	340.3	375.4	359.7	288.6	366.1	333.8
36	381.1	326.9	327.3	310.3	325.6	341.2
48	364.0	330.1	364.3	309.1	329.4	332.9
60	379.9	314.1	350.0	298.1	348.4	316.9
72	360.2	293.6	321.6	305.2	315.6	312.0
84	331.6	298.9	333.9	295.3	354.2	325.8
104	377.7	345.3	340.2	325.0	352.0	339.0
132	304.9	273.7	329.8	279.2	309.8	335.2

APPENDIX I

DISTRIBUTION DIAGRAM OF HYDROGEN SULFIDE AT 25 °C



Note: The pK_{a1}, and pK_{a2} of hydrogen sulfide in this study were selected as 7.04, and 12.9, respectively.

APPENDIX J

RAW DATA, THE EFFECT OF pH 4 ON THE DEGRADATION OF FOUR HERBICIDES AT 21 °C AND 50mM BUFFER ONLY

	Alachlor		Butachlor		Metolachlor		Propachlor	
Time (hours)	Concentration (micrograms/L)	ln(C/Co)	Concentration (micrograms/L)	ln(C/Co)	Concentration (micrograms/L)	ln(C/Co)	Concentration (micrograms/L)	ln(C/Co)
0	301	0.000	283	0.000	296	0.000	319	0.000
12	316	0.049	280	-0.008	299	0.009	317	-0.006
36	296	-0.019	281	-0.007	289	-0.025	311	-0.026
47	289	-0.040	286	0.012	299	0.012	303	-0.053
72	284	-0.059	279	-0.011	286	-0.035	315	-0.013
132	294	-0.024	275	-0.027	297	0.003	311	-0.026
180	280	-0.073	273	-0.034	287	-0.030	307	-0.040
229	287	-0.049	281	-0.005	292	-0.012	303	-0.052

APPENDIX K

RAW DATA, pH 4 EFFECT ON THE DEGRADATION OF FOUR HERBICIDES AT TOTAL SULFIDE CONCENTRATION OF 40 mg/L

	Alachlor		Butachlor		Metolachlor		Propachlor	
Time (hours	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)
0	280	0.000	275	0.000	268	0.000	287	0.000
12	299	0.066	278	0.010	280	0.046	318	0.101
36	287	0.026	284	0.032	273	0.017	301	0.046
47	294	0.052	276	0.003	277	0.033	321	0.112
132	322	-0.051	322	0.156	273	-0.049	343	-0.058
180	266	-0.032	251	-0.091	255	-0.031	271	-0.072
228	271	-0.080	250	-0.096	260	-0.073	267	-0.123

APPENDIX L

RAW DATA, pH 12 EFFECT ON THE DEGRADATION OF FOUR HERBICIDES AT 21 °C AND 50 mM BUFFER ONLY

	Alachlor		Butachlor		Metolachlor		Propachlor	
Time (hours)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)
0	314	0.000	233	0.000	209	0.000	207	0.000
6	290	-0.078	232	-0.004	221	0.056	114	-0.598
7	349	0.107	270	0.148	255	0.195	147	-0.340
8	295	-0.061	231	-0.010	204	-0.026	105	-0.678
9	181	-0.549	249	0.065	369	0.567	94	-0.790
10	280	-0.116	231	-0.008	217	0.037	80	-0.943
11	358	0.131	334	0.360	206	-0.019	159	-0.259
12	341	0.083	255	0.091	234	0.110	226	0.091
15	286	-0.092	216	-0.078	188	-0.110	185	-0.109
21	304	-0.033	228	-0.022	206	-0.017	201	-0.027
29	239	-0.271	262	0.117	257	0.206	162	-0.241

APPENDIX M

RAW DATA, pH 12 EFFECT ON THE DEGRADATION OF FOUR HERBICIDES AT TOTAL SULFIDE CONCENTRATION OF 40 mg/L

	Alachlor		Butachlor		Metolachlor		Propachlor	
Time (hours)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)	Herb. Conc. (micrograms/L)	ln(C/Co)
0	314	0.000	280	0.000	286	0.000	296	0.000
1	299	-0.048	278	-0.006	298	0.041	215	-0.320
2	305	-0.030	314	0.115	337	0.165	145	-0.710
3	313	-0.003	321	0.136	361	0.234	167	-0.573
4	280	-0.115	287	0.026	338	0.169	124	-0.869
8	188	-0.515	172	-0.490	285	-0.003	103	-1.056
10.5	210	-0.404	196	-0.358	321	0.115	109	-0.996
16.5	186	-0.522	159	-0.567	340	0.173	63	-1.552
20.5	74	-1.440	81	-1.243	247	-0.146		
24.5	57	-1.714	60	-1.543	211	-0.301		

APPENDIX N

RAW DATA, COMPARISON AMONG THE ABIOTIC REACTION OF FOUR HERBICIDES AT 21 °C, pH 7 AND SIMILAR BISULFIDE CONCENTRATIONS

	Alachlor			butachlor			Metolachlor			Propachlor	
Time (hours)	Pest.Conc. (micrograms/L)	ln(C/Co)	Time (hours)	Pest.Conc. (micrograms/L)	ln(C/Co)	Time (hours)	Pest.Conc. (micrograms/L)	ln(C/Co)	Time (hours)	Pest.Conc (micrograms/L)	ln(C/Co)
0	315	0	0	317	0.000	0	316	0.000	0	280	0.000
11	215	-0.382	6	224	-0.350	2.5	281	-0.117	11	193	-0.371
33	164	-0.653	16	215	-0.387	14.5	261	-0.193	33	145	-0.661
57	135	-0.847	23	183	-0.549	20.5	259	-0.201	57	121	-0.837
81	86	-1.298	31	185	-0.542	26.5	259	-0.197	81	57	-1.597
129	75	-1.435	43	160	-0.685	30.5	263	-0.182	129	39	-1.974
153	45	-1.946	55	161	-0.678	39.5	255	-0.215	153	29	-2.268
			67	113	-1.029	45.5	266	-0.174			
			79	95	-1.205	53.5	246	-0.250			
			103	95	-1.209	62.5	206	-0.429			
						75	192	-0.500			
						87.5	211	-0.403			
						98	201	-0.451			
						109	181	-0.557			
						121	176	-0.588			

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