WATER RESOURCES research center

Publication No. 76

ALDICARB STUDIES IN GROUNDWATERS FROM CITRUS GROVES IN INDIAN RIVER COUNTY, FLORIDA

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ABSTRACT

The disappearance of aldicarb [2-methyl-2(methylthio)propionaldehyde O-(methylcarbamoyl)oxime] and its two toxic degradation products, aldicarb sulfoxide and aldicarb sulfone, were measured in laboratory studies using groundwaters and subsoils collected from citrus groves in Indian River County, Florida, and incubated under controlled conditions which best represented the in situ environment. The presence of aquifer material on the decomposition of total toxic residues from aldicarb addition in anaerobic groundwaters was pronounced, suggesting bacteria were important in decomposing aldicarb to nontoxic residues. However, aquifer material had only a minor effect on the rate of total toxic residue disappearance when aldicarb sulfoxide or aldicarb sulfone was the primary toxic aldicarb residue, suggesting that chemical hydrolysis in solution was more important in degrading aldicarb sulfoxide and aldicarb sulfone. Based on hydrolysis experiments in sterile pH-buffered distilled water for aldicarb, hydrolysis rate constants became second-order (k_{OH} = 1.94 x 10^3 L $mole^{-1}$ day^{-1} at 20°C) at pH 8 and above; acid-catalyzed hydrolysis occurred at pH 4, but not to the same extent as base-catalyzed hydrolysis. Oximes did not interfere with the analysis of total toxic residues under the conditions of the procedures used in this study; nitriles interfered in a positive fashion, but only when toxic residue concentrations were <10% of the initial concentrati

The half-life times for total toxic residue disappearance of aldicarb and its two sulfur-oxidized derivatives in groundwater-saturated subsoils ranged from 10-26 days, suggesting a resumption to the reported faster aerobic degradation rates in the upper soil layers after having undergone slow degradation in unsaturated subsoils. Based on the degradation rates found in this study, hydrologic parameters obtained for Indian River County subsoils, and amounts

of total toxic residue reported entering Florida groundwaters, it was estimated that toxic residues in aldicarb-contaminated groundwaters in Indian River County would migrate only short distances (1-17 ft) before conversion of toxic residues to non-toxic residues was completed. Thus, the exclusion zone of 300 ft from the nearest drinking water well for applying aldicarb is a reasonable restriction for protecting the groundwater resources in Indian River County.

ACKNOWLEDGEMENTS

This study was supported in part under an annual allotment grant from the Florida Water Resources Research Center to Forrest E. Dierberg, Associate Professor of Environmental Science and Engineering, Florida Institute of Technology. Chris Given served as research assistant and completed his M.S. thesis on this project. The assistance of Brian Combs, Indian River Agricultural Extension Agent, in locating accessible sampling sites and in helping with sample collection is gratefully acknowledged. Larry Pollack, a graduate student in the department, also contributed to the research findings found in this report.

The interest and assistance of Carl Miles, Department of Environmental Engineering Sciences, University of Florida, helped to make this report more complete. The co-operation of Willis Wheeler and David Atherton, of the Pesticide Research Lab, Institute of Food and Agricultural Sciences, University of Florida, Gainesville, and Robert Patton of the Florida Department of Environmental Regulation, Tallahassee, in the inter-laboratory exchange of samples is appreciated. Victor Carlisle of the Soil Science Department, University of Florida, and Carol Wettstein of the U.S. Soil Conservation Service provided the information on the soils in Indian River County. Finally, the U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository, Research Triangle Park, North Carolina, and Union Carbide kindly provided standards for aldicarb and its decomposition products.

INTRODUCTION

Aldicarb (Temik^{R}) is an effective but non-selective systemic insecticide, miticide, and nematicide; its acute mammalian toxicity (rat acute oral LD_{50}, 1 mg/kg; rabbit dermal LD_{50}, 5 mg/kg) (ICET 1983) makes it one of the most toxic of all currently-registered insecticides. Aldicarb and its toxic oxidized metabolites (sulfoxide and sulfone), like other carbamate esters, exert their insecticidal activity through reversible inhibition of the enzyme acetylcholinesterase. There is no evidence that either aldicarb or its metabolites are associated with any adverse mutagenic, carcinogenic, or teratogenic effects. As it stands now, the conditions of exposure can be viewed as a series of low-level exposures rather than continuous chronic exposure. Detailed reviews on the toxicology of aldicarb and its sulfoxide and sulfone metabolites can be found in reports issued by the Institute for Comparative and Environmental Toxicology (ICET 1983) and aldicarb's manufacturer, Union Carbide (1983). Because of its high mammalian toxicity, aldicarb is available only in granular formulations (5-20% active ingredient) for soil incorporation.

Its primary use in Florida is to protect citrus groves (in the central and southern parts of the state) and potatoes (in north Florida) from aphids, mites and nematodes (Jones and Back 1984). Concern for the potential of aldicarb or its toxic metabolites to contaminate underground aquifers used for drinking water in Florida heightened after reports that aldicarb had been detected for the first time in groundwater in Suffolk County, New York, in August 1979 (Zaki et al. 1982). Since the sandy soils in Suffolk County were not too dissimilar from Florida soils and because of the high water solubility ($\simeq$6,000 ppm) and non-volatility (vapor pressure = 1×10^{-4} mm Hg at 25°C) of

the pesticide, both of which would preclude significant adsorption onto soil particles, extensive monitoring, field, and laboratory studies were subsequently undertaken in the state (IFAS 1983). Other states such as Wisconsin (Chesters et al. 1982) also initiated monitoring networks after detecting aldicarb residues in groundwaters.

The regulatory history of aldicarb in Florida can be briefly summarized below:

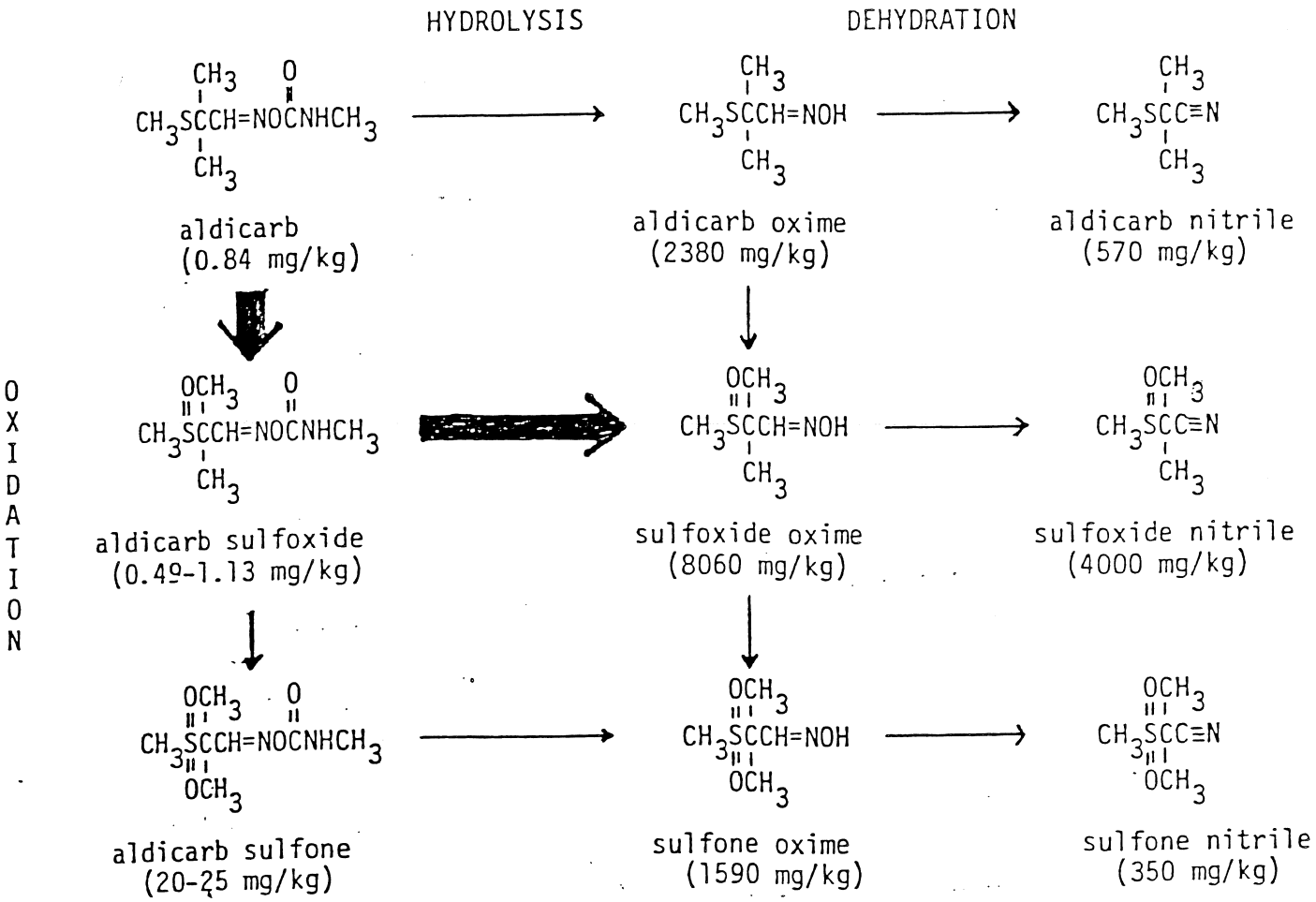
August 1982	Media reported Temik-contaminated water in other states; Florida began testing for - and finding - traces in underground water supplies.
January 28, 1983	State-wide ban went into effect.
October 1983	Nation-wide ban on ethylene dibromide (EDB) increased the potential use of Temik.
January 1, 1984	Ban lifted, but with the following restrictions:

- no more than 5 lbs active ingredient (a.i.) can be used per acre (formerly 15 lbs a.i. per acre).
- applied only once a year between January 1 and April 30 (for citrus).
- cannot be applied within 300 ft of any drinking water well.
- use suspended in an area if drinking water >10 ppb.
- notification of impending treatment must be posted prominently on property where it is to be applied.

The degradation of aldicarb in plants, animals and soil is dominated by two processes: oxidation of sulfur to obtain sulfoxide and sulfone analogs, and cleavage of the carbamate ester bond (Fig. 1). Oxidation is the major pathway for aldicarb metabolism in most systems (ICET 1983). Which degradation pathway predominates is important since hydrolysis of the ester linkage detoxifies aldicarb and its sulfur-oxidized derivatives, while oxidation of sulfur yields metabolites that retain the toxicity of the parent compound. Aldicarb oxidizes readily to sulfoxide in plants (Maitlen et al. 1968) and soils (Smelt et al. 1978c: Bromilow et al. 1980). It is the sulfoxide which is the most potent cholinesterase inhibitor of the group (Fig. 1), and responsible for the high systemic activity and long-term persistence of insecticidal activities.

Much of the research to date on aldicarb and its sulfur-oxidized derivatives in Florida have been fate studies in soils and crops (IFAS 1983). Little is known regarding the chemical behavior of aldicarb and its oxidized metabolites in shallow groundwaters in Florida where drinking water is obtained from many private wells. Funding for the project began in August 1983; field sampling, laboratory studies, and chemical analyses continued through June 1984. Continued research on aldicarb in groundwater is being conducted beyond the funding period of this report. Preliminary data contained in this report were presented at the Florida Academy of Sciences meeting on March 30, 1984, in Boca Raton, Florida.

The practical aspects of the study focused on the degradation of aldicarb and its oxidized metabolites in groundwaters from 3 shallow wells ($\sim$ 20 m deep) located near citrus groves in Indian River County. Two other wells ($\sim$ 1.4 m deep) inside citrus groves were augered to study the effects of aquifer material on the rate of degradation. In one case, groundwaters and aquifer material were



Source: The Institute for Comparative and Environmental Toxicology · 1983

Figure 1. Degradative Pathways of Aldicarb. Large Arrows Indicate Major Pathways. Values in Parentheses are Acute Oral LD_{50}'s for Rats.

sterilized while replicate subsamples were left unsterilized so as to determine what role, if any, the groundwater microflora play in the degradation process. Finally, carefully conducted hydrolysis experiments in pH buffered distilled water of 4, 6, 7, 8, 9 and 10 were carried out at room temperature to further understand the significance of acid or base catalysis and to obtain reliable half-life values for the pH range found for natural waters.

OBJECTIVES

The objectives of this study were as follows:

1. To determine the extent that non-toxic oximes and nitriles interfered in the analysis of total toxic aldicarb residues by gas chromatography;
2. To perform a carefully controlled hydrolysis experiment for understanding what effect pH has on hydrolyzing aldicarb under sterile conditions;
3. To examine shallow groundwaters with and without aquifer material collected in citrus groves for their capacity to degrade aldicarb and its two toxic derivatives, sufoxide and sulfone, to non-toxic residues in laboratory experiments; and
4. To integrate the kinetic expressions of these experiments with a simple groundwater transport model and field data published in the literature in arriving at an estimate of the distances groundwater contaminated with toxic residues of aldicarb would migrate in Indian River County.

SITE DESCRIPTION

Five well sites bordering or within citrus groves in Indian River County (Figure 2) provided groundwaters and aquifer material for aldicarb, aldicarb sulfoxide, and aldicarb sulfone additions in the laboratory degradation studies. Three of the wells - Ryall, Luther, and Sexton - were private water supply wells with attached pumping systems. Two of the wells directly supplied the Luther and Sexton residences; the Ryall well was used for irrigation, but water from it was sometimes consumed by grove workers. Well construction reports were not available to verify their depths, but owners believed that their wells were relatively shallow, ranging between 16 and 20 m, closely approximating the depths which are commonly used in providing drinking water to private homes. Only groundwaters were sampled from the 2-inch diameter piping of these wells. The remaining two wells (BBC and Lindsey Wabasso) were drilled by using a bucket auger, and their very shallow depths (1.3-1.5 m) coincided to the top of the water table in the unconfined aquifer. Any transport of toxic residues to the deeper groundwaters which are used for domestic water supply would have to first pass through this layer.

The soils in Indian River County are currently being mapped by the SCS. The soils in the field sites which were hand-augered (BBC and Lindsey Wabasso groves) are classified as Pineda sand (Arenic Glossaqualfs), Riviera sand (Arenic Glossaqualfs), and Wabasso sand (Alfic Haplaquods). They are all nearly level (slopes less than 2 percent), poorly drained, slowly to very slowly permeable soils. Permeability is rapid (15-51 cm/hr) in the sandy A horizons and slow to very slow in the sandy clay loam B horizons ($<$0.5 cm/hr). Clay content averages 12 to 30% in the B horizon where subsoils representing aquifer material were sampled. The water table is within 10 inches of the

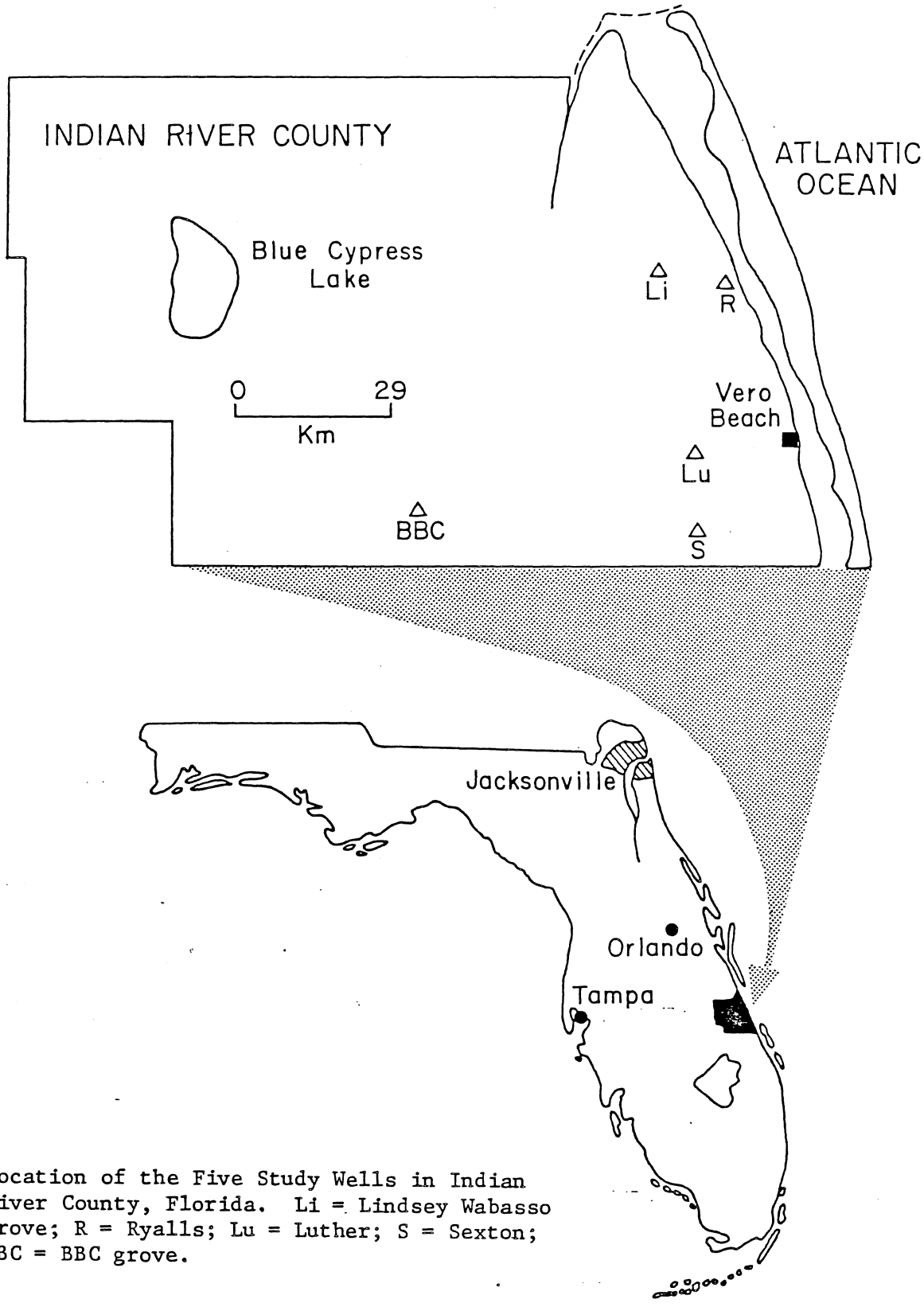


Figure 2. Location of the Five Study Wells in Indian River County, Florida. Li = Lindsey Wabasso grove; R = Ryalls; Lu = Luther; S = Sexton; BBC = BBC grove.

surface for 1 to 6 months in most years and 10 to 30 inches deep most of the rest of the year. Some areas are flooded for periods ranging from a few days to about 3 months.

SAMPLING PROCEDURE

Groundwater samples from the three private water supply wells (Ryall, Luther, Sexton) (Fig. 2) within 30 m of citrus groves were collected on December 9, 1983, and March 26, 1984 after pumping an amount of water greater than three volumes of the water standing in the pipe. Water samples were taken from the closest accessible point to the well head, usually from the pump itself or just after the pump. Care was exercised in avoiding entrapment of air and degassing in the sample containers by flushing several volumes of groundwater before caping each container. Samples to be used in laboratory incubations were put into sterilized 4-L amber-colored glass containers after at least one volume had been allowed to overflow and placed in a cooler filled with ice for transport to the laboratory. Several BOD and Nalgene bottles were filled in the same manner with sample groundwaters for field and laboratory measurements.

In addition to sampling only groundwaters from private water supply wells, two shallow wells each at the BBC and Lindsey Wabasso sites (Fig. 2) were hand-augered on February 22, 1984 and January 30/April 23, 1984, respectively, using a 3-inch (ID) x 14-inch (length of containment area) soil auger. The wells were located in a furrow separating two rows of citrus trees. Groundwater was sampled through 1-inch (OD) Flex PVC heavy wall tubing connected to a 12 gpm maximum flow "Guzzler" hand pump; aquifer material from saturated subsoils was withdrawn from these self-constructed shallow wells (1.3-1.5 m) using the soil auger. The same field and laboratory analyses were done on these augered wells as already described for the private water supply wells.

ANALYTICAL METHODS

Field Measurements

Redox potential was measured with a platinum electrode and a saturated calomel electrode (SCE) as the reference electrode. Calibration of electrodes and potentiometer (Fisher Accumet 640 Mini-Meter) was made against a Fe^{+2}/Fe^{+3} standard solution (Light 1972). Adjustments were made in the measured potentials to a standard hydrogen reference electrode (Light 1972) at pH 7 (Patrick and Mahapatra 1968). In addition to redox potential, dissolved oxygen (Leeds and Northrup 7932 portable dissolved oxygen meter), specific conductance (YSI Model 33 S-C-T meter), and pH (Fisher Accumet 640 Mini-Meter) were also measured potentiometrically using the appropriate sensors. Temperature was recorded using a mercury thermometer.

Laboratory Measurements

General Water Chemistry Analyses

The following chemical constituents were determined titrimetrically according to the procedures given in Standard Methods For the Examination of Water and Wastewater (APHA 1976): total alkalinity (0.02 N H_2SO_4), total hardness (0.02 M EDTA), and sulfide (iodine). Total iron was measured by atomic absorption spectroscopy with a Perkin-Elmer Model 460 atomic absorption spectrometer after preserving sample by acidifying to pH<2 in the field.

Standard plate counts were conducted anaerobically by the Vacuum and Gas Displacement Method (Benson 1973) on the groundwaters and saturated subsoils from the private water supply wells and augered shallow wells before (within 24 hours of field sampling) and at the end of each incubation.

Aldicarb Residue Analyses

After adding 0.10 mg/L of aldicarb or one of its S-oxides (aldicarb sulfoxide and aldicarb sulfone), pH-buffered distilled water, groundwater, and subsoil were analyzed for the sum of aldicarb and its S-oxides at various time intervals according to the methodology developed by Union Carbide (1980). This methodology purports to determine the sum total of toxic aldicarb residues (Fig. 1) (i.e. aldicarb + aldicarb sulfoxide + aldicarb sulfone), which has been referred to as the "total toxic residue" (TTR). It wasn't learned until later into the research period of the potential "positive" interference from non-toxic nitriles. An assessment of the extent that the nitrile may have interfered in those earlier TTR analyses where it hadn't been removed is presented in the RESULTS section.

At appropriate intervals, fifty or one-hundred mL aliquots were removed from each duplicate incubation container (BOD bottle or Mason jar) of pH-buffered distilled water solution or groundwater and placed into a 125-mL or 250-mL separatory funnel. Oxidation of aldicarb and aldicarb sulfoxide to aldicarb sulfone was accomplished by adding 2 mL of peracetic acid. Conversion of aldicarb and aldicarb sulfoxide to aldicarb sulfone is necessary since chromatographic peaks of the former are indistinguishable from the solvent peak using gas chromatograph (GC) (Galoux et al. 1979). The contents in the separatory funnel were mixed and allowed to stand for 30 minutes with occasional mixing. After 30 minutes, 15 mL of 10% $NaHCO_3$ were added, mixed, and allowed to stand with occasional mixing for 15 minutes. Fifty mL of methylene chloride were added with frequent venting to release evolved CO_2. After the layers separated, the lower methylene chloride layer was drained through approximately 80 g of prewet sodium sulfate in a 4-inch funnel with a glass wool plug. The

extraction was repeated with another 50 mL of methylene chloride and the extracts combined. After rinsing the sodium sulfate bed with an additional 20 mL of methylene chloride, the combined extracts and rinse were collected and concentrated in a 45°C water bath by evaporating just to dryness with a stream of dry N_2 gas. The residue was then dissolved in acetone to 1-2 mL and stored in 3-mL septum-capped vials at -5°C until analyzed by GC.

Groundwater-saturated subsoil samples (50 g dry wt) were extracted using the method of Galoux et al. (1979). The subsoils (50 g dry wt) were mixed with 50 mL of acetone-water (40:60), shaken for 30 min and centrifuged for 5 min at 3000 rpm. The extract was transferred to a 250-mL separation funnel. A second extraction was performed with 40 mL of methanol-water (50:50), and the two extracts were combined. The acetone extract was next extracted 3 times with 50 mL methylene chloride in a 500-mL separatory funnel. After draining the methylene chloride fraction through sodium sulfate beds, combining, and concentrating to approximately 2-mL in a 45°C water bath, 10 mg of m-chloroperbenzoic acid was added to oxidize the aldicarb and aldicarb sulfoxide, if present, to aldicarb sulfone (Smelt et al. 1978c). The residue was dissolved in 1-2 mL acetone for GC analysis after taking to dryness under N_2 in a 45°C water bath.

As previously stated, if non-toxic nitrile derivatives of aldicarb and its S-oxides are present in the sample, they would serve as a positive interferent (i.e. included with the toxic residues). The high injection port temperature (260°C) pyrolyzes the toxic aldicarb and its S-oxides to nitriles (Knaak et al. 1966; Trehy et al. 1984), which are then detected by the flame photometric detector in the GC. To remove the nitrile interference, 0.5-cm(ID) x 60-cm glass columns were filled to a depth of 14 cm with 5 g of PR grade Florisil. After pre-washing the columns with 25 mL of methylene chloride but

before it reached the top of the Florisil, the eluted pre-wash was discarded and the sample immediately added to the top of the column. When the sample reached the top of the column, 100 mL of 5% acetone in ethyl ether were added to the column, and the eluate discarded when the solvent reached the top of the Florisil. A second solvent fraction consisting of 50 mL of 50% acetone in ethyl ether was then added to the column, and the eluate collected in a 125-mL Erlenmeyer flask. The second fraction was evaporated under an N_2 gas stream in a 45°C water bath to less than 2 mL and then transferred to a 3 mL septum cap vial. The flask was rinsed with small amounts of acetone and the rinse added to the vial. The volume in the vial was reduced under N_2 gas to a final volume of 1 mL.

Gas chromatography was performed on a Perkin-Elmer Sigma 300 GC equipped with a flame photometric detector with a 394 nm filter to quantify the sulfone. A coiled glass column, 1m x 2mm (ID), packed with 5% SP-1000 on Supelcoport (100/120 mesh) was used for separation. Normal operating conditions were 260°C injector temperature, 175°C column temperature, 250°C detector temperature, and helium, hydrogen, and air flow rates of 35, 20, and 26 mL/min, respectively. The minimum detectable concentration was 1.8 ng absolute or 300 ng/mL in a 6 µL injection, which corresponded to total aldicarb residues extracted from water solutions originally containing 3 to 12 ppb, depending on the volume of water and the final volume of the extract. Chromatograms were reported on a Hewlett-Packard 3390A Integrator in the linearized mode and a Varian 9176 recorder in the non-linearized mode.

Laboratory Incubations of Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone Degradation

Incubation containers consisting of BOD bottles for groundwaters and 946-mL Mason jars for groundwater-saturated subsoils were initially filled to

completely occupy the entire volume of the container. The BOD bottles were stoppered and a small amount of silicone stopcock grease was placed around the outside edge of the stopper and bottle to help prevent any exchange of gases from occuring. All containers were incubated in the dark at the ambient temperatures of the groundwaters measured in the field (22 $\pm$ 2 to 26 $\pm$ 2°C). All pH values were checked before and after each incubation period.

To insure that anaerobic conditions were maintained during those times when aliquots of groundwater and groundwater-saturated subsoil were withdrawn from incubation containers, disposable polyethylene glove bags with a stream of N_2 constantly purging the bag were used. A Leeds and Northrup dissolved oxygen meter equipped with a BOD probe set on "air calibrate" recorded zero oxygen in the bags and headspace of the containers after sampling; also, the water of those samples incubated in Mason jars were devoid of oxygen as recorded by the dissolved oxygen meter.

Sterile and Non-sterile Degradation of Aldicarb

Duplicate sterile and non-sterile groundwaters from Ryall, Sexton, and Luther wells sampled on December 9, 1983, were spiked with aldicarb in BOD bottles to yield a final concentration of 0.10 mg/L, and incubated at measured ambient field temperature of 24 $\pm$ 2°C. Groundwaters (500 mL) with and without saturated subsoils (1800 g dry wt. from 1.1 to 1.5 m depths) obtained from the Lindsey Wabasso grove on January 30, 1984, were also sterilized and left non-sterile at 22 $\pm$ 2°C so as to determine what effects the presence of aquifer material had on aldicarb decomposition. A second site (BBC grove) was cored to retrieve groundwaters with and without saturated subsoil from a depth of 0.9 to 1.2 m on February 22, 1984, but all incubations using water (500 mL) and aquifer material (1200 g dry wt) from this site remained non-sterile. Sterile

and non-sterile controls without added aldicarb were run for each well. Sterilization was accomplished by adding sodium azide (NaN_3) to give a final concentration of 0.1% in the groundwater-only incubations (Sharom et al. 1980) and 0.4% in the groundwater-saturated subsoils. To determine whether sterility was maintained throughout the incubations, thioglycollate broth media was employed on the first and last days to test for contamination in the sterilized samples and was negative in only the groundwater containers.

Fifty-mL aliquots of groundwater from the private water supply wells incubated in the BOD bottles were withdrawn at times 0, 5, 11, 34 and 90 days and analyzed for TTR. In the case of the groundwater with and without aquifer material from the Lindsey Wabasso and BBC sites, subsampling from the 946-mL Mason jars serving as incubation containers at time 0 occurred when the sediment had settled (approximately 1 hour) after being shaken; subsampling occurred again after 30 (Lindsey Wabasso) and 23 (BBC) days had elapsed. Saturated subsoil material was frozen until extraction.

Non-sterile Degradation of Sulfoxide and Sulfone

Duplicate BOD bottles containing non-sterile groundwaters from the private water supply wells were spiked with sulfoxide or sulfone to yield a final concentration of 0.10 mg/L. Shallow groundwaters and saturated subsoils from 0.9- 1.2 m (BBC) and 1.2-1.5 m (Lindsey Wabasso) depths were obtained on February 22 and April 23, 1984, from BBC and Lindsey Wabasso groves, respectively. As before, sulfoxide or sulfone was amended to the Mason jar incubation containers to produce an initial concentration of 0.10 mg/L. Sterile samples were not run because results from the sterile vs. non-sterile aldicarb experiments indicated

sterile conditions were unattainable for incubations where the aquifer material was included. Controls without amended sulfoxide or sulfone were set up in duplicate for all groundwaters from all wells with and without added subsoil. An incubation temperature for the deeper groundwaters from the private water supply wells was 24 $\pm$ 2°C; groundwaters and groundwater-saturated subsoils from the augered wells were incubated at 22 $\pm$ 2°C (BBC) and 26 $\pm$ 2°C (Lindsey Wabasso). Either 50 or 100-mL aliquots were removed at 0, 5, 20 and 40 days from the BOD bottles used to incubate the groundwaters sampled from the private water supply wells. Water and saturated subsoil were withdrawn from the Mason jars used as incubation containers for the augered wells at BBC and Lindsey Wabasso groves at time 0 and after 23 or 25 days, and extracted as previously described.

Aqueous Hydrolysis of Aldicarb

Buffered reaction solutions for the aldicarb hydrolysis experiment were prepared by adding 3 mL of a 30 mg/l aldicarb solution in water to a solution of 297 mL of distilled-deionized-carbon-filtered water and 1.67×10^{-2} M of pH buffer solution (4.1×10^{-3} M buffer for pH 8.85) in duplicate BOD bottles to give a 0.10 mg/L aldicarb concentration. The sterile buffer systems and their final pH values after incubating 15-89 days were potassium hydrogen phthalate-hydrochloric acid (pH 3.95), potassium dihydrogen phosphate-sodium hydroxide (pH 6.02, 7.06, and 7.96), sodium tetraborate-hydrochloric acid (pH 8.85), and sodium bicarbonate-sodium hydroxide (pH 9.85). Buffer solutions and glassware were autoclaved before use. The BOD bottles were plugged with sterilized foam plugs and placed in an incubator in the dark at 20° $\pm$ 2°C. Controls without aldicarb were included. All pH values were checked before and after each kinetic run.

Pseudo-first-order rate constants, k, were obtained from the slope of the line (-2.30 X regression coefficient) obtained by a linear least-squares analysis of the data for those experiments where samples were collected and analyzed over multiple time intervals (i.e., aldicarb hydrolysis in pH-buffered distilled water; Ryall, Sexton, and Luther well-water). For the shallow wells at BBC and Lindsey Wabasso where aquifer material and groundwaters were sampled and analyzed for only one time interval, the integrated first-order rate equation was used

$$-k = \frac{\ln C/C_o}{t} \quad (1)$$

where C_o is the initial concentration of aldicarb or one of its primary oxidation products and C is the remaining concentration at time t, the corresponding half-life was from

$$t_{1/2} = 0.693/k \quad (2)$$

The second-order reaction rate constants, k_{OH} and k_H, were determined from the slope between pH 8 and pH 10 and between pH 4 and pH 6 in a plot of log k vs. pH according to the relationships

$$k_{OH} = \frac{k}{[OH^-]} \quad \text{and} \quad (3)$$

$$k_H = \frac{k}{[H^+]} \quad (4)$$

Migration of TTR in Groundwaters in Indian River County

Lateral movements of theoretical TTR plumes were calculated using Darcy's Law

$$v = -K\frac{dh}{dl}/\alpha \qquad (5)$$

where v = velocity (m day^{-1}); K = hydraulic conductivity (m day^{-1}); $\frac{dh}{dl}$ = hydraulic gradient (m/m); and α = porosity.

Values for the parameter K were obtained from U.S. Soil Conservation Service Soil Interpretation Records for the soil series (Pineda sand, Riviera Sand, and Wabasso sand) surveyed recently to be present at the BBC and Lindsey Wabasso sites. Water table data from observation wells in Indian River County provided by the Soil Survey of the U.S. Soil Conservation Service (C. Wettstein, pers. comm., May 30, 1984) were converted to heights above sea level after adjusting for elevation differences in ground level between well locations. The average of the differences between water table surfaces based on 12 measurements during an 18 month period (November 1982 - May 1984) divided by the distance between two wells generated realistic hydraulic gradients (dh/dl) for the county. A total of five observation wells were used to compute three different hydraulic gradients. Porosity was assumed to be 33%.

QUALITY ASSURANCE

In order to insure reliability in accuracy and precision of analyses, the following quality control measures were carried out:

1. All sample incubations were done in duplicate. Expressed as percentages of their averages, the differences for all aldicarb samples were ±11% (0-30%); for aldicarb sulfoxide samples ±9% (0-33%); and for the aldicarb sulfone samples ±22% (3-62%).
2. Blanks were analyzed for each well water, aquifer material, and aldicarb substrate combination, and were always below the limit of detection (i.e., <3 to <12 ppb, depending on the volume of water extracted and final volume of the extract).
3. A total of 22 spikes were performed (16 with aldicarb spiked into water; 4 with aldicarb sulfone spiked into water; and 2 with aldicarb spiked into saturated subsoils). Recoveries ranged from: 93 to 109% (ave. = 103%) for the aldicarb-spiked water samples, 104% for all the aldicarb sulfone-spiked waters, and 88 to 92% (ave. = 90%) for the aldicarb-spiked subsoils. Results were not corrected for the recovery percentage.
4. Inter-laboratory comparisons with two independent laboratories: 1) Florida Dept. of Environmental Regulation; and 2) Pesticide Research Lab of the Institute of Food and Agricultural Sciences, University of Florida, Gainesville. A total of 4 samples were exchanged (2 samples to each lab), and their results were within ±20%, except for one sample which differed by 29%. The samples, concentrations, and gas/liquid chromatographic systems are presented in Appendix I.
5. Twenty-two groundwater samples underwent separation by liquid chromatography using Florisil columns after oxidation by peracetic acid. Two

eluants were used: one to retrieve the non-toxic aldicarb residues (fraction 1 = 5% acetone in ethyl ether) and the other to elute toxic aldicarb residues (fraction 2 = 50% acetone in ethyl ether). The data from which errors were calculated for recovery of all residues after Florisil separation as well as for not removing nitriles by Florisil separation are provided in Tables 1 and 2 of the RESULTS section. A discussion of the importance of the computed errors is also presented in the RESULTS section.

6. Standards of aldicarb sulfone and aldicarb sulfone nitrile were added to water and separated by Florisil into two fractions: one containing the nitrile and the other containing the sulfone. Recoveries were approximately 111% for the nitrile and 93% for the sulfone. The data are provided in Table 2 of the RESULTS section.

7. Readings of pH for the laboratory experiments were taken at each time a subsample was withdrawn for TTR analysis and pH was found to increase approximately 1 pH unit within 10 days of the initial time in the private water supply wells (Ryall, Sexton, and Luther). The pH hydrolysis experiment for aldicarb and the hand-augered wells showed pH variations within ± 0.2 pH units during the incubation period, except for the Lindsey Wabasso samples taken on January 30, 1984, which had an increase of ~ 0.9 pH unit.

8. A check as to whether positive interferences from oximes would result for those samples not passed through a Florisil column revealed that they would not interfere at the concentrations of toxic aldicarb residues used in this investigation. Details of the check-out procedure are given in the RESULTS section.

9. Anoxic conditions were maintained throughout the laboratory experimental studies since dissolved oxygen could not be detected at the end of the

incubation period in the groundwaters or saturated subsoils from the augered wells which were contained in Mason jars; oxygen was also not detected in the atmospheres in the BOD bottles used for experiments on aldicarb hydrolysis and degradation of TTR in waters from private wells for aldicarb, aldicarb sulfoxide, and aldicarb sulfone amendments.

10. An evaluation of the buffer catalysis contribution to the hydrolysis of aldicarb for each pH-buffered solution indicated that there was minimal contribution, if any, from the nature and concentration of the acid-base system used to buffer the pH. A full account of the evaluation is provided in Appendix II.

11. Tests for enumerating bacterial densities at the end of each incubation period were always conducted to evaluate whether sterilization had been maintained throughout the duration of the experimental period, or, in the case of non-sterile samples, that incubation conditions had closely approximated the in situ environment such that bacterial densities after the incubation period did not differ significantly for densities measured at the beginning of the incubation period. In all cases, bacteria densities remained close to their initial values during the incubation period. Raw data for bacterial counts can be found in Appendix III.

RESULTS

Interferences From Non-toxic Aldicarb Residues: Nitriles and Oximes

Care must be exercised in labeling as total toxic residues any sample extractions which have not been passed through a Florisil column to remove nitriles and oximes (Romine 1974) prior to GC analysis. If a significant proportion of aldicarb residues is comprised of the non-toxic oximes or nitriles, then they would serve as a positive interferent by chromatographing with the toxic aldicarb and its S-oxides; neither nitriles nor oximes should be included in any analytical procedure designed for measuring TTR.

Since the method followed at the beginning of this study was an unpublished one (Union Carbide 1980) which made no mention of removing non-toxic aldicarb residues from the toxic aldicarb residues by Florisil separation, twenty-two groundwater samples collected toward the end of the period of investigation (when the possibility of a nitrile interference became known) were eluted through Florisil columns and fractions 1 and 2 analyzed for aldicarb residues (Table 1). Ten of the 22 samples were split before Florisil separation and one aliquot put through a Florisil column and the other aliquot left without Florisil separation (Table 2).

Large ranges in percentage recoveries (57-129%) were found for the groundwater samples passed through Florisil columns when compared to the aliquots left without separation by liquid chromatography, with an average of 99% for the 10 samples (Table 2). Interferences from nitriles, which would result in an over-estimation of TTR, became quantitatively important only near the end of the incubation period in those samples that had >90% disappearance of the initial TTR (Table 1). Although the absolute error was large for those particular samples because of the low concentrations of TTR remaining (<10 ppb),

Table 1. Amount of Non-toxic Nitriles and Toxic Aldicarb Residues Remaining in Duplicate Groundwaters and Subsoils After Florisil Separation.

		Amount Remaining, ppb				
		Time 0	Time 20 Days		Time 42 Days	
Sample	Compound Added	TTR	TTR[a]	Nitrile[b]	TTR[a]	Nitrile[b]
Ryall-A	aldicarb sulfoxide	97	54	ND	-	-
Ryall-B	aldicarb sulfoxide	105	-	-	4	10
Ryall-A	aldicarb sulfone	81	43	3	ND	5
Ryall-B	aldicarb sulfone	97	28	-	ND	-
Sexton-A	aldicarb sulfoxide	97	34	ND	4	5
Sexton-A	aldicarb sulfoxide	98	35	-	4	-
Sexton-A	aldicarb sulfone	80	12	ND	ND	-
Sexton-B	aldicarb sulfone	92	37	-	ND	13
Luther-A	aldicarb sulfoxide	95	43	6	9	9
Luther-B	aldicarb sulfoxide	92	40	-	13	6
Luther-A	aldicarb sulfone	90	20	5	ND	ND
Luther-B	aldicarb sulfone	94	30	-	ND	ND

		Amount Remaining, ppb		
		Time 0	Time 25 Days	
Sample	Compound Added	TTR	TTR[a]	Nitrile[b]
Lindsey Wab. water-A	aldicarb sulfoxide	79	54	ND
Lindsey Wab. water-B	aldicarb sulfoxide	80	53	3
Lindsey Wab. subsoil-A	aldicarb sulfoxide	51	12	ND
Lindsey Wab. subsoil-B	aldicarb sulfoxide	62	10	5
Lindsey Wab. water-A	aldicarb sulfone	90	30	3
Lindsey Wab. water-B	aldicarb sulfone	90	29	11
Lindsey Wab. subsoil-A	aldicarb sulfone	64	10	5
Lindsey Wab. subsoil-B	aldicarb sulfone	78	16	ND

[a] TTR = eluate from fraction 2 (50% acetone in ethyl ether) of Florisil column

[b] Nitrile = eluate from fraction 1 (5% acetone in ethyl ether) of Florisil column

ND = non-detectable (< 3 ppb)

Table 2. Recovery of Aldicarb Sulfone and Aldicarb Sulfone Nitrile From Water and Sediments After Eluting Through Florisil Columns.

Amount Added To Water	Measured, ppb			Recovery, %		
	No Florisil Separation	Florisil[a] Fraction 1	Florisil[b] Fraction 2	No Florisil Separation	Florisil[a] Fraction 1	Florisil[b] Fraction 2
35 ppb Sn	-	ND	34	-	ND	97
62 ppb Sn nitrile	-	70	ND	-	113	ND
35 ppb Sn + 62 ppb Sn nitrile	-	68	31	-	110	89
Amount Measured in Sample Water or Subsoil						
Lind. Wab. Water Sx added; 25 days	57	ND	54	95	-	-
Lind. Wab. Water Sn added; 25 days	35	11	29	114	-	-
Lind. Wab. Subsoil Sn added; 25 days	15	5	10	100	-	-
Lind. Wab. Subsoil Sx added; 25 days	14	5	10	107	-	-
Ryall Sn added; 20 days	46	3	43	100	-	-
Sexton Sn added; 20 days	21	ND	12	57	-	-
Luther Sn added; 20 days	26	5	20	96	-	-
Luther Sx added; 20 days	65	3	43	71	-	-
Luther Sx added; 42 days	14	9	9	129	-	-
Luther Sx added; 42 days	16	13	6	119	-	-
Average % Recovery For Samples = 99%						

[a] Florisil fraction 1 = 5% acetone in ethyl ether and contains aldicarb Sn nitrile.
[b] Florisil fraction 2 = 50% acetone in ethyl ether and contains aldicarb Sn
ND = non-detectable (<3 ppb)
Sx = Sulfoxide; Sn = Sulfone

the relative error based on the initial TTR concentrations was small (average of 6% with a range of 0-14% for the 8 groundwater samples from the private water supply wells spiked with aldicarb sulfone or aldicarb sulfoxide). Considering that this is less than the individual percentage errors associated with recoveries of aldicarb sulfone nitrile and aldicarb sulfone from Florisil separation of water spiked with standards (111% and 93%, respectively) (Table 2), recoveries of total toxic plus non-toxic residuals remaining in groundwater samples after Florisil separation (57-129%) (Table 2), inter-laboratory comparisons of split samples (~20%), and the average error between duplicate samples (9 and 22% for aldicarb sulfoxide and aldicarb sulfone, respectively), the extra time and effort involved in the Florisil removal of nitriles may not be warranted. Hansen and Spiegel (1983) also observed in their hydrolysis studies that presence of nitriles was important only after 98 to 99% of the aldicarb sulfoxide or sulfone had been degraded. Furthermore, Union Carbide (Romine, pers. comm.; May 1, 1984) has not found nitriles of aldicarb or its sulfoxide or sulfone as residues in potable groundwater from their monitoring of many groundwater sources in several states, including Florida. Neglecting to remove nitriles from some of the earlier samples apparently was not a significant source of error in analyzing for TTR.

Apparently aldicarb oxime does not pose as an interferent since it is not thermally decomposed to nitrile at an injection port temperature of 350°C (Knaak et al. 1966). However, the aldicarb sulfoxide oxime and aldicarb sulfone oxime decompose to nitriles at 350°C (Knaak et al. 1966), and thus could also serve as a positive interferent, especially since any aldicarb oxime and aldicarb sulfoxide oxime present would be oxidized to aldicarb sulfone oxime by the peracetic acid oxidation step. Studies done in our lab using either aldicarb sulfoxide oxime or aldicarb sulfone oxime at final

concentrations of 5 ug/mL in the acetone extract, and without a Florisil separation step, did not elicit a response on the GC under the operating conditions set for the instrument. This was true regardless of whether or not the oxime had undergone oxidation by peracetic acid. Larger amounts of the oxime (100 ug/mL) in acetone did produce a full-scale response by the detector. Clearly, oximes would not have been detected at the low levels of residues (<5-10 ug/mL) that were analyzed in our samples. This could have been due to poor detector sensitivity to oximes; and/or low recovery rates of oximes from extracts (Maitlen et al. 1968); and/or removal of oximes quantitatively by conversion to their respective aldehydes (which do not interfere with the analysis) by acid hydrolysis in the peracetic acid oxidation step (Beckman et al. 1969).

Hydrolysis Rates in Sterile pH-buffered Distilled Water

Plots of log percent remaining vs. time are shown in Figure 3 in an effort to determine the contribution of H^+, OH^-, and H_2O to the rate of degradation. The actual data at each duplicated pH are presented in Table A-2 in the Appendix III. At pH = 6, 7, and 8 aldicarb hydrolyzes slowly, but increases at higher and lower pH levels (Figure 3). Plotting log k vs. pH in Figure 4 demonstrates that there are only slight changes in the pseudo-first-order rate constant in the pH 6 to 8 range. The least squares estimates of all the pseudo-first-order hydrolysis rate constants, half-lives, and coefficients of determination are given in Table 3. Only the tests conducted at pH = 4, 9, and 10 showed degradation sufficient for estimating a rate constant. Therefore, the rates and resulting half-life values for pH 6-8 are only extimates since the slopes of the log percent remaining vs. time regression lines in Figure 3 were probably not significantly different from zero. To accurately estimate the half-life for these pH conditions,

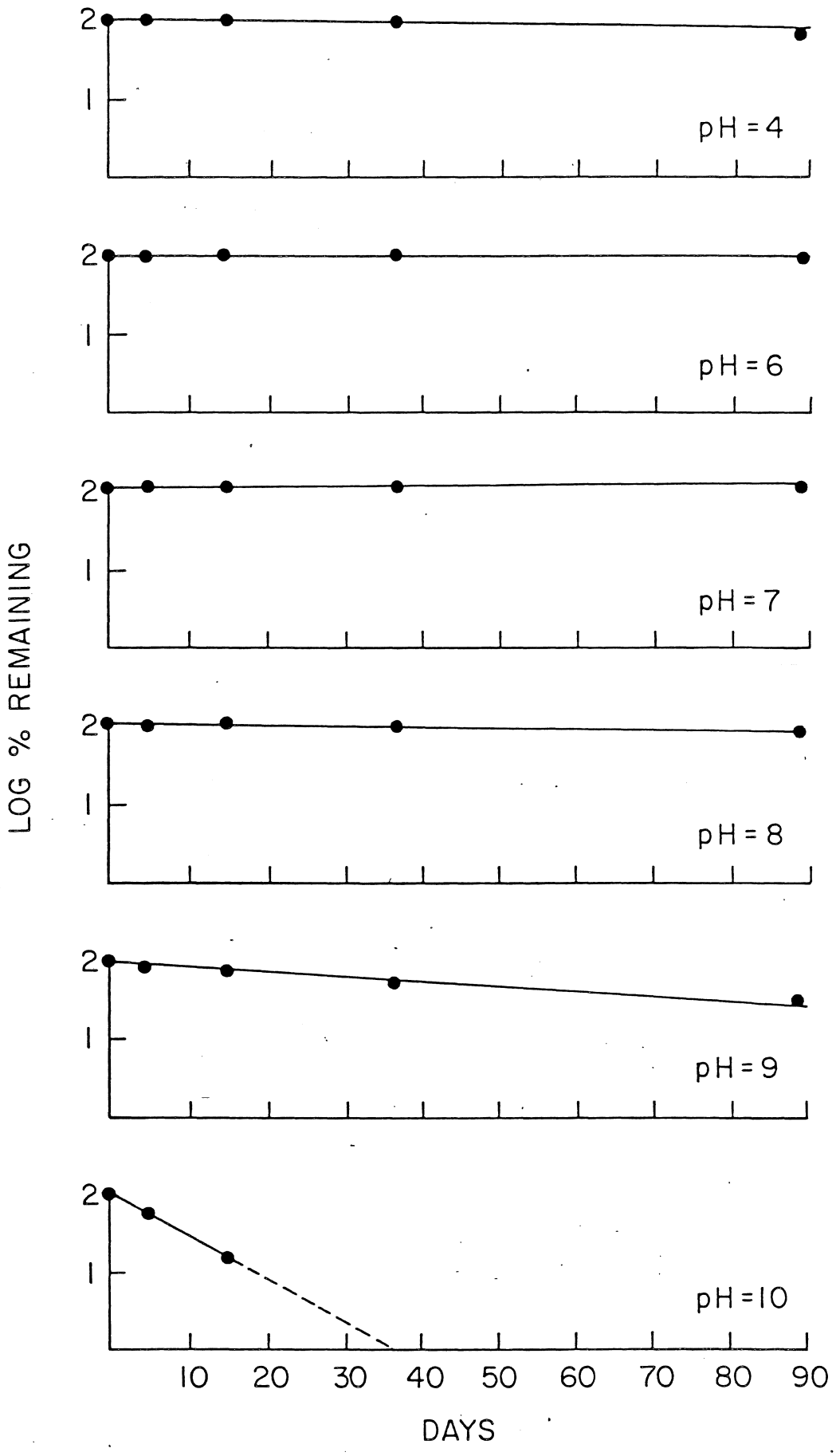


Figure 3. Hydrolysis at 20°C of Aldicarb in Sterile pH-buffered Distilled Water Solutions. Each Data Point is the Mean of Duplicate Samples.

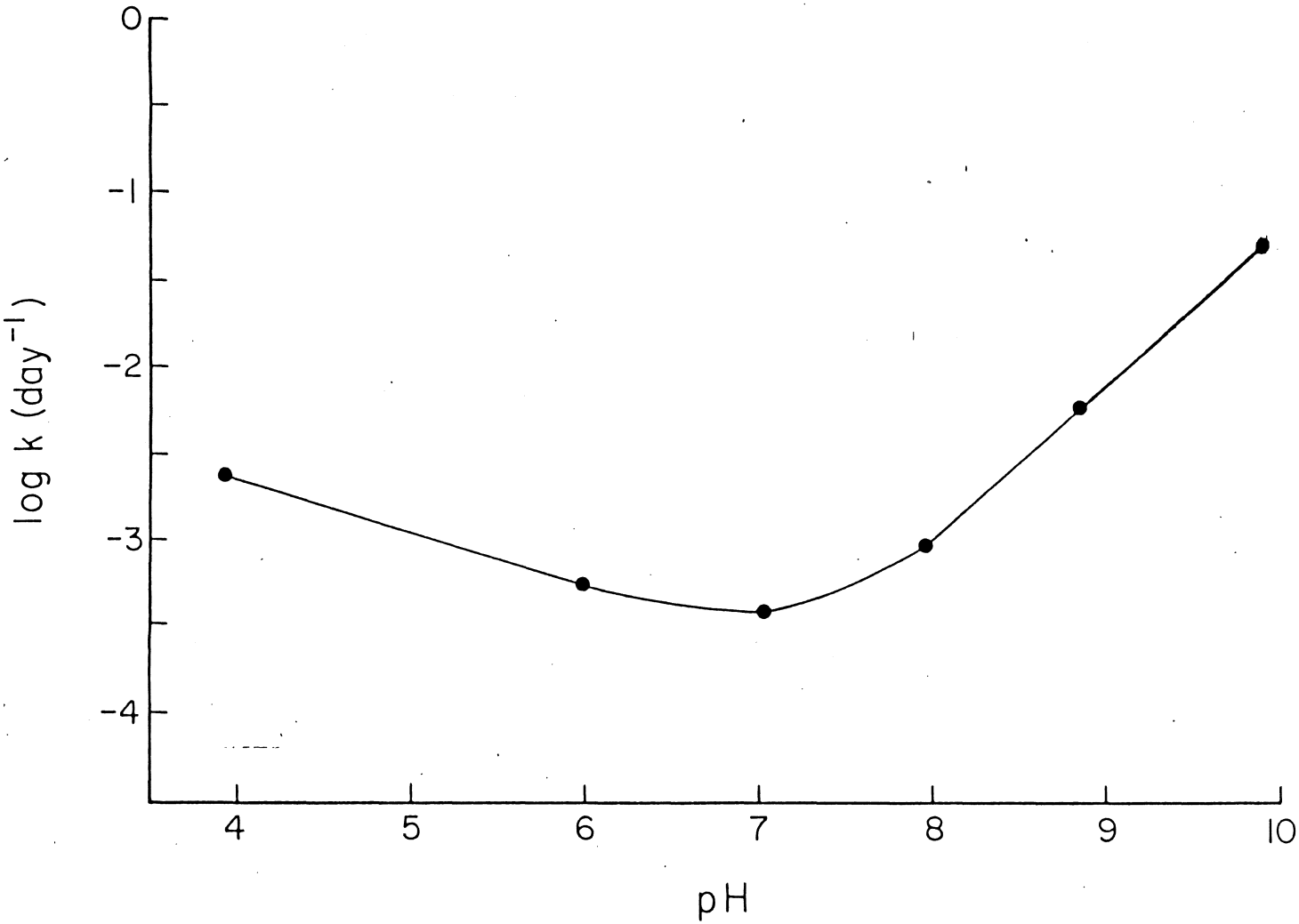


Figure 4. Log k vs. pH for Aldicarb Hydrolysis at 20°C in Sterile pH-buffered Distilled Water Solutions.

Table 3. Pseudo-first-order Rate Constants (d), Half-life Values ($t_{\frac{1}{2}}$), and Coefficient of Determination of the Regression Line (r^2) For Aldicarb Hydrolysis at 20°C in pH - buffered Distilled Water.

pH	Period (days)	k (day^{-1})	$t_{\frac{1}{2}}$ (days)	r^2
3.95	89	5.3×10^{-3}	131	0.86
6.02	89	1.2×10^{-3}	559	0.90
7.06	89	8.1×10^{-4}	861	0.21
7.96	89	2.1×10^{-3}	324	0.62
8.85	89	1.3×10^{-2}	55	0.98
9.85	15	1.2×10^{-1}	6	1.00

experiments lasting longer than 89 days would have to be performed. The data obtained at pH = 7 showed a slight increase in aldicarb and its oxidation products over time, resulting in a low coefficient of determination (r^2 = 0.21) and a positive slope. Above pH 8 the pseudo-first-order rate constant increases with increasing pH and the slope of the line is approximately +1 (Figure 4), indicating aldicarb hydrolysis is sensitive to hydroxyl ions in aqueous solutions. At pH < 6, the rate of hydrolysis appears to be acid catalyzed, but not to the extent as for base catalysis since the slope is less than 1. The nonlinearity of the plot between pH 6 and 8 is interpreted as resulting from competing reactions of aldicarb with water, hydrogen, and hydroxide.

The second-order reaction rate constant for base hydrolysis, k_{OH}, was first-order with respect to hydroxide because the plot of log k vs. pH (Figure 4) yielded a +1 slope at pH > 8. The k_{OH} value calculated from Equation 3, using the data obtained at pH 7.96, 8.85, and 9.85, was $1.94 \times 10^3 \pm 3.54 \times 10^2$ L mole^{-1} day^{-1}. The acid hydrolysis constant, k_H, which was not first-order with respect to hydrogen, had a computed value (based only on the data acquired at pH 3.95) of 4.72×10^1 L mole^{-1} day^{-1}.

Groundwater Characteristics

Private Water Supply Wells

The groundwaters from the three private water supply wells contained similar heat values and concentrations for the following constituents: temperature, specific conductance, pH, alkalinity, and hardness (Table 4). Sexton well, however, exhibited higher levels of total Fe (0.12 mg/L) and sulfide (6.6-8.9 mg/L) while having stronger reducing conditions (-145 to -163 mV). Luther well yielded approximately an order-of-magnitude higher bacteria cell concentration (55-77 cells/mL) than the other two wells, but

Table 4. Physical, Chemical, and Biological Characteristics of Groundwaters Sampled From Private Water Supply Wells.

	WELL SITE					
	Ryall		Sexton		Luther	
Date Sampled	12/9/83	3/26/84	1/9/83	3/26/84	12/9/83	3/26/84
Depth (m)	20	20	17	17	?	?
Temp (^{o}C)	24	24	24	25	24	24
Sp. Cond. (uS/cm)	1126	1363	1073	1049	789	839
D. O. (mg/L)	0.0	0.0	0.0	0.0	0.1	0.1
E_{h7} (mV)	+264	+274	-163	-145	+326	+360
pH	6.8	7.8	7.2	6.8	7.3	7.2
Alkalinity (mg $CaCO_3$/L)	292	292	355	353	219	289
Hardness (mg$CaCO_3$/L)	363	440	298	300	178	272
Total Fe (mg/L)	0.01	0.04	0.11	0.12	0.05	0.20
Sulfide (mg/L)	0.25	0.38	8.88	6.58	0.38	0.57
Bacteria (cells/mL)[a]						
Before	5	4	2	3	55	77
After	11	7	7	6	37	63

[a]Average of two anaerobic plate counts before and after the incubation period.

still was low when compared to cell densities from subsoils (Table 5). The low densities of bacteria were maintained throughout the incubation period, attesting to the sterile techniques and precautions taken not to alter the original temperature and redox potential of the groundwaters during the laboratory incubations. Generally, the groundwaters can be characterized as being hard, anoxic, and reduced, with high alkalinities, low iron, and neutral pH.

Augered Wells

The shallow groundwaters from the augered wells at BBC and Lindsey Wabasso groves differed from the deeper water supply wells by containing more dissolved solids and bacteria cells (Table 5). Oxidation-reduction potential and pH were consistent with those values reported for the deeper groundwaters at Ryall, Sexton, and Luther wells. Lindsey Wabasso groundwater had a higher alkalinity and hardness than of any sampled groundwater.

Degradation of TTR From Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone Amended to Groundwaters From Private Water Supply Wells

The least-squares estimates of the pseudo-first-order rate constants, half-life values, and coefficients of determination of the regression lines when the percent TTR remaining is plotted logarithmically for 0.10 mg/L additions of aldicarb, aldicarb sulfoxide, and aldicarb sulfone are presented in Table 6. The linear coefficients for the straight lines are high (r^2 = 0.88-1.00), indicating that some confidence can be placed on the pseudo-first-order rate constants and half-life values which were determined from the data. The raw data for each duplicate incubation container and at each time that a sample was withdrawn and measured for TTR are presented in Appendix III (Tables A-3 and A-4).

Notwithstanding a high variability in the data during the earlier stages of incubation, Figure 5 depicts that approximately 60% of the initial 0.10 mg/L

Table 5. Physical, Chemical, and Biological Characteristics of Groundwaters Sampled From Augered Shallow Wells.

	Well Site		
	Lindsey Wabasso		BBC
Date Sampled	1/30/84	4/23/84	2/22/84
Depth (m)	1.5	1.5	1.3
Temp (C)	22	26	22
Sp. Cond. (µS/cm)	2750	2462	
D. O. (mg/L)	0.0	0.1	0.4
E_{h_7} (mV)	+111	+83	+321
pH	7.1	7.3	7.4
Alkalinity (mg $CaCO_3$/L)	358	442	106
Hardness (mg $CaCO_3$/L)	836	860	202
Total Fe (mg/L)		0.16	0.12
Bacteria (cells/mL)[a]			
Before	7.5×10^2	1.3×10^3	3.6×10^4
After	2.2×10^2	9.0×10^2	2.0×10^3
Bacteria (cells/g dry wt)[a]			
Before	1.1×10^5	6.0×10^4	4.6×10^4
After	1.5×10^4	8.0×10^3	9.0×10^3

[a]Average of two anaerobic plate counts before and after the incubation period.

Table 6. Pseudo-first-order Rate Constants (k), Half-life Values ($t_{1/2}$), and Coefficients of Determination of the Regression Lines (r^2) at 24°C For the Disappearance of TTR in Sterile and Unsterile Groundwaters Amended With 0.10 mg/L of Aldicarb, Aldicarb Sulfoxide, or Aldicarb Sulfone. Each Value Is a Mean of Duplicate Samples.

Compound	Well	Sterile	Period (days)	k (day^{-1})	$t_{1/2}$ (days)	r^2
Aldicarb	Ryall	Yes	90	5.77×10^{-3}	120	0.96
		No	90	6.74×10^{-3}	103	0.92
	Sexton	Yes	90	6.90×10^{-3}	100	0.90
		No	90	6.88×10^{-3}	101	0.98
	Luther	Yes	90	7.80×10^{-3}	89	0.88
		No	90	6.74×10^{-3}	103	0.92
Aldicarb Sulfoxide	Ryall*	No	42	2.95×10^{-2}	24	1.00
	Sexton*	No	42	7.71×10^{-2}	9	0.98
	Luther*	No	42	5.23×10^{-2}	13	0.99
Aldicarb Sulfone	Ryall*	No	20	4.51×10^{-2}	15	1.00
	Sexton*	No	20	6.65×10^{-2}	10	0.99
	Luther*	No	20	6.46×10^{-2}	11	1.00

*Nitriles removed from sample

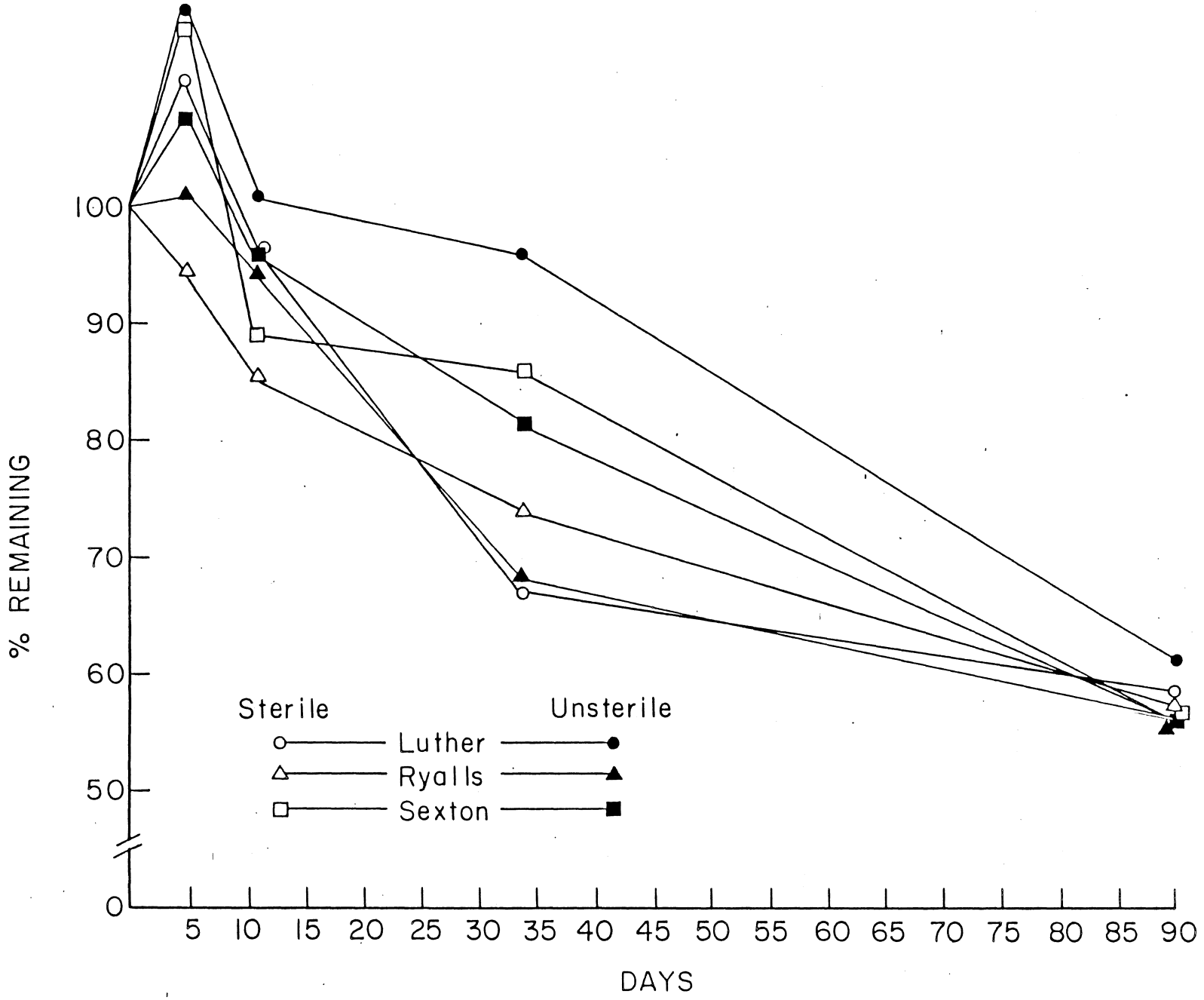


Figure 5. Percent Remaining of TTR From an Initial 0.100 mg/L Aldicarb Inoculum in Sterile and Non-sterile Groundwaters From Three Water Supply Wells. Each Data Point is the Mean of Duplicate Samples.

aldicarb inoculum remained as a toxic residue in all three groundwaters after 90 days at 24°C, regardless of whether the water was sterile or non-sterile. The pseudo-first-order rate constants for the TTR remaining after aldicarb was added to the groundwaters fell within a narrow range of 5.77×10^{-3} to 7.80×10^{-3}/day, which equalled 89 and 120 days when transformed into their respective half-life times. TTR concentrations disappeared at faster rates (half-life of 9-24 days) when either of the S-oxides was added (Table 6); there were no major differences in the degradation of TTR between sulfoxide and sulfone or among wells. The differences in the decomposition of TTR observed for amendments of aldicarb and its S-oxides cannot be from the removal of nitriles in only the S-oxide samples (and not the aldicarb samples) for reasons previously described. It should be pointed out that these measured rates overestimate the true rates of TTR degradation since the pH of the water supply wells increased approximately 1 pH unit in each well water during the incubation period. Still, they represent rates under pH conditions which can exist at different times of the year. For instance, the Ryall well underwent a pH change of 1 (6.8 vs. 7.8) between the two sampling periods in December and March (Table 4).

Degradation of TTR From Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone Amended to Groundwaters and Saturated Aquifer Material

As was found for the private water supply well waters, aldicarb added to groundwaters without the subsoil aquifer material decomposed to non-toxic residuals at very low rates (Table 7): half-life values of 112 days at the BBC and 178 days at Lindsey Wabasso groves. Agreement among the replicate samples was high without any differences being measured (cf. Appendix III). When aldicarb was added to aquifer material consisting of saturated subsoil from the top of the water table, the rate of TTR disappearance was increased by an order-of-magnitude. For example, the half-life times decreased from 112

Table 7. Percent Remaining, Pseudo-first-order Rate Constants (k), and Half-life Values ($t_{1/2}$) For the Disappearance of TTR in Groundwaters and Aquifer Material From Lindsey Wabasso (LW) and BBC Groves Amended With Aldicarb, Aldicarb Sulfoxide, or Aldicarb Sulfone. Each Value Is a Mean of Duplicate Samples.

Aldicarb	Site	Temp (°C)	Period (days)	% TTR Remaining	k (day^{-1})	$t_{1/2}$ (days)
Groundwater	BBC	22	23	87	6.21×10^{-3}	112
Aquifer Material	BBC	22	23	27	5.76×10^{-2}	12
Groundwater	LW	22	30	89	3.88×10^{-3}	178
Aquifer Material	LW	22	30	<3	-	-
Aldicarb Sulfoxide						
Groundwater	BBC	22	23	62	2.09×10^{-2}	33
Aquifer Material	BBC	22	23	54	2.64×10^{-2}	26
Groundwater	LW	26	25	67*	1.60×10^{-2}	43
Aquifer Material	LW	26	25	20*	6.44×10^{-2}	11
Aldicarb Sulfone						
Groundwater	BBC	22	23	54	2.64×10^{-2}	26
Aquifer Material	BBC	22	23	42	3.77×10^{-2}	18
Groundwater	LW	26	25	33*	4.43×10^{-2}	16
Aquifer Material	LW	26	25	18*	6.86×10^{-2}	10

*Nitriles removed from sample

days to 12 days when aquifer material was present from the BBC site. For the Lindsey Wabasso grove, the conversion of TTR to non-toxic residues was so fast that no detectable TTR was found after 30 days when aquifer subsoil was present. This should be compared to a half-life of 178 days without aquifer material being present. Adsorption of aldicarb onto the clays in the subsoil did not occur since extraction of the sediments consistently produced non-detectable levels (< 6 ng/g (dry wt.)).

A similar trend was also noticed for the disappearance of TTR from sulfoxide and sulfone additions to groundwaters with and without aquifer material (Table 7), but not to the extent that was recorded for aldicarb. Instead of the 9-fold difference in the degradation rates with and without aquifer material that was found in the aldicarb amendments, sulfoxide or sulfone amended to saturated aquifer subsoils increased the conversion of TTR to non-toxic products by only 1.3 to 4.0 times. Thus, the presence of aquifer material resulted in only slightly greater rates of degradation of TTR from either sulfone-or sulfoxide-amended groundwaters: half-life times of 16-43 days without aquifer material and 10-26 days in the presence of aquifer material. The removal of nitriles from some of the S-oxide amended samples but not from the aldicarb-amended samples could not have accounted for the differences in the rates of TTR disappearance measured for aldicarb amended and S-oxide amended samples since the percentage of the initial TTR comprised by nitriles was small (Table 1). The small differences between the rate constants from the two groves for sulfoxide and sulfone amendments in Table 7 were probably due more to the higher incubation temperature (26^{o}C) used for the Lindsey Wabasso samples than from the removal of nitriles from the Lindsey Wabasso samples. Adsorption onto clays was negligible: no aldicarb sulfoxide or aldicarb sulfone was found above the limits of detection (6 ng/g (dry wt.)).

DISCUSSION

Hydrolysis Rates in pH-buffered Distilled Water

Laboratory hydrolysis studies of any xenobiotic using sterile pH-buffered distilled water can only be interpreted as representing a "worst case" situation since all the environmental factors such as volatilization, adsorption, plant uptake, leaching, and microbial degradation present under field conditions have been omitted. Moreover, laboratory studies of hydrolysis reaction rates are not only a function of pH, but also of the nature and concentration of the acid-base system used to buffer the pH, which is called buffer catalysis (Perdue and Wolfe 1983). A detailed account showing the effect of buffer catalysis was negligible under the experimental conditions used in this investigation (Appendix II). The extent of error in not considering the environmental conditions in the field and not using actual well waters and aquifer material when interpreting hydrolysis data will be discussed later in this report. Still, as Hansen and Spiegel (1983) point out, hydrolysis rates obtained from laboratory studies can be used to establish upper bounds for the half-lives of aldicarb in groundwater.

Comparisons of hydrolytic half-life values reported by other investigators for aldicarb in sterile, pH-buffered distilled water are presented in Table 8. For those cases when the raw data were available, the rate constants derived for temperatures other than 20°C were adjusted to a temperature of 20°C by constructing Arrhenius plots. Not only is there a scarcity of published literature on aldicarb hydrolysis, but only a few of the published studies included the range of pH values which bracket the pH of natural waters.

Carbamates such as aldicarb typically are quite resistant to hydrolysis at neutral pH values, but are relatively unstable under alkaline conditions of

Table 8. A Comparison of Hydrolytic Half-lives for the Disappearance of TTR in Sterile pH-buffered Distilled Water Amended With Aldicarb.

pH	Temp(°C)	Half-life(days)	Reference
3.95	20	131	This study
6.02	20	559	This study
7.06	20	861	This study
7.96	20	324	This study
8.85	20	55	This study
9.85	20	6	This study
12.90	15	4.0 min	Lemley and Zhong 1983
13.39	15	1.3 min	Lemley and Zhong 1983
8.5	20	69	Hansen and Spiegel 1983
8.2	None given	43	Trehy et al. 1984

pH (Faust and Gomaa 1972), yielding aldicarb oxime (which is stable in basic medium), methylamine, and carbonate from the cleavage of the $-\overset{O}{\overset{\|}{C}}-O$ bond (Lemley and Zhong 1983). Trehy et al. (1984) found from GC/MS analysis that the degradation product for aldicarb in sterile anaerobic water was also aldicarb oxime. Oximes can undergo a dehydration to become another non-toxic aldicarb residue: nitriles. Hansen and Spiegel (1983) felt that sulfoxide nitrile and sulfone nitrile became important only after 98 or 99% of the aldicarb sulfoxide or aldicarb sulfone had been hydrolyzed at pH 8.5; however, they never measured the nitriles. Presumably, aldicarb nitrile would also become a dominant degradation product under similar circumstances.

The Hansen and Spiegel (1983) work is the closest data set comparable to the conditions of our experiment. Their data (adjusted to 20°C) for pH 8.5 yield a half-life of 69 days, which is almost twice as fast as the pseudo-first-order rate constant extrapolated from Figure 4 at pH 8.5 ($k = 5.8 \times 10^{-3}$/day), corresponding to a half-life of 120 days. Little confidence can be placed on the rate constants obtained at pH 7.5 in either study since the slope of the regression line, which is equal to k, was not significantly different from zero in the Hansen and Spiegel study and also was probably not so in this study; having only two replicates precluded statistically testing the hypothesis of whether the slope was significantly different than zero.

To the authors' knowledge, the only published values for second-order rate constants of aldicarb hydrolysis is from Lemley and Zhong (1983). Based on using high hydroxide and aldicarb concentrations, and a different method (i.e., titrimetric) to measure the progress of hydrolysis, they found k_{OH} for aldicarb to be $1.35 \times 10^3 \pm 0.03 \times 10^3$ L mole^{-1} day^{-1} at 15 °C. After adjusting to a temperature of 20°C (assuming the activation energy of the aldicarb is the same as the activation energy measured by Lemley and Zhong for aldicarb

sulfoxide (= 15.2 $\pm$ 0.1 kcal/mol), the k_{OH} becomes 2.12 x 10^3 L $mole^{-1}$ day^{-1}, which compares favorably to the 1.94 x 10^3 L $mole^{-1}$ day^{-1} rate measured by us.

There is some confusion in the literature as to whether acid-catalyzed hydrolysis of aldicarb and its S-oxides occur. Lemley and Zhong (1983) have measured proton-catalysis for aldicarb sulfone, but the reaction rates were slow and unmeasurably low when the acid concentrations were below 2M. Hansen and Spiegel (1983), based on their communications with L. Tobler (1980), reported no acid-catalysis of aldicarb at 77°C down to a pH of 2, a finding which is inconsistent with the results of this study.

Disappearance of Toxic Residues of Aldicarb in the Saturated Zone

Although hydrolysis experiments using pH-buffered sterile distilled water are easier to perform than experiments using groundwaters and their aquifer material from specific sites, their results are not as meaningful because microbiological and aquifer catalytic effects are not taken into consideration. Neither do field studies lend themselves to the accurate degradation rate of TTR in groundwaters since the residues are subject to dispersion, dilution, and recharge, all of which are beyond the control of the investigator. Therefore, TTR degradation rates are best measured by laboratory studies using actual groundwaters and saturated subsoils collected in the field and incubated under controlled conditions which best represent the *in situ* environment.

The half-life values for groundwaters and aquifer material obtained from the well sites are compared to the hydrolytic degradation half-life times in Table 9 after appropriate adjustments for pH and temperature differences. In those samples which experienced an upward shift in the pH during the incubation period, an average pH was used for the basis of comparison to the hydrolysis studies in sterile, pH-buffered distilled water. The pH shift to more alkaline

Table 9. Comparison of Degradation Rates For TTR Estimated by Hydrolysis With Degradation Rates Measured in Groundwaters in the Absence and Presence of Aquifer Material.

Site	Residue Added	pH Initial	pH Ave.	Study Temp (°C)	Measured Half-life (days)	Estimated Half-life Based on Distilled Water Hydrolysis (days)[a]	Estimated / Measured
Ryall	aldicarb	6.8	8.0	24	103	211	2
Sexton	aldicarb	7.2	7.9	24	101	238	2
Luther	aldicarb	7.3	8.0	24	103	211	2
BBC	aldicarb	7.4	7.3	22	112	648	6
Lind. Wab.	aldicarb	7.1	7.5	22	178	456	3
BBC[b]	aldicarb	7.4	7.4	22	12	515	43
Ryall[c]	aldicarb	6.8	8.0	24	120	211	2
Sexton[c]	aldicarb	7.2	7.9	24	100	238	2
Luther[c]	aldicarb	7.3	8.0	24	89	211	2
Ryall	sulfoxide	7.8	7.9	24	24	30	1
Sexton	sulfoxide	7.2	7.9	24	9	30	3
Luther	sulfoxide	7.4	7.6	24	13	50	4
BBC	sulfoxide	7.4	7.3	22	33	140	4
Lind. Wab.	sulfoxide	7.4	7.4	26	43	70	2
BBC[b]	sulfoxide	7.4	7.4	22	26	110	4
Lind. Wab.[b]	sulfoxide	7.4	7.3	26	11	140	11
Ryall	sulfone	7.8	7.9	24	15	12	1
Sexton	sulfone	7.2	7.9	24	10	12	1
Luther	sulfone	7.4	7.6	24	11	23	2
BBC	sulfone	7.4	7.3	22	26	70	3
Lind. Wab.	sulfone	7.4	7.4	26	16	38	2
BBC[b]	sulfone	7.4	7.4	22	18	62	3
Lind. Wab.[b]	sulfone	7.4	7.3	26	10	44	4

[a]Aldicarb half-life times based on data presented in Fig. 4 and Table 3; sulfoxide and sulfone half-life times based on data presented by Porter et al. (1984).

[b]Aquifer material present

[c]Sterilized groundwater

values by as much as one pH unit was unexpected. It indicated the waters were not well buffered at their initial neutral pH values, the high alkalinities notwithstanding. It is assumed the pH shift occurred because of losses of CO_2 during sequential subsamplings for TTR analysis. Apparently the change occurred within the first 10 days of the incubation period. If a buffer had been added to maintain the pH at its initial value, even more of an error may have been introduced because of: 1) changing the ionic strength of the waters (which may affect rate constants); 2) exerting a buffer catalysis effect; and 3) serving as a nutrient or energy source to the microbiota.

For the locations listed, the half-life times measured in the groundwater only and groundwater + aquifer samples are a factor of 1 to 43 shorter than half-life estimates based on distilled water hydrolysis. Metabolic activities of the microbiota cannot be invoked in explaining the faster degradation of aldicarb in well waters since there were no differences between the rates of aldicarb disappearance between sterile and non-sterile groundwaters (estimated $t_{\frac{1}{2}}$/measured $t_{\frac{1}{2}}$ was 2 in all cases). Even though the anaerobic plate counts probably underestimated bacterial cell densities because of the bias toward gram-negative bacteria when a high proportion of the total bacteria in the unconsolidated sediments of the saturated zone has been reported to be gram-positive (White et al. 1983), the low bacteria densities found for the three private water supply wells (Table 4) indicate a negligible microbiological influence on TTR degradation rates. Therefore, the well waters contained dissolved constituents which, when incubated under conditions closely resembling those found in the field, increased the rate of degradation of aldicarb and its toxic derivatives.

Based solely on the degradation rates for aldicarb-amended groundwaters, a substantial risk of contaminating groundwaters would exist if aldicarb should

leach into the saturated zone. However, in the presence of aquifer material, which is a more realistic condition, aldicarb and its toxic residues disappeared 9 times faster at the BBC site where the estimated $t_{\frac{1}{2}}$/measured $t_{\frac{1}{2}}$ ratio was increased to 43 (Table 9). The higher densities of bacteria in the groundwater-saturated subsoils (Table 5) probably accounted for the faster decay of TTR, since aldicarb was not significantly sorbed on the sandy clay loam subsoil ($<$6 ng/g (dry wt)) which served as the water table aquifer at this site, thereby reducing the likelihood that surface catalyzed degradation was responsible for the faster subsoil degradation rate. Sterile conditions (through NaN_3 additions) were not achieved in the subsurface soils from Lindsey Wabasso (see Appendix III) probably because of the protection afforded to the microbiota by extracellular polysaccharide polymers secreted under the conditions of unbalanced growth (i.e. nutrient deprivation) usually found in underground waters (Uhlinger and White 1983).

It was not the objective of this investigation to determine the individual degradation products, although such a study on these groundwaters would be useful. Since the incubations were anaerobic, oxidation of aldicarb to sulfoxide by bacteria would be less likely than bacterially-mediated hydrolysis to aldicarb oxime. Oxidation processes cannot be entirely ruled out, but an oxidizing agent other than oxygen would have to serve as the terminal electron acceptor.

TTR concentrations in aldicarb sulfone- or aldicarb sulfoxide-enriched well waters decreased at rates which were more consistent with expected values published for hydrolysis in sterile, pH-buffered distilled water (Table 9). By using a detailed study on the effects of pH and temperature on the hydrolysis of aldicarb sulfoxide and aldicarb sulfone (Porter et al. 1984), we interpolated the estimated half-life times for Ryall, Sexton, and Luther wells to

be 30-50 days for aldicarb sulfoxide and 12-23 days for aldicarb sulfone. These should be compared to the nearly equal measured half-life times of 9-24 days and 10-15 days for aldicarb sulfoxide and aldicarb sulfone, respectively (Table 9). Since these samples were not sterilized, the role which microbiota in the groundwaters had in the degradation was unknown. However, the low bacteria densities (6-63 cells/mL) measured for the March 26, 1984 well water samples (Table 4) indicated only a negligible contribution from the microbiota could have occurred. It is therefore believed that most of the increase in degradation rates was due to non-biological effects, with chemical hydrolysis accounting for much of it. This is consistent with the findings of Delfino and co-workers (1984), who found aldicarb sulfoxide to have a half-life of 13-15 days in autoclave aerobic groundwaters.

When aldicarb sulfoxide and aldicarb sulfone were separately added to saturated subsoils obtained from Lindsey Wabasso and BBC groves (containing 5-100 times more bacteria than without aquifer material), only slightly higher rates of TTR disappearance ($\sim$50% higher for 3 of the 4 site-substrate combinations) than what had been observed for well waters alone were recorded (Tables 7 and 9). This differs sharply from the 9-fold increase in TTR rate of degradation previously described for aldicarb-amended saturated subsoils. The exception was for sulfoxide at the Lindsey Wabasso site, where the decomposition rate for TTR was increased 4 times by the presence of aquifer material. These data indicate that using only groundwaters may suffice in testing the potential of sulfoxide and sulfone to degrade in aquifers. The 50% overestimation of half-life values may be an acceptable error (especially since it is a conservative one) considering the time and expense expended in obtaining aquifer material from deep wells and that contaminated groundwaters have been found to contain 50% each of aldicarb sulfoxide

and aldicarb sulfone (Porter et al. 1984). However, more studies are necessary before this procedure could be routinely practiced because the nature of the aquifer material can be important. Miles (pers. comm., April 4, 1984) found limestone decreased the hydrolysis rate of aldicarb sulfoxide and aldicarb sulfone five-fold. This may be true only for deep limestone aquifers such as the Floridan, and not for the shallower unconfined aquifers that are composed of sands and clays.

In summary, the effect of the presence of aquifer material on the decomposition of TTR from aldicarb addition was pronounced; however, aquifer material had only small effects on rates of TTR disappearance for sulfone and sulfoxide. Because aldicarb, aldicarb sulfoxide, and aldicarb sulfone sorb weakly in sandy and clay soils with low organic matter, surface catalyzed degradation is less likely to be more important than microbial or solution processes in causing faster aldicarb degradation in saturated subsoils. If bacteria are essential in the anaerobic degradation of aldicarb to non-toxic oximes in groundwaters, they are relatively unimportant in degrading sulfone and sulfoxide, a finding consistent with studies conducted on Long Island (Porter et al. 1984). Also, for sulfoxide and sulfone, chemical hydrolysis in solution proceeds fast enough to be a major degradation pathway by itself. Since all the experiments were conducted under anaerobic conditions, oxidation reactions would probably be unimportant relative to hydrolysis reactions, which produce oximes (Figure 1). It therefore appears that without bacteria, aldicarb hydrolysis is slow compared to sulfoxide and sulfone hydrolysis in anaerobic groundwaters, which conforms to the findings reported by Hansen and Spiegel (1983), Delfino (1984), Porter et al. (1984), and this investigation. Bacteria are necessary for catalyzing the hydrolysis of only aldicarb. When this occurs, the rate of TTR disappearance equals that for chemical hydrolysis of aldicarb sulfoxide and aldicarb sulfone.

Comparison of Degradation Rates of TTR in the Unsaturated and Saturated Zones

To understand the significance of the findings in this report, the broader picture of the likelihood of aldicarb or one of its toxic residues reaching the water table from the vadose zone should be presented. The susceptibility of groundwaters to aldicarb contamination is a combination of the potentials for TTR to reach the water table and to persist after it has entered the groundwater system. Numerous studies of aldicarb behavior in soils in the unsaturated zone have demonstrated rapid conversion to sulfoxide, which in turn is more slowly biodegraded to sulfone (Bromilow et al. 1980; Smelt et al. 1978 b, c). However, one study (Coppedge et al. 1967) reported aldicarb to decompose slowly in a fine sand soil: 27% of the applied aldicarb remained after 4 weeks. Smelt et al. (1978c) calculated 91-100% of aldicarb was converted to its sulfoxide, which was higher than the 60-80% values given by Coppedge et al. (1967) and Bull et al. (1970), and the 67-92% conversion reported by Bromilow et al. (1980). For two studies which investigated aldicarb sulfone degradation in soils, both found rates to be slower than what had been reported for aldicarb sulfoxide (Smelt et al. 1978a) and aldicarb (Hornsby et al. 1984).

Generally, soil scientists have found slower rates in the degradation of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in deeper soil layers than in corresponding top layers of the soil profile (Smelt et al. 1978a,b; Hornsby et al. 1984), presumably because of the lower microbial activity in the subsoil. Typical half-life values reported in the literature for laboratory studies of aldicarb, aldicarb sulfoxide, and aldicarb sulfone losses in the upper soil layers were 1-23, 13-14, and 24-158 days, respectively. For deeper soil layers (70-180 cm) in the unsaturated zone, aldicarb sulfoxide had a reported half-life of 53-475 days (Smelt et al. 1978b), while half-life times of 46-∞

(Smelt et al. 1978a) and 54-296 days for aldicarb sulfone (Hornsby et al. 1984) have been published. These data imply that once TTR penetrate to the deeper layers of the aerated soil zone, little further degradation can be expected. When compared to the half-life times found in the upper soil layers of the unsaturated zone, the half-life range of 10-26 days for TTR disappearance measured for saturated subsoils in this study suggest a resumption to the faster degradation rates recorded for the upper soil layers can be expected for TTR entering the shallow water table.

Field Monitoring Studies and Models For TTR Intrusion into Florida Groundwaters

Based on the laboratory degradation studies for deep soils in the unsaturated zone and field investigations in Florida (Jones and Back 1984; Hornsby et al . 1984) and other states (Rothschild et al. 1982; Porter et al. 1984), the question no longer is whether toxic aldicarb residues are reaching water tables, but at what concentrations are they entering water tables, how fast is the TTR decomposing to non-toxic residues in groundwaters, and how far would TTR travel in groundwaters before it is degraded to non-toxic products.

Jones and Back (1984) reported degradation rates of aldicarb residues in Florida soils decreased as they moved down through the soil column due to fewer soil biota available to metabolize the residues. After several months, when most of the remaining residues are 60 to 120 cm below the soil surface, the disappearance of the residues became immeasurably low. Their data, which encompassed six citrus grove sites throughout Florida, clearly indicated significant percentages of TTR (i.e., aldicarb + aldicarb sulfoxide + aldicarb sulfone) can remain in the lower 1.2-2.2 m of unsaturated soil. Contamination of groundwaters from wells near the six citrus groves during a 1.5 year period was slight: out of 67 groundwater samples taken from a total of 21 wells in

the 6 locations, waters from only two wells (at the Hillsborough site) had intermittent trace amounts (1 ppb) of aldicarb residues.

Although the field data were too variable to make predictions of the amount of aldicarb residues which will leach into the saturated zone, Jones and Back (1984) estimated that, based on a computer model (PESTAN), < 1% of the aldicarb applied to citrus groves will leach more than three feet below the soil surface. However, many assumptions were made in reaching this conclusion. These included using average soil and climatic properties, applying soil characteristics to Florida soils from sandy soil on Long Island, and adopting the faster degradation rates found for the upper soil horizons. Considering that the selection of input parameters for the modeling produced a "best case" simulation, the conclusion that < 1% of the applied aldicarb would leach below three feet of the soil surface would have to be viewed with a large degree of uncertainty. Furthermore, the field data provided by Jones and Back (1984) show that from 0.5 to 5.7% of the applied aldicarb remains as TTR in the unsaturated zone from 166 to 344 days after application. Most of the remaining residues would be located at the lower depths of the unsaturated zone, where degradation is slow and migration to the nearby saturated zone is likely to occur. The importance of looking at site-specific contamination, rather than relying on generalized computer simulations or averages of field data, can be readily recognized by noting that the highest fraction of aldicarb residues remaining (5.3% in Hillsborough County) at any of the six field sites, was associated with the longest time after application (344 days). Another example of the variability of different soils to degrade aldicarb and its toxic residues is given by Hornsby et al. 1984, where 4-8 percent of the applied aldicarb residues reached groundwater in a citrus grove on ridge soils in Seminole County, Florida, while no TTR were detected in the upper portion of the saturated zone at a flatwoods soil site in Polk County, Florida.

In further modeling efforts, Jones et al. (1984) recognized that the model PESTAN, although simpler and easier to use than other models, is generally not appropriate for predicting the leaching of aldicarb residues in Florida citrus groves. By comparing three existing simulation models (PESTAN, PISTON, and PRZM) with each other and with field monitoring and laboratory studies, they found using site-specific factors such as soil hydraulic properties, soil organic matter, pesticide degradation rates, and daily rainfall data were important in determining the extent of pesticide leaching.

Lateral Transport of TTR in Shallow Groundwaters in Indian River County

The results of this investigation showed measured TTR half-life times of 10-26 days in the presence of aquifer material, regardless of whether the initial toxic residue had been aldicarb or one of its S-oxides. Using the number of half-lives (7) required to reduce the highest TTR concentration (1.26 mg/L) reported for Florida groundwaters (Hornsby et al. 1984) to levels less than the state standard of 10 ppb, and our measured half-life times, 70-182 days would have to elapse before TTR concentrations in that water (without dilution or dispersion) could decrease to acceptable TTR levels. This means that if Temik was applied only once a year, and toxic residues of this magnitude moved into the saturated zone as a pulse over a short time interval, TTR would be below the state drinking water standard (10 ppb) after one-half year. How far would such a plume travel in that period of time? Considering the calculated hydraulic gradients of 0.00019-0.00078 m/m derived from observation wells in Indian River County and reported hydraulic conductivities of 3.6-12.2 m/day for the overlying sandy soils located at the BBC and Lindsey Wabasso groves, and assuming a porosity of 33%, the plume of contaminated water would travel 0.0021-0.029 m/day from the boundaries of application. Thus, a distance of 0.38-5.3 m (1.3-17 ft) would

be traveled by a contaminated plume during the one-half year required for the TTR to decrease to concentrations < 10 ppb. These calculated distances of lateral plume migration are well within the 300 ft exclusion zone adopted by the state for applying aldicarb near drinking water wells. This simple calculation assumes a homogeneous and isotropic shallow groundwater aquifer with no contribution from dispersion or dilution toward reducing TTR concentrations. It therefore represents the travel distance of TTR in the most extreme case, especially since the highest reported concentration of TTR in Florida groundwaters was used.

Another approach to evaluating the extent of migration of contaminated groundwater in Indian River County is by calculating how much of the 5 lb a.i./acre per year application rate as required under the new restrictions may enter into the groundwater and be transmitted laterally. If 8% of the applied aldicarb were to enter into the groundwater as reported by Hornsby et al. (1984), then 352 ppb of TTR would be concentrated in the surface to 0.1 m layer of groundwater. Rothschild et al. (1982) concluded that most TTR leached to groundwaters under aldicarb-treated fields was near the water table. If an average half-life of 16 days measured in this study for a TTR comprised of 50% each of aldicarb sulfoxide and aldicarb sulfone (Porter et al. 1984) is assumed, then it would require 80 days (or five half-lives) for the TTR to degrade to a concentration that is in compliance with the 10 ppb standard adopted by Florida for potable waters. Using the same hydraulic conductivities and gradients and porosity as before, then only 0.17-2.3 m (0.6-8 ft) distance would be traveled by the contaminated plume. Considering the slow rate of groundwater movement in Florida soils, coupled with any further reduction in concentration within the contaminated plume from dilution and dispersion, there should be little chance that wells used for potable water would

be contaminated above the 10 ppb standard if the present restrictions are observed. Even if a larger hydraulic gradient exists because of downward gradients artificially created during well pumping (Rothschild et al. 1982), the effect of a 10-fold increase in the hydraulic gradient increases the distance traveled by the TTR plume to 6-80 ft, still well within the 300 ft exclusion zone. Apparently the restriction that aldicarb cannot be applied within 300 ft of any drinking water well seems reasonable. It should be emphasized that the estimated small distances of plume migration apply only to Indian River County, which in turn are further limited to those few sandy soils used to derive the TTR degradation rates.

SUMMARY AND RECOMMENDATIONS

Laboratory degradation experiments were conducted for the purpose of measuring the degradative activity of a small concentration (0.10 mg/L) of aldicarb and its toxic oxidation products (sulfoxide and sulfone) in groundwaters from five wells located near citrus groves in Indian River County.

The experiments were designed to evaluate what effect microbiota and aquifer material would have in influencing the rate of detoxification of toxic residues. Attention was given to mimick as closely as possible the actual *in situ* conditions of the shallow groundwaters during the incubations in the lab so that realistic reaction rates could be projected. Reliable predictions of the duration of aldicarb contamination in groundwater could then be made. Once having arrived at the reaction rates, converting to half-lives facilitated comparisons to other degradation rates reported in the literature for the saturated and unsaturated zones.

Our measured rates for total toxic residue disappearance were also combined with data from the literature which stated the amounts and concentrations of toxic residues entering the water table in another Florida county to yield the time required to degrade the toxic residues to less than 10 ppb. Using field measurements of water table fluctuations and hydraulic conductivities reported for Indian River County, the daily distance of groundwater flow could be calculated which, when multiplied by the amount of time necessary to reduce toxic residues to less than 10 ppb, gave the total distance moved by the contaminated plume.

Two companion studies sought to: 1) adequately describe the hydrolysis of aldicarb in various pH-buffered solutions; and 2) evaluate the suspected interferences of non-toxic nitriles and oximes in the methodology used for the

analysis of toxic residues.

To best summarize the results of this investigation, four recommendations are given. Following each recommendation the pertinent conclusions are provided upon which the recommendation was based.

Recommendation 1

The positive interferences from non-toxic oximes and nitriles in being included with the total toxic residue (TTR) are minor, suggesting that the liquid chromatography step used in the analytical procedure to remove them may be omitted under some experimental circumstances.

Oximes did not interfere in the analysis of TTR under the conditions used in this investigation; nitriles did interfere, but only when $>$90% of the TTR had disappeared. The percentage error of the initial TTR contributed by non-toxic nitriles rarely exceeded 10%, and was on the average, less than the percentage errors associated with either: i) the Florisil separation method; ii) agreement between duplicate samples; iii) inter-laboratory analyses of split-samples; or iv) recoveries of known standards without Florisil separation.

Recommendation 2

The best method for determining the degradation rate of toxic pesticides in groundwaters and gaining an understanding of the mechanisms is from laboratory experiments using groundwater-saturated aquifer material incubated under *in situ* environmental conditions. However, in cases where obtaining aquifer material is difficult or impossible, incubating only groundwater may be sufficient in producing realistic TTR degradation rates for aldicarb sulfoxide and aldicarb sulfone. This does not apply to aldicarb, where incubating in the absence of aquifer material would cause a large underestimation of the rate of degradation in anaerobic groundwaters.

TTR disappearance in anaerobic groundwaters containing low densities of bacteria and without aquifer material was slow (half-life times = 101-178 days) for aldicarb and fast (half-life times = 9-43 days) for aldicarb sulfoxide and aldicarb sulfone, indicating that chemical hydrolysis in the slightly alkaline groundwaters was responsible for converting the sulfoxide and sulfone into non-toxic derivatives but was not operating to the same extent in aldicarb deactivation. The persistence of aldicarb in neutral to slightly alkaline (pH 8) waters was supported by an hydrolysis experiment in sterile pH-buffered distilled waters. At pH 7, the rate of TTR disappearance from the parent compound was immeasurable; a half-life of 324 days was measured at pH 8, with rates of TTR disappearance increasing as the pH increased. The second-order reaction rate (k_{OH}) for base-catalyzed hydrolysis was 1.94×10^{3} L mole^{-1} day^{-1}.

When aquifer material was added, rates of TTR disappearance increased 9-fold to 5.76×10^{-2} day^{-1} for aldicarb in one shallow well, indicating microbes were essential in degrading the parent compound to non-toxic residues. However, aldicarb sulfoxide and aldicarb sulfone degraded only slightly more in the presence of aquifer material (half-life times = 10-26 days) than they did in the absence of aquifer material, suggesting chemical hydrolysis is more prominent in reducing TTR associated with these S-oxides than any microbially-mediated pathway.

Recommendation 3

Restricting the application rate of Temik to 5 lb a.i./acre and not applying it within 300 ft of a potable water supply well should be continued.

Shallow groundwaters of Indian River County apparently possess the capability to rapidly degrade TTR from aldicarb and its S-oxides. Half-life times of 10-26 days stand out in contrast to the 2-3 year half-life projected by Porter

et al. (1984) for TTR disappearance in groundwater on Long Island. The reasons for the faster degradation rates of TTR in Florida are probably the more favorable temperatures and pH. The neutral to slightly alkaline pH of Florida's groundwaters (6.8-7.8) serves to hydrolyze the sulfoxide and sulfone, whereas the acid pH of Long Island groundwater (4.2-5.9) inhibits hydrolysis.

A combination of slow groundwater movement and fast degradation rates limits the migration distances of aldicarb-contaminated plumes in Indian River County. Estimates of lateral distances traversed in the saturated zone of the soils studied in this investigation by a plume of groundwater contaminated with TTR were only 1-17 ft since the TTR was converted to non-toxic residues within one-half year. The 300 ft exclusion zone and application rate of 5 lb a.i./acre insure adequate protection of the groundwater resources in Indian River County.

Recommendation 4

Studies on surface and ground water contamination by aldicarb and its oxidized toxic products should be continued.

Although these results point to rapid degradation and slow transport of TTR in groundwaters, care should be exercised in extrapolating this conclusion to other sites and soils in Florida. The danger of generalizing results obtained at one site to other sites has been discussed. Even for the specific soils used in the degradation experiments, the limited number of replicates and field samplings performed in the short study period warrant a cautious interpretation of the fast degradation rates.

Monitoring the groundwaters of some citrus fields receiving annual aldicarb applications should be performed for a period of several years to provide a long-term data base which includes the extremes in meteorological conditions affecting residue transport and deactivation.

Future experimental studies should be directed toward evaluating the effect of salt content on the hydrolysis rate and the chemical or biological reductive conversion of sulfone to sulfoxide and sulfoxide to aldicarb. There is some evidence that both could have an effect on aldicarb. Fukuto et al. (1967) reported that the observed first-order rate constants for the hydrolysis of p-nitro-N-methylcarbamate increased upon decreasing the ionic strength of the phosphate buffer. He suggested that a lowering of the rate constant was from decreasing activities of hydroxide ion and/or the carbamate because of increasing ionic strength, and not from catalysis of the phosphate ions present in the buffer. The environmental implication is that the hydrolysis rate of toxic aldicarb residues may be inhibited in estuarine environments.

Reductive conversion of a sulfoxide to its parent compound has been reported for phorate (Walter-Echols and Lichtenstein 1977) in sediments. The prevailing evidence of this occurring in reduced environments for sulfoxide or sulfone is to the contrary. Studies such as this one have shown rapid disappearance of TTR under anaerobic conditions and no one has published any data implying that this mechanism is operating in the chemistry of sulfoxide or sulfone conversions. Still, there is an abundance of reduced compounds in groundwaters (e.g. sulfides, ferrous iron) which could serve as a reductant, and with the possibility of marketing sulfone as the active ingredient (instead of aldicarb) in commercial insecticides, more research should be done on evaluating whether reductive conversion could occur. Even if a reductive pathway was not found, the information that would be generated on the conversion rates to other toxic and non-toxic compounds for each toxic residue species in an anaerobic aquifer system would be beneficial.

Given the shallow distances between land surface and the water table, the geographical closeness of residential and agricultural land uses,

permeability of sandy soils, low adsorption potential, and field studies in Florida showing 4-8% of the applied aldicarb available to enter the groundwater, a continuing scientific effort directed toward monitoring, modeling, and reaching best management practices is prudent.

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APPENDIX I

SUMMARY OF COMPARISONS BETWEEN LABORATORIES IN THE SPLIT SAMPLING PROGRAM

Sample	FIT	FDER[a] Tallahassee	IFAS Pesticide Research Lab[b] Gainesville
Ryal well-B Aldicarb amended Non-sterile T = 0 days	101 ppb	120 ppb	
Aldicarb hydrolysis pH = 10 Time = 5 days	49 ppb	60 ppb	
Aldicarb hydrolysis-A pH = 10 Time = 15 days	18 ppb		16 ppb
Luther well-B Aldicarb amended Non-sterile Time = 90 days	51 ppb		36 ppb

[a] TTR determination using a Hewlitt-Packard model 5700 GC with a nitrogen-phosphorus detector and a 1% SP1000 on Carbopack B 60/80 mesh column; injector, column and detector temperatures were 250, 200, and 300°C, respectively.

[b] TTR determination using a Perkin-Elmer Series 4 high pressure liquid chromatograph with a Gilson 121 fluorometer (excitation: 305-395 nm; emission: 430-470 nm) and a Zorbax C-8 (15 cm x 4.6 mm) stationary phase. The mobile phase consisted of a 10 min. linear gradient with an initial composition of 4% CH_3CN, 16% CH_3OH, 80% H_2O and ending with a final composition of 14% CH_3CN, 56% CH_3OH, 30% H_2O. A post-column derivitization step included 0.5 mL/min of 0.05 M NaOH at 95°C followed by 0.5 mL/min of OPA at ambient temperature.

APPENDIX II

EFFECT OF BUFFER CATALYSIS ON THE HYDROLYSIS OF ALDICARB IN STERILE, pH-BUFFERED SOLUTIONS

EFFECT OF BUFFER CATALYSIS ON THE HYDROLYSIS OF ALDICARB IN STERILE, pH-BUFFERED SOLUTIONS

In laboratory studies of hydrolysis of the aldicarb, conditions of constant pH are desired to simplify kinetic interpretations. Pseudo-first-order kinetics are usually observed only at a constant pH for acid-base-catalyzed hydrolysis of a pollutant, P:

$$\frac{d[P]}{dt} = -k_{obsed}\,[P] \qquad \text{(A-1)}$$

where $K_{obsed} = k_{H_2O}[H_2O] + k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH] + \sum_i (k_{HB_i}[HB_i] + k_{B_i}[B_i])$ (A-2)

and HB_i and B_i are the ith Bronsted acid-base pair in solution. Eq. A-2 states that hydrolysis reaction rates are a function not only of pH (the first three terms) but also of the nature and concentration of the acid-base system used to buffer the pH, called buffer catalysis. The first three terms of Eq. A-2 can contribute to k_{obsed} in all aqueous solutions, their contribution being predictable if the second-order rate constants (k_{H_2O}, $k_{H_3O^+}$, and k_{OH^-}) and pH are known. At constant pH, the combined contributions of H_2O, H_3O^+, and OH^- to k_{obsed} are constant and can be represented by a pseudo-first-order rate constant, k_w:

$$k_w = k_{H_2O}[H_2O] + k_{H_3O^+}[H_3O^+] + k_{OH^-}[OH^-] \qquad \text{(A-2)}$$

Thus, the observed pseudo-first-order rate constant (k_{obsed}) equals the pseudo-first-order rate constant for catalysis by solvent species (k_w) plus the buffer catalysis contribution (the last two terms of Eq. A-2).

Perdue and Wolfe (1983) developed a theoretic basis for assessing a <u>maximum</u> contribution of buffer catalysis for hydrolysis reactions in aqueous systems. They derived a buffer catalysis factor (BCF) for the buffers commonly employed to buffer solutions to a constant pH. The potential significance of

buffer ctalysis in aqueous solutions can be expressed;

$$k_{obsed}/k_w = 1 + C_B(BCF) \qquad (A-4)$$

where C_B is the concentration of the buffer catalyst. When $k_{obsed}/k_w \tilde{\sim} 1$, then the contribution from buffer catalysis to the rate of hydrolysis is negligible. Perdue and Wolfe suggested that when $k_{obsed}/k_w > 1.10$ (i.e., buffer catalysis contribution that equals or exceeds 10% of the combined kinetic contribution of H_2O, H_3O^+, and OH^-), then a 10% or greater increase in k_{obsed} results from buffer catalysis, and should be viewed as having potential significance.

Substituting the molar concentrations and published BCFs for the buffers used in the aldicarb hydrolysis investigation yielded k_{obsed}/k_w ratios ranging from 1.23 to 2.67 (Table A-1). Even though these represent a potential for significant buffer catalysis of 23 to 167% in k_{obsed}, the pH buffers which exhibited the highest ratios (i.e., pH = 6.02, 7.06, and 7.96) corresponded to the slowest k_{obsed}, while those buffers which had faster k_{obsed} (i.e., pH = 3.95, 8.85, 9.85) were associated with lower k_{obsed}/k_w ratios, indicating that the potential for buffer catalysis was not realized. It is important to recognize that the relative contribution of buffer catalysis to k_{obsed} is a function of pH, catalyst, and substrate, but that the preceding calculations predict the maximum contribution of buffer catalysis for a particular catalyst and pH only (ignoring the type of substrate). Buffer catalysis would be somewhat less important for any real substrate, such as aldicarb, and our data indicate a negligible contribution from the buffers at the strength used in our hydrolysis experiment. Fukuto et al.(1967) found varying concentrations of phosphate buffer anions did not participate in the hydrolytic reaction of p-nitrophenyl N-methycarbamate, which supports our conclusion that buffer catalysis is probably unimportant in hydrolyzing carbamates.

Table A-1. Potential for Maximum Contribution of Buffer Catalysis to the Observed Pseudo-first-order Rate Constants (k_{obsed}) in the Hydrolysis of Aldicarb Using Various pH Buffers in Distilled Water.

pH	Buffer Concentration (C_B)	Buffer Catalysis Factor[a] (BCF)	k_{obsed}/k_w (=1 + C_B(BCF))
3.95	1.67×10^{-2} M phthalate	30	1.50
6.02	1.67×10^{-2} M phthalate	50	1.84
7.06	1.67×10^{-2} M phosphate	100	2.67
7.96	1.67×10^{-2} M phosphate	80	2.34
8.85	4.10×10^{-3} M borate	55	1.23
9.85	1.67×10^{-2} M carbonate	25	1.42

[a]Perdue and Wolfe (1983)

APPENDIX III

RAW DATA

Table A-2 Hydrolysis Data for Aldicarb in Sterile pH-buffered Distilled Water at $20^{o} \pm 2^{o}$ C.

	Aldicarb Remaining, ppb				
pH	Day 0	Day 5	Day 15	Day 37	Day 89
3.95-A	111	121	112	120	72
3.95-B	117	118	128	106	76
6.02-A	133	133	122	127	120
6.02-B	-	139	150	130	124
7.06-A	108	121	128	130	132
7.06-B	117	130	137	127	124
7.96-A	130	133	-	127	100
7.96-B	-	127	150	134	120
8.85-A	88	84	72	54	32
8.85-B	120	95	78	57	32
9.85-A	108	59	18	<3	
9.85-B	108	62	18	<3	

Table A-3 Raw Data For Aldicarb Degradation in Duplicate Sterile and Non-sterile Groundwaters at 24 ± 2°C.

Well	Sterile	TTR Remaining, ppb				
		Day 0	Day 5	Day 11	Day 34	Day 90
Ryall -A	Yes	94	92	84	73	54
Ryall -B	Yes	99	90	81	70	56
Ryall -A	No	99	95	91	57	58
Ryall -B	No	101	107	98	80	54
Sexton -A	Yes	83	85	78	80	51
Sexton -B	Yes	92	118	78	70	47
Sexton -A	No	80	89	88	73	51
Sexton -B	No	99	104	84	73	49
Luther -A	Yes	97	98	95	77	56
Luther -B	Yes	97	118	91	53	49
Luther -A	No	97	118	95	97	66
Luther -B	No	95	124	98	87	51

Table A-4. Raw Data For Aldicarb Sulfoxide and Aldicarb Sulfone Degradation in Duplicate Non-Sterile Groundwaters at 24 ± 2°C.

Well	Aldicarb S-Oxide	TTR Remaining, ppb			
		Day 0	Day 5	Day 20	Day 42
Ryall - A	Sulfoxide	97	85	54*	--
Ryall - B	Sulfoxide	105	92	--	4*
Ryall - A	Sulfone	81	68	43*	<3*
Ryall - B	Sulfone	97	79	28*	<3*
Sexton -A	Sulfoxide	97	83	34*	4*
Sexton -B	Sulfoxide	98	84	35*	4*
Sexton -A	Sulfone	80	63	12*	<3*
Sexton -B	Sulfone	92	81	37*	<3*
Luther -A	Sulfoxide	95	92	43*	9*
Luther -B	Sulfoxide	92	82	40*	13*
Luther -A	Sulfone	90	65	20*	<3*
Luther -B	Sulfone	94	60	30*	<3*

* Nitrile removed from sample.

Table A-5. Raw Data For Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone Degradation in Duplicate Non-sterile Groundwaters With and Without Subsoil From the BBC and Lindsey Wabasso Groves.

Well	Substrate	Subsoil	TTR Remaining, ppb Day 0	Day 23
BBC-A	Aldicarb	Absent	89	77
BBC-B	Aldicarb	Absent	100	87
BBC-A	Aldicarb	Present	73	20
BBC-B	Aldicarb	Present	93	24
BBC-A	Aldicarb Sulfoxide	Absent	82	54
BBC-B	Aldicarb Sulfoxide	Absent	104	59
BBC-A	Aldicarb Sulfoxide	Present	73	37
BBC-B	Aldicarb Sulfoxide	Present	72	42
BBC-A	Aldicarb Sulfone	Absent	67	38
BBC-B	Aldicarb Sulfone	Absent	88	46
BBC-A	Aldicarb Sulfone	Present	80	37
BBC-B	Aldicarb Sulfone	Present	90	34
			Day 0	Day 30
Lind. Wab.-A	Aldicarb	Absent	100	89
Lind. Wab.-B	Aldicarb	Absent	100	89
Lind. Wab.-A	Aldicarb	Present	62	<3
Lind. Wab.-B	Aldicarb	Present	65	<3
			Day 0	Day 25
Lind. Wab.-A	Aldicarb Sulfoxide	Absent	79	54*
Lind. Wab.-B	Aldicarb Sulfoxide	Absent	80	53*
Lind. Wab.-A	Aldicarb Sulfoxide	Present	51	12*
Lind. Wab.-B	Aldicarb Sulfoxide	Present	62	10*
Lind. Wab.-A	Aldicarb Sulfone	Absent	90	30*
Lind. Wab.-B	Aldicarb Sulfone	Absent	90	29*
Lind. Wab.-A	Aldicarb Sulfone	Present	64	10*
Lind. Wab.-B	Aldicarb Sulfone	Present	78	16*

*Nitrile removed from sample.

Table A-6. Bacterial Counts on Groundwater Samples.

Sampling Date	Well	Pour Plate (cells/mL for water and cells/g (dry wt) for sediments)	
9 December 1983	Ryall	start: 6; 5; 4	$\bar{x}$=5
		finish: 10; 12	$\bar{x}$=11
	Sexton	start: 2; 3; 2	$\bar{x}$=2
		finish: 7; 8	$\bar{x}$=7
	Luther	start: 58; 51; 55	$\bar{x}$=55
		finish: 42; 33	$\bar{x}$=37
26 March 1984	Ryall	start: 3; 5	$\bar{x}$=4
		finish: 6; 8	$\bar{x}$=7
	Sexton	start: 1; 4	$\bar{x}$=3
		finish: 6; 7	$\bar{x}$=6
	Luther	start: 75; 79	$\bar{x}$=77
		finish: 63; 64	$\bar{x}$=63
30 January 1984	Lind. Wab. (sed.)	start: 1.2×10^5; 1.0×10^5	$\bar{x}=1.1 \times 10^5$
		finish: 1.4×10^4; 1.6×10^5	$\bar{x}=1.5 \times 10^4$
	Lind. Wab. (water)	start: 800; 700	$\bar{x}$=750
		finish: 228; 219	$\bar{x}$=223
23 April 1984	Lind. Wab. (sed.)	start: 6.3×10^4; 5.7×10^4	$\bar{x}=6.0 \times 10^4$
		finish: 8.0×10^3; 8.0×10^3	$\bar{x}=8.0 \times 10^3$
	Lind. Wab. (water)	start: 1500; 1200	$\bar{x}$=1350
		finish: 800; 1100	$\bar{x}$=950
22 February 1984	BBC (sed.)	start: 3.9×10^4; 5.4×10^4	$\bar{x}=4.6 \times 10^4$
		finish: 9.0×10^3; 9.0×10^3	$\bar{x}=9.0 \times 10^3$
	BBC (sater)	start: 31,000; 42,000	$\bar{x}$=36,000
		finish: 1800; 2300	$\bar{x}$=2,050