Tome, D.; Naulet, N.; Kozlowski, A. *Int. J. Pept. Protein Res.*, in press.
Trezl, L.; Rusnak, I.; Tyihak, E.; Szarvas, T.; Szende, B. *Biochem. J.* **1983**, *214*, 289.
Tyihak, E.; Trezl, L.; Rusnak, I. *Pharmazie* **1980**, *35*, 18.
Walker, J. F. "Formaldehyde"; Krieger, R. E., Publishing Co.: Huntington, NY, 1964.
Wrenn, T. R.; Weyant, J. R.; Wood, D. L.; Bitman, J. *J. Dairy Sci.* **1975**, *59*, 627.
Zelter, S. L.; Leroy, F.; Tissier, J. P. *Ann. Biol. Anim., Biochim., Biophys.* **1970**, *10*, 111.

Received for review July 6, 1984. Accepted December 26, 1984.

Fate of Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone in Floridan Groundwater

Carl J. Miles* and Joseph J. Delfino

The fate of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in Floridan groundwater microcosms was determined. One reaction mechanism observed was base hydrolysis and degradation rates decreased in the order sulfone > sulfoxide >> aldicarb. Appearance of oximes followed the disappearance of corresponding parent compounds while appearance of nitriles was minor and rarely observed. Microcosms amended with crushed limestone showed rates of hydrolysis that were 4–5 times slower than microcosms without limestone. Oxidation of aldicarb to the sulfoxide was minimal within 70 days whereas in separate experiments, the reduction of the sulfoxide to aldicarb was significant over the same time period. The sorption of aldicarb, aldicarb sulfoxide, and aldicarb sulfone onto limestone was not observed.

Recent detection of aldicarb (2-methyl-2-(methylthio)-propionaldehyde *O*-(methylcarbamoyl)oxime, Temik) in Florida groundwater related to its use in citrus agriculture has renewed interest in the fate of this pesticide in the subsurface environment. Although there has been considerable study on the degradation of aldicarb in soils (Coppedge et al., 1967, 1977; Bull et al., 1970; Andrawes et al., 1971; Smelt et al., 1978a, 1978b, 1978c), similar research for natural water matrices is lacking. In Florida, porous, sandy, low organic soils allow rapid penetration of water soluble materials into aquifers where physicochemical conditions differ from most surface waters (i.e., lower temperatures, absence of light, lack of oxygen, and potentially active surfaces).

Several studies have shown that the major metabolic pathway of aldicarb (AS) in soils is rapid oxidation of the parent compound to aldicarb sulfoxide (ASO) followed by slower oxidation to aldicarb sulfone (ASO_2) or hydrolysis to ASO oxime (Figure 1) (Union Carbide, 1983). Additional work has suggested that ASO oxime is degraded further to the corresponding nitrile (Coppedge et al., 1967; Andrawes et al., 1971). Since all of the carbamoyl oximes (AS, ASO, and ASO_2, sometimes called total toxic residue) have a high mammalian toxicity, the hydrolysis step represents a major detoxification mechanism.

Recently, several studies have discussed the degradation of AS, ASO, and ASO_2 in abiotic, reagent grade water solutions (Chapmen and Cole, 1982; Lemley and Zhong, 1983, 1984; Porter et al., 1984; Hansen and Spiegel, 1983). These investigators reported that base hydrolysis is an important reaction mechanism in water and that acid hydrolysis occurs at a lower rate. Most of these authors found that pseudo-first-order kinetics described degradation; experiments with other carbamate pesticides showed that cleavage of the carbamate ester bond is first order with respect to hydroxide and pesticide concentration (Aly and El-Dib, 1972). Studies on the effect of pH on hydrolysis rate allowed calculation of second-order rate constants which showed that base hydrolysis reaction rates decreased in the order ASO_2 > ASO >> AS (Lemley and Zhong, 1983; Porter et al., 1984). Degradation of ASO and ASO_2 was significantly affected by temperature and the reaction followed the Arrhenius relationship. Also, several investigators have reported that increased ionic strength significantly decreases the hydrolysis rate of carbamate pesticides (Fukuto et al., 1967; Aly and El-Dib, 1972; Lemley and Zhong, 1983).

Trehy et al. (1984) investigated the degradation of AS in aerobic and anaerobic Floridan groundwater microcosms, some of which were enriched with microorganisms or limestone. In the presence of high concentrations of microorganisms (pH 6.8) or in the presence of ground limestone (pH 7–7.4), they found that AS degraded rapidly to AS nitrile under anaerobic conditions. In anaerobic groundwater (pH 8.2), AS degraded to AS oxime. These degradation products accounted for a large part (ca. 80%) of the degraded AS. These results contrast with AS degradation rates found by others but can be ascribed to the high concentrations of microbes. The Trehy et al. (1984) investigation demonstrates the importance of naturally occurring factors (i.e., limestone, microorganisms, H_2S, etc.) on AS degradation.

Most of the aforementioned investigators, with the exception of Trehy et al., reported that base hydrolysis of carbamoyl oxime was the major mechanism without ever measuring the actual appearance of the resulting oxime. In short, no pesticide speciation measurements were performed. Soil studies have shown that oxidation is a major metabolic pathway for AS and ASO, suggesting that similar processes should occur in aerobic natural waters. Speciation of AS oxidation products by a gas chromatography (GC) method, not mentioned heretofore (Maitlen et al., 1968), requires an additional liquid chromatograpy (LC) fractionation which apparently was not performed in previous studies. Recently, we developed a high performance liquid chromatography (HPLC) method capable of measuring AS, ASO, ASO_2 and their corresponding oximes and nitriles in groundwater at submilligram per

Department of Environmental Engineering Sciences, University of Florida, Gainesville, Florida 32611.

0021-8561/85/1433-0455$01.50/0

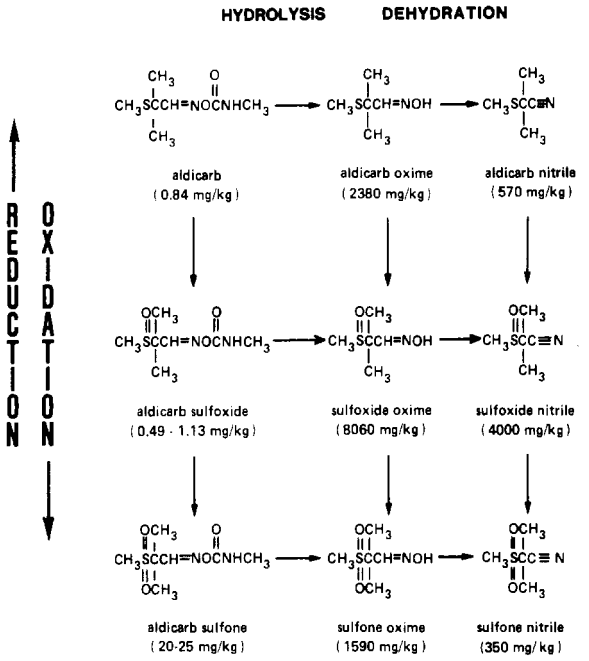

Figure 1. Degradative pathways of aldicarb. Values in parentheses are acute oral LD_{50}'s for rats (after Union Carbide, 1983).

liter concentrations (Miles and Delfino, 1984). This procedure allows observation of the oxidation, hydrolysis, and dehydration (nitrile formation) of AS in groundwater microcosms without prior fractionation steps.

All of the previous studies, except for Trehy et al. (1984), used unbuffered reagent grade water or buffered solutions to determine degradation rates of AS in water. Although such studies are useful and simplify kinetic description, they omit many of the inorganic and organic constituents in natural waters that may influence degradation rates and patterns. Our goal was to study the fate of AS, ASO, and ASO_2 in groundwater microcosms under conditions similar to those found in the Floridan aquifer.

Degradation experiments were performed in aerobic and anaerobic groundwater, in the presence and absence of crushed limestone, and with and without native microorganisms. Further experiments were designed to measure the effect of inorganic ions on hydrolysis rate and to determine the possibility for reduction of ASO and ASO_2. Also, the potential sorption of AS, ASO, and ASO_2 onto limestone was studied by using a batch equilibration technique.

EXPERIMENTAL SECTION

All chemicals used were reagent grade or higher quality. Distilled deionized water was obtained from a laboratory reagent water system (Millipore Milli-Q). AS, AS oxime, ASO oxime, and ASO_2 were obtained from the United States Environmental Protection Agency (Research Triangle Park, NC). ASO, ASO nitrile, ASO_2 oxime, and ASO_2 nitrile were provided by Union Carbide. AS nitrile was synthesized by M. Trehy (Trehy et al., 1984). Stock standard solutions (ca. 4000 mg/L) of these compounds were prepared in acetonitrile and stored at −20 °C when not in use. Working standards were made periodically to maintain accuracy and stored at 4 °C when not in use.

Raw groundwater was collected from an intake line at the Murphree Water Treatment Plant in Gainesville, FL. The city wells draw water from the Floridan aquifer, some 150–160 m below the ground, and the water contains at least 2 mg/L total hydrogen sulfide. Anaerobic conditions were maintained by flushing 160-mL glass bottles 5–6 times with groundwater prior to applying a Teflon-coated crimp-seal cap. Limestone was collected from an outcrop of the Floridan aquifer near Ocala, FL. The limestone was crushed and sieved into three size fractions: 20–50 mesh; 50–100 mesh; >100 mesh (Tyler equivalent).

Degradation. All sample processing was done in an atmosphere of dry, filtered (0.2-μm pore size and charcoal) nitrogen (Atmosbag, Aldrich Chem. Co.) to prevent introduction of oxygen into the anaerobic samples and to minimize microbial contamination of all samples. All materials used in the bag, except groundwater, were autoclaved (30 min, 250 °C) before use. In some cases, groundwater was passed through 0.2-μm membrane filters (Millipore) to remove microorganisms. Also, some bottles were sparged with sterile air until the oxygen concentration was about 4 mg/L (22 °C). Glass bottles (150 mL) filled with groundwater were fortified with AS, ASO, or ASO_2 (ca. 2 mg/L each) and mixed well. Small vials (2 mL, Wheaton) with and without limestone (12 mg each, 20–50 mesh) were completely filled with the various groundwater solutions and capped with Teflon-lined crimp-seal caps. All samples were incubated in the dark in a 20 °C water bath. Periodically, individual samples were removed and analyzed for AS and its derivatives.

Reduction. Experiments designed to observe reduction of ASO and ASO_2 followed the above sample preparation scheme with a few modifications. Only anaerobic groundwater was tested and some bottles were amended with 0.1% (w/v) glucose followed by an incubation period to 22 days to increase microbial populations. Also, some abiotic, buffered (0.1 M phosphate, pH 7.0) solutions were fortified with ferrous iron and hydrogen sulfide to create conditions that might be favorable for the chemical reduction of ASO and ASO_2.

Effect of Inorganic Ions. The effect of inorganic ions on the hydrolysis rate of ASO_2 was measured by adding different amounts of various salts to buffer solutions (0.020 M borate, pH 8.5) containing 2 mg/L of ASO_2. Ions tested were Na, K. Ca, Mg, Ba, Cu^{II}, Co^{II}, Cd^{II}, Mn^{II}, Fe^{II}, and Fe^{III}, and all were added as chloride salts. Also, the effect of carbonate concentration was determined by varying the concentration of a bicarbonate/carbonate buffer (both sodium salts, pH 10.3) while maintaining the ionic strength at 0.10 with additions of KCl. Aerobic solutions were placed in Teflon-sealed bottles and incubated in darkness at 20 °C. Samples were analyzed periodically for ASO_2 and ASO_2 oxime.

Sorption. Sorption experiments were performed by adding 10.0 g of 50–100 mesh limestone to glass culture tubes followed by 10.0 mL of aerobic groundwater that was previously equilibrated with limestone for about 1 month. Samples were fortified with AS, ASO, or ASO_2 at concentrations ranging from 0.1 to 2.0 mg/L. Samples were prepared in duplicate and controls consisted of 10.0 mL of the same groundwater without limestone. After shaking for 24 h, the tubes were centrifuged and supernatant was analyzed by HPLC.

Determination of the parent compounds and their metabolites was performed by reverse-phase HPLC (C-8 Zorbax, DuPont) by using an acetonitrile/water mobile phase. Detection was achieved by UV absorption at 200 nm and concentrations were measured by comparing peak heights of standards to samples. Details of this procedure are reported elsewhere (Miles and Delfino, 1984).

RESULTS AND DISCUSSION

Environmental parameters for the degradation experiments were chosen to represent the natural biogeochemistry of a major aquifer in Florida (Table I). Some alterations of these conditions were made to help isolate the major mechanisms for the degradation of AS, ASO, and ASO_2. These modifications included addition of air and/or limestone and removal of native microorganisms. Initially, we autoclaved the groundwater to achieve sterile conditions, but found that degassing of CO_2 and H_2S significantly increased the pH of the water and modified the degradation patterns. Thus, 0.2-μm membrane filtration was employed for removal of microorganisms in most of the water used for our experiments although no sterility test was performed. Anaerobic conditions were assumed because of the presence of H_2S.

An additional feature of our experimental design was subdividing the samples into small vials. Preliminary experiments suggested that subsampling a single large sample bottle resulted in the introduction of oxygen into anaerobic samples and led to microbial contamination.

Table I. Physical-Chemical Characteristics of Floridan Groundwater from the Murphree Water Treatment Plant, Gainesville, FL[a]

parameter	value(s)
temp	21–23 °C
conductivity	350–450 μmho/cm
ionic strength[b]	0.0056–0.0072
pH	7.6–7.8
total alkalinity	170–180 mg/L as $CaCO_3$
color	5 CPU
Ca	65–75 mg/L
Mg	19 mg/L
Na	9 mg/L
SO_4^{2-}	30–70 mg/L
Cl^-	12–15 mg/L
F^-	0.35–0.37 mg/L
H_2S	0.25 mg/L
Fe	0.01–0.06 mg/L
Mn	0.03–0.05 mg/L

[a] Raw water comes from a field of six wells ranging in depth from 150–160 m. Data provided by plant personnel. [b] By $\mu = 1.6 \times 10^{-5}$ (conductivity as μmho/cm) (Snoeyink and Jenkins, 1980).

Table II. Sorption Study of Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone on Limestone

compound	K_p[a] ($n = 2$)
aldicarb	0.05 ± 0.04
aldicarb sulfoxide	0.03[b]
aldicarb sulfone	0.03[b]

[a] K_p = X/C = (ng/g on 10 g of limestone)/(ng/g in 10 g of groundwater). [b] No standard deviation; identical results.

Several individual vials within each set of conditions allowed each sample vial to be discarded after analysis.

Sorption. Test compound–limestone equilibration experiments with solutions of AS, ASO, and ASO_2 in contact with the crushed Ocala limestone showed negligible difference in soluble pesticide concentration when compared with solutions without the limestone, indicating that sorption was not detectable (Table II). These low values of the sorption coefficients, K_p, agree with soil sorption studies (Hornsby et al., in press) which showed that Florida soils low in organic matter do not significantly retain AS. Although the Ocala limestone was mostly inorganic, significant concentrations of metals such as iron (1200 mg/kg) could have bound these pesticides by complexation processes. Since our experiments showed negligible sorption of AS compounds, we assumed these effects were absent in subsequent experiments.

Degradation. Degradation experiments showed that one reaction mechanism in groundwater microcosms was base hydrolysis. The conditions of the various degradation experiments and the pseudo-first-order rate constants for each experiment are listed in Table III. Reaction rates decreased in the order ASO_2 > ASO >> AS which agree with other studies. Porter et al. (1984) constructed graphs of half-life vs. pH for ASO and ASO_2 in buffered laboratory water at various temperatures and Table III shows that our results for ASO_2 compare favorably with those prediced from their graphs. This close agreement suggests that the Carmody buffer (citrate, phosphate, and borate) used by Porter et al. (1984) had little or no effect on the hydrolysis rate of ASO_2. Conversely, we found faster hydrolysis rates for ASO, which could be due to some naturally occurring factor.

To maintain natural conditions, no buffer was used to control pH in our initial experiments. As a result, pH values for different test conditions varied and these pH differences are an important consideration in interpretation of the results. Buffer-free water was used because of the concern raised by Perdue and Wolfe (1983) over the effect of buffer catalysis in laboratory studies of pollutant hydrolysis reactions. Although this effect was calculated to be minimal at low buffer concentrations, laboratory investigations that use buffer solutions should resolve this question with additional experiments or by appropriate calculations.

The pH values of the various microcosms at the beginning of the experiments are listed in Table III. Aeration of groundwater in the laboratory degassed carbon dioxide and hydrogen sulfide and caused the pH to rise to 8.5; the same water with added limestone yielded an equilibrium pH also at 8.5. Anaerobic groundwater showed a pH = 7.7 at the well intake but the addition of limestone (predominantly $CaCO_3$) raised the pH to 8.3. Calculations of pH for pure water with solid $CaCO_3$ in equilibrium with a fixed atmospheric content of carbon dioxide (0.032%) yielded a pH of 8.4 (Stumm and Morgan, 1981). Thus, with the exception of the anaerobic groundwater without limestone, the microcosm solutions were near equilibrium pH values, indicating that the pH remained relatively constant throughout the incubation period.

Degradation rates for AS in the groundwater microcosms were the slowest of all the compounds tested with half-lives ranging from 38–1300 days, although some of these rates may be imprecise due to high standard deviations recorded. AS degradation rates were faster in water without limestone and in microcosms at pH 8.3–8.5. The major degradation product of AS observed after 40–50 days was AS oxime. AS nitrile was not observed under any of the conditions investigated. Most samples fortified with AS showed small amounts of oxidation to ASO. Although this contrasts with soil studies, the low microbe population in groundwater relative to soil can account for this difference and this suggests that oxidation of AS to ASO is microbially mediated. Also, since both anaerobic and aerobic samples showed only about 1% conversion of AS to ASO, further evidence is provided that oxidation of AS is microbially mediated rather than being strictly an abiotic chemical reaction.

ASO and ASO_2 degradation followed similar trends (Figures 2 and 3). One advantage of using HPLC with

Table III. Pseudo-First-Order Rate Constants and Half-Lives for Degradation of Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone in Groundwater Microcosms

microcosm conditions[a]	pH	AS		ASO			ASO_2		
		k, $days^{-1}$	$t_{1/2}$	k, $days^{-1}$	$t_{1/2}$	$t_{1/2}$[b]	k, $days^{-1}$	$t_{1/2}$	$t_{1/2}$[b]
AF	8.5	0.018 ± 0.018	38	0.071 ± 0.007	9.8	15	0.159 ± 0.010	4.4	6
A		0.011 ± 0.005	63	0.061 ± 0.002	11.3		0.123 ± 0.012	5.7	
AFL	8.5	0.007 ± 0.006	94	0.015 ± 0.006	47		0.022 ± 0.014	32	
AL		0.015 ± 0.014	44	0.020 ± 0.002	35		0.027 ± 0.008	26	
ZF	7.7	0.011 ± 0.006	62	0.028 ± 0.006	25	90	0.021 ± 0.023	33	35
Z		0.001 ± 0.004	635	0.026 ± 0.007	26		0.027 ± 0.003	26	
ZFL	8.3	0.002 ± 0.005	433	0.021 ± 0.004	32		0.014 ± 0.018	49	
ZL		0.001 ± 0.004	1300	0.024 ± 0.004	29		0.006 ± 0.011	109	

[a] A = aerobic; Z = anaerobic; L = limestone added; F = filtered to remove microorganisms. [b] Obtained from graphs in Porter et al. (1984).

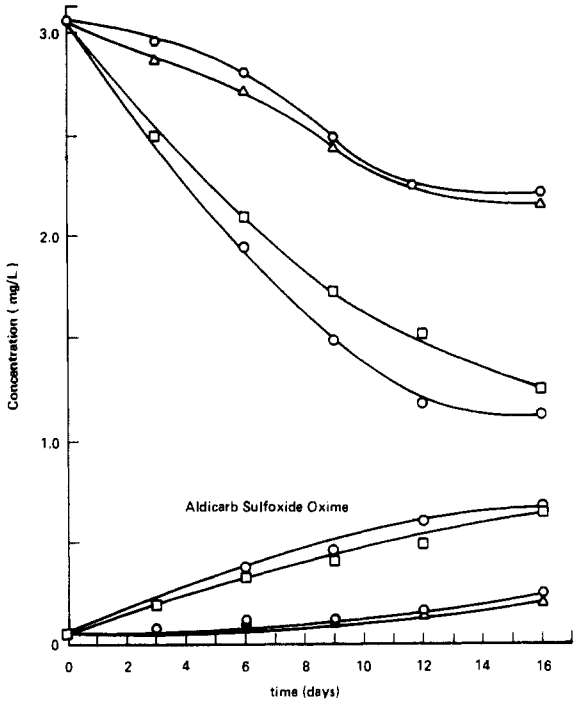

Figure 2. Degradation of ASO in aerobic groundwater microcosms at 20 °C and pH 8.5 (O = AF = 0.2 μm filtered; ○ = AFL = 0.2 μm filtered with limestone; □ = A = raw groundwater; Δ = AL = raw groundwater with limestone).

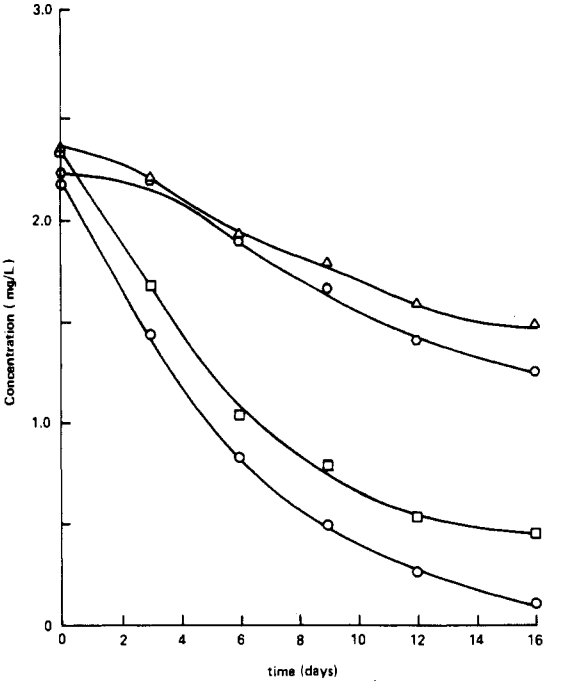

Figure 3. Degradation of ASO_2 in aerobic groundwater microcosms at 20 °C and pH 8.5 (O = AF = 0.2 μm filtered; ○ = AFL = 0.2 μm filtered with limestone; □ = A = raw groundwater; Δ = AL = raw groundwater with limestone.

UV detection in the AS series hydrolysis experiments (rather than postcolumn fluorescence HPLC or the GC technique) is that measurement of the hydrolysis products (the corresponding oximes) can be sensitively measured without further sample preparation. For ASO, the oxime accounted for about 30% of the loss of the initial concentration while ASO nitrile only represented 10–15% of the original fortification. Formation of other degradation products such as alcohols, amides, aldehydes, and acids (Union Carbide, 1983) could account for the remaining degradation products. For ASO_2, the oxime accounted for only 10–15% of the initial loss of fortified compound. In addition, ASO_2 oxime reached maximum concentrations shortly after the start of the experiments and decreased thereafter, suggesting that this compound is unstable in groundwater. Formation of ASO_2 nitrile could account for this difference but this species had poor detection limits under the conditions used.

An interesting observation was that samples with addition of limestone showed rates of hydrolysis that were 4–5 times slower than those without limestone (Table III). Since limestone (mostly $CaCO_3$) is basic, we predicted that limestone addition to groundwater would increase the base hydrolysis rate. Filtered samples showed slightly faster rates of degradation in most cases, suggesting that filtration removed a solution component that retarded hydrolysis (i.e., particulate limestone). Differences in pH were too small to account for the different rates. Examination of the hydrolysis reaction shows that carbonate is a product in an alkaline medium. Assuming that the law of mass

$$ASO_2 + 2OH^- = ASO_2 \text{ oxime} + CH_3NH_2 + CO_3^{2-} \quad (1)$$

action applies to this process, then addition of carbonate to a closed system should retard the overall reaction rate. Experiments in which the carbonate concentrations were varied from 0.001 to 0.100 M showed that increased carbonate concentrations did not have a significant effect on the hydrolysis rate of ASO_2. Since the hydrolysis rate of ASO_2 under the conditions tested (pH 10.3) was much faster than was observed in the groundwater microcosms (pH 8.3–8.5), the mass action effect was not readily apparent. Thus, under the conditions examined, ASO_2 hydrolysis was not significantly affected by increases in carbonate concentration.

Ionic Strength. In experiments where ionic strength was increased by addition of sodium or calcium chloride to buffered solutions, a significant decrease in rate was observed (Figure 4). An increase of NaCl concentration from 0.05 to 1.0 M decreased the hydrolysis rate by 54%. In a similar study, Lemley and Zhong (1983) reported a 36% decrease in the hydrolysis rate of ASO_2. An increase in $CaCl_2$ concentration over the same ionic strength range decreased the rate of hydrolysis by 82% suggesting that divalent ions decrease hydrolysis more efficiently.

Fukuto et al. (1967) reported that rate constants for the hydrolysis of *p*-nitro-*N*-methylcarbamate increased with decreasing concentrations of phosphate buffer. They postulated that phosphate anions did not participate in the hydrolytic reaction and that the lowering of rate constants with increasing ionic strength was due to a decrease in the activity of hydroxide ion or carbamate. Also, Aly and El-Dib (1972) reported that the half-life of Sevin (Union Carbide) (1-naphthyl-*N*-methylcarbamate) in low ionic strength water (pH 8.0, 20 °C) was 1.3 days while Karinen et al. (1967) reported a half-life of 4 days for the same compound in sea water at the same temperature and pH. Thus, an increase in ionic strength significantly decreases the hydrolysis rate of carbamate-type pesticides and this would be expected to be significant mostly in estuarine or marine systems.

Perdue and Wolfe (1983) developed a mathematical model for determining the maximum contribution of buffer catalysis in laboratory studies of pollutant hydrolysis reactions. In this model, the potential significance of buffer catalysis in aqueous solution is expressed as

$$k_{obsd}/k_w = 1 + C_B(BCF) \quad (2)$$

where k_{obsd} is the observed pseudo-first-order rate constant, k_w is the pseudo-first-order rate constant for catalysis by

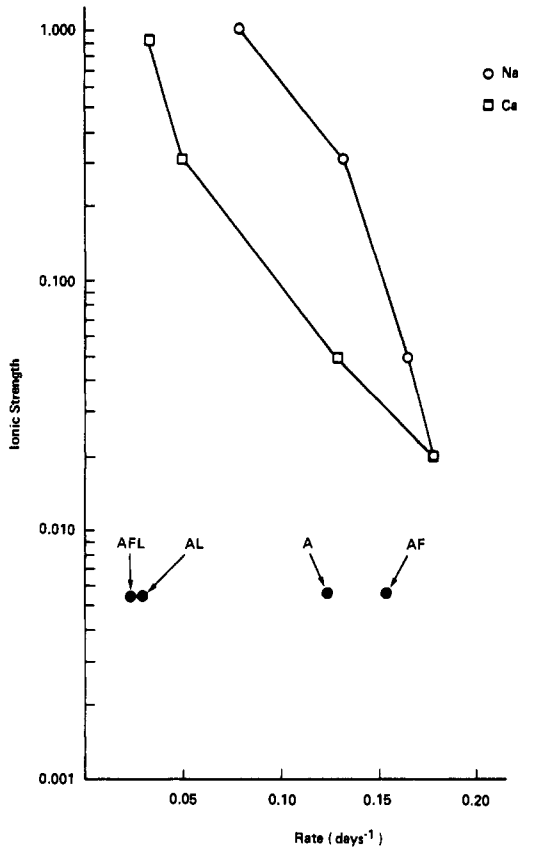

Figure 4. The effect of ionic strength on hydrolysis rate of ASO_2 in buffered, aerobic microcosms (0.020 M borate, pH 8.5, T = 20 °C). Hydrolysis rates for ASO_2 in 0.2 μm filtered groundwater (AF), 0.2 μm filtered groundwater with limestone (AFL), raw groundwater (A), and raw groundwater with limestone (AL) are shown for comparison.

solvent species H_2O, OH^-, and H_3O^+, C_B is the molar buffer concentration, and BCF is a buffer catalysis factor. When k_{obsd}/k_w is much greater than 1, buffer catalysis can be significant.

According to Perdue and Wolfe (1983), borate buffer at pH 8.5 has a BCF of about 50. At a concentration of 0.020 M, k_{obsd}/k_w is 2.0 indicating that up to 50% of the observed hydrolysis rate can be attributed to buffer catalysis. Comparison of the rates of ASO_2 hydrolysis in buffered (μ = 0.020) vs. unbuffered (μ = 0.006) solutions indicates that buffer catalysis increased the hydrolysis rate by 12%.

Groundwater and groundwater equilibrated with limestone for 30 days had similar conductivity and calcium and iron concentrations. This indicates that increased ionic strength cannot account for slower rates in samples amended with limestone. It appears that some other factor associated with the added limestone significantly retards hydrolysis.

A possible explanation of these results could be complexation of the carbamoyl oximes by trace metals in the limestone. Shih and Carr (1984) demonstrated that certain thiocarbamates can strongly complex with metals. If this is occurring with AS, complex formation and subsequent dissociation could control, and therefore retard, the overall hydrolysis rate.

To test this hypothesis, 1×10^{-6} M concentrations of various metal salts (all chlorides) were added to solutions of ASO_2 in borate buffer (0.020 M, pH 8.5) and the effects on hydrolysis were noted. No significant changes in hydrolysis rates were observed for the metals and conditions tested. Apparently, some other factor or combination of factors accounts for the significant decrease in hydrolysis rate observed in groundwater amended with limestone. Further studies are needed to elucidate this mechanism since much of Florida's groundwater is in contact with limestone.

Reduction. As a result of anaerobic microbial action, many soils, sediments, and natural waters have highly reducing environments which can transform organic chemicals such as pesticides (Alexander, 1981). Walter-Echols and Lichtenstein (1977) reported that phorate sulfoxide was reduced to its phorate precursor in lake sediment microcosms. Since AS has two oxidation products, we hypothesized that ASO and ASO_2 might be similarly reduced. This step would represent a toxification enhancement mechanism, particularly in the case of ASO_2.

Preliminary experiments showed that aerobic groundwater fortified with ASO (1.88 mg/L) had an AS concentration of 0.33 mg/L after 71 days, representing an 18% reduction. AS was qualitatively and quantitatively confirmed by a postcolumn fluorescence HPLC technique (Moye et al., 1977). After about 40 days, this sample showed the presence of increased microbial growth (turbidity) suggesting that microbial action was responsible for reduction. Also, experiments in which ferrous iron and hydrogen sulfide were added to abiotic, buffered (phosphate pH 7.0) solutions of ASO showed no reduction. This further supports the microbial reduction pathway hypothesis.

In subsequent experiments, ASO and ASO_2 were tested for reduction in anaerobic Floridan groundwater with additions of glucose and/or limestone. ASO_2 did not reduce to ASO under the conditions tested, but similar retention times of ASO and ASO_2 oxime in the HPLC chromatograms made quantitation difficult. ASO was reduced to AS, though only in solutions with glucose added. This is not surprising since microbial populations in raw Floridan groundwater are often low (Dierberg, 1984). Addition of glucose presumably increased the microbial population and this likely enhanced the subsequent reduction reaction. After 33 days incubation, 3% of the added ASO was reduced to AS in glucose-fortified groundwater, while the same glucose amended water with limestone added showed a 12% reduction of ASO to AS. This observation suggests that addition of limestone promotes the reduction reaction and this could be due to microbes on the limestone. Although we autoclaved the limestone for 30 min at 250 °C, even more extensive autoclaving of soils and sediments is often necessary to achieve sterile conditions (Walter-Echols and Lichtenstein, 1977).

It is interesting to compare these results with a study on the reduction of phorate sulfoxide to phorate in soil–lake sediment microcosms (Walter-Echols and Lichtenstein, 1977). These investigators found that only small amounts of phorate were produced in flooded loam soil treated with phorate sulfoxide. However, the addition of lake sediment to the soil system dramatically increased reduction of phorate sulfoxide to phorate (44% in 2 weeks). Sterilized soil–sediment microcosms had no detectable phorate indicating that the reduction reaction was microbially mediated. Also, addition of glucose (0.5% w/w) to the unsterilized microcosms further enhanced reduction of phorate sulfoxide to phorate indicating that microbial reduction depended on the supply of organic nutrients. Finally, they found that phorate sulfone was not reduced to phorate sulfoxide in the systems examined.

CONCLUSIONS

This study is one of the few to have observed degradation of AS, ASO, and ASO_2 in a natural water maintained close to the original field conditions. The results demon-

strated base hydrolysis of these three compounds by measurement of both the disappearance of the parent carbamoyl oxime and the appearance of the corresponding oxime. Aquifer material (limestone) did not adsorb the test compounds although it significantly retarded the hydrolysis rate by a presently unknown mechanism. Furthermore, oxidation of AS and ASO was shown to be minor while reduction of ASO was observed in glucose and limestone amended groundwater environments. This sudy indicates that the fate of AS, ASO, and ASO_2 in Floridan groundwater is a complex process. Further research is needed to assess the environmental and toxicological impact of the AS series compounds.

ACKNOWLEDGMENT

The authors wish to thank David Atherton of the Pesticides Research Laboratory (University of Florida) for postcolumn fluorescence HPLC analyses, and Michael Trehy, Michael Corbett, and Forrest Dierberg for helpful discussions.

Registry No. AS, 116-06-3; ASO, 1646-87-3; ASO_2, 1646-88-4.

LITERATURE CITED

Alexander, M. *Science (Washington, D.C.)* **1981**, *211*, 132–138.
Aly, O. M.; El-Dib, M. A. "Fate of Organic Pesticides in the Aquatic Environment"; Faust, S. D., Ed.; American Chemical Society: Washington, D.C., 1972; Advances in Chemistry Series No 111, pp 210–243.
Andrawes, N. R.; Bagley, W. P.; Herrett, R. A. *J. Agric. Food Chem.* **1971**, *19*, 727–730.
Bull, D. L.; Stokes, R. A.; Coppedge, J. R.; Ridgway, R. L. *J. Econ. Entomol.* **1970**, *63*, 1283–1289.
Chapmen, R. A.; Cole, C. M. *J. Environ. Sci. Health, Part B* **1982**, *B17(5)*, 487–504.
Coppedge, J. R.; Bull, D. L.; Ridgway, R. L. *Arch. Environ. Contam. Toxicol.* **1977**, *5*, 129–140.
Coppedge, J. R.; Lindquist, D. A.; Bull, D. L.; Dorough, H. W. *J. Agric. Food Chem.* **1967**, *15*, 902–910.
Dierberg, F. E., personal communication, 1984.
Fukuto, T. R.; Fahmey, M. A. H.; Metcalf, R. L. *J. Agric. Food Chem.* **1967**, *15*, 273–281.
Hansen, J. L.; Spiegel, M. H. *Environ. Toxicol. Chem.* **1983**, *2*, 147–153.
Hornsby, A. G.; Rao., P. S. C.; Wheeler, W. B.; Nkedi-Kizza, P.; Jones, R. L. In "Proceedings of a 1983 Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone"; Nielson, D. M., Ed.; National Water Well Association: Worthington, OH; in press.
Karinen, J. F.; Lamberton, J. G.; Stewart, N. E.; Terriere, L. C. *J. Agric. Food Chem.* **1967**, *15*, 148–156.
Lemley, A. T.; Zhong, W. Z. *J. Environ. Sci. Health, Part B* **1983**, *B18*, 189–206.
Lemley, A. T.; Zhong, W. Z. *J. Agric. Food Chem.* **1984**, *32*, 714–719.
Maitlen, J. C.; McDonough, L. M.; Beroza, M. *J. Agric. Food Chem.* **1968**, *16*, 549–553.
Miles, C. J.; Delfino, J. J. *J. Chromatogr.* **1984**, *299*, 275–280.
Moye, H. A.; Scherer, S. J.; St. John, P. A. *Anal. Lett.* **1977**, *10*, 1049–1073.
Perdue, E. M.; Wolfe, N. L. *Environ. Sci. Technol.* **1983**, *17*, 635–642.
Porter, K. S.; Lemley, A. T.; Hughes, H. B.; Jones, R. L. In "Proceedings on the Second International Conference on Groundwater Quality Research"; U.S. Environmental Protection Agency: Washington, D.C., 1984; in press.
Shih, Y. T.; Carr, P. W. *Anal. Chim. Acta* **1984**, *159*, 211–228.
Smelt, J. H.; Leistra, M.; Houx, N. W. H.; Dekker, A. *Pestic. Sci.* **1978a**, *9*, 279–285.
Smelt, J. H.; Leistra, M.; Houx, N. W. H.; Dekker, A. *Pestic. Sci.* **1978b**, *9*, 286–292.
Smelt, J. H.; Leistra, M.; Houx, N. W. H.; Dekker, A. *Pestic. Sci.* **1978c**, *9*, 293–300.
Snoeyink, V. L.; Jenkins, D. "Water Chemistry"; John Wiley and Sons: New York, 1980; pp 463.
Stumm, W.; Morgan, J. J. "Aquatic Chemistry", 2nd ed.; Wiley-Interscience: New York, 1981; pp 780.
Trehy, M. L.; Yost, R. A.; McCreary, J. J. *Anal. Chem.* **1984**, *56*, 1281–1285.
Union Carbide, Agricultural Products Company, Inc. "Temik Aldicarb Pesticide: A Scientific Assessment"; Union Carbide: Research Triangle Park, NC, 1983; pp 71.
Walter-Echols, G.; Lichtenstein, E. P. *J. Econ. Entomol.* **1977**, *70*, 505–509.

Received for review July 27, 1984. Revised manuscript received Oct. 24, 1984. Accepted February 19, 1985. This research was funded by the University of Florida College of Engineering through a grant from the Engineering and Industrial Experiment Station.