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REDUCTION OF PHORATE SULFOXIDE IN ANAEROBIC SEDIMENT SLURRIES

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ABSTRACT

The fate of phorate sulfoxide in anaerobic sediment slurries was studied in order to further define the role of reduction reactions in the environmental fate of organic pollutants. The primary transformation pathway of phorate sulfoxide in slurries of anaerobic stream and pond sediments was reduction of the sulfinyl moiety to the thioether. There was no evidence for oxidation of the thioether (phorate) back to phorate sulfoxide, although phorate was degraded by hydrolysis. Autoclaving and amendments of formaldehyde, toluene, nitrate, and sulfate to separate aliquots of sediment slurry indicated that the reduction of phorate sulfoxide was the result of microbial cometabolism or extracellular soil enzymes, whereas the subsequent hydrolysis of phorate was abiotic. At initial phorate sulfoxide concentrations of 10^{-4} M, it could not be determined whether the reduction kinetics were zero-order or first-order, but the kinetics appeared to be first-order at 10^{-5} M. The hydrolysis of phorate conformed to first-order kinetics. The reduction rate of the dissolved phorate sulfoxide was effectively first-order in sediment concentration, which indicates the reducing agent was sediment associated. The K_{OC} was 58 L/kg for phorate sulfoxide and 990 L/kg for phorate. Phorate sorption apparently inhibited hydrolysis. Further experiments suggested that the fate of carbophenothion and its sulfoxide in anaerobic sediments is analogous to that of the phorate system.

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KEYWORDS

Phorate sulfoxide Phorate Carbophenothion sulfoxide Reduction Anaerobic sediment

INTRODUCTION

It has gradually been recognized that abiotic reduction is a transformation pathway that contributes significantly to the fate of several classes of pollutants [1]. In a series of studies reported in this journal, Wolfe and coworkers [2-4] have sought to characterize the realm of this class of reactions. This work extends the series to include deoxygenation of sulfoxides to thioethers.

In principle, thioethers, sulfoxides, and sulfones are interconvertible by means of oxidation-reduction reactions (Figure 1), although the reduction of sulfones is particularly difficult to achieve in the laboratory. Synthetic techniques for the reduction of sulfoxides to thioethers involve strong reducing agents like $SnCl_2/HCl$, $TiCl_3$, and H_2/Pd [5].

Environmentally important organic chemicals that contain sulfinyl moieties include the solvent dimethyl sulfoxide and the pesticides demeton-S-methylsulfoxide, oxydisulfoton, and fensulfothion. Anthropogenic sulfoxides (and sulfones) also can result from environmental oxidation of thioethers. This has been reported for aldicarb [6], butocarboxim [7], carbophenothion [8], disulfoton [7], fenamiphos [9], fenthion [7], methiocarb [7], and phorate [10,11,12].

Reduction of organic sulfoxides to thioethers has been

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reported in several environmental media. Phorate sulfoxide reduction can be the major reaction in anaerobic soil and lake mud mixtures [13] but appears to be a minor pathway in aerobic soil [12,13,14 but cf. 15]. Disulfoton sulfoxide and fenthion sulfoxide reduction have been demonstrated in glucose-amended flooded paddy soil [16]. In axenic cultures of various soil bacteria, fensulfothion exhibits reduction of its sulfoxide moeity [17], but demeton S-methyl sulfoxide yields only hydrolysis and oxidation products [18]. The carbamate pesticide aldicarb sulfoxide has been reported to undergo reduction in limestone amended groundwater [6,19], but products other than the sulfide have sometimes been observed, indicating that the reaction is complex in comparison to those of the phosphorothioates. The important industrial solvent dimethyl sulfoxide has been shown to be reduced by a variety of microbial cultures, including some isolated from lake mud [20,21].

Despite these reports of sulfoxide reduction in the environment, a general understanding of the reaction pathway(s) has not emerged. In this work, we have used anaerobic techniques to study the fate of phorate and carbophenothion sulfoxides in reducing sediments. The goals were to characterize the kinetics of transformation and determine the balance of physico-chemical and/or microbiological controls on the reaction.

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EXPERIMENTAL METHODS

Materials

The sulfide, sulfoxide, and sulfone of phorate and carbophenothion (all analytical reference standards from the U.S. Environmental Protection Agency Pesticides and Industrial Chemicals Repository) were used to prepare standard solutions of the reactants and expected products. Liquid chromatographic analysis indicated that none of the standards contained significant amounts of either of its congeners. Hydrolysis studies were performed in 0.05 M buffers prepared from premixed dry salts (Fisher Certified Gram-pacs^{R}). The buffer solutions used were: pH 4.01, potassium acid phthalate; pH 6.86 and 7.41, potassium phosphate monobasic and sodium phosphate dibasic; pH 9.18, sodium tetraborate; and pH 10.4, tris(hydroxymethyl)aminomethane. The chemicals used to treat the sediments were 37% (v/v) aqueous formaldehyde (Baker, analyzed, stabilized with 12% methanol), potassium nitrate (Baker, analyzed), potassium sulfate (Baker, analyzed), and toluene (Burdick and Jackson, high purity). The solvents used were acetonitrile (Burdick and Jackson, high purity) and deionized water distilled in glass with potassium permanganate.

Sediments were sampled from three sites near Athens, GA. Beaver Dam refers to an eutrophic, abandoned stream channel in a lowland area that is heavily used as a watering-hole by cattle. Cherokee Park refers to a large, eutrophic artificial pond in an open area. Bar-H refers to a small mesotrophic pond in a wooded area away from agricultural land. Samples from the two ponds

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were taken from the littoral zone 1 to 2 m off shore where the mud was about 0.5 m below the surface. The mud in the abandoned channel and two ponds was sapropelic and, when disturbed, ebullition was apparent. The sample jars were submerged, used to mix the top 5 cm of sediment into a thin slurry, and then capped while submerged. The samples were stored and manipulated in a glove box with a nitrogen-purged atmosphere that typically was about 1% oxygen. Leaves, twigs, and other large items were removed from the samples but the sediments were not sieved.

Reaction Kinetics

Each experiment was begun in the glove box. Portions of sediment and water were transferred from the sample jar to a large beaker such that the approximate desired sediment to water ratio was obtained. While the contents of the beaker were mixed with a magnetic stir-bar, 10-mL aliquots of slurry were pipetted into 16 x 125-mm screw-cap culture tubes. Each tube was spiked with 1 mL of substrate standard in 65/35 acetonitrile and water. The resulting nominal, initial concentrations of substrate varied from 6.1×10^{-5} to 1.1×10^{-4} M (based on suspension volume) depending on the concentration of the standard solution.

The tubes were sealed with butyl rubber stoppers (for Hungate tubes, from Bellco) secured with linerless plastic screw caps and moved from the glove box to a covered, 27°C, shaker-water bath. At appropriate times, tubes were prepared for analysis by adding 4 mL of acetonitrile, shaking by hand for 1 min, and vortexing for 5 to 10 s. The samples were centrifuged for 10 min at 1240 G, the supernatant was transferred to a

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clean culture tube, and the centrifugation was repeated.

The supernatant was analyzed for substrate and products by isocratic liquid chromatography with uv-absorbance detection. The analytical column was 4.1 x 250-mm, 10-um particle size, poly(styrene-divinylbenzene) copolymer (Hamilton PRP-1). Various combinations of acetonitrile and water were used to elute the analytes. The most useful eluent was 65/35 acetonitrile in water because it could be used to analyze all three phorate congeners at once. Absorbance was monitored at 230 nm for all compounds. Concentrations were quantified by comparison of peak areas to calibration curves determined with standard solutions and were not corrected for extraction efficiency.

Treatment Effects

Treatments were applied to the sediment slurry after it was dispensed into culture tubes and before the substrate was added. The treated slurry was well mixed but no additional time was allowed for the treatment to take effect. Sediment slurries were made 8.5 mM in toluene by adding the neat liquid, 0.4 M in formaldehyde by adding a 37% (v/v) solution, and 0.99 mM in KNO_3 and 0.85 mM in K_2SO_4 by adding 0.1 M aqueous solutions of the salts. Moist-heat sterilization was performed by capping a set of tubes, removing them from the glove box, autoclaving twice at 120°C (20 psi) with 24 h incubation in between, and returning them to the glove box to spike with substrate. The effect of temperature was determined by incubating sets of tubes in 5, 27, 45, 55, and 86°C. The influence of the acetonitrile added as part of the substrate solution was tested by treating sets of

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tubes with 1 mL of water, with 50/50 and 60/40 acetonitrile and water, and with acetonitrile. In this series of experiments, substrate was introduced by adding 10 uL of 0.0474 M phorate sulfoxide in acetonitrile.

Sediment Parameters

The weight fraction of organic carbon was determined by coulometric titration [22] on sediment samples that were air dried and sieved with a No. 18 (1 mm) screen. Sediment to water ratios were calculated from the weight of dry sediment divided by the weight of water in the slurry. The role of sorption was investigated by an experiment similar to those used in reaction kinetics studies but using a Beaver Dam sediment that had been oven dried at 100°C, gently ground, sieved with a No. 18 mesh (1-mm) screen, and then resuspended in distilled water. The analysis was performed periodically over 6 d by centrifuging, separating the supernatant from the pellet, and extracting both with acetonitrile. The extracts were analyzed by liquid chromatography as described above. The amount of analyte sorbed to the sediment was calculated from the moles in the extracted pellet (assuming 100% extraction efficiency) less the moles in solution with the residual water (assuming the solid is responsible for 0.25 mL of the slurry volume). The partition coefficient, K_d, is reported as moles/kg of sediment per moles/L of water.

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RESULTS AND DISCUSSION

Sorption to Sediments

For moderately reactive compounds like phorate and phorate sulfoxide, it is desirable to inhibit transformation reactions in order to isolate and measure sorption to the sediment. This was attempted by thoroughly drying the sediment at 100°C and then adding distilled water to restore the slurry. The resultant slurry was spiked with substrate and the concentrations in solution and sorbed to the sediment were determined periodically. For both phorate and phorate sulfoxide, the amount recovered from the supernatant declined exponentially over a week. The amount of substrate extracted from the pellet increased exponentially for about 2 days and then declined; perhaps due to some restored transformation pathway. Total phorate sulfoxide recovery remained about 80% over one week. However, total phorate recovery declined from 114% to 73%. The most important contributor to the decreased recovery of phorate is probably hydrolysis. The calculated values of K_d reached their maximum values of 49 L/kg for phorate after 6 days and 2.9 L/kg for phorate sulfoxide after 3 days. The weight fraction of organic carbon for the Beaver Dam sediment sample was 0.05. This fraction was used to calculate K_{OC} from the distribution coefficients. For phorate, our value was 990 L/kg, which is somewhat higher than the literature values of 250 [23], 380 [24], and 510 [26]. Our K_{OC} for phorate sulfoxide is 58 L/kg but we found no values in the literature for comparison. In the reduction studies that follow, phorate sulfoxide sorption is

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presumed to be largely complete after about 2 h with about 10% on the sediment and sorption-desorption rates being fairly rapid. Phorate sorption levels off after about 1 h and about 70% is sediment sorbed.

Hydrolysis in Buffer Solutions

We performed a series of hydrolysis studies in buffer solutions for phorate and phorate sulfoxide before using sediment slurries (Table 1). The disappearance rates were first-order. Hydrolysis of phorate sulfoxide was negligible over 18 days below a pH of about 8, but showed significant base-catalyzed hydrolysis at higher pH. Phorate exhibits predominantly neutral (pH independent) hydrolysis from pH 4 to 10 with a half-life of about 3.4 days. These observations agree with those reported in the literature [26]. The significance to this work is that abiotic, neutral hydrolysis of phorate sulfoxide is very slow and is not likely to be an important process in anaerobic sediment slurries, but hydrolysis of phorate occurs at a moderate rate and may be a significant pathway.

Fate in Fresh Sediment

Determination of the reaction order for the disappearance of phorate sulfoxide and phorate was made by comparison between plots and regression analysis for concentration versus time (zero-order) and ln concentration versus time (first-order) data. In those cases where enough substrate was reacted to clearly indicate first-order kinetics, the rate constant was taken from the slope of the linear regression line for all data. In other cases, the reaction order could not be determined unambiguously;

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however, the data were consistent with first-order kinetics, so a disappearance rate constant was computed by assuming the rate was first-order. These rate constants are used for comparison of treatment effects only. In all cases, the uncertainties reported with the rate constants are one standard deviation of the regression line slope.

Phorate. The most important transformation of phorate in aerobic soil is reported to be microbiological oxidation to the sulfoxide or sulfone [10,12]. This reaction also has been reported in anaerobic systems [11]. In contrast, we found no evidence for the formation of the sulfoxide or sulfone 1 week after spiking anaerobic Beaver Dam sediment slurry with phorate. Phorate concentration decreased, however, and the kinetics appeared to be first-order contrary to the results of several previous studies [summarized and discussed at length in reference 12]. It is likely that the transformation processes and their associated kinetics are different in our anaerobic sediments from those in aerobic soil systems. However, it also should be noted that the duration of our experiments was shorter than that of most studies that have reported non-first-order kinetics so our results may correspond to initial rates and these conditions may degenerate at longer reaction times.

Disappearance rate constants for phorate are given in Table 2. The values agree closely with those that Chapman et al. [12] calculated after discarding the first observations of each of their data sets. The small differences between the rate constants in Table 2 suggest the disappearance of phorate in

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Beaver Dam sediment slurries is not biological and not dependent on anaerobic conditions. As suggested previously in the sorption section, we believe the degradation process is hydrolysis. The phorate disappearance rates are about three times slower in sediment slurries (Table 2) than in buffers (Table 1), and this is consistent with the fact that only 30% of the phorate in these sediment slurries was in solution, assuming that sorbed phorate is not subject to hydrolysis [27].

Phorate Sulfoxide. The fate of phorate sulfoxide in untreated anaerobic sediment slurries was observed many times in the course of this work using a liquid chromatographic method that separated the sulfide, sulfoxide, and sulfone peaks with each injection. In all runs at 27°C, there was no indication of sulfone formation. The sulfoxide response usually declined; in which case, the sulfide response increased (Figure 2). At the beginning of the experiment, the combined concentration of phorate sulfoxide and phorate gave good agreement with the nominal, initial concentration of phorate sulfoxide, but the sum fell increasingly short of mass balance as the experiment progressed. These results are consistent with reduction of phorate sulfoxide to phorate, without reoxidation of the sulfide back to the sulfoxide, and subsequent hydrolysis of phorate.

The reaction order for disappearance of phorate sulfoxide could not be determined unambiguously because the duration of most experiments was only one half-life. Typically, the data fit zero-order and first-order disappearance kinetics equally well. However, when the experiment was performed with 10^{-5} M initial phorate sulfoxide concentration, instead of the usual 10^{-4} M,

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unequivocally first-order kinetics were observed over three half-lives. The disappearance rate constant was $1.08(\pm 0.05) \times 10^{-4}$ min^{-1}, an order-of-magnitude faster than was typically observed at 10^{-4} M initial concentrations. These observations suggest a transition from first-order to zero-order disappearance kinetics at higher substrate concentrations. Such a transition may occur at high substrate concentrations because the substrate reacts rapidly with a reducing agent that is formed continuously but slowly so that the supply of reducing agent is rate limiting, or it may occur because there are a limited number of sites (enzyme or surface) and the sites become saturated [28]. An equivalent dependence of reduction rate on initial concentration has been observed for halogenated ethanes in anaerobic slurries of Bar-H sediment [3]. The range of concentrations where transitional kinetics were encountered in this work is typical of microbiological transformation pathways that exhibit saturation of enzyme sites and conform to Michaelis-Menton kinetics [30].

To be able to make predictions about the fate of anthropogenic sulfoxides, the role of the sediment medium in the transformations must be determined. The results of selected phorate sulfoxide disappearance studies in various sediment samples are given in Table 3. Except for one atypically reactive sample, the half-lives do not appear to depend on the time or place of sample collection or length of the incubation period between when the sample was collected and when it was used in a disappearance study.

Two previous papers [3,4] in this series have reported that

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disappearance due to reduction is faster in more concentrated sediment slurries and the results in Table 3 suggest that the same is true here. A deliberate effort to test this hypothesis by varying the sediment to water ratio as much as possible and analyzing only the phorate sulfoxide in solution, without extracting the sediment, resulted in the data in Figure 3. Apparently there is a direct, linear relationship between the disappearance rate constant of phorate sulfoxide in solution and the sediment to water ratio. In effect, the reaction is first-order in sediment concentration and, therefore, the reducing agent is sediment associated [30]. Sediment associated kinetics can result when the reducing agent is sediment bound, as are most microorganisms and extracellular enzymes in soil, or when the reducing agent is released at the particle surface and forms a narrow diffusion zone of low concentration in the surrounding solution.

Antimicrobial Treatments

To determine the role that microorganisms play in the reduction of phorate sulfoxide, disappearance kinetics were determined in treated sediment slurries. Because the sediment sample is a dynamic and not usually reproducible medium, treatment effects were determined in sets of parallel disappearance studies performed with the same starting material. Each set included an untreated control against which the results from treated runs were compared. The results (Table 4) favor an enzymatic pathway for the reduction of phorate sulfoxide, but they still allow a wide range of possible reducing agents.

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Autoclaving is a very severe treatment that alters the sediment in many ways. Sediment slurries that were autoclaved twice with 24 h of incubation in between produced no reduction of phorate sulfoxide. Apparently, some heat labile substance is responsible for the reaction.

Formaldehyde is a very reactive substance that combines with amines, carboxylic acids, phenols, and sulfides [31]. It also may alter the sediment medium significantly, although the mechanism is presumably different than that of autoclaving. Treatment levels used to sterilize sediments vary from 0.075% v/v [3,4] to 4% [32]. In this work, 0.15% formaldehyde decreased the rate of reduction about five-fold, suggesting that most of the reducing agent is formaldehyde-labile.

Toluene alters the permeability of cell membranes and has been used extensively at 5 to 20% (v/v) to distinguish soil enzyme activity from endocellular enzymatic processes in active soil microorganisms [33]. Enough toluene was added to make a 0.1% (v/v) sediment slurry and the treatment decreased the reduction rate 28%. This result may be evidence that the reaction is due to extracellular enzymes, but it is also possible that not enough toluene was added to completely inhibit microbial activity.

The effect of acetonitrile concentration on the kinetics of phorate sulfoxide reduction was determined because some acetonitrile was present in all experiments as a consequence of the way substrate was added to the slurries. It is apparent from the data in Table 4 that acetonitrile inhibits the reaction. Not enough is known about the effect of acetonitrile in sediments to

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speculate on the mechanism of this inhibition. Due to the presence of acetonitrile and relatively high initial concentrations of substrate, it can be presumed that environmental reduction of phorate sulfoxide in situ will be faster than has been observed in these laboratory experiments.

Nitrate and sulfate were added as alternative electron acceptors for microbial metabolism. Neither treatment significantly affected the rate of phorate sulfoxide reduction. These results, and the fact that no lag phase was ever observed in our work, are consistent with a reaction that is cometabolic [34]. Zinder and Brock [20,21] came to this conclusion regarding the reduction of dimethyl sulfoxide by enrichment cultures of various microorganisms. However, in sediment systems, other reducing agents are possible that will not be affected by sulfate and nitrate.

Brock [32] has suggested that the most incisive way to distinguish enzymatic reactions in soil or sediment media is by the effect of temperature on reaction rate. Barring any changes in mechanism, a chemical reaction rate increases monotonically with temperature, whereas an enzymatic reaction (and biological reactions in general) exhibit a maximum rate at intermediate temperatures. However, the effect of temperature on the fate of phorate sulfoxide in anaerobic sediment slurries (Figure 4) is not so easily interpreted because the dominant reaction pathway apparently changes twice between 5 and 86^{o}C. Below 45^{o}C, phorate was the observed product so the disappearance is certainly due to reduction. Around 55^{o}C, phorate sulfone was the major product,

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suggesting oxidation is the important pathway. Above 70°C, the lack of detected oxidation or reduction products indicates that disappearance is due to hydrolysis. The Arrhenius plot of the same data (Figure 5) suggests, if there are three different rate controlling steps, that they all have activation energies equal to about 12 kcal/mole. In general, these results are consistent with the expectation that the reduction and oxidation are due to enzymes or similar agents while the hydrolysis is abiotic, but they demonstrate that temperature effects are not necessarily an unambiguous way to distinguish biological from abiotic reactions.

Carbophenothion Sulfoxide

To add perspective, experiments were done with carbophenothion and carbophenothion sulfoxide. The thioether, carbophenothion, has a K_{om} more than 100 times greater [35] and a hydrolysis half-life about 60 times greater [36] than phorate. The disappearance of carbophenothion in anaerobic Beaver Dam sediment slurry was very slow (half-life of 50 days). By analogy to the phorate system, we expect the slow disappearance is due to hydrolysis partially inhibited by sorption to the sediment. However, carbophenothion sulfoxide recovery declined in the reducing sediment system with a concomitant increase in carbophenothion peak area. No evidence for carbophenothion sulfone formation was observed. The disappearance of the sulfoxide fit first-order kinetics with a half-life of 1.4 days. In the same sediment slurry, phorate sulfoxide was reduced with a half-life of 2.5 days. We conclude from these results that carbophenothion sulfoxide and its redox congeners are subject to

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the same set of transformations as the phorate compounds in anaerobic sediment slurries.

CONCLUSIONS

Organophosphorothioate pollutants with a sulfinyl moiety are subject to reduction to thioethers. The reduction of phorate sulfoxide is probably due to enzymes or similar agents. If microorganisms are directly involved, the reduction is likely to be cometabolic; but sediment-bound extracellular reducing substances also may be responsible. In anaerobic sediment slurries, this reaction appears to be the primary transformation process. Not enough phorate sulfoxide is sorbed to significantly affect the reduction rate, but the reducing agent is clearly sediment associated. Presumably, this results from the concentration of microorganisms or soil enzymes on the sediment. The thioether (phorate) is not detectably oxidized to the sulfoxide, but it is degraded by abiotic hydrolysis. Phorate is mostly sorbed to the sediment and this apparently retards hydrolysis.

The kinetics of phorate sulfoxide reduction are first-order for substrate concentrations at or below 10^{-5} M, but were not distinguishable from zero-order at 10^{-4} M. This transition is probably due to saturation of available reductant. The hydrolysis of the reduction product, phorate, proceeds with first-order kinetics.

Carbophenothion and its sulfoxide behave analogously to phorate and phorate sulfoxide in these systems. It is likely

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that pathways described here apply generally to the fate of organophosphorothioate sulfoxide pesticides in anaerobic environments.

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Table 1. Hydrolysis rate constants for phorate and phorate sulfoxide in buffer solutions at 25.4°C.

	k_{obs} (min^{-1}) x 10^{-4}				
pH	4.01	6.86	7.41	9.18	10.4
phorate sulfoxide	--[a]	--[a]	-- [a]	1.33±0.04	14.6±0.2
phorate	1.64±0.08	1.39±0.22	1.39±0.18	1.40±0.08	2.10±0.16

[a]slopes calculated from regression analysis were not significantly different from zero.

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Table 2. Neutral hydrolysis rate constants for phorate in anaerobic sediment slurries[a]

treatment	$k_{obs}(min^{-1}) \times 10^{-5}$	half-life (days)
untreated	3.52±0.26	13.6
untreated	4.34±0.24	11.1
autoclaved	3.77±0.32	12.8
0.4 M CH_2O	4.73±0.25	10.2
dried	3.18±0.68	15.1

[a]in Beaver Dam sediment slurries with sediment to water ratio about 0.04 and temperature 27.0°C.

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Table 3. Reduction rate constants for phorate sulfoxide in anaerobic sediment slurries[a]

sample site	date collected	age[b] (days)	sediment to water ratio	k_{obs} x 10^{-5} (min^{-1})	half-life (days)
Beaver Dam	1 July 88	3	0.04	24.9±0.6	1.9
		12	0.04	19.4±0.17	2.5
	21 July 88	10	0.01	2.96±0.38	16.3
		14	0.01	2.63±0.29	18.3
		15	--	5.66±0.81	8.5
Cherokee Park	19 July 88	16	0.10	2.53±0.18	19.0
	19 July 88	20	0.05	1.15±0.09	41.9
	8 Sept 88	0	0.04	1.17±0.13	41.2

[a]at 27.0°C and assuming first-order disappearance kinetics.

[b]the amount of time between sample collection and when it was used in kinetics studies.

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Table 4. Antimicrobial treatment effects on phorate sulfoxide reduction rate constants for anaerobic sediment slurries[a]

sediment treatment	sediment to water	k_{obs} (min^{-1}) x 10^{-5}	half-life (days)
control	0.04	19.4±1.7	2.5
autoclaved	0.04	--[b]	--[b]
0.05 M CH_2O	0.04	1.07±0.10	45.0
control	0.01	2.63±0.29	18.3
0.1% (v/v) toluene	0.01	2.08±0.31	23.2
control	0.04	1.17±0.13	41.2
$1x10^{-3}$ M nitrate	0.04	1.32±0.25	36.5
$8x10^{-4}$ M sulfate	0.04	1.22±0.13	39.6
0.1% acetonitrile	0.02	13.9±0.19	3.5
4.4% acetonitrile	0.02	2.58±0.15	18.7
5.9% acetonitrile	0.02	1.37±0.13	35.1
9.1% acetonitrile	0.02	0.88±0.12	54.4

[a]at 27.0°C and assuming first-order disappearance kinetics.

[b]no significant disappearance was detected over 12 days.

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FIGURE CAPTIONS

Figure 1. Structures of the three redox interconvertible congeners of phorate: phorate (left), phorate sulfoxide (center), and phorate sulfone (right).

Figure 2. Disappearance of phorate sulfoxide, appearance of phorate, and decline in combined phorate and phorate sulfoxide in Beaver Dam sediment slurry at 27.0°C.

Figure 3. Effect of sediment to water ratio on the rate of reduction of dissolved phorate sulfoxide in Beaver Dam sediment slurries at 27.0°C.

Figure 4. Effect of temperature on phorate sulfoxide disappearance rate in a Cherokee Park sediment slurry.

Figure 5. Arrhenius plot for phorate sulfoxide disappearance kinetic data in a Cherokee Park sediment slurry.

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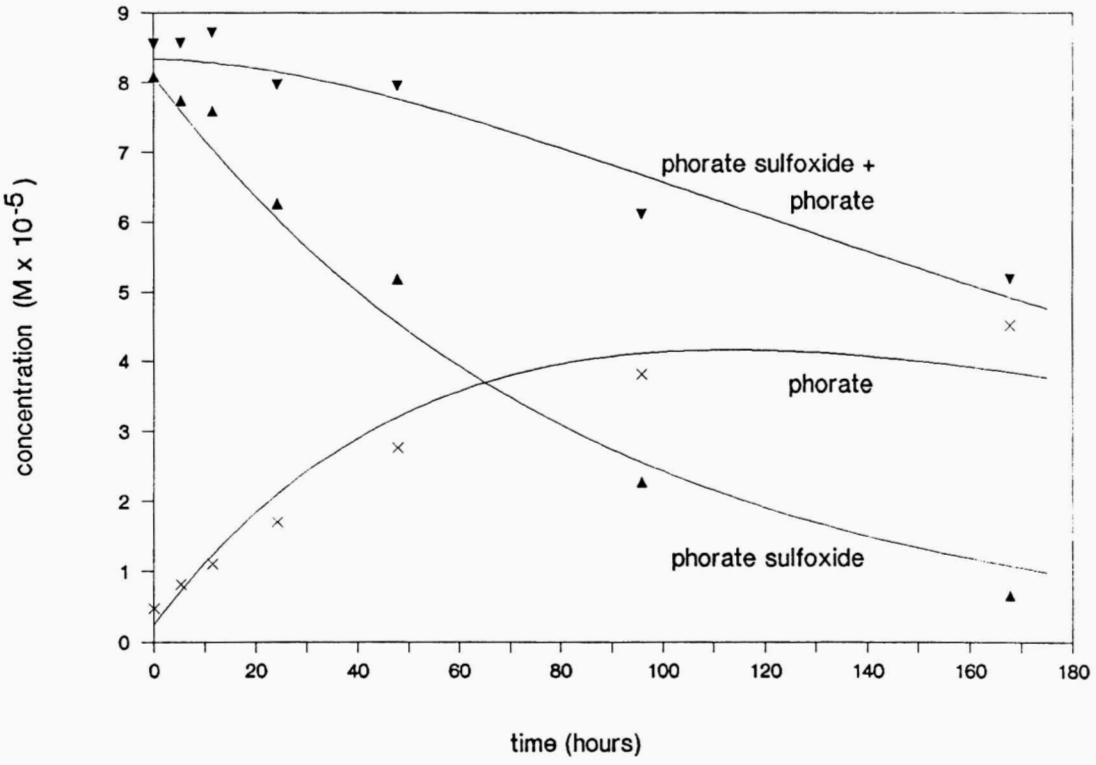
Figure 2



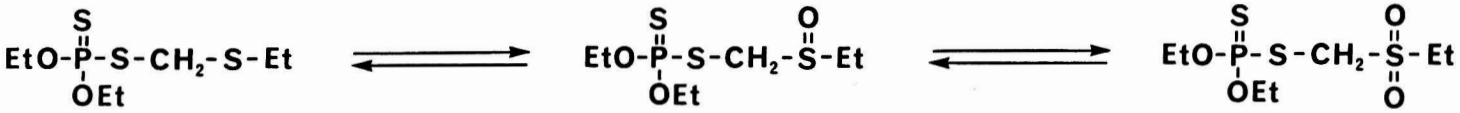


Fig. 1

Tratnyek and Wolfe (1988)

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Figure 3

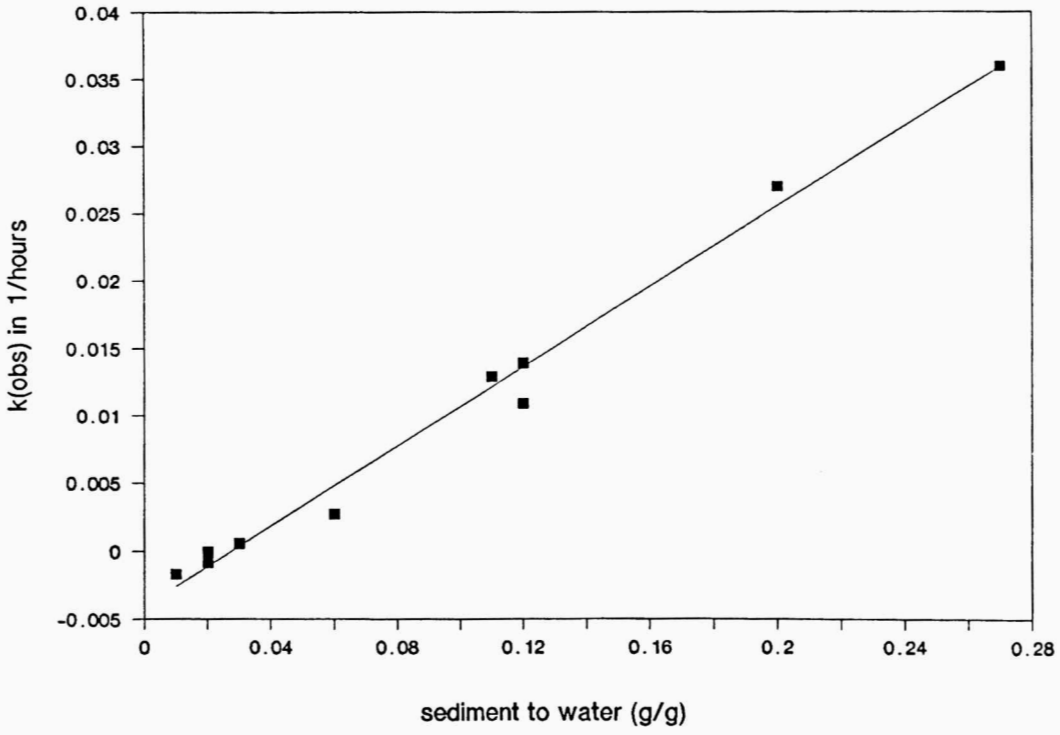

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Figure 4

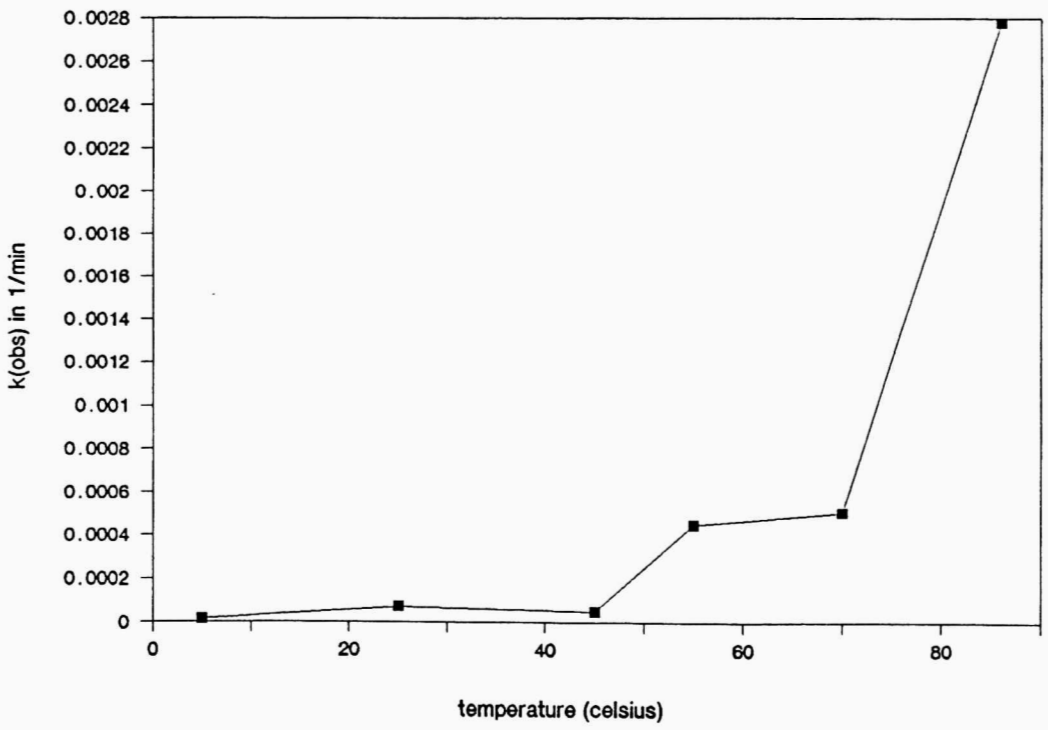

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Figure 5