

- Cook, A. M.; Hütter, R. In "Microbial Degradation of Xenobiotics and Recalcitrant Compounds"; Leisinger, Th.; Cook, A. M.; Nüesch, J.; Hütter, R., Eds.; Academic Press: London, 1981; Chapter 14.
- Cowan, S. T.; Liston, J. In "Bergey's Manual of Determinative Bacteriology", 8th ed.; Buchanan, R. E.; Gibbons, N. E., Eds.; Williams and Wilkins: Baltimore, 1974; pp 10-13.
- Cripps, R. E.; Roberts, T. R. In "Pesticide Microbiology"; Hill, I. R.; Wright, S. J. L., Eds.; Academic Press: London, 1978; Chapter 11.
- da Fonseca-Wollheim, F.; Bergmeyer, H. U.; Gutmann, I. In "Methoden der enzymatischen Analyse", 3rd ed.; Bergmeyer, H. U.; Gawehn, K., Eds.; Verlag Chemie: Weinheim, 1974; pp 1850-1853.
- Daughton, C. G.; Hsieh, D. P. H. *Appl. Environ. Microbiol.* 1977a, 34, 175-184.
- Daughton, C. G.; Hsieh, D. P. H. *Bull. Environ. Contam. Toxicol.* 1977b, 18, 48-56.
- Esser, H. O.; Dupuis, G.; Ebert, E.; Marco, G. J.; Vogel, C. In "Herbicides: Chemistry, Degradation and Mode of Action"; Kearney, P. C.; Kaufman, D. D., Eds.; Marcel Dekker: New York, 1975; Chapter 2.
- Fishbein, L. "Chromatography of Environmental Hazards"; Elsevier: Amsterdam, 1975; Vol. III, Chapter 17.
- Giardina, M. C.; Buffone, R. *Ann. Microbiol. Enzimol.* 1977a, 27, 127-130.
- Giardina, M. C.; Buffone, R. *Chemosphere* 1977b, 9, 589-594.
- Guillemat, J. C. R. *Hebd. Seances Acad. Sci., Ser. D* 1960, 250, 1343-1344.
- Guillemat, J.; Charpentier, M.; Tardieux, P.; Pochon, J. *Ann. Epiphyt.* 1960, 11, 261-295.
- Harris, C. I.; Kaufman, D. D.; Sheets, T. J.; Nash, R. G.; Kearney, P. C. *Adv. Pest Control Res.* 1968, 8, 1-55.
- Hughes, D. E.; Stafford, D. A. *CRC Crit. Rev. Environ. Control* 1976, 6, 233-257.
- Hulbert, M. H.; Krawiek, S. J. *Theor. Biol.* 1977, 69, 287-291.
- Jensen, H. J.; Abdel-Ghaffar, A. S. *Arch. Microbiol.* 1969, 67, 1-5.
- Jordan, L. S.; Farmer, W. J.; Goodin, J. R.; Day, B. E. *Residue Rev.* 1970, 32, 267-286.
- Kaufman, D. D.; Blake, J. *Soil Biol. Biochem.* 1970, 2, 73-80.
- Kaufman, D. D.; Kearney, P. C. *Residue Rev.* 1970, 32, 235-265.
- Kaufman, D. D.; Kearney, P. C.; Sheets, T. J. *Science (Washington, D.C.)* 1963, 142, 405-406.
- Kaufman, D. D.; Kearney, P. C.; Sheets, T. J. *J. Agric. Food Chem.* 1965, 13, 238-242.
- Kearney, P. C.; Kaufman, D. D.; Sheets, T. J. *J. Agric. Food Chem.* 1965, 13, 369-372.
- Kennedy, S. I. T.; Fewson, C. A. *Biochem. J.* 1968, 107, 497-506.
- Knuesli, E.; Berrer, D.; Dupuis, G.; Esser, H. In "Degradation of Herbicides"; Kearney, P. C.; Kaufman, D. D., Eds.; Marcel Dekker: New York, 1969; Chapter 2.
- Lehninger, A. L. "Biochemistry", 2nd ed.; Worth: New York, 1975; pp 19, 208.
- Luria, S. E. In "The Bacteria"; Gunsalus, I. C.; Stanier, R. Y., Eds.; Academic Press: New York, 1960; Vol. I, Chapter 1.
- Mickovski, M.; Verona, O. *Agric. Ital. (Pisa)* 1967, 67, 67-76.
- Munnecke, D. M. *Biotechnol. Bioeng.* 1979, 21, 2247-2261.
- Munnecke, D. M. *J. Agric. Food Chem.* 1980, 28, 105-111.
- Payne, W. J. *Annu. Rev. Microbiol.* 1970, 24, 17-52.
- Pfennig, N.; Lippert, K. D. *Arch. Microbiol.* 1966, 55, 245-256.
- Ramsteiner, K. A.; Hörmann, W. D.; Eberle, D. *Z. Pflanzenschutz, Sonderh.* 1972, 6, 43-52.
- Saldick, J. *Appl. Microbiol.* 1974, 28, 1004-1008.
- Stanier, R. Y.; Adelberg, E. A.; Ingraham, J. L. "The Microbial World", 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1976; Chapter 9.
- Stanier, R. Y.; Palleroni, N. J.; Doudoroff, M. *J. Gen. Microbiol.* 1966, 43, 159-271.
- Strzelec, A. *Acta Microbiol. Pol., Ser. B* 1975, 7, 91-96.
- Vionova, G.; Bakalivanov, D. *Meded. Fac. Landbouwwet., Rijksniv. Gent* 1970, 35, 839-846.
- Weatherburn, M. W. *Anal. Chem.* 1967, 39, 971-974.
- Wise, L. E.; Walters, E. H. *J. Agric. Res. (Washington, D.C.)* 1917, 10, 85-92.
- Wolf, D. C.; Martin, J. P. *J. Environ. Qual.* 1975, 4, 134-139.
- Zeyer, J. Ph.D. Dissertation No. 6446, Eidgenössische Technische Hochschule, Zürich, Switzerland, 1979.

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## s-Triazine Solubility in Chloride Salt Solutions

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Terbutryn [2-(*tert*-butylamino)-4-(ethylamino)-6-(methylthio)-*s*-triazine], atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], and secbumeton [*N*-ethyl-6-methoxy-*N'*-(1-methylpropyl)-1,3,5-triazine-2,4-diamine] solubility was determined as a function of temperature, salt type, and concentration. The aqueous solubility of the *s*-triazines increased in the order terbutryn  $\leq$  atrazine  $<$  secbumeton. As the ambient temperature increased from 1 to 29 °C, solubility increased by 11% (secbumeton), 42% (atrazine), and 52% (terbutryn). Salt up to ionic strength ( $\mu$ ) 0.1 did not greatly affect solubility while values  $>$  0.1  $\mu$  reduced solubility. Sodium chloride and KCl at 2.5  $\mu$  reduced solubility by 85%, whereas CaCl<sub>2</sub> reduced solubility by 58% for the herbicides studied.

The distribution of the *s*-triazine herbicides in soil solution is influenced by soil reaction, mineralogy, organic matter, moisture content, hydrous oxides, and chemical form and concentration of ions in solution. Under low rainfall conditions or irrigated agriculture, the salt con-

centration in the soil solution could be appreciable because of low-quality irrigation water, high evaporation, or banded fertilizer application. Thus, it is of interest to study the effect of solute concentration on *s*-triazine solubility to differentiate between adsorption and precipitation reactions which affect herbicide concentration in the soil solution.

*s*-Triazine solubility has been extensively studied as a function of molecular structure (Ward and Weber, 1968). The solubility of the methoxy analogues was found to be 1 order of magnitude greater than that for the methylthio

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analogues, whereas chloro-*s*-triazines generally were least soluble. Monoalkylamino substituted *s*-triazine solubility decreased in the order  $\text{OCH}_3 > \text{SCH}_3 > \text{OH} > \text{Cl}$  but changed to  $\text{OH} > \text{OCH}_3 > \text{Cl} > \text{SCH}_3$  as the *N*-alkylamino complexity of the two side chain functional groups increased (Ward and Weber, 1968; Ward and Holly, 1966).

The solubility of polar basic nonelectrolytes may be reduced (salted out) or increased (salted in) by electrolyte solutions (Long and McDevit, 1952; Harned and Owen, 1958). The hydration of the cations and anions, the orientation of the water molecules in the hydration sphere, and the polarity of the nonelectrolyte influence solute solubility.

This study was initiated to determine the effect of temperature and potassium, sodium, and calcium chloride salts on the solubility of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], terbutryn [2-(*tert*-butylamino)-4-(ethylamino)-6-(methylthio)-*s*-triazine], and secbumeton [*N*-ethyl-6-methoxy-*N'*-(1-methylpropyl)-1,3,5-triazine-2,4-diamine] in aqueous solution.

#### MATERIALS AND METHODS

**Solubility-Temperature Relationships.** Atrazine (0.05 g), terbutryn (0.05 g), and secbumeton (0.10 g) in duplicate were added to 100 mL of deionized water, adjusted to pH 6 with 1 N NaOH or HCl, and equilibrated 6 days at room temperature in 250-mL Erlenmeyer flasks. After equilibration, the samples were placed in a constant-temperature room at 1, 8, 20, and 29 °C for 3 days, then filtered (Whatman No. 5), and analyzed on a Cary Model 11 recording spectrophotometer at 219, 222, and 224 nm for secbumeton, atrazine, and terbutryn, respectively. Particles greater than 2–3  $\mu\text{m}$  were retained by the filter paper. Preliminary studies showed no *s*-triazine was adsorbed by the filter paper and that maximum solubility was reached before 6 days. Samples of the herbicide solutions were diluted with deionized water to a range of 1–5 ppm. Absorbance measurements were made at 206 and 255 nm for background correction utilizing the base-line technique (Knüsli et al., 1964).

**Solubility in Sodium, Potassium, and Calcium Chloride.** Sufficient sodium, potassium, and calcium chloride salts and atrazine (0.05 g), terbutryn (0.05 g), and secbumeton (0.10 g) were added to 100-mL volumetric flasks to give final salt ionic strengths ( $\mu$ ) of 0.005, 0.05, 0.1, 0.5, 1.0, and 2.5. The equation  $\mu = \frac{1}{2} \sum (MZ^2)$ , where  $M$  is the molarity of the ion species (moles/liter) and  $Z$  is the valence of the cation or anion, was used to calculate the ionic strength. After an initial 6-h equilibration, the pH of the salt systems which were greater than pH 6 was adjusted with 0.2 N HCl. The Na and Ca systems at pH less than 6 were adjusted with 1 N NaOH and the K systems with 1 N KOH. In all systems <0.2 mL was required for the pH adjustment. The Ca systems were adjusted with NaOH because of the low solubility of  $\text{Ca}(\text{OH})_2$ . After the pH adjustment, the samples were transferred to 250-mL Erlenmeyer flasks and shaken for 6 days at room temperature. Upon removal from the shaker, the samples were placed in a constant-temperature room at 20 °C for 3 days without shaking, filtered, and analyzed as above. Duplicate samples were prepared for each herbicide at each ionic strength. Blank solutions of salts with ionic strength similar to that of the herbicide systems were used for background correction.

#### RESULTS AND DISCUSSION

**Solubility-Temperature Relationships.** Structurally, the three chemicals differ in two substituents of the *s*-triazine ring but possess a common ethylamino group in the third position (Table I). The solubility of the *s*-tri-

Table I. Chemical Structure and Melting Points of the *s*-Triazines

common name	ring substituents			mp, °C
	R	R'	R''	
atrazine	Cl	Et	<i>i</i> -Pr	175
terbutryn	$\text{SCH}_3$	Et	<i>t</i> -Bu	104
secbumeton	$\text{OCH}_3$	Et	<i>sec</i> -Bu	88

Table II. Temperature Effects on *s*-Triazine Solubility at pH 6

temp, °C	<i>s</i> -triazine solubility, $M \times 10^4$		
	atrazine	terbutryn	secbumeton
1	1.39 (30) <sup>a</sup>	1.09 (26)	29.3 (659)
8	1.41 (30)	1.10 (27)	32.5 (731)
20	1.58 (34)	1.46 (35)	30.7 (691)
29	1.97 (42)	1.66 (40)	33.0 (743)

<sup>a</sup> Values in parentheses are in ppm.

azines investigated increased in the order  $\text{SCH}_3 < \text{Cl} < \text{OCH}_3$  (Table II) which corresponds to the solubility order for *s*-triazines with a complex alkylamino functional group (Ward and Weber, 1968; Ward and Holly, 1966). The chloro and methylthio analogues had similar solubilities, but the solubility of the methoxy analogue was 1 order of magnitude greater.

The most recently published solubilities (Weed Science Society of America, 1979) for these herbicides are  $1.53 \times 10^{-4}$  M (27 °C, atrazine),  $1.04 \times 10^{-4}$  M (20 °C, terbutryn), and  $27.5 \times 10^{-4}$  M (20 °C, secbumeton) which, except for terbutryn, are in good agreement with solubilities at the corresponding temperatures reported herein. The pH of the solutions for the published solubilities were not reported, and since *s*-triazine solubilities increase as pH decreases (Ward and Weber, 1968; Weber, 1970), discrepancies may reflect differences in methodologies and environmental conditions.

For the *s*-triazines studied, the  $\text{pK}_a$  and basicity increased in the order  $\text{Cl}$  (1.68) <  $\text{SCH}_3$  (4.10) <  $\text{OCH}_3$  (4.36), indicating, as Ward and Weber (1968) found, that increased basicity did not always result in increased solubility. The lower solubility of terbutryn relative to atrazine is because of the higher hydrophobicity of the *tert*-butylamino group, since it has been shown that for structurally related compounds the *N*-alkylamino functional groups played a more significant role in solubility than did basicity (Ward and Weber, 1968). For example, for the methoxy-*s*-triazines, simeton [2-methoxy-4,6-bis(ethylamino)-*s*-triazine;  $\text{pK}_a = 4.15$ ] and trietaton [2-methoxy-4-(ethylamino)-6-(diethylamino)-*s*-triazine;  $\text{pK}_a = 4.51$ ], solubilities were  $132 \times 10^{-4}$  and  $10.6 \times 10^{-4}$  M, respectively.

Within each of the *s*-triazines studied, the solubility increased as temperature increased from 1 to 29 °C (Table II). A 28 °C increase in temperature increased solubility 52, 42, and 13% for terbutryn, atrazine, and secbumeton, respectively.

The relatively small temperature effect and much greater solubility of secbumeton ( $30.7 \times 10^{-4}$  M at 20 °C) relates to the methoxy functional group. Finkel'shtein and Boitsov (1962) showed that the ring nitrogen atoms carried a partial negative charge, while the ring substituents retained a partial positive charge. The methoxy oxygen atom is more electronegative than the methylthio sulfur; thus,

Table III. *s*-Triazine Solubility ( $M \times 10^4$ ) at 20 °C in Chloride Salt Solutions

salt ionic strength, $\mu$	atrazine			terbutryn			secbumeton		
	Na	K	Ca	Na	K	Ca	Na	K	Ca
0	1.58	1.58	1.58	1.46	1.46	1.46	30.7	30.7	30.7
0.005	1.67	1.69	1.61	1.54	1.40	1.56	31.3	30.8	31.0
0.05	1.59	1.63	1.61	1.37	1.37	1.45	29.3	29.2	30.3
0.1	1.60	1.65	1.67	1.32	1.27	1.43	26.7	26.9	29.7
0.5	1.11	1.17	1.30	0.96	0.95	1.20	20.9	20.6	25.6
1.0	0.79	0.81	1.23	0.67	0.68	0.99	13.7	14.5	22.0
2.5	0.28	0.24	0.67	0.24	0.22	0.61	3.9	4.3	13.1

the overall more negative polarity of the methoxy-*s*-triazine would result in less intermolecular attraction in the solid phase. The attractive forces in the solid phase were greater for the methylthio- and chloro-*s*-triazines as inferred from their lower solubilities and higher melting points. An increase in temperature would reduce these attractive forces to a greater extent, as manifested by a greater relative increase in solubility. This same analogy (i.e., the weaker the bonds, the less the effect of temperature) has also been observed for temperature effects on adsorption (Goring and Hamaker, 1972).

**Solubility in Sodium, Potassium, and Calcium Chloride.** At equivalent ionic strengths ( $\mu$ ), the *s*-triazine solubility increased in the order  $SCH_3 < Cl < OCH_3$  (Table III), the same as that observed for the electrolyte-free systems. No salt-*s*-triazine complexes were detectable from the ultraviolet spectra, but the absence of such complexes was not confirmed by other analytical techniques.

Salt at  $<0.1 \mu$  had only minimal effects on solubility. At ionic strength  $> 0.1$ , the *s*-triazine solubility decreased faster in sodium and potassium chloride than in calcium chloride. At a salt ionic strength of 2.5, *s*-triazine salting out appeared to be independent of *s*-triazine type since the percent reduction in herbicide concentration was similar in the presence of their respective salts. Calcium reduced *s*-triazine solubility 58%, where Na and K reduced solubility 85%.

Nonelectrolyte salt solubility can be expressed by

$$\log (f/f^0) = \log (S^0/S) = K_s\mu + K_i(S - S^0) \quad (1)$$

where  $f^0$  and  $f$  are the activity coefficients of the nonelectrolyte (*s*-triazine) in distilled water and salt solution,  $S^0$  and  $S$  are the corresponding solubilities, and  $K_s$  and  $K_i$  are the salt and solute interaction parameters, respectively (Long and McDevit, 1952). A plot using the empirical Setschenow equation (eq 2)

$$\log (S^0/S) = K\mu \quad (2)$$

of  $\log (S^0/S)$  against ionic strength ( $\mu$ ) was linear, with its intercept near 1. The Setschenow equation (eq 2), which is empirically derived, cannot be equated to the term relating the activity coefficient to the ionic strength, except at infinite dilution or where the solubility differential approaches zero.

The salt parameter  $K_s$  in eq 1 is not the same as the Setschenow parameter ( $K$ ), which includes ion-solute as well as molecule-solute interactions (self-interactions), i.e., a combination of  $K_i$  and  $K_s$ . The molecular self-interaction term,  $K_i$ , may be as large as the salt parameter term,  $K_s$ , and becomes more significant as solute polarity increases. Relative values for the Setschenow constant,  $K$ , can be compared for different salts within each *s*-triazine compound because the interaction term,  $K_i$ , i.e., molecule-solute interaction, is constant and independent of salt (Long and McDevit, 1952).

The parameter  $K$  was determined for the *s*-triazine data by the method of least-squares fit (Table IV). The  $K$

Table IV. Salt Coefficients ( $K$ ) for *s*-Triazines<sup>a</sup>

salt	atrazine	terbutryn	secbumeton
NaCl	0.310a	0.317a	0.354a
KCl	0.339a	0.320a	0.337a
CaCl <sub>2</sub>	0.155b	0.156b	0.149b

<sup>a</sup> Coefficients followed by the same letter are not significantly different at the 1% level.

values for NaCl and KCl were similar for each of the *s*-triazines (0.310–0.354) and were significantly higher than those for Ca (0.149–0.156) (Table IV). The higher  $K$  values for the Na and K ions indicate these cations more effectively salt out *s*-triazines than Ca. In a similar study, the addition of 0.3 and 0.6  $\mu$  chloride salts of  $NH_4$ , K, and Ca decreased the solubility of three structurally related *s*-triazines with the reduction in solubility following the expected cation order  $Ca < NH_4 < K$  (Hurle and Freed, 1972). Long and McDevit (1952) also observed that monovalent cations suppressed solubility more than divalent cations for polar basic nonelectrolytes.

Several qualitative and quantitative approaches have been proposed to explain the effects of electrolytes on polar nonelectrolyte solubility. Two qualitative approaches adequately explain this data: the concept of preferred orientation of the water molecules in the hydration sphere of an ion (Kruyt and Robinson, 1926) and the "localized hydrolysis" concept (Harned and Owen, 1958).

The preferred orientation concept suggests that strongly hydrated cations, such as Li and Ca, orient water molecules about themselves with protons exposed to the solute (dissolved *s*-triazine). Basic nonelectrolytes will be attracted to the protons, thereby reducing the salting out effect. The effect of salt type will be dependent upon their hydration energies. Hydration energies for Li, Na, K, Ca, and Cl are 127, 101, 81, 389, and 86 kcal/mol (Pauling, 1970). The *s*-triazine herbicides accept protons and by the Lowry-Bronsted definition are considered bases. The cations, because of their high hydration energy, orient the water dipoles and the *s*-triazines to reduce the salting out effect. Na and K cations would have a lesser effect on water orientation and thus reduce *s*-triazine solubility more than Ca. The activity coefficient of the *s*-triazines, as reflected by the  $K$  value (Table IV), increased less for the Ca than for the Na or K ions, hence a higher solubility. *s*-Triazine solubility was reduced similarly by the Na and K cations because of their similar hydration energies (101 and 81 kcal/mol). The preferred orientation concept agrees with the conclusions of Ward and Weber (1968) in which protonation of the one and/or three ring nitrogen atoms increased solubility at low pH.

It is recognized that the hydration concept only explains relative salt effects on nonelectrolyte solubility. Other proposals to explain observed effects of salts on polar nonelectrolyte solubility have considered expressions of changes in dielectric constant of the solution, (i.e., a decrease in dielectric constant results in salting out), dipole moment and polarizability of the nonelectrolyte (i.e., in-

creased solubility as dipole moment increases), and van der Waals forces.

Although anion and cation combinations may have different effects on *s*-triazine salting out, the solubility values obtained with the chloride salts indicate that salts in the soil solution (~0.02 N) would have an insignificant effect on solubility. Richards (1954) reported that saturated saline soils do not exceed 0.1 N salt concentration and that most agricultural soils have salt levels below 0.02 N.

It may be possible, however, that under the right management conditions, i.e., band application of fertilizers with herbicides and low-moisture conditions, salt levels may become high enough to precipitate the *s*-triazines. The condition would probably be relieved upon application of water.

#### LITERATURE CITED

- Finkel'shtein, A. I.; Boitsov, E. N. *Russ. Chem. Rev. (Engl. Transl.)* 1962, 31, 712.  
 Goring, C. A.; Hamaker, J. W., Eds. "Organic Chemicals in the Soil Environment"; Marcel Dekker: New York, 1972; Vol. 2, pp 49-143.

- Harned, H. S.; Owen, B. B., Eds. *ACS Monogr.* 1958, No. 137.  
 Hurle, K. B.; Freed, V. H. *Weed Res.* 1972, 12, 1.  
 Knüsel, E.; Burchfield, J. P.; Storrs, E. E. In "Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives"; Zweig, G., Ed.; Academic Press: New York, 1964; Vol. IV, pp 213-233.  
 Kruyt, H. R.; Robinson, C. *Akad. Wetenschappen, Amsterdam* 1926, 29, 1244.  
 Long, F. A.; McDevit, W. F. *Chem. Rev.* 1952, 51, 119.  
 Pauling, L., Ed. "General Chemistry", 3rd ed.; W. H. Freeman: San Francisco, 1970.  
 Richards, L. A., Ed. *U.S. Dep. Agric., Agric. Handb.* 1954, No. 60.  
 Ward, T. M.; Holly, K. J. *Colloid Interface Sci.* 1966, 22, 221.  
 Ward, T. M.; Weber, J. B. *J. Agric. Food Chem.* 1968, 16, 959.  
 Weber, J. B. *Residue Rev.* 1970, 32, 93.  
 Weed Science Society of America "Herbicide Handbook of the Weed Science Society of America", 4th ed.; Weed Science Society of America: Champaign, IL, 1979.

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## Fate of the Insecticide *O*-[4-[(4-Chlorophenyl)thio]phenyl] *O*-Ethyl *S*-Propyl Phosphorothioate (RH-0994) in Water

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The stability of a radiolabeled preparation of the organic phosphate insecticide *O*-[4-[(4-chlorophenyl)thio]phenyl] *O*-ethyl *S*-propyl phosphorothioate (RH-0994) was determined in buffered water, in the dark, at pH 4.0, 7.0, and 10.0. RH-0994 degraded rapidly at neutral or alkaline pH but much more slowly under acidic conditions. The half-lives of 0.5-ppm solutions of RH-0994 under the conditions of study were as follows: pH 10.0, <1 day; pH 7.0, ~14 days; pH 4.0, >>28 days. Degradation occurred primarily by hydrolysis of the phosphorus-O-phenyl ester linkage and by oxidation of the diphenyl thioether sulfur to sulfoxide derivatives.

There is a continual need for the development of insect control agents that are both efficacious and highly selective in toxicity toward pest species. Further, as pest insects acquire resistance to existing insecticides, the development of newer chemicals that circumvent resistance becomes a highly desirable and in fact critical need.

Certain major insect pests of cotton, such as the cotton bollworm, *Heliothis zea* (Boddie), and the tobacco budworm, *Heliothis virescens* (F.), have developed a high degree of resistance to many of the insecticides used against them for the past two or more decades. Due to resistance, control strategies for these insects must be adaptable as the insects themselves change. The *Heliothis* complex in cotton is presently managed by a number of approaches, including continued reliance on older insecticides, the use of newer chemicals such as the synthetic pyrethroids, and various integrated pest management

(IPM) techniques. There is little doubt that management of the *Heliothis* complex in cotton will, in the future, require further refinements; thus, research toward the development of newer and more efficacious insecticides is clearly warranted.

The experimental organic phosphate insecticide *O*-[4-[(4-chlorophenyl)thio]phenyl] *O*-ethyl *S*-propyl phosphorothioate (RH-0994 of the Rohm and Haas Co., Philadelphia, PA) is being developed for possible use in controlling *Heliothis* populations, as well as other insect species. The compound has good selectivity, particularly in its relatively low toxicity to mammals (Bull and Ivie, 1981). RH-0994 thus offers promise as an environmentally acceptable insecticide for use against *Heliothis* and other insects attacking cotton and other crops. As a necessary prerequisite to its potential commercial use, environmental studies are needed. We have previously reported on the fate of RH-0994 in cotton (Bull and Ivie, 1981); the current studies were designed to evaluate the fate of the chemical in water, in the dark, under acidic, neutral, and alkaline conditions.

#### MATERIALS AND METHODS

**Chemicals.** [<sup>14</sup>C]RH-0994 (6.15 mCi/g) was supplied for these studies by the Rohm and Haas Co., Spring House, PA. The radiochemical was uniformly incorporated into

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