Adsorption of Glyphosate by Soils and Clay Minerals

Robert L. Glass

The adsorption of glyphosate by several soils and clay minerals was investigated with a high-performance liquid chromatographic method. Freundlich adsorptive capacities (K) were determined as 138, 115, and 8, respectively, for the clay minerals montmorillonite, illite, and kaolinite; and 76, 56, and 33, respectively, for Houston clay loam, Muskingum silt loam, and Sassafras sandy loam. Adsorption by the soils appeared to be related to the clay content and the cation-exchange capacities of the soils. Adsorption of glyphosate by illite was found to be independent of pH. The loss of solution protons as revealed by the increase in pH of the glyphosate solutions equilibrated with illite suggested the existence of a cation-exchange reaction. Saturating montmorillonite with various cations increased glyphosate adsorption in the order $Na^+ < Ca^{2+} < Mg^{2+} < Cu^{2+} < Fe^{3+}$. The complexation of glyphosate by cations released from cation-saturated clays via a cation-exchange reaction with solution protons was proposed as an adsorption mechanism. The formation of a new absorbance band (λ_{max} = 226 nm) in the UV spectra of glyphosate solutions (pH 4) equilibrated with Cu^{2+}–montmorillonite provided additional evidence for complex formation between glyphosate and cations.

The adsorption of the herbicide glyphosate, N-(phosphonomethyl)glycine, by soils was first reported by Sprankle et al. (1975) who found that [^{14}C]glyphosate adsorbed more readily to a clay loam soil than a sandy loam. Additions of cations to bentonite clay were shown to increase the adsorption of glyphosate in the following order: $Ca^{2+} < Mn^{2+} < Zn^{2+} < Mg^{2+} < Fe^{3+} < Al^{3+}$. The authors postulated that the cations assisted in forming new adsorption sites on the clay minerals. Hensley et al. (1978) also studied the effects of cations on the behavior of glyphosate in soils and concluded that the inactivation of glyphosate by Fe^{3+}- and Al^{3+}-saturated soils was caused by the chelation of glyphosate. Shoval and Yariv (1979), utilizing Fe^{3+}- and Al^{3+}-saturated montmorillonite, investigated several glyphosate–cation complexes by infrared spectrophotometry and concluded that complexes formed within the interlayer spaces of the clay minerals.

In a recent adsorption study, McConnell and Hossner (1985), utilizing a high-performance liquid chromatographic (HPLC) method for quantitating glyphosate, demonstrated that glyphosate adsorption on cation-saturated clays was a function of the charges of the individual cations based on the observed adsorptive capacities of 1155.6, 112.8, and 100.7 for Al^{3+}-, Ca^{2+}-, and Na^+-saturated montmorillonites (pH 4.5), respectively. In another adsorption study, Miles and Moye (1986), who also used a HPLC method, reported that glyphosate adsorption varied inversely with the pH of the clay suspensions and that a cation-exchange mechanism played a significant role in the adsorption process of glyphosate on cation-saturated clays.

In this paper the adsorption phenomenon of glyphosate is further explored with a new HPLC technique (Glass, 1983). The objectives of this investigation were to (1) determine the adsorptive capacities of glyphosate of several agricultural soils and clay materials and (2) examine the effects of pH and saturating cations on the adsorption of glyphosate by the clay minerals illite, kaolinite, and montmorillonite.

EXPERIMENTAL SECTION

Materials. Analytical-grade glyphosate (94% purity) was obtained from Monsanto Chemical Co. and was used without further purification. All other chemicals were

U.S. Department of Agriculture—Agricultural Research Service, Agricultural Environmental Quality Institute, Beltsville, Maryland 20705.

Table I. Properties of Three Agriculture Soils[a] Used for Glyphosate Adsorption

soil type	CEC,[b] mequiv/ 100 g	pH	particle size anal.,[c] %			
			C	silt	clay	sand
Houston clay loam (TX)[d]	29.0	7.5	1.56	37.5	52.6	9.9
Muskingum silt loam (OH)[d]	11.0	5.8	1.64	55.0	17.0	28.0
Sassafras sandy loam (MD)[d]	6.6	5.6	1.24	17.0	7.1	75.9

[a] Soil samples were taken from a repository of former U.S. Soils Laboratory, Beltsville, MD. [b] Cation-exchange capacities were determined by Cooperative Extension Service of the University of Maryland. [c] Values were obtained from unpublished soil data of former U.S. Soils Laboratory, Beltsville, MD. [d] Origin of soil samples.

reagent grade. The names of the three soils used in the investigation, including their origin and properties, are given in Table I. The clay minerals kaolinite, illite, and montmorillonite obtained from Ward's Science Establishment originated as follows: kaolinite (no. 3) from Oneal Pitt, Macon, GA; illite (no. 36) from Morris, IL; montmorillonite (no. 20) from Polkville, MS. The natural clays were ground in a mortar and passed through a 20-mesh sieve. The cation-saturated clays were prepared by combining 25-g samples of the clays with 50-mL volumes of 1 M concentrations of the selected cations. The samples were mixed for 1 h on a rotary shaker. The suspensions were then dialyzed against water until the dialysates were free of chloride ions, which were tested by adding aliquots of a dilute silver nitrate solution. After the clay samples were dried overnight in an oven, they were ground again and passed through the 20-mesh sieve. The clays were stored in jars over anhydrous P_2O_5. In the preparation of the soil samples, the soils were first air-dried until they contained about 15% moisture. The soils were passed through a 20-mesh sieve and then stored in jars over anhydrous P_2O_5.

Adsorption. Weighed quantities of the soils (2.0 g) and the clay minerals (0.5–1.0 g) were combined with 25-mL aliquots of glyphosate solutions of varying concentrations and pH values. All of the soil and clay samples were prepared in duplicate. The pH values of the glyphosate solutions were adjusted with either 0.1 N NaOH or 0.1 N HCl before combining with the adsorbents. The suspensions were then shaken in polypropylene tubes (29 × 103 mm) on a rotary shaker for 1-h time periods at room
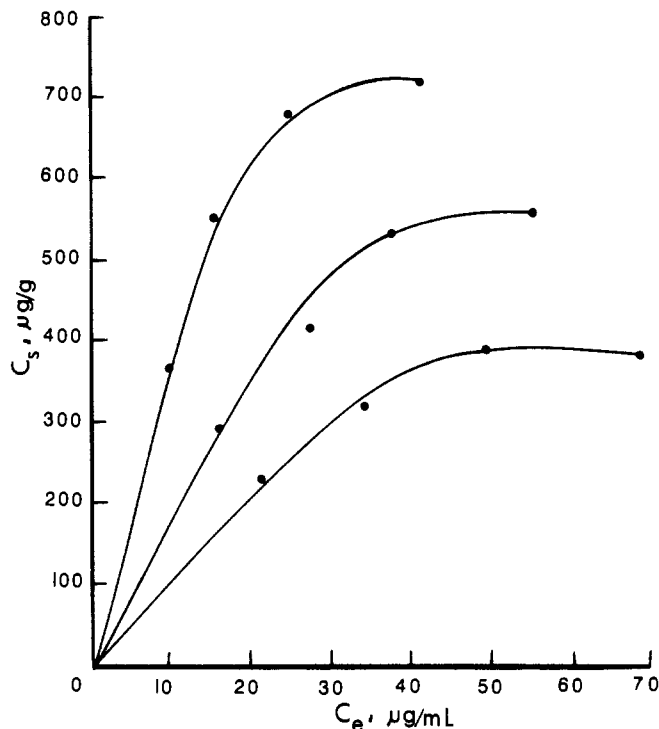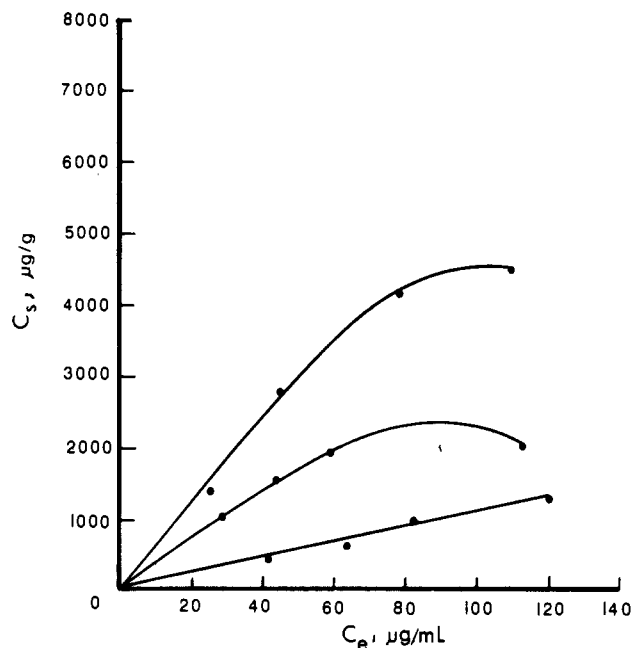
Figure 1. Adsorption isotherms for glyphosate on soils: (a) Sassafras sandy loam; (b) Muskingum silt loam; (c) Houston clay loam.

temperature. The samples were subsequently centrifuged for 15 min at 2000 rpm. After the suspensions were re-adjusted to ca. pH 5, 5-mL aliquots of 0.1 M $CaCl_2$ were added to flocculate the remaining suspended substances. The samples were centrifuged again, and the liquid phases were then passed through filter paper. The liquid phases were subsequently passed through anion-exchange resin (8 g; Bio-Rad AG 1-X8 in HCO_3^- form) and then eluted wiith a 150-mL aliquot of 0.2 M NaCl.

Glyphosate Analysis. The fluorescent derivative of glyphosate prepared with 9-fluorenylmethyl chloroformate (Aldrich) was measured by a high-performance liquid chromatographic (HPLC) method as reported in an earlier paper (Glass, 1983). In the early stages of the investigation, an Aminco filter fluorometer (excitation 254 nm, emission 300–400 nm) was used but was later replaced with a dual monochromatic spectrofluorometer (S.I./McPherson Model 750; excitation 270 nm, emission 315 nm). The excitation light was supplied by a 150-W xenon arc lamp equipped with an arc stabilizer. The chromatographic column was an Alltech NH_2 column (25 cm × 4.6 mm). The mobile phase was a mixture (v/v) of 75% 0.1 M KH_2OP_4/25% acetonitrile (Burdick & Jackson Laboratories).

RESULTS AND DISCUSSION

Adsorption Isotherms. In Figures 1 and 2, the adsorption isotherms for glyphosate on the three soils and the clay minerals are presented. The isotherms were curvilinear for all of the soils, montmorillonite, and illite, but it was linear for kaolinite. The adsorption data over the range of concentrations studied here conformed to Freundlich equation $C_s = KC_e^{1/n}$ or the logarithmic form $\log C_s = \log K + (1/n) \log C_e$, where C_s is the amount of glyphosate adsorbed (μg/g of adsorbent), C_e is the equilibrium concentration of glyphosate (μg/mL), and K and n are constants that give estimates of the adsorptive capacity and intensity, respectively. Freundlich K and $1/n$ values were obtained from the intercepts (where $\log C_e =$

Figure 2. Adsorption isotherms for glyphosate on clay minerals: (a) kaolinite; (b) illite; (c) montmorillonite.

Table II. Freundlich K Values, 1/n Values, and Correlation Coefficients (r^2) for the Adsorption of Glyphosate by the Various Samples (pH 4.0)

sample	K	$1/n$	r^2
clay minerals			
montmorillonite (117)[a]	138	0.75	0.93
illite (24)[a]	115	0.59	0.99
kaolinite (6)[a]	8	1.08	0.99
soils			
Houston clay loam	76	0.67	0.98
Muskingum silt loam	56	0.51	0.67
Sassafras sandy loam	33	0.46	0.81

[a] Values in parentheses are cation-exchange capacities (mequiv/100 g). Courtesy of Dr. Van King, Wards Science Establishment, Rochester, NY.

0 or $C_e = 1$ μg/mL) and the slopes of the adsorption plots (not shown), respectively. These Freundlich values for the soils and the clays are shown in Table II. Freundlich K values for the soils reveal that the adsorption of glyphosate decreased in the following order: Houston > Muskingum > Sassafras. After properties of the soils (Table I) were compared, adsorption appears to be related to the clay content of the various soils as suggested earlier by Sprankle et al. (1975), who reported that more [14C]glyphosate was absorbed by a clay loam than a sandy loam. In addition, glyphosate adsorption by these soils appears to be related to the cation-exchange capacities of the various soils (Table I).

An examination of the Freundlich K values (Table II) for the clay materials shows that montmorillonite has the highest adsorptive capacity for glyphosate and that the order of adsorption is montmorillonite > illite > kaolinite. These results were consistent with the findings from earlier adsorption studies of herbicides of widely different chemical character (Bailey et al., 1968). However, the present results disagree with the findings of Sprankle et al. (1975) who reported nearly twice as much adsorption of [14C]-glyphosate by kaolinite than illite. Differences in the purity and origin of the kaolinite samples may account for these variations.

When the results from the present study were compared with those from the earlier adsorption study by McConnell

Table III. Effect of Solution pH on the Adsorption of Glyphosate[a] by Illite (0.5 g)

| sample no.	pH_1[b]	pH_2	pH	amt ads,[c] $\mu g/g$ (av ± SD)
1	1.8	1.9	+0.1	1638 ± 180
2	2.0	2.3	+0.3	1425 ± 313
3	3.0	4.2	+1.2	1514 ± 66
4	4.0	5.4	+1.4	1590 ± 159
5	5.0	6.1	+1.1	1350 ± 16
6	6.1	5.9	−0.2	1533 ± 128
7	8.1	6.6	−1.5	1235 ± 344
8	10.0	8.6	−1.4	1380 ± 180
				LSD = 648[d]

[a] Initial concentration of glyphosate solutions was 100 $\mu g/mL$. [b] pH_1 and pH_2 are the pHs before and after equilibrium, respectively. [c] Values are means and standard deviations for two or more determinations. [d] LSD ($p = 0.05$) value is to be used for comparing the amounts of glyphosate adsorbed at various pHs; $f = 0.58$ with 6 df as derived from ANOVA.

and Hossner (1985), some of the data were in agreement; however, a large portion of the results differed significantly. For instance, the K value observed here for montmorillonite was 138.0 (pH 4.0) in comparison to 100.7 (pH 4.5) reported in the earlier study for Na^+–montmorillonite, which probably is very similar to montmorillonite in adsorptive behavior. On the other hand, the K value for kaolinite was 8.0 (pH 4.0) in this work but was 519.3 (pH 4.5) in the earlier study. The validity and reliability of the analytical procedure used to quantitate glyphosate in the study by McConnell and Hossner are highly questionable. Aliquots of the supernatant liquid of thee clay–glyphosate slurries were injected directly into the HPLC, which was equipped with a UV detector set at 254 nm. Because it is well-known that glyphosate alone is UV inactive and that the derivatization of the substance is necessary for HPLC detection (Miles et al., 1986), it is uncertain what species was observed in the earlier investigation. A review of the paper by McConnell (1984) describing the initial work did not provide any useful information. Attempts to duplicate their results were unsuccessful under similar experimental conditions (unpublished results). However, the detector responses in earlier work by McConnell and Hossner may have been caused by metallic complexes of glyphosate as observed in an earlier spectrochemical study of glyphosate (Glass, 1984). The strong UV absorbance band observed at 226 nm resulting from the addition of cupric ions to aqueous solutions of glyphosate was attributed to the formation of a Cu(II)–glyphosate complex.

Effects of pH and Saturating Cations. The effect of pH on the adsorption of glyphosate is shown in Table III. Although the adsorption data show differences at the various pH values, an analysis of variance reveals that these differences are statistically insignificant. Therefore, it is concluded that glyphosate adsorption is independent of pH on illite. It was also observed that the pH values of the supernatant liquid changed after equilibrating the solutions with illite as shown in Table III. The positive pH values indicated a loss of solution protons, suggesting the existence of a cation-exchange reaction.

Saturating the clay minerals with various cations increased glyphosate adsorption, in particular with divalent and trivalent cations as shown in Table IV. Adsorption by cation-saturated montmorillonites increased as

$$Na^+ < Ca^{2+} < Mg^{2+} < Cu^{2+} < Fe^{3+}$$
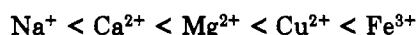
These results generally agree with the findings of Sprankle et al. (1975), who conducted an adsorption study on cation-saturated bentonite using a bioassay technique. They did not find any adsorption of $[^{14}C]$glyphosate by Na^+-

Table IV. Adsorption of Glyphosate[a] by Cation-Saturated Clay Minerals

clay minerals	amt ads,[b] $\mu g/g$	cation clay/clay[c]
montmorillonites (M)		
M^d	4015 ± 38	1.0
Na^+–	3683 ± 250	0.9
Mg^{2+}–	4802 ± 57	1.2
Ca^{2+}–	4679 ± 109	1.2
Cu^{2+}–	8038 ± 89	2.0
Fe^{3+}–	9341 ± 15	2.3
illites (I)		
I^d	2837 ± 39	1.0
Na^+–	2896 ± 44	1.02
Ca^{2+}–	2948 ± 24	1.04
kaolinites (K)		
K^d	792 + 82	1.0
Na^+–	1150 ± 86	1.3
Ca^{2+}–	1685 ± 114	1.5
Cu^{2+}–	3713 ± 37	2.5
Fe^{3+}–	2647 ± 74	1.6

[a] Initial concentration of glyphosate was 200 $\mu g/mL$, pH 4.0. [b] Means of two or more determinations and standard deviations. [c] The ratio of the amounts of glyphosate adsorbed by the cation-saturated clays to the natural clays. [d] M, I, and K are abbreviations for the natural clays montmorillonite, illite, and kaolinite, respectively.
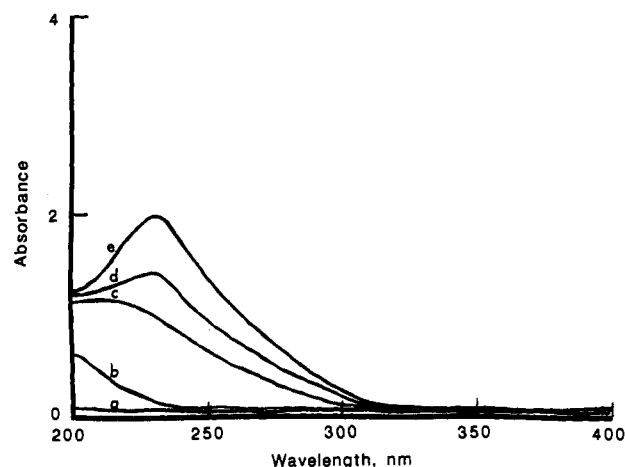
Figure 3. Comparison of UV spectra of glyphosate solutions (pH 4) equilibrated with Cu^{2+}–montmorillonite and copper oxide: (a) 100 $\mu g/mL$ glyphosate solution; (b) aqueous solution (pH 4) equilibrated with Cu^{2+}–montmorillonite; (c) 50 $\mu g/mL$ glyphosate solution equilibrated with Cu^{2+}–montmorillonite; (d) 100 $\mu g/mL$ glyphosate solution equilibrated with Cu^{2+}–montmorillonite; (e) 100 $\mu g/mL$ glyphosate solution equilibrated with copper oxide (1.0 g), which is fully described in an earlier paper (Glass, 1984).

saturated bentonite. The data in Table IV also reveal that Cu^{2+}–kaolinite adsorbed more glyphosate than Fe^{3+}–montmorillonite. No explanation can be made at this time for the observed differences. The ability of the cations to form coordination compound or complexes is believed to be a factor responsible for the adsorption of glyphosate by these cation-saturated clays.

In an earlier study, Shoval and Yariv (1979) proposed that complex formation was responsible for the adsorption of glyphosate by Fe^{3+}– and Al^{3+}–montmorillonite but discounted complex formation and adsorption by mono- and divalent cation montmorillonites from aqueous solutions. On the other hand, the present results demonstrate that the adsorption of glyphosate occurs on clays saturated with both di- and trivalent cations. In addition, the formation of a new absorbance band ($\lambda_{max} = 226$ nm) in the UV spectra of solutions of glyphosate equilibrated with Cu^{2+}–montmorillonite in Figure 3 provides new evidence of complex formation between glyphosate and copper

cations. A similar absorbance band, also shown here, was observed earlier in the absorbance spectra of glyphosate solutions equilibrated with CuO, which was interpreted as belonging to a Cu(II)–glyphosate complex (Glass, 1984). The mechanisms in which the complexes of glyphosate are formed from CuO- and Cu^{2+}-saturated clays are uncertain, but one speculation is that a surface interaction between glyphosate and the metal at the liquid/solid interface plays a vital role in the process.

In a similar adsorption study with several amino acids, Bodenheimer and Heller (1967) suggested that the extraction of copper ions was the first stage of the reaction that occurred when amino acids were brought in contact with Cu^{2+}-montmorillonite. The amount of copper extracted from the clay increased with increasing concentrations of glycine and glutamic acids. Cu^{2+} ions that were released into solution after equilibrating Cu^{2+}-montmorillonite with glyphosate solutions in the present study increased with higher glyphosate concentrations (unpublished results) as was found in the earlier investigation with CuO. It is proposed that Cu^{2+} ions are brought into solution from the Cu^{2+}-montmorillonite via a cation-exchange action with solution protons and that the increased adsorption of glyphosate is attributed to the formation of complexes in solution between glyphosate and cations. Motekaitis and Martell (1985) reported that glyphosate formed 1:1 and 1:2 chelates with 13 selected divalent and trivalent metal ions. The equilibrium stability constants for these chelates ranged from 3.29 for Ca(II)–glyphosate to 16.09 for Fe(III)–glyphosate.

In summary, the results of this investigation demonstrate that the order of adsorption for glyphosate on soils is Houston > Muskingum > Sassafras and on the clay minerals is montmorillonite > illite > kaolinite. The results are consistent with reported evidence that suggests that glyphosate adsorbs within the interlayer spaces of the clay minerals. However, the increased glyphosate adsorption on cation-saturated clay minerals suggests that glyphosate is complexed by cations released from the clays via a cation-exchange reaction with solution protons. The new absorbance band (λ_{max} = 226 nm) in the UV spectra of glyphosate solutions equilibrated with Cu^{2+}-montmorillonite provides supporting evidence for the formation of glyphosate complexes.

LITERATURE CITED

Bailey, G. W.; White, J. L.; Rothberg, T. Soil Sci. Soc. Am. Proc. **1968**, 32, 222–233.

Bodenheimer, W.; Heller, L. Clay Miner. **1967**, 7, 167–176.

Glass, R. L. J. Agric. Food Chem. **1983**, 31, 280–282.

Glass, R. L. J. Agric. Food Chem. **1984**, 32, 1249–1253.

Hensley, D. L.; Beuerman, D. S. N.; Carpenter, P. L. Weed Res. 18, 287–291.

McConnell, J. S. Ph.D. Thesis, Texas A&M University, College Station, Tx, 1984.

McConnell, J. S.; Hossner, L. R. J. Agric. Food Chem. **1985**, 33, 1075–1078.

Miles, C. J.; Moye, H. A. Abstracts of Papers, 191st National Meeting of the American Chemical Society, New York, NY, 1986; American Chemical Society: Washington, DC, 1986; AGRO 59.

Miles, C. J.; Wallace, L. R.; Moye, H. A. J. Assoc. Off. Anal. Chem. **1986**, 69, 458–461.

Motekaitis, R. J.; Martell, A. E. J. Coord. Chem. **1985**, 14, 139–149.

Shoval, S.; Yariv, S. Clays Clay Mineral **1979**, 27, 19–28.

Sprankle, P.; Meggit, W. F.; Penner, D. Weed Sci. **1975**, 23, 229–234.

Synthesis, Resolution, and Toxicological Properties of the Chiral Isomers of O,S-Dimethyl and -Diethyl Ethylphosphonothioate

David J. Armstrong[1] and T. Roy Fukuto*

The effect of chirality on the toxicological properties of O,S-dimethyl (1) and O,S-diethyl ethylphosphonothioate (2) was determined. The resolved esters were prepared from the respective O-methyl and O-ethyl ethylphosphonothioic acids, and absolute configurations of the esters were assigned by relating them to the known configuration of the resolved acids. The S_P (−) enantiomers of both 1 and 2 were more acutely toxic and were stronger anticholinesterases than the R_P (+) enantiomers. No delayed deaths were observed with the resolved compounds, but all treated animals lost weight for 3–4 days following dosing.

The work of Mallipudi et al. (1979) and Aldridge et al. (1979) on the toxicity of the malathion impurities O,O,S-trimethyl phosphorothioate and O,S,S-trimethyl phosphorodithioate has prompted investigation of low molec-

Division of Toxicology and Physiology, Department of Entomology, University of California, Riverside, California 92521.

[1]Present address: S-CUBED, La Jolla, CA.

ular weight organophosphates that may be formed as byproducts in the synthesis of technical insecticides. Previous papers from this laboratory on phosphonothioate analogues of some malathion impurities, which may also be found as impurities in technical phosphonothioate insecticides, described the unusually high acute toxicity of the O,S-dialkyl alkylphosphonothioate esters (Armstrong and Fukuto, 1984) and the insidious delayed toxic effect attributable to O,S-diethyl ethylphosphonothioate (Hollingshaus et al., 1981). Since these phosphonothioate esters