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X-ray Diffraction and Infrared Spectroscopic Studies of Adsorbed Glyphosate

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X-ray diffraction (XRD) and infrared (IR) spectroscopy were used to investigate the bonding mechanism of glyphosate onto clay sized Al³⁺-, Ca²⁺-, and Na⁺-saturated smectites, kaolinite, hematite, gibbsite, and goethite. Aqueous solutions of glyphosate (0.5%) were buffered at pH 2.0, 4.5, 7.0, or 11.5 and used to treat the clays. Adsorbed glyphosate bands in the infrared spectra of treated smectites were reduced in frequency, indicating a hydrogen-bonding mechanism. X-ray diffraction analysis showed interlayer expansion of both Al³⁺-saturated smectites treated with glyphosate solutions buffered at pH 2.0. The interlayer spacing of Al³⁺ montmorillonite was also expanded by treatment with glyphosate solutions buffered at pH 4.5. Treated samples of kaolinite, hematite, goethite, and gibbsite exhibited no additional IR bands due to adsorbed glyphosate. Further, X-ray diffraction of glyphosate-treated kaolinite showed no interlayer expansion.

The active ingredient of Roundup, a widely used non-selective herbicide, is the monoisopropylamine salt of glyphosate (Mullison et al., 1979). Glyphosate has been shown to have no herbicidal activity in soils. The speed

of deactivation of glyphosate in soil indicates adsorption to be the primary mechanism of deactivation (Sprankle et al., 1975a). Both minerals and whole soils have both been shown to adsorb glyphosate under a variety of conditions (Hance, 1976; Sprankle et al., 1975b; Nomura and Hilton, 1977).

Sprankle et al. (1975b) also identified the pK_a values for the equilibria of the acid functionalities of glyphosate. The pK_a of cationic glyphosate (HO₂CCH₂NH₂⁺CH₂PO₃H₂) and neutral glyphosate (HO₂CCH₂NH₂⁺CH₂PO₃H⁻) was

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assumed in these studies to be less than 2.0. A pK_a of 2.6 was determined for the equilibrium of neutral glyphosate and the 1- charged anion ($^-O_2CCH_2NH_2^+CH_2PO_3H^-$). Other pK_a values assigned were 5.6 for the equilibrium between the 1- and 2- charged ($^-O_2CCH_2NH_2^+CH_2PO_3^{2-}$) anions and 10.6 for the 2- and 3- ($^-O_2CCH_2NHCH_2PO_3^{2-}$) species. Through the use of these values the concentration of a specific ionic species can be calculated if the pH of the system and the initial glyphosate concentration are known. Adjusting the pH of the system can then be used to specify the ionic status of the glyphosate as well as to influence the adsorption characteristics of the minerals by affecting surface properties. Investigations of the effects of pH on glyphosate adsorption by clay minerals have generally shown greater adsorption in conjunction with lower pH (McConnell and Hossner, 1985). These studies found substantial differences in adsorption of glyphosate by smectites with different saturating cations at the same system pH. Further, adsorption by the smectites, kaolinite, hematite, and goethite was also shown to be pH-dependent, and anion exchange was found to be a likely mechanism.

The infrared spectra of glyphosate and its salts have been studied and functional groups correlated with various absorption bands (Shoval and Yariv, 1981). Bands assigned to the carboxyl group of free acid glyphosate were found at 1733, 1716, 1422, 1202, and 861 cm^{-1} . Similar assignments were made for the carboxylate moiety of the potassium salt of glyphosate at 1630, 1400, and a shoulder at 670 cm^{-1} . Bands indicative of the protonated secondary amine group were found at 1560 and 1484 cm^{-1} in the spectra of the free acid. A band representing the deprotonated secondary amine was located at 820 cm^{-1} in the spectra of the glyphosate salt. Bands of the phosphono functional group ($-PO_3H^-$) of the free acid were found at 1268, 1231, 1162, 1091, 1000, and 798 cm^{-1} . The deprotonated phosphono moiety ($-PO_3^{2-}$) was found to produce infrared absorption bands at 1179 and 1080 cm^{-1} .

Infrared studies of glyphosate and several saturations of montmorillonite indicated adsorption could occur from both alcohol and aqueous solutions (Shoval and Yariv, 1979). These experiments did not report or regulate the pH of the adsorbing system and may have allowed interstitial glyphosate to be dried on the clay. Infrared bands and their functional group assignments indicating glyphosate was adsorbed from ethanol solutions by montmorillonite were reported at 1236 and 1260 ($-PO_3H^-$), 1700-1734 ($-CO_2H$), and 1475 and 1545 cm^{-1} ($-NH_2^+$). Montmorillonite was found to adsorb glyphosate from aqueous solutions of Roundup. Infrared bands at 1416 cm^{-1} ($-CO_2H$), shoulders of this peak near 1440 and 1470 cm^{-1} (both $-CH_2-$), and another weak $-CH_2-$ band near 1320 cm^{-1} occurred in the spectra of glyphosate-treated Fe^{3+} , Al^{3+} , and H^+ -saturated montmorillonite.

The objectives of this study were to examine the interactions of glyphosate with clay minerals under highly controlled conditions. An assessment of pH on clay-glyphosate bonding was made. Further, the effects of homoionic saturations of the smectite minerals were examined.

EXPERIMENTAL SECTION

Instrumentation. The infrared spectrometer employed in these studies was a Perkin-Elmer Model 283. A Perkin-Elmer data station equipped with a Model 250 microcomputer was lined to the spectrometer. The data station was used to enhance and refine spectra taken by averaging several spectra of the same sample. Averaging several scans greatly reduced background noise, clarified

the absorbance bands, and allowed the position of each band to be specified to ± 1 cm^{-1} . All spectra reported are the average of five 12-min scans in the percent transmission mode from 2500 to 800 cm^{-1} on AgCl windows unless otherwise stated.

The X-ray equipment used was a Phillips-Norelco XRG 3000 X-ray diffractometer with a copper target generating Cu $K\alpha$ wavelength X-rays. Scan speed of the goniometer was calibrated to 1° 2θ /min for all scans. The number of cycles per second was varied up to 10 000, as necessary, for the particular sample.

Minerals. The minerals selected for examination in this study were an Oklahoma montmorillonite, Washington nontronite, Georgia kaolinite, synthetic hematite, goethite, and gibbsite. The montmorillonite, nontronite, and kaolinite were purchased from Wards Natural Science Establishment. Reagent-grade Fe_2O_3 was the source of hematite. Goethite was synthesized by a modified method of Atkinson et al. (1968). The gibbsite was obtained from the Reynolds Metal Co., Bauxite, AR.

Clay fractions (< 2 μm) of all the minerals were obtained by differential sedimentation in water. The nontronite and montmorillonite clays were treated with chloride salts of Al^{3+} , Ca^{2+} , and Na^+ to prepare homoionic saturations of the smectites. The kaolinite clay was washed with NaCl solutions and dialyzed free of chloride. All the clay minerals were then freeze-dried for future analyses.

Glyphosate solutions, 0.5% (w/v), were prepared by dissolution of the organic acid in distilled water. These solutions were treated with dilute HCl and NaOH to adjust to pH 2.0, 4.5, 7.0, or 11.5. This allowed the Na^+ salt of glyphosate to act as the buffer for the clay-glyphosate system. Approximately 20 mg of each clay was treated with the glyphosate solutions. The pH of the clay-glyphosate mixture was then measured to ensure the clays had not affected any changes in the system acidity. No additional pH adjustment was found to be necessary in any of the samples. Control samples were slurried in water, and the pH was adjusted to correspond with the glyphosate-treated samples. All samples were then equilibrated for 16 h, centrifuged, and filtered. Small portions of the treated clays (approximately 2 mg) were slurried and washed in approximately 0.5 mL of deionized water and pipetted onto AgCl windows. Excess water was carefully poured off the windows after the clays settled, thereby removing excess glyphosate. Slow-settling clays such as the high-pH smectites required repetition of the process until a suitable film was formed. The remainder of each silicate clay was slurried in 3-5 mL of deionized water and pipetted onto an XRD slide. The clays were allowed to settle, and the water was poured off in a manner similar to the IR washing procedures.

The clay samples on the AgCl windows and XRD slides were air-dried (approximately 16 h) to form oriented films. The dry clay films on the windows and slides were then analyzed by IR spectroscopy and XRD. The XRD slides were then heated for 18-24 h at 200-250 °C to remove interlayer water, cooled under desiccation, and reanalyzed by X-ray diffraction.

IR Spectra of Glyphosate. Technical-grade glyphosate (95% pure) was furnished by the Monsanto Chemical Corp., St. Louis, MO. The method used in the preparation of glyphosate for the IR spectroscopy was incorporation of the organic acid (1 mg) into a KBr pellet (250 mg).

RESULTS AND DISCUSSION

Band Assignments of Glyphosate. The infrared spectra of the glyphosate sample was taken in a KBr matrix. Correlations between adsorbance bands and the

Table I. Functional Groups and Their IR Bands in the Spectra of Glyphosate in a KBr Matrix

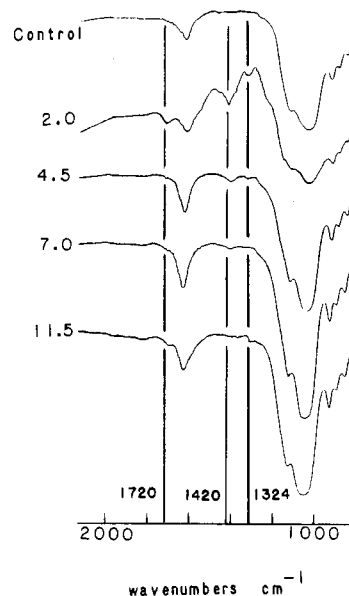
functional group	abs band, cm ⁻¹
carboxyl acid (-CO ₂ H)	
C=O str	1729
C—O—H bend	1422
C—O str	1262
O—H out of plane	915
carboxylate (-CO ₂ ⁻) ^a	
-CO ₂ ⁻ asym str	1630
-CO ₂ ⁻ sym str	1400
-CO ₂ ⁻ deformn	717, 965 sh, 670 sh
methyl (-CH ₂ -)	
-CH ₂ - deformn	1468, 1430, 1334
protonated secondary amine (-NH ₂ ⁺ -)	
-NH ₂ ⁺ - deformn	1555, 1484
-NH ₂ ⁺ - rock	796
phosphonic acid (-PO ₃ H)	
P=O str	1285
P—C asym deformn	1269
deprotonated phosphonic acid (-PO ₃ ²⁻) ^a	
-PO ₃ ²⁻ str	1179, 1080

^aFrom Shoal and Yariv (1981).

functional groups of glyphosate were made using the data of Bellamy (1960) and a previous IR study of glyphosate by Shoal and Yariv (1981) and are reported in Table I.

IR Spectra of Glyphosate-Treated Smectites. The IR spectra of the untreated controls of montmorillonite saturated with Al³⁺, Ca²⁺, and Na⁺ had identical band positions. Intensities of the bands varied due to the thickness of the sample, but there were no differences between samples. The IR spectra of nontronite were similar to the spectra obtained from montmorillonite. Like montmorillonite, the untreated saturations (Al³⁺, Ca²⁺, Na⁺) of nontronite did not give appreciably different spectra. Differences between the intensities of the bands of the three nontronite samples were due to the thickness of the film, and not true differences between the nontronite samples.

The infrared spectra of an Al³⁺ montmorillonite control and the treated clay samples can be seen in Figure 1. The bands indicating adsorbed glyphosate for all three initial

**Figure 1.** Infrared spectra of Al³⁺ montmorillonite treated with 0.5% glyphosate solutions.

saturations of montmorillonite and nontronite are organized in Table II. Aluminum-saturated montmorillonite was chosen to discuss all montmorillonite samples because of the exaggerated absorbance bands compared to the Ca²⁺- and Na⁺-saturated montmorillonite.

Absorbance bands in addition to the spectra of the clay at pH 2.0 are found at 1720, 1420, and 1324 cm⁻¹. A new absorbance shoulder is also evident in the region of 1269 cm⁻¹. These absorbance bands indicate that montmorillonite retained and adsorbed glyphosate at pH 2.0. The 1720- and 1420-cm⁻¹ bands represent protonated carboxyl groups (-CO₂H). Both bands are shifted downward from their position in the glyphosate spectra. The 1324-cm⁻¹ absorbance band indicates the presence of the -CH₂- groups of glyphosate. This band is also shifted down 10 cm⁻¹ from its glyphosate spectral position. The shoulder at 1269 cm⁻¹ may represent the partially deprotonated phosphonic acid moiety, -PO₃H⁻ (Shoal and Yariv, 1979).

Table II. IR Bands (cm⁻¹) of Adsorbed Glyphosate in the Spectra of Montmorillonite and Nontronite

mineral	init saturation	pH	functional group			
			-CO ₂ H	-CO ₂ ⁻	-CH ₂ -	-PO ₃ H ⁻
montmorillonite	Al ³⁺	2.0	1720, 1420		1324	1269 sh ^a
		4.5		1414	1321	1262 sh
		7.0		1417		1265 sh
		11.5				
	Ca ²⁺	2.0	1420 ^b		1441, 1328	
		4.5		1415		
		7.0		1443	1461, 1360	
	Na ⁺	11.5		1440	1461	
		2.0	1721, 1425			
		4.5		1418		1261 sh
		7.0		1410		
		11.5		1422		
nontronite	Al ³⁺	2.0				
		4.5		1414		1260 sh
		7.0		1408		1262 sh
	Ca ²⁺	11.5		1417		
		2.0	1725, 1460		1320	
		4.5		1415	1324	
		7.0		1413		1265 sh
		11.5		1414		
	Na ²⁺	2.0	1721, 1424		1319	
		4.5		1407		
		7.0		1413		1260 sh
		11.5		1418		

^ash = shoulder. ^bIdentification of these bands is not completely certain.

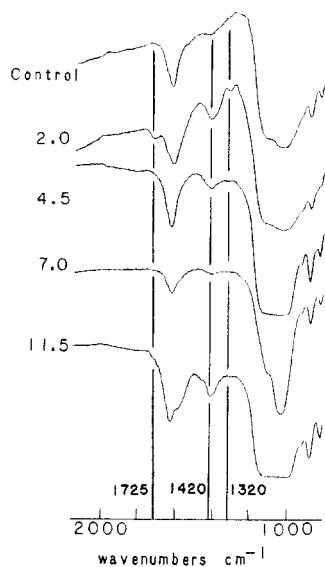


Figure 2. Infrared spectra of Ca^{2+} nontronite treated with 0.5% glyphosate solutions.

The downscale shift of the two carboxylic acid bands and the possible phosphonic acid band indicate that these functionalities are participating in hydrogen bonding (Bellamy, 1960). Shoval and Yariv (1979) indicate that glyphosate will hydrogen bond to interlayer cations of montmorillonite through a water bridge. A water-bridging mechanism also seems likely for these experiments. The carboxyl and phosphono groups of glyphosate would readily conform to water bridges as might the secondary protonated amine moiety.

Aluminum-saturated nontronite degraded rapidly when treated with 0.5% glyphosate solution buffered at pH 2.0. The IR spectra of the degraded clay prevented clear band identification. For this reason Ca^{2+} nontronite is used to represent the treated nontronite clays (Figure 2).

Infrared absorbance bands for the pH 2.0 treatment of Ca^{2+} nontronite that are a result of adsorbed glyphosate are found at 1725, 1420, and 1320 cm^{-1} . The two bands at 1725 and 1420 cm^{-1} indicate the presence of the protonated carboxyl group of glyphosate and are similar to bands found in the pH 2.0 treatment of Al^{3+} montmorillonite. The band at 1320 cm^{-1} is evidence of $-\text{CH}_2-$ moieties and is shifted down 14 cm^{-1} . The bonding mechanism of glyphosate to nontronite appears to be similar to that postulated for montmorillonite. Nontronite apparently adsorbs glyphosate by a water-bridging mechanism similar to montmorillonite.

Smectites placed in buffered acid systems such as the pH 2.0 glyphosate solutions begin dissolution (Borchardt, 1977). The first phase of the dissolution of smectites is the release of octahedral cations from the clay lattice. These cations are prone to migrate to exchange sites and resaturate the clay (Bohn et al., 1979). This process probably resulted in Al^{3+} and Fe^{3+} montmorillonite and nontronite, respectively, regardless of the initial saturating cation.

Glyphosate solutions (0.5%) were buffered at pH 4.5 by addition of NaOH and used to treat the minerals. Absorbance bands found in the treated Al^{3+} montmorillonite spectra as a result of adsorbed glyphosate are located at 1414 and 1321 cm^{-1} . At pH 4.5 the carboxyl acid group of glyphosate deprotonates to function as a carboxylate moiety in bulk solution. The carboxylate functional group of glyphosate has been shown to produce an intense band in the IR spectra at 1400 cm^{-1} (Shoval and Yariv, 1981). The shape of the 1414- cm^{-1} peak and the absence of the

1720- cm^{-1} band are due to the carboxylate functionality of glyphosate. The upscale shift of 14 cm^{-1} from 1400 cm^{-1} indicates that the carboxylate is participating in a hydrogen-bonding adsorption mechanism. The very small band at 1321 cm^{-1} represents the $-\text{CH}_2-$ group of glyphosate.

The Ca^{2+} nontronite spectra was similar to the treated Al^{3+} montmorillonite spectra after treatment with a pH 4.5 glyphosate solution. New absorbance bands are located at 1415 and 1324 cm^{-1} , representing the carboxylate and methyl moieties of adsorbed glyphosate, respectively. The similarities in shape, intensity, and shifts of glyphosate absorbance bands of Ca^{2+} nontronite and Al^{3+} montmorillonite indicate similar mechanisms of adsorption. Hydrogen bonding of the glyphosate to the interlayer cation by a water bridge is postulated to be a primary adsorption mechanism for nontronite at pH 4.5.

The spectra of pH 7.0, glyphosate-treated Al^{3+} montmorillonite shows the 1417- cm^{-1} band to be barely identifiable and is shifted upscale (17 cm^{-1}). As in the previous discussions of IR spectra, this type shift indicates that the carboxylate functionality is participating in a hydrogen-bonding adsorption mechanism. The treated Ca^{2+} nontronite spectra show band intensity and location similar to that of the Al^{3+} montmorillonite. The carboxylate band in this spectrum is located at 1415 cm^{-1} and upshifted 15 cm^{-1} , showing that hydrogen bonding was retaining the glyphosate.

A 0.5% solution of glyphosate buffered at pH 11.5 by addition of NaOH was used to treat the smectites. The quantity of Na^+ added from NaOH was calculated to be 0.89 mequiv to each 10 mL slurry of clay. This amount of Na^+ was necessary to ensure buffering of the glyphosate solution at pH 11.5. The total CEC of the 20-mg sample of nontronite was calculated as 0.03 mequiv, while the montmorillonite had a CEC of 0.02 mequiv. The excess of Na^+ added with the glyphosate should have had a profound influence on the saturating cation of the smectites. Since the Na^+ concentration exceeded the CEC by 30–45 times, the treated smectites were probably converted to Na^+ clays.

The spectra of glyphosate (pH 11.5) treated Al^{3+} montmorillonite showed no absorbance bands due to the adsorption of the herbicide. However, the spectra of Ca^{2+} and Na^+ montmorillonite showed bands due to the glyphosate treatment. These bands are found at 1440 and 1461 cm^{-1} for the Ca^{2+} clay and 1422 cm^{-1} in the Na^+ clay and indicate the presence of the carboxylate moiety of glyphosate. The mechanism of attachment between glyphosate and montmorillonite at pH 11.5 is not clear from the infrared data.

The spectra of treated Ca^{2+} nontronite shows a single band at 1414 cm^{-1} , signifying an upscale shifted carboxylate functionality. The shift observed indicates hydrogen bonding between the glyphosate and exchangeable cation on the clay surface through water bridging is again the main mechanism of attachment.

X-ray Diffraction Patterns of Glyphosate-Treated Smectites. All layer silicate minerals treated with glyphosate were also examined by X-ray diffraction. Comparisons were made between buffered, glyphosate-treated smectite samples and analogous samples adjusted to the corresponding pH with HCl and NaOH. Only three treatments showed expanded interlayers. Al^{3+} nontronite treated with glyphosate at 0.5% pH 2.0 had an air-dry *d*-spacing of 14.8 Å. When this sample was heated, two peaks became apparent. The first peak was diffuse but had a spacing of 14.7 Å. The second peak at 10.2 Å was

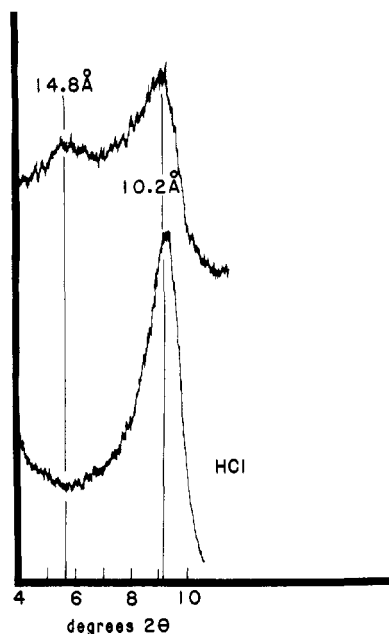


Figure 3. X-ray diffraction patterns of glyphosate (pH 2.0) and HCl (pH 2.0) treated Al^{3+} nontronite after oven drying.

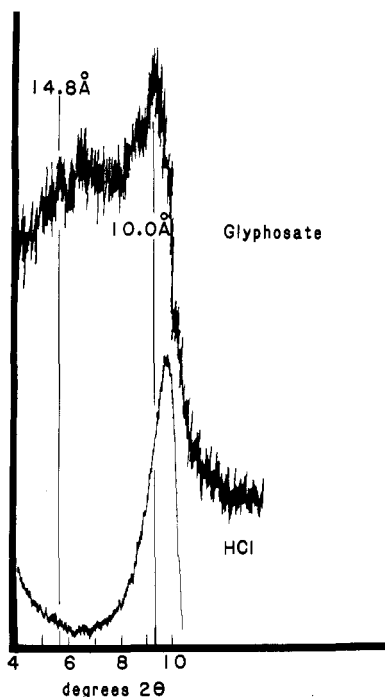


Figure 4. X-ray diffraction patterns of glyphosate (pH 2.0) and HCl (pH 2.0) treated Al^{3+} montmorillonite after oven drying.

specific for a dehydrated smectite. The pH 2.0 Al^{3+} nontronite check had an air-dry spacing of 13.0 Å but completely collapsed to 9.9 Å with heating. The incomplete collapse of the treated nontronite after heating is confirmation that glyphosate is adsorbed into the interlayer region (Figure 3).

The second and third cases of expanded interlayers occurred with Al^{3+} montmorillonite. The air-dry spacing of Al^{3+} montmorillonite treated with glyphosate at pH 2.0 was 14.8 Å, and 13.0 Å for the HCl-treated control. The glyphosate-treated sample peak of 14.8 Å collapsed after heating and was replaced by peaks at 14.7 and 10.0 Å. The extra peak at 14.7 Å of the heated and treated sample indicates interlayer adsorption of glyphosate as it did for the similarly treated Al^{3+} nontronite (Figure 4). Aluminum-saturated montmorillonite also exhibited evidence of

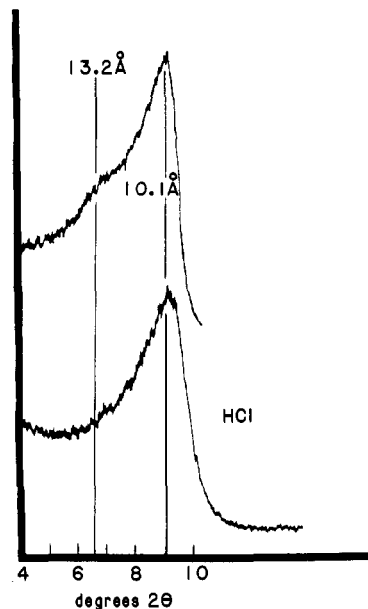


Figure 5. X-ray diffraction patterns of glyphosate (pH 4.5) and HCl (pH 4.5) treated Al^{3+} montmorillonite after oven drying.

interlayer adsorption when treated with glyphosate buffered at pH 4.5. The glyphosate-treated Al^{3+} montmorillonite was found to have an air-dry basal spacing of 13.2 Å and the control a basal spacing of 13.0 Å. After heating, the control completely collapsed to a spacing of 9.9 Å. Most of the treated montmorillonite had collapsed to 10.1 Å; however, a shoulder at 13.1 Å confirmed glyphosate in the interlayer of the clay (Figure 5).

Glyphosate-Treated Kaolinite, Hematite, Goethite, and Gibbsite. There was no evidence by IR spectroscopy or XRD that treated kaolinite, hematite, goethite, or gibbsite had adsorbed any glyphosate regardless of pH. No IR bands in the spectra of the treated minerals could be attributed to glyphosate adsorption, and XRD showed no interlayer expansion of the treated kaolinite.

Previous studies have shown these minerals to be capable of adsorbing glyphosate at the pH levels employed in this study (Sprankle et al., 1975b; Hance, 1976; McConnell and Hossner, 1985), but no absorption was detectable by IR. This indicates that the glyphosate concentration on these clays was below the detection limits of the IR spectrometer. A probable cause for these low levels may have been the method of sample preparation, which may have allowed replacement of the glyphosate by water through mass action during the washing phase.

CONCLUSIONS

Smectites (montmorillonite, nontronite) were shown to adsorb glyphosate from aqueous buffered solution by IR spectroscopy and XRD. Substantial glyphosate was adsorbed into interlayer regions of both Al^{3+} smectites at pH 2.0 and Al^{3+} montmorillonite at pH 4.5. The primary bonding mechanism of glyphosate to the smectites was hydrogen bonding of the acid functionalities, probably through a water bridge to the exchangeable cations as suggested by Shoal and Yariv (1979). Hydrogen bonding of this type is suggested by the downscale shift of frequency of adsorbed glyphosate bands in the IR spectra. As the pH was increased to 11.5, the IR bands of adsorbed glyphosate became less intense due to reduced adsorption of glyphosate by the clays.

The minerals with pH-dependent charge, kaolinite, hematite, goethite, and gibbsite, probably adsorbed glyphosate through an anion-exchange mechanism. As the minerals were washed with deionized water, the glyphosate was

replaced by water on the mineral surface and consequently no bands indicating adsorbed glyphosate were found in the IR spectra of these minerals.

Registry No. Glyphosate, 1071-83-6; montmorillonite, 1318-93-0; nontronite, 12174-06-0.

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Determination of Fumigants and Related Chemicals in Fatty and Nonfatty Foods

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Mean recoveries for 22 fumigants and related industrial chemicals were determined from various fatty and nonfatty foods by liquid extraction and gas chromatography. Results were sorted according to sample type, e.g., fat or nonfat, and the extraction or cleanup techniques used. The overall mean recovery was 73% from fatty foods and 78% from nonfatty foods; the recovery from both sample types after further cleanup by Florisil chromatography was 55%. Actual fumigant residues were also determined in 549 samples examined; 849 residues were found in 372 samples; no residues were found in 177 samples. Findings were sorted and cross-referenced by sample type, i.e., fat, nonfat, grain-based, and non-grain-based. Findings included 10 different residues: carbon disulfide, carbon tetrachloride, chloroform, chloropicrin, ethylene dibromide, ethylene dichloride, methylene chloride, methylchloroform, tetrachloroethylene, and trichloroethylene. Mean finding amounts ranged from 7 to 799 ng/g. The average number of findings per fat and nonfat sample was 2.31 and 0.72 and per grain-based and nongrain-based sample was 2.22 and 1.04, respectively.

Traces of toxic fumigant residues are being found in several food products, e.g., spices (Stijve et al., 1976; Reeves et al., 1985), citrus fruit (Iwata et al., 1983; Tonogia et al., 1986) drinking and process water (Kroneld, 1986; Uhler and Diachenko, 1987), and dairy and grain-based products (Rains and Holder, 1981; Entz and Hollingfield, 1982; Heikes, 1987). Most residues are found in products containing 0-10% fat because existing methods work best on nonfat or low-fat foods and generally do not work well on high-fat types. For example, the acetone-soaking or back-extracting methods used for analyzing whole grain, milled products, and low-fat foods (Berck, 1974; Newsome and Panopio, 1977; AOAC, 1980; Clower, 1980; Daft, 1987) do not efficiently partition fumigants from samples containing more than 10% fat, e.g., corn chips, which contain 28% fat. Extractions from these high-fat-containing foods either contain too much fat or the excess fat is not com-

pletely soluble in the extracting solutions, resulting in lost determinations or low fumigant recoveries through poor, fat-distorted gas chromatography (GC).

Since the compounds used as fumigants are quite fat soluble, fat-containing foods that have been exposed to them would be expected to contain these kind of residues. Therefore, fumigant methods should be capable of analyzing all foods, including high-fat types.

In this study, the method used, a rapid aqueous-nonaqueous coextraction of sample with acetone and isooctane (Daft, 1988b), satisfactorily partitions halogenated fumigants and related chemicals from a wide variety of food types. The gas chromatograms from samples containing as much as 20% fat generally are free of fat effects such as band broadening and delayed retention times; further cleanup is not necessary.

Experimentally, however, several of these 20% or less fat extracts were taken through a Florisil cleanup step to determine whether the gas chromatography was improved or analyte recovery changed. An improvement seen was the removal of endogenous background peaks from gas chromatograms. An impairment seen was the lowering of

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