a solution of this film on a 3% OV-1 column (3-mm i.d. × 2 ft) gave five peaks with fragmentation patterns and weak molecular ions characteristic of straight-chain hydrocarbons. No further effort was made to characterize these compounds.

From an environmental safety point of view, the photolysis of I poses no danger. As a thin film, the compound rapidly photolyzed without producing detectable amounts of any other photolyte other than CO_2.

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Registry No. I, 72542-56-4; II, 16752-77-5; III, 72542-64-4; IV, 59669-26-0; V, 68789-90-2; VI, 944-23-0.

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Application of a High-Performance Liquid Chromatographic System with an On-Line Infrared Detector to the Residue Analysis of Permethrin

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The first application of a high-performance liquid chromatographic system (HPLC) with an on-line infrared (IR) detector for pesticide residue analysis is reported. The system was applied to the residue analysis of permethrin in lettuce which was field-treated with an emulsifiable concentrate formulation. Permethrin residues were extracted with acetone, the extract was liquid–liquid partitioned with hexane and CH_3CN, and the coextracted chlorophyll was removed with charcoal. The extract was then concentrated, filtered through a silica gel Sep-PAK, and analyzed by HPLC on a 5-μm Partisil column which was eluted with a solvent mixture composed of 3% 1-tetradecene, 70% CH_2Cl_2, and 27% cyclohexane. Under these conditions the cis and trans isomers of permethrin were separated and quantified. With the IR detector operated at 5.8 μm and 0.025 absorbance unit full scale, a minimum detectable level of 0.2 μg/g was obtained based on a 20-μL injection volume and a concentration factor of 0.2 mL/100 g of fresh lettuce. A tandem ultraviolet detector operated at 254 nm was also used as a second on-line detection system.

Permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] was the first pyrethroid insecticide developed which was appropriate for field use (Elliott et al., 1978). Residue analyses for permethrin have been conducted principally by gas chromatography (GC) with electron-capture detection. GC analyses for permethrin residues in extracts prepared from plant and animal tissues, soil, and water have been reported (Bélanger and Hamilton, 1979; Chapman and Harris, 1978, 1979; Chiba, 1978; Estesen et al., 1979; Fujie and Fullmer, 1978; Oehler, 1979; Reichel et al., 1981; Siegel et al., 1980; Williams, 1976; Williams and Brown, 1979). The use of high-performance liquid chromatography (HPLC) with an ultraviolet (UV) detector has been reported only by Kikta and Shierling (1978) for the analysis of permethrin in extracts from plant deposits.

An HPLC–infrared (IR) system reported for the analysis of pyrethroid and carbamate insecticides in formulations and technical-grade materials (Papadopoulou-Mourkidou et al., 1980, 1981a,b) has now been used for residue analysis with permethrin serving as a test compound. This report represents the first application of such a system to pesticide residue analysis.

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EXPERIMENTAL SECTION

Materials. Analytical standards of *cis*- and *trans*-permethrin (99%) and Pounce 3.2 EC formulation [0.38 kg of active ingredient (AI)/L] were obtained from FMC Corp. HPLC solvents were purchased from J. T. Baker Chemical Co. 1-Tetradecene was obtained from Aldrich Chemical Co., Inc. Acetone, CH_2Cl_2, hexane, CH_3CN, and cyclohexane were used for residue extractions, and sample preparations were of reagent grade and were redistilled prior to use.

A 250 × 4.6 mm i.d. analytical column packed with 5-μm Partisil and a 50 × 4.6 mm i.d. guard column packed with 35–50-μm HC Pellosil were obtained from Whatman. Other chromatographic materials used were Celite 545 (AW) (Supelco, Inc.), Norit A acid-washed charcoal (Phanstiehl Laboratories, Inc.), silica gel Sep-PAK (Waters Associates), attaclay, and anhydrous Na_2SO_4.

Instrumentation. The liquid chromatographic system (Waters Associates) consisted of two Model 6000A pumps controlled by a Model 660 solvent programmer. A Rheodyne 7125 valve-type injector equipped with 10-, 20-, or 200-μL loops was used.

A Rheodyne 7000A valve with a guard column in the loop was inserted between the injector and the analytical

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column so that the guard column could be isolated and back-flushed, in case such an operation was required for protection of the analytical column or for in situ sample cleanup. To back-flush the guard column, a second solvent delivery circuit connected to one of the pumps was used.

A Wilks Miran-1A variable-wavelength (Foxboro) IR spectrophotometer with a 9-μL capacity, 3-mm path length, NaCl cell was used unless it is specifically noted that a 4.5-μL, 1.5-mm, BaF_2 cell was used instead. A dual-wavelength (254 and 280 nm) Model 151 Altex UV detector with a 9-μL capacity flow cell was used as the second on-line detector. The IR and UV detectors were separately connected to recorders operated at chart speeds of 1 cm/min and 1 in./min, respectively.

Field Application. Lettuce was sown in mid-April 1981 at the University of California agricultural field station at Riverside, CA. Plants were thinned and allowed to grow without any pesticide treatment and were watered by furrow irrigation every other day.

Twelve rows (40 × 0.75 m) of plants were used. A single application with Pounce 3.2 EC was made on July 7, 1981. Four rows were sprayed at the rate of 0.22 kg of AI/ha and four at 0.34 kg of AI/ha; four rows were untreated and kept as controls. Plants were treated with a hand-operated, compression sprayer with a 15-L capacity tank and a three-nozzle gun.

The air temperature during the morning spray operation was ~32 °C. High temperatures (34 °C) persisted over the 6-day postapplication period.

Sampling and Processing. Samples were collected 1, 2, 3, 4, and 6 days postapplication. For each sampling date, 10 lettuce heads were randomly collected from each plot. Two to three outer wrapper leaves of the lettuce heads were removed, and the rest of the plant material was chopped in a food processor. Each sample of chopped lettuce was mixed thoroughly and subdivided into 100-g subsamples. Twenty subsamples from each treatment and at each sampling date were stored frozen, and 10–15 subsamples were processed.

Control samples were also collected and processed at each sampling date. Collection of control samples was particularly necessary because of the rapid growth and aging of the plants.

Sample Processing. A 100-g subsample was macerated with 200 mL of acetone for 3 min in a blender jar. The extract was vacuum-filtered through a Büchner funnel lined with a No. 2 Whatman filter paper and a layer of Celite 545. The filtrate was placed in a 2-L separatory funnel, and the filtration cake was reextracted by blending for 1 min with 200 mL of acetone. The second extract was filtered. The blender jar was rinsed twice with 25 mL of acetone, and the rinsings were poured onto the filter cake. All filtrates were combined in the 2-L separatory funnel. The extract was diluted with 200 mL of 4% aqueous NaCl solution and partitioned with 200 mL of hexane. The mixture was shaken very gently for 1 min each time so as to avoid the formation of a heavy emulsion. The lower aqueous phase was drawn into a second separatory funnel and repartitioned with 200 mL of hexane. The aqueous phase was discarded. The hexane phases from both funnels were combined into a 1-L flask by passing through a funnel containing 30 g of Na_2SO_4. Both separatory funnels were each rinsed with 50 mL of hexane, and the rinses were combined with the hexane extract in the flask by passage through the funnel containing the Na_2SO_4.

The hexane solution was reduced to about 350 mL with a rotary evaporator and transferred to a storage bottle. The flask was rinsed twice with 25 mL of hexane, and the rinses were also added to the storage bottle. Processed samples were stored at 8 °C until analyzed.

Twenty control subsamples collected on the first sampling date were processed and fortified with 0.5–10 ppm of permethrin and stored at 8 °C along with the processed, treated, field samples.

Cleanup. The hexane solution was reduced to 100 mL with a rotary evaporator and placed in a 250-mL separatory funnel containing 200 mL of CH_3CN. The mixture was shaken for 1 min. The lower phase was drawn into a flask, and the hexane phase was repartitioned with 100 mL of CH_3CN. The hexane phases were discarded; the two CH_3CN extracts were combined and then either concentrated to 2–5 mL, filtered through a silica gel Sep-PAK, and analyzed directly by HPLC or concentrated to 10–15 mL, placed on a sintered-glass funnel containing a layer of 10 g of Na_2SO_4 and a layer of 20 g of a 1:1 mixture of acid-washed charcoal–attaclay, and vacuum-filtered with the addition of 200 mL of CH_2Cl_2. The adsorbents in the funnel were prewashed with 100 mL of CH_2Cl_2. The CH_2Cl_2 filtrate was concentrated to 1–2 mL and filtered through a silica gel Sep-PAK. The flask was rinsed twice with 4 mL of a 1:1 mixture of CH_2Cl_2–cyclohexane, and the rinses were filtered as above. The volume of the combined filtrate was reduced to 0.5 or 0.2 mL in a graduated tube.

Analysis. Sample extracts in 20-μL volumes were injected onto the HPLC system operated at ambient temperature and eluted under isocratic conditions at a flow rate of 0.9 mL/min with a mobile phase which consisted of 3% 1-tetradecene, 70% CH_2Cl_2, and 27% cyclohexane. The IR detector was operated at 5.8 μm, the strongest usable IR absorption band, and 0.025 absorbance unit full scale (AUFS) and the UV detector at 254 nm and 0.64 AUFS. Quantitative measurements were made by the external standard technique and by measuring peak heights. Under the described chromatographic conditions, *cis*- and *trans*-permethrin were separated and quantified.

Standard solutions in CH_2Cl_2 containing both permethrin isomers in concentrations ranging from 0.05 to 2 mg/mL were used for the construction of calibration curves and calculation of the calibration factors. The calibration factor and the minimum detectable amount for the IR detector for both permethrin isomers were 0.42 cm/μg and 0.5 μg/20-μL injection volume at the linear response range of 0.5–20 μg/20-μL injection volume.

Method Verification. All steps of the method were verified as described below by fortification and recovery studies. Lettuce samples fortified with CH_2Cl_2 solutions of permethrin at the 2- and 5-ppm levels gave 100% recoveries.

The hexane–(acetone–water) partitioning step gave recoveries ranging from 98 to 100%. Permethrin is virtually insoluble [<1 ppm (Elliott, 1977)] in water, and therefore, the partitioning ratio in the above system was expected to be close to 1.0. Other solvents such as heptane, cyclohexane, and 2,2,4-trimethylpentane were also tested, but they did not show special advantages over hexane.

The CH_3CN–hexane partitioning system gave recoveries close to 90%. Beroza's p values (Beroza and Bowman, 1965) determined in the 1:1 CH_3CN–hexane system were found to be 0.39 for *cis*-permethrin and 0.29 for *trans*-permethrin. The charcoal adsorption cleanup step gave recoveries ranging from 90 to 100%. The overall recovery of the method ranged from 80 to 90%. Fortified samples at 10-, 5-, and 1-ppm levels gave an average recovery of 88%, whereas the recovery at the 0.5-ppm level of fortification was 80%. Analysis of fortified samples stored at

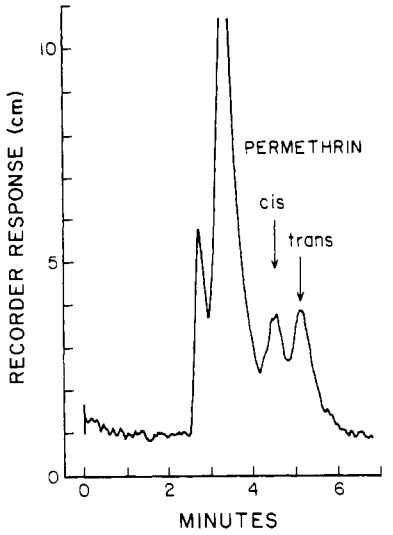

Figure 1. IR chromatogram obtained after injection of 200 μL of 5-ppm-fortified lettuce extract (concentration factor: 1 mL/10 g of fresh lettuce). The analytical column was eluted with a mobile phase which consisted of 0.7% CH_3CN in CCl_4 and a flow rate of 0.8 mL/min. The detector, operated at 8.65 μm and 0.1 AUFS, was equipped with a BaF_2 cell.

8 °C showed that no decomposition of permethrin occurred during 1 month of sample storage.

RESULTS AND DISCUSSION

Method Development. Initial attempts were to develop a system that required minimal sample preparation for the analysis of permethrin residues with the HPLC–IR system. Hexane extracts, prepared from control lettuce samples and fortified just prior to the CH_3CN partitioning step, were used during the developmental stages of this procedure. First, the possibility of analyzing the hexane extract directly by HPLC with no further sample preparation was examined. The hexane extract was concentrated to 5–10 mL and filtered through a silica gel Sep-PAK, and a 20- or 200-μL aliquot was injected directly onto the guard column of the HPLC system. The guard column was connected on line with the analytical column during the injection, but immediately after the injection it was isolated and back-flushed with a stronger solvent. A sample chromatogram obtained after injection of 200 μL of lettuce fortified at 5 ppm (concentration factor of 1 mL/10 g of fresh lettuce) is shown in Figure 1. Permethrin was eluted with a mobile-phase system consisting of 0.7% CH_3CN in CCl_4 and at a flow rate of 0.8 mL/min. The guard column was back-flushed with a solvent system consisting of 10% CH_3CN in CH_2Cl_2 at a flow rate of 1 mL/min. The IR detector operated at 8.65 μm and 0.1 AUFS was equipped with a BaF_2 cell. The minimum detectable level of this system was 2 ppm based on a concentration factor of 1 mL/20 g of fresh lettuce and a 200-μL injection volume.

Hexane extracts from commercial head lettuce, due to a lower overall chlorophyll content, could be concentrated to 1 mL/40 g fresh weight without forming a precipitate and thus improved the detectability level by a factor of two. Precipitates could be removed by centrifugation; however, massive precipitation of the more polar components of the extract resulted in loss of permethrin, probably through adsorption to the precipitate.

Removal of the relatively polar coextractives, primarily chlorophyll, by use of charcoal adsorbent allowed a better minimum detectability level and an easier handling of sample. A sample chromatogram obtained from the injection of 20 μL of hexane extract fortified at 5 ppm and cleaned up by charcoal adsorption is shown in Figure 2.

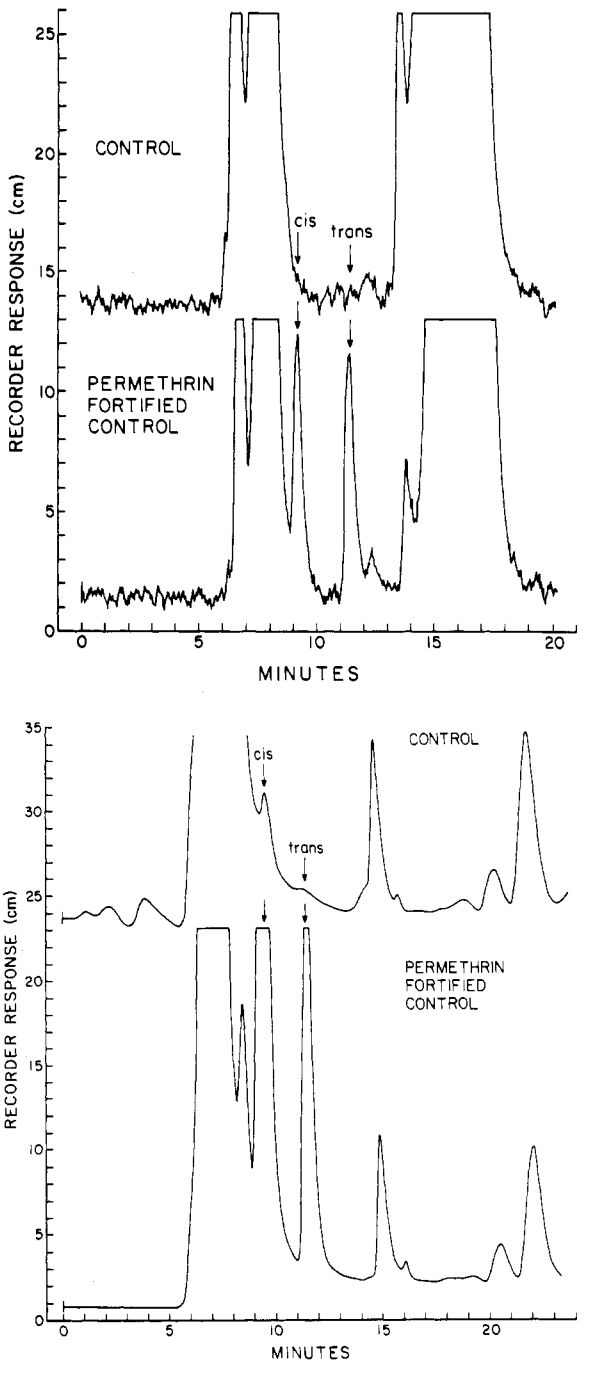

Figure 2. Chromatograms obtained after injection of 20 μL of control and 5-ppm-fortified lettuce extracts (concentration factor: 1 mL/200 g of fresh lettuce) and eluted with 3% 1-tetradecene, 70% CH_2Cl_2, and 27% cyclohexane and at a flow rate of 0.5 mL/min. Top: IR chromatograms of control and fortified samples obtained with the detector operated at 5.8 μm and 0.025 AUFS. Bottom: Corresponding UV chromatograms obtained with the detector operated at 254 nm and 0.32 AUFS.

The IR detector was operated at 5.8 μm and 0.025 AUFS. The mobile phase consisted of 3% 1-tetradecene, 70% CH_2Cl_2, and 27% cyclohexane and had a flow rate 0.5 mL/min. Under these conditions permethrin isomers were eluted with retention times of 6.1 (cis) and 7.5 (trans) min. Figure 2 was obtained without isolation of the guard column after injection. The two late-eluting peaks, due to the plant coextractives, were IR active at 5.8 μm and had small molar extinction coefficients at 254 nm, as shown in the UV chromatogram of Figure 2. The elimination of chlorophyll allowed the increase of concentration factor to 1 mL/200 g and easily brought down the minimum

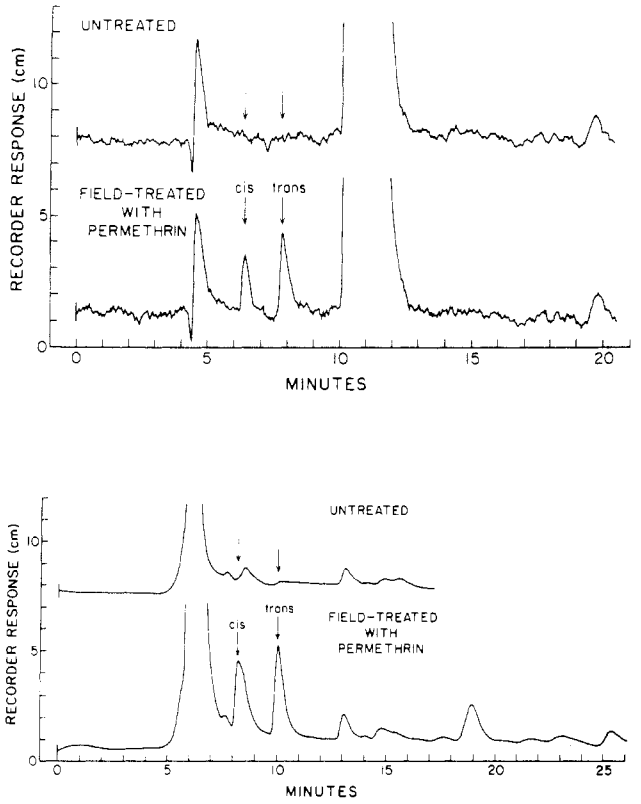

Figure 3. Chromatograms obtained after injection of 10 μL of control and field-treated lettuce extracts (concentration factor: 0.2 mL/100 g of fresh lettuce), eluted with a mobile phase which consisted of 3% 1-tetradecene, 70% CH_2Cl_2, and 27% cyclohexane and at flow rate of 0.9 mL/min. Top: IR chromatograms of control and field-treated samples were obtained with the detector operated at 5.8 μm and 0.025 AUFS. Bottom: Corresponding UV chromatograms obtained with the detector operated at 254 nm and 0.64 AUFS.

detectability level to 0.5 ppm. At higher concentration factors, the *cis*-permethrin was obscured by the early-eluting coextractive peak.

Different procedures were tested to eliminate the bulk of the coextractives interfering with *cis*-permethrin analysis. Liquid–liquid partitioning of the hexane extract with CH_3CN removed the early-eluting peak. Sample chromatograms from the analyses of a control and a field-treated lettuce extract are shown in Figure 3. A 100-g lettuce subsample extract concentrated to a final volume of 0.2 mL gave no precipitate and thus improved the minimum detectable level to 0.2 ppm for both permethrin isomers. The other conditions for these analyses are given in the caption of Figure 3.

Another major factor that greatly affected the sensitivity of the detector and the minimum detectability level of the overall procedure was the detector base-line noise. The base-line noise can be controlled to some degree by various means. One factor that greatly contributed to the increase of the base-line noise was the mobile-phase composition. Some mobile-phase systems generated more base-line noise than others. Thus, numerous isoeluotropic mobile phases which had the same selectivity were examined. Systems such as *n*-tetradecane–heptane–CH_2Cl_2, heptane–CH_2Cl_2, cyclohexane–CH_2Cl_2, heptane–$CHCl_3$, cyclopentane–heptane–CH_2Cl_2, and tetrahydrofuran–heptane–CH_2Cl_2 generated very noisy base lines. The system CH_3CN–CCl_4 gave the least noisy base line. Another equally good system consisted of 1-tetradecene–CH_2Cl_2–cyclohexane. A mobile-phase system consisting of CH_3CN–heptane–CH_2Cl_2 was very attractive in terms of separation selectivity and base-line noise, but the sensitivity of the detector was relatively low and gave a minimum detectable level of 10 μg with a 200-μL injection volume.

The detector noise was also aggravated by variations in laboratory air composition caused by the operation of the laboratory hood, especially when the relative humidity of the air was over 70%. Isolation of the IR detector in a nitrogen-purged environment increased the detector sensitivity to below the 1-μg level and eliminated virtually all the base-line noise; however, the resultant overheating of the IR cell caused solvent evaporation, especially of the highly volatile solvents, and created erroneous detector responses.

Another factor that could increase the detector sensitivity was the mobile-phase flow rate. Generally, flow rates above 1.5 mL/min drastically reduced the sensitivity. Optimum flow rates ranged from 0.7 to 1.2 mL/min.

The use of an in-line voltage stabilizer was also found to improve the base-line noise and detector sensitivity.

Permethrin Residues in Field-Treated Lettuce. The chromatograms shown in Figure 3 were obtained from the analysis of a sample collected 24 h after treatment from the plot treated at 0.22 kg of AI/ha. The residues found in this sample were 0.4 ppm for *cis*-permethrin and 0.6 ppm for *trans*-permethrin. Samples from the plot treated at 0.34 kg of AI/ha gave residues of 1.0 ppm for *cis*-permethrin and 1.6 ppm for *trans*-permethrin. Analysis of samples collected 48 h after treatment at 0.34 kg of AI/ha were found to have 0.6 ppm of the *trans*-permethrin and no detectable level (>0.2 ppm) of *cis*-permethrin. Samples collected at later dates showed no detectable amounts of residues.

The relatively low residue levels found were attributed to rapid residue dissipation resulting from high temperatures and intense incident radiation, to residue dilution due to rapid plant growth, and to removal of the outer wrapper leaves of the plant. FMC Corp. has proposed a tolerance of 20 ppm on lettuce (*Fed. Regist.*, 1981).

CONCLUSIONS

The HPLC–IR system has been demonstrated to be efficient in analyzing permethrin residues. Fortified samples at the 1-ppm level could be analyzed very easily with minimum sample preparation and in situ cleanup on the guard column. The removal of chlorophyll from the plant extract permitted the detection of permethrin at the 0.5-ppm level, and a liquid–liquid partitioning step with CH_3CN allowed the detection and quantification of both isomers as low as 0.2 ppm.

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Comparison of Solvent Systems for the Extraction of Diclofop Acid, Picloram, Simazine, and Triallate from Weathered Field Soils

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The extraction of diclofop acid [2-[4-(2,4-dichlorophenoxy)phenoxy]propionic acid], picloram (4-amino-3,5,6-trichloropicolinic acid), simazine (2-chloro-4,6-diethylamino-1,3,5-triazine), and triallate (*S*-2,3,3-trichloroallyl diisopropylthiocarbamate) from three field soils that had received treatments of the individual herbicides 12 months previously was compared by using different solvent systems. The highest recoveries for dicolofop acid and triallate were achieved with 30% aqueous acetonitrile containing 2.5% of glacial acetic acid. The same extraction solvent was also the most effective for recovering weathered residues of picloram and simazine from a clay soil. For the extraction of picloram and simazine from treated clay loam and sandy loam soils, acetonitrile containing 18% of water and 12% of ammonium hydroxide proved to be the most effective solvent system. In all cases for maximum recoveries, the soils were initially extracted for 0.5 h on a wrist-action shaker and then allowed to stand for 18 h before being shaken for a further 0.5-h period.

When a pesticide residue remains in contact with field soils for prolonged periods of a phenomenon kown as aging, or weathering, can occur which renders the chemical residue more resistant to solvent extraction (Hamaker et al., 1966; Chiba and Morley, 1968; Chiba, 1969; Saha et al., 1969; Mattson et al., 1970). This resistance to solvent extraction has been considered to result from an increased adsorption of the pesticide to soil colloids and a diffusion into the interior of humic colloids (Hamaker et al., 1966; Chiba, 1969; Adams, 1973; Khan, 1973).

Inadequate extraction procedures present problems to analysts monitoring persistent pesticide residues in the soil. In addition, unextracted residues could be considered to be bound to the soil [cf. Kearney (1976)] when, in fact, they are merely being inefficiently extracted. A practical solution to this problem has been to take samples of field soils that have received previous applications of pesticides and compare several extraction systems, selecting for general analytical use that procedure which recovers the greatest amounts of the particular residue (Mattson et al., 1970; Johnsen and Starr, 1970, 1972; Khan et al., 1975; Smith, 1978, 1981; Cotterill, 1980). The results from such studies provide more reliable information on the solvent extractability of residues than do those which simply rely on the recovery of pesticide residues from recently fortified soils. In the latter case the test chemicals are allowed to equilibrate with the soil for a few hours, or a few days, before extraction, and although a particular procedure may indicate that over 90% of the applied pesticides is being recovered, there are no means of knowing whether the recovery efficiency of the same pesticide from field soils treated several months previously is the same (Hamaker et al., 1966; Saha et al., 1969).

In the studies to be reported, field plots were separately treated with the commonly encountered herbicides diclofop-methyl (Figure 1, 1, R = CH_3), picloram (Figure 1, 2), simazine (Figure 1, 3), and triallate (Figure 1, 4), all of which can persist for over a year in Canadian field soils (Smith, 1982). Following natural weathering in the field for over 12 months, the soils were sampled and various solvent systems compared to determine which extractant resulted in the highest amounts of herbicide recovered. Since diclofop-methyl (Figure 1, 1, R = CH_3) undergoes rapid hydrolysis in soils (Smith, 1977) to diclofop acid (Figure 1, 1, R = H), the extraction of the acid, rather than the ester, was investigated. Triallate was included in this study since its extraction from weathered field soils was previously reported (Smith, 1978) from a single soil.

MATERIALS AND METHODS

Soils. The composition and physical characteristics of the clay (C), clay loam (CL), and sandy loam (SL) have already been described (Smith, 1981).

Field Treatments. Commercial formulations of diclofop-methyl, picloram, and simazine were applied as unicorporated treatments of 1.25 kg/ha to the surface of fallow plots at three locations in Saskatchewan. In the case of diclofop-methyl, treatments were made only on the clay. All applications were made during the second week of May 1981. At the same time, and at the same locations,

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