the potentially high levels of nutsedge activity inherent in this series of compounds.

Greenhouse tests have indicated residual weed control for a period of several months with the phenylpyrazole amides; this was confirmed under field conditions. Fox silty clay loam soil treated with 0.8 lb/acre of compounds **3**, **4**, **5**, **12**, and **74** was collected 14, 77, and 155 days after application. Residual activity was determined by bioassaying with yellow nutsedge. The plots received 25 in. of rainfall during the experiment. Yellow nutsedge control exceeded 95% 14 or 77 days after treatment. Control percentages 155 days after treatment varied with compound and in order of increasing magnitude were: **5** (0%) < **12** (12%) < **3** (33%) < **74** (37%) < **4** (71%).

Field results similar to those presented for corn were also obtained for cotton, peanuts, and soybeans. In general, the compounds performed well on light to medium soils under conditions of adequate rainfall. While potential utility was demonstrated in several tests, performance of the compounds was inconsistent from site to site across a wide range of geographic locations.

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Clean-Up Techniques for the Determination of Parts per Trillion Residue Levels of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

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Clean-up techniques are described for gas chromatography–mass spectrometric measurement of parts per trillion levels of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in nonfat and fat tissue, milk, cream, grain, feed, dry plant material, wet plant material, soil, and blood. A sensitivity of 10 parts per trillion TCDD was obtained for most types of samples. Animal tissue, milk, and cream are digested in an alkaline solution and a hexane extract is cleaned up using sulfuric acid and chromatography on silica gel and alumina. Grain and other plant material are extracted with hexane first and the oil obtained is digested with alkali. Recovery of 10 to 900 parts per trillion TCDD added to beef fat, soil, and rice averaged 76%. The types of interferences encountered are discussed.

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) is a trace contaminant in 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) herbicides. Because of its interesting biochemical properties, TCDD has been extensively studied (Blair, 1973; Environmental Health Perspectives, 1973). Early attempts to determine TCDD in biological samples using electron-capture gas chromatography had a detection limit of 50 ppb (Crummett and Stehl, 1973; Watts and Storherr, 1973; Woolson et al., 1973). This sensitivity was not low enough to detect TCDD in animal tissues from the feeding studies that were being carried out. In 1973, a method for TCDD was described which had a sensitivity approaching 1 part per trillion using direct probe introduction of a cleaned-up sample extract into a high-resolution mass spectrometer (Baughman and Meselson, 1973). In this method 1 ppb ^{37}Cl TCDD was added to the sample to provide a "carrier" and to provide recovery data. This implied that the use of ^{37}Cl TCDD was necessary to recover parts per trillion levels of TCDD but later data showed that recoveries were the same with and without the addition of ^{37}Cl TCDD (Baughman, 1974). Measurement of TCDD using gas chromatography–mass spectrometry (GC–MS) confirmed that parts per trillion levels of TCDD could be carried through a cleanup without using ^{37}Cl TCDD and most cleaned-up extracts could be analyzed using a gas chromatograph–low-resolution mass spectrometer. Use of ^{37}Cl TCDD as an internal standard is not necessary when using gas chromatographic introduction of the sample into the mass spectrometer because there is no variation in ion source pressure which would change the sensitivity for TCDD.

The objective of this study was to develop and validate procedures which could be used to analyze a wide variety of environmental samples and tissue samples for TCDD.

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The environmental samples were analyzed to determine whether TCDD was present from registered uses of 2,4,5-T herbicides while animal tissues, milk, and cream from TCDD or 2,4,5-T feeding studies were analyzed to obtain residue data. The procedures developed as a result of this study have been used to analyze over 700 samples with most of the analyses having a detection limit of 10 parts per trillion or lower. The clean-up techniques used for different types of samples are described here. The digestion and extraction conditions have to be varied depending on sample type in order to obtain an extract low in solids for the liquid chromatographic cleanup on small columns. Details of the GC–low-resolution MS measurement of TCDD used routinely and the GC–high-resolution MS techniques used for confirming the presence of TCDD or for overcoming low-resolution interferences are described by Shadoff and Hummel (1975, 1977a). A clean-up procedure for fish, shrimp, and oysters similar to the one described here reports a sensitivity of 1.5 ppb for electron-capture GC measurement and 10 parts per trillion for GC–MS measurement, but no recovery data below 20 ppb are given (Fukuhara, 1975). Recently a neutral extraction procedure for milk and animal tissue using ^{37}Cl TCDD as an internal standard and direct probe introduction of the sample extract into a high-resolution mass spectrometer was described (O'Keefe et al., 1976).

EXPERIMENTAL SECTION

Reagents. The hexane, acetone, and benzene used were Mallinckrodt Nanograde, and carbon tetrachloride, methylene chloride, and *o*-xylene were Burdick and Jackson distilled-in-glass. Ethanol was Matheson, Coleman and Bell pesticide quality. Silica gel was Curtin Scientific Co. high purity 100–200 mesh. The alumina was Fisher Scientific Co. A-540. The potassium hydroxide, ammonium chloride, and sulfuric acid were ACS grade. Deionized water was used in gallon lots, so all samples of a series used the same water. With all reagents, satisfactory performance and freedom from interferences is the only requirement, so other grades would probably be suitable. The TCDD standard was supplied by the Agricultural Products Department, Dow Chemical USA. It was 98% pure by gas chromatography and mass spectrometry (Muelder and Shadoff, 1973). The structure of a crystal prepared from material synthesized in the same manner as the standard was determined by x-ray diffraction to be 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Boer et al., 1972a,b). The ^{37}Cl TCDD was prepared by chlorination of dibenzo-*p*-dioxin in chloroform using a ferric chloride–iodine catalyst. The $^{37}Cl_2$ was generated by the oxidation of $Na^{37}Cl$ with H_2SO_4–H_2O_2. Standard solutions of TCDD in xylene standing on the laboratory bench decrease in concentration after a few months; therefore, periodic checks against a fresh standard are necessary.

Instrumentation (Shadoff and Hummel, 1975, 1977a). An LKB 9000 GC–MS with a 6 ft (1.8 m) by 3 mm 3% OV-3 silicone column was used for routine measurement of TCDD. An AEI MS-30 interfaced to a Pye 104 gas chromatograph was used for high-resolution measurements. A 1024 channel analyzer was used with the MS-30 to store repetitive scans of a narrow mass range at m/e 320 or 322 during the time that TCDD would elute from the GC column.

Sample Digestion and Extraction. *Nonfat Tissue.* Tissue samples were ground when it was necessary to obtain a representative subsample of a large sample. Ten grams was weighed into a 125-mL boiling flask, 10 mL of ethanol (20 mL for catfish tissue) and 20 mL of 40% potassium hydroxide solution were added, and the flask was heated on a steam bath for 30 min. A whole small animal or small fish was digested in a wide-mouth bottle, increasing the amounts of ethanol and 40% potassium hydroxide in proportion to sample weight. When the digested solution had cooled slightly, 10 mL of ethanol was added. If on cooling to room temperature the solution turned into a gel, it was liquified by warming and an additional 10 mL of ethanol and 10 mL of water added. When cool, the solution was extracted with four 10-mL portions of hexane (15-mL portions for liver tissue) or with proportionately larger volumes of hexane if the sample weighed more than 10 g. Samples high in skeletal debris which would clog the stopcock of a separatory funnel were extracted by shaking with hexane in a screw-cap bottle and drawing off the hexane with a pipet.

Milk. A 20- to 40-g sample in a 125-mL boiling flask was heated 4 h with 10 mL of ethanol and 20 mL of 40% potassium hydroxide solution using a steam bath. After cooling, the solution was extracted with four 10-mL portions of hexane. If an emulsion formed, ethanol was added in 1-mL increments, followed by mixing until the emulsion broke.

Cream. A 10-g sample in a 125-mL boiling flask was heated 30 min with 10 mL of ethanol and 20 mL of 40% potassium hydroxide solution using a steam bath. When the solution had cooled slightly, 10 mL of ethanol and 20 mL of water were added. The solution was cooled to room temperature and extracted with four 10-mL portions of hexane.

Fat Tissue (Higginbotham et al., 1967). Samples were ground or rendered when it was necessary to obtain a representative subsample of a large sample. Ten grams was weighed into a 250-mL boiling flask, 10 mL of ethanol and 20 mL of 40% potassium hydroxide were added, and the flask was heated on a steam bath until the sample had dissolved (usually 15 to 30 min). When the solution had partially cooled, 20 mL of ethanol and 125 mL of water were added and the warm solution was extracted with 40 mL of hexane, followed by three 20-mL portions. Any emulsion that formed was broken by addition of 1-mL portions of ethanol. If the fat solution began to solidify during the extraction, it was warmed on the steam bath.

Grain, Feed, Dry Leaves, Dry Grass. The sample was ground in a blender and a 10-g portion weighed into a cellulose extraction thimble and extracted with 90 mL of hexane for 4 h using a Soxhlet apparatus. A few pieces of 10 mesh carborundum were used in the boiling flask to promote smooth boiling. The hexane extract was evaporated to dryness under a stream of air at room temperature, 10 mL of ethanol and 20 mL of 40% potassium hydroxide solution were added, and the solution was heated on a steam bath for 30 min. Ten milliliters of ethanol was added to the warm solution and the solution was cooled and extracted with four 10-mL portions of hexane.

Wet Plant Material. Samples such as onion bulbs, potatoes, and leaves that had not been dried were chopped into small pieces and 10 to 15 g weighed into a jar and batch extracted with two 25-mL portions of acetone. The acetone extracts were added to 100 mL of water in a 250-mL separatory funnel. The plant material was transferred to a cellulose extraction thimble and extracted 4 h with 90 mL of hexane using a Soxhlet apparatus. The hexane was cooled and used to extract the acetone–water solution. The hexane plus two 25-mL of hexane washes of the acetone–water was evaporated, the residue digested, and the resulting solution extracted as described for grain, etc.

Soil (Kearney et al., 1972; Nash et al., 1973). Soil samples were not dried before analysis. A 10- to 20-g sample plus 7 mL of 1% ammonium chloride was extracted with 100 mL of 1:1 hexane–acetone (v/v) for 2 h, followed by extraction with 30 mL of 1:1 hexane–acetone for 15 min. The combined organic layers were washed with 100 mL of water, followed by two 25-mL portions of water to remove acetone. The hexane was then washed with concentrated sulfuric acid as described in the clean-up section.

Blood. To adequately recover parts per trillion levels of TCDD added to blood, parts per billion amounts of ^{37}Cl TCDD had to be added to enhance recovery. A 1-g portion of whole blood was weighed into a 1-oz bottle, and 20 μL of 100 ppb ^{37}Cl TCDD in *o*-xylene, 10 mL of 0.1 N hydrochloric acid, and 15 mL of chloroform were added and the mixture shaken for 30 min. If necessary, the layers were separated by centrifuging. The chloroform layer was withdrawn with a pipet and the solution extracted with two additional 15-mL portions of chloroform. The combined chloroform extracts were washed with 10 mL of 0.1 N potassium hydroxide solution and the chloroform was evaporated under a stream of air at room temperature. Only alumina column cleanup of the residue was necessary so the residue was dissolved in hexane and transferred to an alumina column prepared as directed in the clean-up section. Elution of the column and transfer of the fraction containing the TCDD to a cone-shaped vial was carried out as described in the clean-up section.

Cleanup. The combined hexane extracts obtained as described in the sample digestion and extraction section were washed with 10 mL of water and then washed with 10 mL portions of concentrated sulfuric acid until the acid was only faintly colored (usually three or four washes). After a 10-mL water wash, the hexane was evaporated in a screw-cap bottle at room temperature using a stream of air. The bottle was kept capped except when evaporating the hexane or removing the residue. A 5-cm silica gel column was prepared using a 0.4-cm diameter disposable pipet. The hexane residue was transferred to the column using three 0.5-mL portions of hexane. The effluent from the column was discarded. The column was eluted with 2 mL of 20% benzene in hexane (v/v) and the eluate evaporated under a stream of air at room temperature. An alumina column the same size as the silica gel column was prepared using alumina activated at 140 °C. One milliliter of hexane was added to the column. The residue from the silica gel column was transferred to the alumina column using three 0.5-mL portions of hexane and the column was then washed with 12 mL of 20% carbon tetrachloride in hexane (v/v), followed by 1 mL of hexane. The washings were discarded. The column was eluted with 4 mL of 20% methylene chloride in hexane (v/v). The eluate was collected in a screw-top vial, evaporated to 0.2 mL, transferred to a 0.3-mL cone-shaped vial using hexane as solvent and the contents of the cone-shaped vial evaporated to dryness under air at room temperature. All vials were kept capped except when evaporating solvent or transferring a residue.

Measurement of TCDD (Shadoff and Hummel, 1975, 1977a). The mass spectrometer was tuned to monitor m/e 320 and 322 ions. A 10- or 20-μL portion of *o*-xylene was added to the cone-shaped vial containing the sample residue and, after mixing with a syringe, a 2- or 5-μL aliquot was injected into the GC column. Quantitation was by peak height ratio using standard solutions of 10, 50, or 100 ppb TCDD in *o*-xylene. When ^{37}Cl TCDD was added to obtain recovery data, it was monitored at m/e 328 on a separate injection. If an environmental sample showed a low ppt positive result by GC–low-resolution MS, the same extract was also examined by GC–high-resolution MS.

DISCUSSION

Many different types of samples have been analyzed for the presence of parts per trillion levels of TCDD. Results of analyses of whole fish, fish muscle, viscera and eggs, crayfish, tadpoles, snails, racerunners, rat and mouse liver, mouse pelts, bird liver and stomach, insects, diving beetles, seeds, soil, water, and bovine and human milk have been included in reports on feeding studies (Rose et al., 1976) and environmental studies (Mahle et al., 1977; Shadoff and Hummel, 1975; Shadoff et al., 1977b; Young, 1974; Young et al., 1976). Shrimp, beef tissue, sheep tissue, cream, blood, rice, grass, and animal feed have also been analyzed. In most analyses the limit of detection for TCDD was 10 parts per trillion (ppt) or less and a limit of detection of 1 ppt was attained with bovine milk. Generally, samples were analyzed with the least amount of sample preparation necessary in order to reduce the amount of time spent on sample preparation and to reduce the possibility of cross contamination or loss of TCDD. Samples containing moisture were not dried before analyzing. When moisture content was needed as part of a particular study, moisture was determined on a separate portion of the sample.

Detection limits are relatively easy to assign when suitable control samples are available but with environmental samples it was usually not possible to obtain controls. In such cases the limit of detection for TCDD was calculated according to criteria developed at a meeting of academic, government, and industrial scientists called to discuss the determination of low levels of TCDD (Collier, 1974). These criteria specify (1) a signal to noise ratio of at least 2.5 to 1, (2) a clearly defined change in slope of a TCDD peak on the side of a contaminating peak, (3) duplicate analyses if the signal to noise ratio is between 2.5 to 1 and 10 to 1, and (4) duplicate analyses if the ratio of the peak heights at m/e 320 and 322 is not in the proper isotopic proportion.

Gas chromatography–low-resolution mass spectrometry has proven satisfactory for rapidly screening sample extracts and does not give false negative results but it does not have sufficient specificity to positively identify 5 to 50 ppt levels of TCDD in environmental samples, contrary to a statement by Fukuhara et al. (1975). Results of the analysis of catfish for the presence of TCDD by GC–low- and high-resolution MS showed several apparent positive results by low resolution while high-resolution results on the same extracts were negative (Shadoff and Hummel 1975; Shadoff et al., 1977b). Thus an apparent positive result for TCDD in an environmental sample by GC–low-resolution MS should be confirmed by GC–high-resolution MS.

Recovery Data. Recovery data for known amounts of TCDD added to fish and milk have been reported (Mahle et al., 1977; Shadoff and Hummel, 1975; Shadoff et al., 1977b). Recoveries from these samples fortified at 10 to 100 ppt averaged 65%. The standard deviation calculated using differences between percent recovered and the average percent recovery was 25% relative. Table I gives data on the recovery of TCDD added to beef fat, soil, and rice and determined by the appropriate procedures in the Experimental Section (soil low in moisture was used in the soil recovery experiments). The data for native TCDD was obtained without using ^{37}Cl TCDD. The ^{37}Cl isotope of TCDD has been added to occasional samples of a series to obtain recovery data, and these data are included in

Table I. Recovery of TCDD Added to Beef Fat, Soil, and Rice

TCDD added,[a] ppt	TCDD found, ppt[b] (% recovery)		
	Beef fat	Soil	Rice
0	n.d.[c]	n.d.	n.d.
5	n.d. (0)	4 (80)	n.d. (0)
5	n.d. (0)		6 (120)
10	7 (70)	10 (100)	9 (90)
10	8 (80)	7 (70)	7 (70)
10	7 (70)		7 (70)
10	8 (80)		7 (70)
10	8 (80)		10 (100)
10	9 (90)		
20	16 (80)		18 (90)
20			12 (60)
25		20 (80)	
30[d]			26 (87)
40	26 (65)		34 (85)
50	35 (70)	41 (82)	
50[d]			46 (92)
50[d]			37 (74)
50[d]			41 (82)
100	78 (78)	87 (87)	
100	60 (60)	90 (90)	
100	54 (54)		
100	63 (63)		
100[d]	69 (69)	75 (75)	48 (48)
100[d]	74 (74)	61 (61)	88 (88)
100[d]	75 (75)	77 (77)	74 (74)
200	156 (78)		
300	222 (74)		
300[d]	183 (61)		
900	650 (72)		

[a] TCDD = 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. [b] ppt = parts per trillion. [c] n.d. = not detected. [d] ^{37}Cl TCDD.

Table II. Response from Possible Environmental Contaminents

Compound	Retent. time diff. from TCDD,[a] s	TCDD equivalent peak height[b]	
		m/e 320	*m/e* 322
Chlordane	−251, −194, −184	n.d.[d]	n.d.
p,p'-DDE[e]	−158	1	0.2
p,p'-DDD[f]	−83	0.07	0.03
p,p'-DDT[g]	−16	0.01	0.003
Dieldrin	−155	0.005	0.003
Endrin	−120	0.060	0.024
Endosulfan	−96	0.0002	0.0009
Mirex	+257	0.00028	0.00022
PCB's[h]			
Aroclor 1242		n.d.	n.d.
Aroclor 1254		n.d.	n.d.
Aroclor 1260	−35	0.001	0.020
	+15	0.001	0.015
	+85	n.d.	0.032
	+187	0.0005	0.008
Toxaphene[c]	−85	0.000002	0.000002
	−38	0.00001	0.00001
	+9	0.00005	0.000005
	+57	0.000005	n.d.

[a] TCDD retention time 390 s. Peak width at half-height = 30 s. [b] The ratio of response of the compound at its retention time to the response of an equal weight of TCDD measured at 390 s. [c] Only those peaks near TCDD are listed. [d] n.d. = not detected; no peaks were detected at *m/e* 320 or 322. [e] *p,p'*-DDE = 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene. [f] *p,p'*-DDD = 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane. [g] *p,p'*-DDT = 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane. [h] PCB's = polychlorinated biphenyls.

Table I. The GC column used gives background at *m/e* 328, so it is necessary to add at least 25 ppt ^{37}Cl TCDD to samples to obtain good recovery data. Liver from rats fed ^{14}C enriched TCDD has been analyzed by ^{14}C counting, GC–MS and electron-capture GC and the results showed that the extraction and clean-up procedure, when corrected for recovery determined in separate experiments, gave an accurate measure of TCDD present at 20 and 200 ppb (Rose et al., 1976).

As with all methodology, the procedures were set up for samples requiring extensive cleanup; however, some types of samples do not require all the clean-up steps. Many soil samples were analyzed, omitting the sulfuric acid wash, and some water extracts required only cleanup on alumina. The shorter cleanup was tried when a soil or water sample gave a colorless hexane extract and no visible residue on evaporation of the hexane. A few soils from stream bottoms high in organic matter required extra sulfuric acid washes and a second alumina chromatography step. Small fat samples (up to 1 g) have been dissolved in hexane and the hexane shaken with concentrated sulfuric acid, omitting the saponification step. The use of carbon tetrachloride in place of 20% carbon tetrachloride in hexane to wash the alumina column reduces the volume needed and would save time but the elution of PCB's and DDE from the alumina has varied with the sample matrix so this change would require standardization for each type of sample. Higher limits of detection result if the TCDD retention time is on the tail of a large DDE peak or is close to PCB peaks. If too much carbon tetrachloride is used, some TCDD is lost. Florisil (Firestone, 1976) and charcoal (Stalling et al., 1974), which have been suggested for use with TCDD, have not been tried with sample extracts. Florisil shows promise of separating aromatics and TCDD better than alumina. The difficulty of recovering TCDD from charcoal does not make its use attractive if a large number of samples are to be analyzed.

Interferences. Pesticides that would not decompose on heating with alkali and that have molecular weights greater than 315 were checked by GC–MS to see if they were potential interferences in the method (Table II). Most such pesticides are separated sufficiently from TCDD on the gas chromatography column so that they should not interfere but DDT and a minor component of the toxaphene tested had almost the same retention time on an OV-3 silicone column as TCDD. DDT is dehydrohalogenated to DDE by alkaline digestion, so it is a potential interference only when the digestion step is omitted. On other GC columns, i.e., OV-210 silicone, DDT and TCDD have different retention times. The minor component in the toxaphene was carried through the clean-up procedure with TCDD; however, this material does have a different *m/e* 320/322 ratio than TCDD.

The only compounds that have been identified in extracts of samples that were analyzed are DDE and PCB's. DDE elutes early enough from the GC column so that it does not interfere in the low-resolution mass spectrometry measurement but a large amount of DDE can interfere in the high-resolution mass spectrometry measurement because of the different technique used. PCB's give several peaks at *m/e* 322, so they can interfere with the low-resolution as well as the high-resolution measurement. The interference most often encountered in the low-resolution mass spectrometry method appeared to be a higher molecular weight aliphatic material which would slowly break down on the GC column, giving a very broad peak. This increased the background signal resulting in increased noise level and a higher limit of detection. The aliphatic material did not interfere with high-resolution measurements. This interference was encountered most often in fat samples and could be reduced using a second alumina

column clean-up step. With the majority of the fat samples analyzed, it was not necessary to use this second alumina cleanup to attain 10 parts per trillion sensitivity.

Determination of Other Chlorinated Dioxins. This clean-up procedure for TCDD has not been tried with small amounts of other chlorinated dioxins. The procedure is similar to a procedure used to determine hexachlorodibenzo-*p*-dioxin (HCDD) and octachlorodibenzo-*p*-dioxin (OCDD) in chicken tissue (Firestone et al., 1971). Firestone (1977) reports that HCDD and OCDD are lost on alkaline digestion and recommends shaking with an alkali solution at room temperature to dissolve tissue samples.

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