Community air monitoring for pesticides.
Part 2: Multiresidue determination of pesticides in air by gas chromatography, gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry

M. Hengel and P. Lee

Address Correspondence to: Matt Hengel, Department of Environmental Toxicology,
University of California, Davis, CA 95616
Email: mjhengel@ucdavis.edu

ABSTRACT

Two multiresidue methods were developed to determine pesticides in air collected in California. Pesticides were trapped using XAD-4 resin and extracted with ethyl acetate. Based on an analytical method from the University of California Davis Trace Analytical Laboratory, pesticides were detected by analyzing the extract by gas chromatography-mass spectrometry (GC-MS) to determine chlorothalonil, chlorthal-dimethyl, cycloate, dicloran, dicofol, EPTC, ethalfluralin, iprodione, mefenoxam, metolachlor, PCNB, permethrin, pronamide, simazine, trifluralin, and vinclozolin. A GC with a flame photometric detector was used to determine chlorpyrifos, chlorpyrifos oxon, diazinon, diazinon oxon, dimethoate, dimethoate oxon, fonophos, fonophos oxon, malathion, malathion oxon, naled and oxydemeton. Trapping efficiencies ranged from 78 to 92% for low level (0.5 µg) and 37 to 104% for high level (50 and 100 µg) recoveries. Little to no degradation of compounds occurred over 31 days; recoveries ranged from 78 to 113%. In the California Department of Food and Agriculture (CDFA) method, pesticides were detected by analyzing the extract by GC-MS to determine chlorothalonil, chlorpyrifos, cypermethrin, dichlorvos, dicofol, endosulfan 1, endosulfan sulfate, oxyfluorfen, permethrin, propargite, and trifluralin. A liquid chromatograph coupled to a MS was used to determine azinphos-methyl, chloropyrifos oxon, DEF, diazinon, diazinon oxon, dimethoate, dimethoate oxon, diuron, EPTC, malathion, malathion oxon, metolachlor, molinate, norflurazon, oryzalin, phosmet, propanil, simazine and thiobencarb. Trapping efficiencies for compounds determined by the CDFA method ranged from 10 to 113, 22 to 114, and 56 to 132% for 10, 5 and 2 µg spikes, respectively. Storage tests yielded 70 to 170% recovery for up to 28 days. These multiresidue methods represent flexible, sensitive, accurate, and cost-effective ways to determine residues of various pesticides in ambient air.

Keywords: air sampling, gas chromatography, liquid chromatography, mass spectrometry, pesticides, XAD resin, multiresidue

1. Introduction

In the present study, multiresidue methods were developed to trap selected pesticides from ambient air using XAD resin, and analyze them in a timely manner to assist in various California Department of Pesticide Regulation air monitoring projects. The method developed by the University of California Davis Trace Analytical Laboratory (TAL) utilized gas chromatography with flame photometric detection (GC-FPD) and gas chromatography with mass spectrometry (GC-MS) to determine pesticide residues. Alternatively, the method developed by the California Department of Food and Agriculture (CDFA) utilized liquid chromatography with mass spectrometry and GC-MS for residue determination.

2. Experimental Procedures

2.1 Chemicals

All analytical standards were of analytical grade from various sources. Reagents and solvents were reagent grade or better. For TAL methodology, neat standards were kept at approx. -20°C until use. Stock and working solutions were prepared in ethyl acetate and kept at ~ 5°C. Calibration solutions were prepared in the presence of extracted XAD resin to correct for enhancement effect associated with GC-MS. The CDFA methodology prepared stock and working solutions in methanol and kept them at ~ 5°C. As with the TAL method, the CDFA method produced calibration standards in the presence of XAD resin extract.

2.2 Trapping medium

XAD-4 (100-120 mesh, Rohm and Haas, Amberlite, Philadelphia, PA), a macro-reticular resin, was employed as the trapping medium. XAD-4 resin was prepared prior to use according to Seiber et al. (1989), with modifications. Resin was initially rinsed with methanol in a 40 L container. The fines were removed by placing a hose at the bottom of the container, overfilling with deionized water and stirring vigorously. Two liters of 0.25 *N* hydrochloric acid were added and the resin was stirred for 30 min. Again, water was added to remove fines. The water steps above were repeated until the water above the resin was clear and the pH was that of the deionized water. The resin was then transferred with methanol to gallon bottles. Next, the resin was Soxhlet extracted twice with fresh methanol for 24 h, then extracted twice with fresh ethyl acetate for 24 h. The resin was dried in a vacuum oven (64 cm Hg) for four days at 60ºC. Resin was stored at room temperature in clean, dry jars with Teflon®-lined lids.

2.3 Trapping efficiency tests

Preparation of cartridges is described in Hall et al. (1997a) and Wofford et al. (2003). The resin cartridge consisted of a resin bed (~30 ml) held in position with a stainless steel mesh screen. The cartridges were connected in tandem with Teflon® tubing. Tygon® tubing was connected to a Staplex high-volume air pump fitted with a manifold that allowed for a flow rate of approximately 20 L/min.

Compounds were trapped in the resin either by direct application or by fortifying glass wool above the resin bed, usually at 50 µg for TAL and between 2 and 10 µg for CDFA. After collecting the air sample for 24 h, the resin was extracted as described below and analyzed as described in the quantitation section.

2.4 Determination of method detection limit (MDL)

For the TAL MDL determination, 8 samples were fortified with 0.2 or 0.1µg quantities of each pesticide and air was pulled through the cartridges at approximately 15 L/min for 24 h. Samples were extracted and quantitated as described below. The CDFA MDL determinations were based on seven samples fortified with 0.4 or 0.2 µg quantities of each pesticide of interest and processed in a similar fashion as the TAL samples.

2.5 Collection of air samples

Air samplers were as described by Sieber et al. (1989) and were placed at various sample locations as described by Wofford et al. (2003, 2013) in Lompoc and Parlier.

2.6 Extraction of air samples (TAL)

Sample cartridges were removed from the freezer (approx. -20ºC) and the cap and screen were removed from the cartridge and the resin was poured into a 4-oz jar. The remaining resin was transferred by rinsing the cartridge using 75 ml of ethyl acetate and the jar was secured with a Teflon® cap. For each set, one resin blank and 3 laboratory concurrent resin fortification samples were prepared by adding 30 mL of clean XAD-4 resin to an appropriate jar and fortifying the resin with a standard mixture of a known concentration. Fortifications were made between one and five times the Estimated Quantitation Limit (EQL). To each fortified jar, 75 mL of ethyl acetate was added and the jars were capped. Samples were swirled for 1 h on a rotary platform shaker at moderate speed.

A 37.5-mL aliquot was quantitatively transferred to a 100-mL round bottom flask and the solvent was evaporated to dryness using a rotary evaporator (water bath at ~35°C). Two milliliters of ethyl acetate were added to the flask, which was then capped and swirled. An aliquot was transferred from the flask to an autosampler vial to inject on the GC-FPD or the GC-MS.

For analysis of dioxydemeton-methyl, 18.75 mL of extract were quantitatively transferred to a 100-mL round bottom flask and the solvent was evaporated to dryness using a rotary evaporator as above. One milliliter of ethyl acetate, 5 mL of 20% magnesium sulfate solution and 20 mL of 0.5 *N* potassium permanganate solution were added with swirling. After sitting for 30 min with occasional swirling, the oxidized mixture was transferred to a 125-mL separatory funnel. The oxidation flask was rinsed with 20 mL chloroform and the rinsate added to the separatory funnel. After shaking the funnel for 30 s, the layers were left to separate. The lower layer (chloroform) was drained through No. 541 filter paper containing a small amount of granular, anhydrous sodium sulfate into a 100-mL round bottom flask. The extraction was repeated twice more with 20 mL portions of chloroform. The sodium sulfate was rinsed with 5 mL of chloroform. The combined extracts were rotary evaporated to dryness, as above. One milliliter of ethyl acetate was added to the flask, which was capped and swirled. An aliquot was transferred to an autosampler vial and analyzed using the GC-FPD.

2.7 Extraction of air samples (CDFA)

Sample tubes were removed from the refrigerator (0–5ºC) and allowed to reach ambient temperature. The tube was secured to a lab rack and the end caps were removed. A 250-mL round bottom flask was positioned below the sample tube and a 250-mL separatory funnel was placed above the tube such that the tip was just inside the sample tube. Ethyl acetate (100 mL) was then added to the separatory funnel and the flow was adjusted to maintain ~ 13 mm of solvent above the resin bed. Once all the ethyl acetate had passed through the sample tube and collected into the round bottom flask, the sample extract was concentrated to ~ 10 mL by a rotary evaporator (water bath at 45ºC). The sample was quantitatively transferred to a 15-mL conical centrifuge tube and evaporated to ~ 1 mL with nitrogen (water bath at 40ºC). A solvent exchange was performed with methanol and the final volume was adjusted to 2 mL with methanol. The final sample was vortexed and transferred into autosampler vials.

2.8 Instrumentation and analysis (TAL)

Two separate instruments were used for analysis to provide sufficient resolution and quantitation:

1) Chlorpyrifos, chlorpyrifos oxon, diazinon, diazinon oxon, dimethoate, dimethoate oxon, fonophos, fonophos oxon, malathion, malathion oxon, naled, and oxydemeton were analyzed with a Hewlett Packard (HP) 5890 Series II GC (HP, Avondale, PA) equipped with a 30 m × 0.53 mm i.d. (d_f = 1.5 µm) DB-210 megabore column (J&W Scientific, Folsom, CA) and a flame photometric detector (FPD), phosphorus mode. The injector and detector were operated at 250 and 225°C, respectively. An HP model 7673 autoinjector was used to inject 3 µl of sample in splitless mode. The oven temperature program was initially held at 170°C, held for 0.5 min, ramped at 5°C /min to 200°C, and then ramped at 8°C/min to 225°C where it was held for 4.0 min. The FPD gases consisted of air at 101 mL/min and hydrogen at 79 mL/min. The carrier gas was helium at a rate of 12.1 mL/min. See Table 1a for retention times.

2) Chlorothalonil, chlorthal-dimethyl, cycloate, dicloran, dicofol (as dicofol and dichlorobenzophenone), EPTC, ethalfluralin, iprodione, mefenoxam, metolachlor, PCNB, permethrin, pronamide, simazine, trifluralin, and vinclozolin were analyzed with a HP 6890-5972A GC-MSD, equipped with a 15 m × 0.25 mm i.d. (d_f = 0.25 µm) DB-17ms column (J&W Scientific, Folsom, CA). The injector was held at 250°C. The MSD interface was held at 280°C, operated in positive electron ionization mode with selective ion monitoring (SIM) for the compounds of interest. An HP6890 Series autoinjector was programmed to inject 2 µL of sample in splitless mode. Oven temperature was initially 70°C, then ramped 10°C/min to 280°C and held for 4 min. The carrier gas was helium at a flow rate of 1.0 mL/min. See Table 1b for compound retention times and ions monitored.

2.9 Instrumentation and Analysis (CDFA)

Two separate instruments were used for analysis to provide sufficient resolution and quantitation:

1) Azinphos methyl, chlorpyrifos oxon, DEF, diazinon, diazinon oxon, dimethoate, dimethoate oxon, diuron, EPTC, malathion, malathion oxon, metolachlor, molinate, norflurazon, oryzalin, phosmet, propanil, simazine, and thiobencarb were determined by a Waters 2695 liquid chromatograph (Waters Corp., Milford, MA) coupled to a Finnigan DECA ion trap mass spectrometer (MS; Thermo-Scientific, USA) via an atmospheric pressure ionization source (APCI). The APCI source was operated in positive mode with a capillary temperature of 200°C and vaporizer temperature of 500°C. The MS was operated in MS/MS

mode. Chromatographic separation was accomplished with a Waters Symmetry Shield RP_{18} column (150 × 3.9 mm i.d., 5 µm particle size) fitted with a Waters Symmetry Shield RP_{18} (20 × 3.9 mm i.d., 5 µm particle size) guard column. Initial mobile phase composition was 85:15 (v/v) at 5% methanol, 0.1% formic acid, and 0.01 M ammonium formate in water/10% water, 0.1% formic acid and 0.01 M ammonium formate in methanol with a flow rate of 0.75 mL/min. The mobile phase program consisted of 0–3.0 min 85:15, 3.0–4.0 min ramp gradient to 50:50, 4.0–10.0 min hold 50:50, 10.0–21.0 min ramp gradient to 25:75, 21.0–22.0 min ramp gradient to 5:95, 22.0–27.0 min hold 5:95, 27.0–30.0 min ramp gradient back to 85:15, 30.0–34.0 min hold 85:15. Injection volume was 10 µL. See Table 1c for compound retention times and ions monitored.

2) Chlorothalonil, chlorpyrifos, cypermethrin, dichlorvos, dicofol, endosulfan, endosulfan sulfate, oxyflurofen, permethrin, propargite, and trifluralin were analyzed with an Agilent 6890-5973 GC-MSD equipped with a 30 m × 0.25 mm i.d. (d_f = 0.25 µm) HP-5 ms column (Agilent, Wilmington, DE). The injector was held at 250°C. The MSD interface was held at 280°C and operated in positive electron ionization mode with SIM for the compounds of interest. An Agilent 6890 Series autoinjector was programmed to inject 1 µL of sample in splitless mode. Oven temperature was initially 70°C for 2 min, then ramped 15°C/min to 190°C (5 min hold), then ramped 15°C/min to 250 °C (5 min hold), then finally ramped 15°C/min to 270°C and held for 8 min. The carrier gas was helium at a flow rate of 1.2 mL/m^{-1}. See Table 1d for compound retention times and ions monitored.

3. Results and discussion

Trapping efficiencies of pesticides in the TAL procedure ranged from 78 to 92% for the low level (0.5 µg) and 37 to 104% for the high level (50 and 100 µg) recoveries as shown in Table 2a. For the CDFA procedure trapping efficiencies ranged from 10 to 113, 22 to 114, and 56 to 132% for 10, 5 and 2µg fortifications, respectively (Table 2b). These trapping efficiency recovery levels were sufficient and are comparable to Egea Gonzalez et al. (2004), Foreman et al. (2000), Hall et al. (1997a, b), Le Noir et al. (1999), and Royce et al. (1993).

The TAL MDLs for the selected pesticides were determined with 0.1 or 0.2 µg for each pesticide (Table 3a). The MDL (in micrograms per sample) ranged from 0.007 to 0.041 µg. The EQL was calculated as five times the MDL and ranged from 0.033 to 0.203 µg/sample. The CDFA procedure, with fortifications of 0.2 or

0.4 µg for each pesticide (*n*=7), yielded an MDL range of 0.025 to 0.295 µg/sample and a RL range of 0.250 to 2.00 µg/sample (Table 3b). In both cases, the MDL was calculated using the following formula:

MDL = standard deviation of replicates × *t*-value for *n* samples.
t-values were obtained from tables of Students *t*-values.

Method validation was performed by CDFA over six levels of fortification (0.5, 1, 2, 5, 10 and 20 µg). Overall recoveries ranged from 68 to 206% (Table 4). Generally, the CDFA method produced acceptable recoveries for the majority of the compounds screened. Conversely, the TAL procedure utilized the MDL and trapping efficiency results to show how the method could capture residues over a relatively wide range for each compound. The method was verified over five levels of fortification (one to five times EQL) by concurrent fortifications and quality assurance (QA) field/trip spikes (samples which were fortified and were collocated at various sampling sites) that were analyzed with each sampling set. The average recoveries for concurrent fortification ranged from 55 to 166% (Table 5) while the QA spikes ranged from 52 to 179% (Table 6). As with the CDFA results, the TAL sample produced generally acceptable recoveries.

The TAL storage stability study samples were analyzed after 30 to 31 days, with 0 days representing the concurrent recoveries (Table 7). Average concurrent recoveries analyzed with storage stability study samples ranged from 78 to 113%. The CDFA storage samples were analyzed at 0-, 7-, 14-, and 2-day intervals after fortification. The average recoveries ranged from 70 to 170% recovery (Table 8). All the air samples collected from the field in TAL studies were analyzed within five days of receipt. Samples collected in CDFA studies were analyzed within 19 days of receipt. No apparent degradation of pesticides occurred over the storage intervals.

Overall, both the CDFA and TAL methodologies proved to be comparable and adequate to determine pesticide residues in air samples.

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Table 1a Compound Retention Times for TAL GC-FPD Analysis.

Compound	Retention Time (min)
Diazinon	2.36
Naled	2.73
Fonofos	2.81
Fonofos Oxon	3.25
Diazinon Oxon	3.64
Chlorpyrifos	4.20
Dimethoate Oxon	4.47
Dimethoate	4.80
Malathion	5.99
Chlorpyrifos Oxon	6.67
Malathion Oxon	6.94

Table 1b Selected Ion Monitoring and Retention Times for TAL GC-MS Analysis.

Compound	Retention Time (min)	Selected Ions
EPTC	9.38	132, 189
Ethafluralin	12.42	276, 292
Trifluralin	12.43	264, 306
Cycloate	13.34	154, 215
Pronamide	14.94	175, 254
PCNB	15.32	237, 295
Simazine	15.56	186, 201
Dichloran	15.56	206, 208
Vinclozolin	16.34	285, 287
Chlorothalonil	16.74	264, 266
Mefenoxam	17.22	206, 279
Metolachlor	17.31	238, 240
Chlorthal-dimethyl	17.46	299, 301
Dichlorobenzophenone	18.02	139, 250
Iprodione	22.03	244, 246
Dicofol	22.74	139, 251
Permethrin	24.78, 25.03	163, 183

Table 1c Selected Ion Monitoring and Retention Times for CDFA GC-MS Analysis.

Compound	Retention Time (min)	Selected Ions
Dichlorvos	7.25	109, 145, 185
Trifluralin	11.02	264, 306, 335
Dimethoate	11.86	87, 125, 229
Chlorothalonil	12.76	109, 229, 266
Chlorpyrifos	15.98	197, 258, 314
Dicofol	16.46	111, 139, 250
Endosulfan I	18.02	195, 241, 261, 339
Oxyfluorfen	18.68	252, 300, 361
Endosulfan Sulfate	20.04	229, 272, 387, 422
Propargite	20.50	135, 173, 350
Permethrin	24.80, 25.09	127, 163, 183
Cypermethrin	26.41	161, 163, 209

Table 1d Selected Ion Transitions and Retention Times for CDFA LC-MS Analysis.

Compound	Retention Time (min)	Molecular Ions	Product Ions
Dimethoate Oxon	3.16	213	183
Dimethoate	7.40	229	199
Malathion Oxon	10.04	314	127, 173, 269
Simazine	11.55	201, 203	124, 132, 174
Diazinon Oxon	15.06	288	153, 261, 289
Norflurazon	16.23	303, 305	284, 286, 302, 304, 316, 317
Diuron	17.06	232, 234	72
Phosmet	17.40	317	160, 286
Azinphos-methyl	17.18	317	160, 171, 261
Molinate	18.05	187	126
Malathion	18.56	330	285
Metolachlor	19.59	283, 285	252
Propanil	19.63	217, 219	162
Chlorpyrifos Oxon	20.35	333, 335, 337	306, 308, 310
EPTC	20.55	189	128
Oryzalin	21.53	346	247, 288, 305
Diazinon	22.39	304	153, 169
Thiobencarb	24.43	257, 259	100, 125, 258
DEF	27.00	314	201, 257, 259

Table 2a Trapping Efficiencies for TAL Analytical Procedure.

Compound	% Recovery[1]
Chlorothalonil[2]	78±4[3]
Chlorpyrifos	95±4
Chlorpyrifos Oxon	58±5
Chlorthal-dimethyl	104±2
Cycloate	37±6
Diazinon	83±6
Diazinon Oxon	89±3
Dichloran	93±4
Dicofol	102±1
Dimethoate	88±6
Methoate Oxon	90±3
EPTC	53±2
Ethalfluralin	60±3
Fonofos	67±10
Fonofos Oxon	87±3
Iprodione	82±2
Malathion	86±6
Malathion Oxon	104±4
Mefenoxam	91±3
Metolachlor	93±2
Naled	75±4[4]
Oxydemeton methyl	92±18[3]
PCNB	94±4
Permethrin	78±2
Pronamide	77±2
Simazine	90±2
Trifluralin	77±2
Vinclozolin	89±2

[1]Replicates (average ± standard deviation), *n*=4
[2]Recovery from direct resin only
[3]Recovery at 0.5 µg fortification
[4]Recovery at 100 µg fortification

Table 2b Trapping Efficiencies for CDFA Analytical Procedure.

	% Recovery[1]		
Compound	**10 µg**	**5 µg**	**2 µg**
Azinphos Methyl	69±3	59±5	85±5
Chlorothalonil	90±24	77±19	86±7
Chlorpyrifos	103±12	101±4	67±16
Chlorpyrifos Oxon	---[2]	---[2]	---[2]
Cypermethrin	97±4	114±9	132±10
DEF	97±5	93±2	96±6
Diazinon	99±11	94±5	83±11
Diazinon Oxon	---[2]	---[2]	---[2]
Dichlorvos	113±5	111±7	78±9
Dicofol	105±8	102±2	78±15
Dimethoate	91±5	94±3	94±13
Dimethoate Oxon	---[2]	---[2]	---[2]
Diuron	83±6	76±11	103±4
Endosulfan	104±10	104±4	72±14
Endosulfan Sulfate	107±10	102±11	80±13
EPTC	89±1	79±4	90±5
Malathion	90±18	83±10	101±11
Malathion Oxon	---[2]	---[2]	---[2]
Metolachlor	75±10	85±10	92±5
Molinate	85±0	80±3	93±8
Norflurazon	10±3	22±15	78±33
Oryzalin	14±3	25±18	64±35
Oxyfluorfen	23±5	42±16	68±13
Permethrin	93±7	100±7	78±18
Phosmet	103±4	87±8	106±16
Propanil	100±6	98±5	98±16
Propargite	90±9	77±4	56±7
Simazine	109±6	103±4	112±3
Thiobencarb	90±1	87±2	99±8
Trifluralin	76±14	85±8	72±9

[1]Replicates (average ± standard deviation), *n*=3
[2]Oxon compounds were not separately fortified during trapping efficiency testing; they were analyzed and summed with their corresponding parent residues.

Table 3a Determination of Method Detection Limit (MDL) and Estimated Quantitation Limit (EQL) for TAL Procedure.

Compound	Average (µg/Sample)	S.D.[1] (µg/Sample)	MDL[2] (µg/Sample)	EQL[3] (µg/Sample)
Chlorothalonil[4]	0.136	0.012	0.036	0.179
Chlorothalonil[5]	0.089	0.011	0.032	0.161
Chlorpyrifos[4]	0.097	0.006	0.019	0.097
Chlorpyrifos[5]	0.098	0.006	0.017	0.087
Chlorpyrifos Oxon[5]	0.101	0.004	0.012	0.061
Chlorthal-dimethyl[5]	0.100	0.002	0.007	0.033
Cycloate[5]	0.100	0.014	0.041	0.203
Diazinon[4]	0.078	0.007	0.022	0.109
Diazinon[5]	0.093	0.005	0.016	0.081
Diazinon Oxon[5]	0.097	0.004	0.012	0.059
Dicloran[5]	0.120	0.010	0.029	0.143
Dicofol[5]	0.105	0.010	0.030	0.149
Dimethoate[4]	0.086	0.007	0.021	0.103
Dimethoate[5]	0.097	0.004	0.012	0.062
Dimethoate Oxon[5]	0.102	0.004	0.011	0.053
EPTC[5]	0.092	0.004	0.014	0.069
Ethalfluralin[5]	0.112	0.004	0.013	0.067
Fonofos[4]	0.065	0.007	0.020	0.098
Fonofos[5]	0.090	0.005	0.015	0.074
Fonofos Oxon[5]	0.094	0.004	0.012	0.060
Iprodione[5]	0.121	0.011	0.034	0.170
Malathion[5]	0.098	0.006	0.019	0.093
Malathion Oxon[5]	0.102	0.003	0.009	0.045
Mefenoxam[5]	0.098	0.004	0.013	0.067
Metolachlor[5]	0.111	0.004	0.013	0.065
Naled[5]	0.088	0.007	0.022	0.108
Oxydemeton[4]	0.193	0.007	0.021	0.104
PCNB[5]	0.111	0.006	0.019	0.095
Permethrin[4]	0.128	0.012	0.037	0.184
Permethrin[5]	0.112	0.011	0.032	0.161
Pronamide[5]	0.125	0.013	0.038	0.189
Simazine[5]	0.109	0.004	0.014	0.068
Trifluralin[5]	0.114	0.012	0.034	0.171
Vinclozolin[5]	0.104	0.003	0.009	0.043

[1] Standard Deviation, *n*=8

[2] Method Detection Limit (MDL) is t-value (2.998 for *n*=8) × standard deviation; t-value obtained from Tables of Students t-values

[3] Estimated Quantitation Limit (EQL) is MDL × 5

[4] Determined during 1998 sampling project at 0.2 µg/sample

[5] Determined during 2000 sampling project at 0.1 µg/sample

Table 3b Determination of Method Detection Limit (MDL) and Reporting Limit (RL) for CDFA Procedure.

Compound	Average (µg/Sample)	S.D.[1] (µg/Sample)	MDL[2] (µg/Sample)	RL[3] (µg/Sample)
Azinphos Methyl[4]	0.345	0.052	0.164	1.000
Chlorothalonil[4]	0.556	0.094	0.295	2.000
Chlorpyrifos	0.193	0.035	0.109	1.000
Chlorpyrifos Oxon	0.189	0.020	0.063	0.250
Cypermethrin[4]	0.487	0.032	0.101	1.000
DEF	0.198	0.012	0.038	0.250
Diazinon	0.190	0.008	0.025	0.250
Diazinon Oxon	0.218	0.014	0.045	0.250
Dichlorvos	0.196	0.022	0.070	1.000
Dicofol	0.212	0.015	0.046	1.000
Dimethoate	0.186	0.016	0.050	0.250
Dimethoate Oxon	0.199	0.013	0.042	0.250
Diuron	0.184	0.035	0.111	0.250
Endosulfan	0.200	0.022	0.070	1.000
Endosulfan Sulfate	0.207	0.032	0.100	1.000
EPTC	0.165	0.011	0.036	0.250
Malathion	0.141	0.015	0.047	0.250
Malathion Oxon	0.189	0.009	0.028	0.250
Metolachlor	0.184	0.019	0.059	0.250
Molinate	0.163	0.012	0.039	0.250
Norflurazon	0.187	0.026	0.081	0.250
Oryzalin	0.227	0.010	0.030	0.250
Oxyfluorfen[4]	0.370	0.044	0.138	1.000
Permethrin[4]	0.464	0.050	0.156	1.000
Phosmet[4]	---[5]	---[5]	---[5]	---[5]
Propanil	0.184	0.016	0.050	0.250
Propargite[4]	0.369	0.026	0.082	1.000
Simazine	0.186	0.008	0.026	0.250
Thiobencarb	0.200	0.038	0.121	0.250
Trifluralin	0.264	0.011	0.036	0.500

[1] Standard Deviation, n=7

[2] Method Detection Limit (MDL) is t-value (3.143 for n=7) × standard deviation; t-value obtained from Tables of Students t-values

[3] Reporting Limit (RL) is roughly 2–22 × MDL, depending on each compound

[4] Determined at 0.4 µg/sample, all other compounds were fortified at 0.2 µg/sample

[5] No data were reported for phosmet.

Table 4 Method Validation for CDFA Procedure.

	% Recovery[1]					
Compound	**20 µg**	**10 µg**	**5 µg**	**2 µg**	**1 µg**	**0.5 µg**
Azinphos Methyl[2]	86±9	91±14	84	93±10	72±17	77
Chlorothalonil[2]	94±40	111±30	101	102±6	127±20	206
Chlorpyrifos	N/A	100±17	90±20	N/A	99±13	104±14
Chlorpyrifos Oxon	N/A	93±17	95±8	N/A	113±14	111±21
Cypermethrin[2]	100±19	103±11	97	99±7	109±18	119
DEF	N/A	96±8	93±9	N/A	94±3	95±5
Diazinon	N/A	99±13	90±13	N/A	89±7	83±7
Diazinon Oxon	N/A	103±5	97±13	N/A	103±9	106±14
Dichlorvos	N/A	98±22	83±17	N/A	92±24	104±35
Dicofol	N/A	101±12	95±9	N/A	94±10	92±11
Dimethoate	N/A	94±9	89±8	N/A	93±14	94±10
Dimethoate Oxon	N/A	100±6	97±10	N/A	101±10	103±12
Diuron	N/A	97±15	97±13	N/A	106±9	99±15
Endosulfan	N/A	108±8	100±7	N/A	100±15	102±18
Endosulfan Sulfate	N/A	111±13	100±7	N/A	99±9	116±13
EPTC	N/A	85±11	73±20	N/A	68±22	75±14
Malathion	N/A	90±17	95±19	N/A	87±15	85±21
Malathion Oxon	N/A	102±5	101±5	N/A	104±7	103±13
Metolachlor	N/A	92±17	95±15	N/A	96±8	88±15
Molinate	N/A	90±10	81±17	N/A	75±12	75±11
Norflurazon	N/A	93±11	94±11	N/A	98±12	97±18
Oryzalin	N/A	101±16	95±15	N/A	100±5	107±12
Oxyfluorfen[2]	103±11	100±8	103	96±5	106±4	122
Permethrin[2]	106±16	103±7	105	101±9	99±8	97
Phosmet[2]	116±45	118±16	99	139±41	118±23	83
Propanil	N/A	97±12	89±11	N/A	92±8	97±9
Propargite[2]	95±12	95±16	88	105±3	107±21	94
Simazine	N/A	96±9	94±4	N/A	97±11	96±9
Thiobencarb	N/A	94±7	92±9	N/A	90±6	94±8
Trifluralin	N/A	109±13	93±8	N/A	98±9	110±12

[1]Replicates (average ± standard deviation), *n*=5
[2]Fortifications at 20 µg (*n*=3); at 10 µg (*n*=5); at 5 µg (*n*=2); at 2 µg (*n*=3); at 1 µg (*n*=5); at 0.5 µg (*n*=2)
N/A not fortified at these levels

Table 5 Concurrent Recoveries for TAL Procedure.

	% Recovery[1]				
Compound	**1 EQL**	**2 EQL**	**3 EQL**	**4 EQL**	**5 EQL**
Chlorothalonil[2]	N/A	92±4	95±2	N/A	N/A
Chlorothalonil[3]	91±2	87±2	85±3	89±4	55±27
Chlorpyrifos[2]	N/A	120±6	105±5	N/A	N/A
Chlorpyrifos[3]	93±4	95±7	92±4	97±3	100±4
Chlorpyrifos Oxon[3]	98±5	95±5	93±10	108±9	98±4
Chlorthal-dimethyl[3]	112±6	100±3	99±2	98±3	88±5
Cycloate[3]	92±4	89±2	98±8	89±2	82±1
Diazinon[2]	N/A	103±5	97±4	N/A	N/A
Diazinon[3]	86±5	93±6	90±9	98±4	97±3
Diazinon Oxon[3]	96±2	95±6	93±5	99±4	98±4
Dichloran[3]	117±11	94±3	90±6	86±3	75±2
Dicofol[3]	97±23	85±5	101±13	89±14	100±12
Dimethoate[2]	N/A	111±4	96±4	N/A	N/A
Dimethoate[3]	92±5	94±6	92±8	100±4	96±3
Dimethoate Oxon[3]	106±7	101±6	96±8	109±4	99±5
EPTC[3]	93±1	87±4	87±2	95±8	79±3
Ethalfluralin[3]	166±12	144±8	150±25	121±39	123±12
Fonofos[2]	N/A	97±4	89±2	N/A	N/A
Fonofos[3]	82±7	92±10	88±11	91±5	92±4
Fonofos Oxon[3]	95±3	98±8	90±3	97±2	97±3
Iprodione[3]	91±8	93±3	92±14	87±4	77±4
Malathion[3]	92±5	94±7	90±8	97±2	96±3
Malathion Oxon[3]	105±5	102±7	99±8	109±6	99±3
Mefenoxam[3]	119±4	101±12	101±10	92±3	89±3
Metolachlor[3]	137±5	110±3	103±7	103±3	86±2
Naled[3]	89±4	86±5	82±9	100±9	87±9
Oxydemeton[2]	N/A	152±29	125±6	N/A	N/A
Oxydemeton[3]	N/A	120±5	N/A	N/A	N/A
PCNB[3]	126±5	97±7	96±6	91±2	80±4
Permethrin[2]	N/A	102±7	101±2	N/A	N/A
Permethrin[3]	101±2	95±3	94±7	89±6	76±2
Pronamide[3]	102±2	97±4	97±10	91±2	78±2
Simazine[3]	110±3	96±3	100±10	100±10	87±3
Trifluralin[3]	106±12	85±3	89±7	84±4	72±5
Vinclozolin[3]	119±7	106±3	105±4	104±3	91±1

[1]Replicates (average ± standard deviation), *n*=6
[2]Analyzed during 1998 sampling project
[3]Analyzed during 2000 sampling project
N/A not fortified at these levels

Table 6 Quality Assurance Field/Trip Spike Recoveries for TAL Procedure.

	%Recovery					
Compound	**2 EQL[1]**	**2.5 EQL[2]**	**3 EQL[1]**	**3.5 EQL[2]**	**4 EQL[1]**	**5 EQL[1]**
Chlorothalonil[3]	90±5	76±7	87±7	N/A	93±13	N/A
Chlorothalonil[4]	82±8	78±4	82±9	65±17	89±9	83±6
Chlorpyrifos[3]	129±8	111±18	175±76[5]	N/A	125±11	N/A
Chlorpyrifos[4]	110±5	111±8	107±9	100±7	102±4	71±24
Chlorpyrifos Oxon[4]	100±11	104±2	104±7	104±17	106±4	72±24
Chlorthal-dimethyl[4]	107±11	90±5	110±20	102±5	117±13	155±84
Cycloate[4]	90±5	82±5	85±9	92±9	93±9	84±3
Diazinon[3]	122±2	118±13	120±23	N/A	98±11	N/A
Diazinon[4]	91±10	94±3	94±7	85±5	99±6	62±21
Diazinon Oxon[4]	103±9	104±6	103±10	102±9	103±4	75±29
Dichloran[4]	90±14	79±11	93±23	92±8	96±15	89±20
Dicofol[4]	98±16	179±12	93±12	102±11	90±9	112±28
Dimethoate[4]	83±12	84±12	84±12	90±2	94±7	60±20
Dimethoate Oxon[4]	113±11	114±7	112±11	111±17	117±8	83±31
EPTC[4]	92±7	82±8	88±9	92±3	102±20	88±7
Ethalfluralin[4]	155±24	142±22	135±24	140±14	160±32	131±26
Fonofos[3]	94±4	95±3	95±2	N/A	88±11	N/A
Fonofos[4]	72±17	70±16	70±13	84±4	82±13	52±12
Fonofos Oxon[4]	88±17	112±15	112±15	120±13	123±16	91±16
Iprodione[4]	96±3	93±2	96±8	102±5	111±15	95±2
Kerb[4]	105±4	102±5	107±9	109±10	119±27	101±7
Malathion[4]	101±20	94±1	96±6	101±7	100±2	70±25
Malathion Oxon[4]	109±15	106±6	108±9	114±15	115±6	78±27
Mefenoxam[4]	97±5	82±2	93±10	108±4	115±25	99±9
Metolachlor[4]	113±1	107±4	109±8	109±5	125±24	108±3
Naled[4]	90±10	95±2	96±5	85±20	104±7	66±19
Oxydemeton[3]	117±3	149±3	135±13	N/A	118±12	N/A
Oxydemeton[4]	N/A	N/A	121±2[6]	N/A	N/A	N/A
PCNB[4]	89±10	89±5	127±60	100±5	113±11	122±52
Permethrin[3]	109±5	95±7	86±11	N/A	79±6	N/A
Permethrin[4]	100±1	92±15	101±10	100±3	109±15	96±4
Simazine[4]	101±2	97±1	99±6	102±0	108±9	97±4
Trifluralin[4]	87±12	82±11	88±25	88±8	99±27	79±13
Vinclozolin[4]	116±10	105±5	107±8	110±7	141±64	114±15

N/A not fortified at these level.
[1]Replicates (average ± standard deviation), *n*=6
[2]Replicates (average ± standard deviation), *n*=3
[3]Analyzed in 1998, for 2 EQL, *n*=2, for all other values, *n*=3
[4]Analyzed in 2000, see Footnotes 1-3 for *n* values
[5]Not corrected for chlorpyrifos ambient background
[6]Oxydemeton analysis for Weeks 8, 9 & 10, *n*=3

Table 7 Storage Stability Recoveries for TAL Procedure.

Compound	%Recovery 0 Days[1]	31 Days
Chlorothalonil	93±4	100±5[3]
Chlorpyrifos	104±19	93±4[3]
Chlorpyrifos Oxon	86±8	89±5[2]
Chlorthal-dimethyl	97±3	92±2[2]
Cycloate	89±4	113±2[2]
Diazinon	94±8	92±5[2]
Diazinon Oxon	88±11	91±5[3]
Dichloran	88±6	85±2[2]
Dicofol	78±2	74±2[2]
Dimethoate	98±8	94±4[3]
Dimethoate Oxon	89±12	90±6[2]
EPTC	91±3	107±2[2]
Ethalfluralin	83±5	96±2[2]
Fonofos	90±5	89±5[3]
Fonofos Oxon	87±9	89±4[2]
Iprodione	88±7	89±3[2]
Malathion	90±10	92±6[2]
Malathion Oxon	88±9	91±4[2]
Menfoxam	91±4	91±2[2]
Metolachlor	83±4	90±2[2]
Naled	113±6	103±8[4]
Oxydemeton	104±16	99±6[3]
PCNB	87±4	83±1[2]
Permethrin	98±4	98±4[3]
Pronamide	85±5	87±2[2]
Simazine	95±5	92±2[2]
Trifluralin	85±5	95±2[2]
Vinclozolin	93±4	92±2[2]

Samples fortified at 50 µg/compound unless noted.
[1]Replicates (average ± standard deviation), *n*=3
[2]Replicates (average ± standard deviation), *n*=5
[3]Replicates (average ± standard deviation), *n*=6, fortified with 0.2 µg of each compound, except 4 µg for oxydemeton
[4]Replicates (average ± standard deviation), *n*=4, fortified with 2 µg for naled

Table 8 Storage Stability Recoveries for CDFA Procedure.

	% Recovery[1]			
Compound	**0 Days**	**7 Days**	**14 Days**	**28 Days**
Azinphos Methyl	104±6	115±0	98±9	101±5
Chlorothalonil	129±11	107±22	115±24	123±7
Chlorpyrifos	108±11	96±24	102±24	83±3
Chlorpyrifos Oxon	N/A	N/A	N/A	N/A
Cypermethrin	117±13	104±17	105±19	74±3
DEF	99±4	100±3	106±4	99±4
Diazinon	94±4	97±4	96±4	111±5
Diazinon Oxon	N/A	N/A	N/A	N/A
Dichlorvos	108±7	89±16	108±24	73±10
Dicofol	110±6	113±16	112±15	85±8
Dimethoate	96±9	95±2	94±13	101±5
Dimethoate Oxon	N/A	N/A	N/A	N/A
Diuron	94±6	103±9	109±6	95±5
Endosulfan	110±14	101±23	106±21	84±8
Endosulfan Sulfate	109±16	98±14	98±25	99±12
EPTC	84±7	80±5	75±1	93±5
Malathion	80±6	76±3	89±14	100±4
Malathion Oxon	N/A	N/A	N/A	N/A
Metolachlor	109±11	96±4	96±5	100±2
Molinate	82±6	83±6	83±3	99±6
Norflurazon	101±6	95±3	105±2	106±5
Oryzalin	94±6	104±4	105±1	116±3
Oxyfluorfen	114±9	104±24	103±17	83±8
Permethrin	111±7	105±17	108±18	90±14
Phosmet	101±9	125±13	170±9[2]	119±5
Propanil	105±7	101±6	101±7	90±1
Propargite	82±10	93±12	99±19	70±2
Simazine	99±4	99±7	101±3	104±3
Thiobencarb	90±4	99±2	102±9	99±1
Trifluralin	108±7	97±13	104±18	82±10

N/A compounds were not fortified for storage stability determination
[1]Replicates, *n*=3
[2]High recovery due to calibration standard stability.