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PESTICIDE RESIDUE ANALYSIS OF STORM-DRAIN WATERS, 1975

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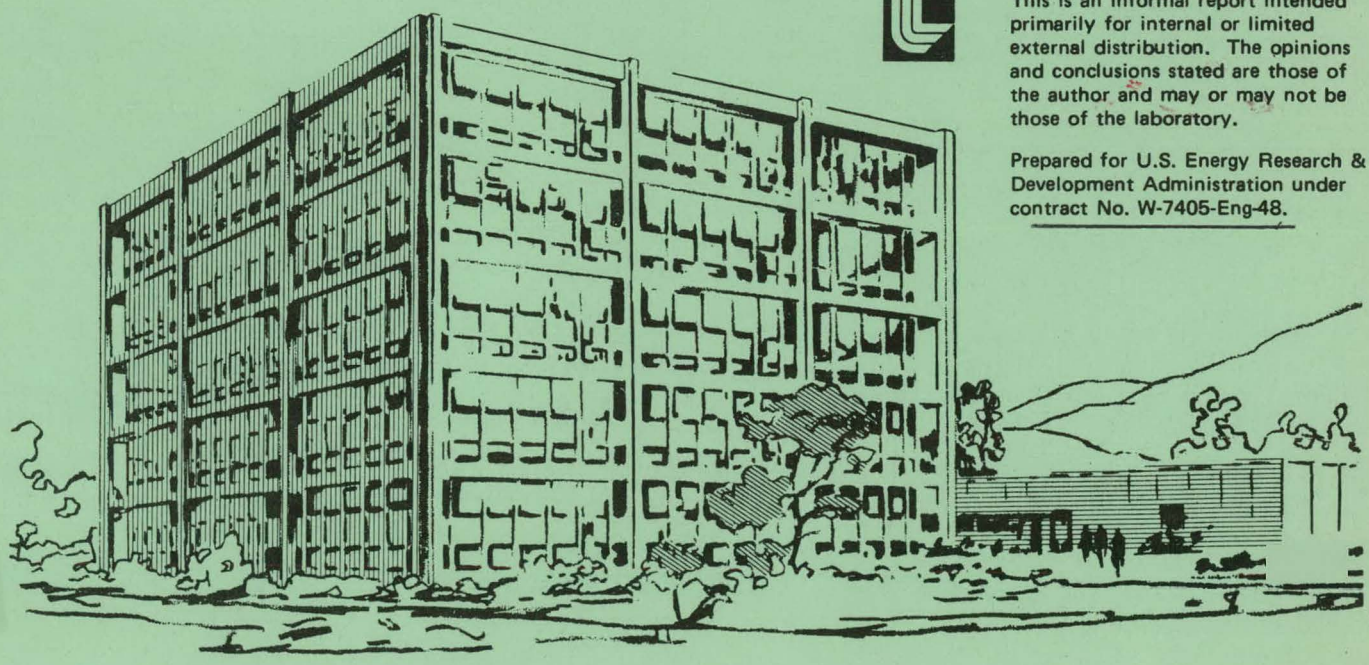

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INTRODUCTION

Pesticide use at the Lawrence Livermore Laboratory (LLL) is not heavy, but over the years has been highly diverse and has included approximately 35 herbicides, insecticides, and fungicides. This diversity has been gradually reduced in part as a result of the restrictions on the use of persistent pesticides, especially chlorinated hydrocarbons.

In the past 2 years, environmental monitoring of effluents from the Laboratory grounds has been extended to include pesticide residues.[1] Surface waters drain at the northwest corner of the site, and quarterly samples of effluent are taken at this point and assayed for free pesticides. The pesticides used at LLL during 1974-1975 were the following:

Bromacil	2,4-D
Chlordane	2,4-D butoxyethyl ester
Dicofol	Amitrole
Diuron	Amizine
Folpet	Arsenicals
Malathion	Benefin
Simazine	Carbamates

METHODS

General

Sample-preparation techniques have, during the past 2 years, evolved to a point where they are similar to the procedures used for such samples by the U.S. Environmental Protection Agency (EPA) laboratories. The EPA methods are described in Ref. 2, and current methods used at LLL will be detailed in a future report. The 1975 quarterly samples described here differ somewhat from one another in the methods used for collection, extraction, concentration, and cleanup, and thus can be expected to show varying quantities of nonpesticide organic materials.

Sampling

In general, effluent samples are collected in 1-gal glass bottles with Teflon-lined caps and are refrigerated until they can be extracted with an organic solvent.*

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research and Development Administration to the exclusion of others that may be suitable.

Attempts are made to sample runoff from the first heavy rain, though samples of streambed soil have been taken in dry quarters.

Sample Extraction and Concentration

At the time the sample is extracted, a water blank is simultaneously extracted by identical procedures. Several solvent systems may be used for the extraction, resulting in differences in organic compounds coextracted with the pesticide residues and possibly introducing interfering peaks in the gas-chromatography analysis. A mixture of hexane and ethyl ether is presently favored as coextracting fewer contaminants than the mixture of hexane and benzene used earlier.

After the extraction, a column-chromatography cleanup procedure is employed if the extract is expected to be grossly contaminated (e.g., a soil sample). Sodium sulfate and Florisil columns have been used to selectively adsorb such interfering compounds as fats, waxes, and coloring matter. Considerable losses of certain pesticides have, however, been reported.[3]

After the (optional) cleanup procedure, the extract is concentrated to 5 ml in a Kuderna Danish evaporator and finally further evaporated over a water bath to 1 ml; it is then ready for analysis. Variations from these procedures will be noted in the description of the samples.

Description of Quarterly Samples, 1975

The samples collected in 1975 were given letter designations, as described below.

First Quarter (January-March 1975)

A. A total of 12 liters of water and sediment, collected during the first quarter in plastic containers, was filtered to separate water and sediment. The glass-fiber filter paper and 2.2 g of sediment were extracted with 300 ml of 9:1 hexane-benzene and concentrated to 1 ml in a current of air.

B. The 12 liters of filtrate from A was extracted with 9:1 hexane-benzene and evaporated to 1 ml in a current of air.

C. Deionized water blank treated as B.

Second Quarter (April-June 1975)

D. A sample of soil collected during the second quarter and weighing 640 g was extracted with 9:1 hexane-benzene. The extract underwent Florisil-column cleanup with two elutions: 6% ethyl ether in hexane and 15% ethyl ether in hexane. The first fraction was lost through breakage, but the second fraction (15% ether) was saved.

Third Quarter (July-September 1975)

E. A total of 9.5 liters of drainage water was collected in glass bottles with Teflon caps and extracted with 9:1 hexane-benzene. The extract was concentrated to 1 ml.

Fourth Quarter (October-December 1975)

F. A sample consisting of 3 liters of drain water was collected in a glass bottle with a Teflon cap, extracted with hexane-ethyl ether, column chromatographed on sodium sulfate, and evaporated to 1 ml.*

G. The blank consisted of 3 liters of deionized water, treated similarly to sample F.

Additional blanks for all samples were available but not needed.

Analytical Standards

Analytical standards were obtained from the EPA and included malathion, chlordane, dicofol, folpet, bromacil, and diuron. Stock solutions in hexane at a concentration of 1000 ppm were prepared and kept refrigerated. Working standards were prepared by diluting stock solutions with hexane when needed and were then kept only a few days.

Controls

Concentrated extracts as well as several mixed standards were each divided into two portions, one of which was retained for analysis at LLL and the other submitted to the LFE Environmental Analysis Laboratory in Richmond, California, an EPA-certified laboratory. The EPA standards were supplied to LFE in order to provide a common reference point. Analyses at LFE were based entirely on gas chromatography using electron-capture detection.

Analytical Procedures

Analyses at LLL were performed with a Finnigan model 3000D gas chromatograph-mass spectrometer (GC/MS) system with a 1.5-m glass column packed with 3% OV-210 on 80/100-mesh Supelcoport. With some exceptions, noted below, most of the organic pesticides used during the past 2 years are analyzable on such columns. Sample volumes of between 1 and 2 microliters were injected.

The extracts were analyzed in the following two ways:

1. Each sample was separately analyzed for each of the pesticides for which standards were available, optimizing the GC/MS conditions with respect to separation and sensitivity for a single compound. Characteristic ion fragments were monitored as far

*Work performed during a visit at the EPA laboratory in Alameda, California.

as possible to avoid interferences by coextracted organic matter with similar gas-chromatography retention times. The upper limits quoted for these compounds in the concentrated extracts are based on the criteria of fragment intensity and gas-chromatographic retention time. The total-ion-current chromatogram was used to quantitate the material relative to the working standard.

2. Each sample was run conventionally--that is, by temperature-programmed gas chromatography with ion-current monitoring from 88 amu (just above the solvent spectrum) to 500 amu. Mass spectra were obtained for all peaks in the chromatogram and checked for expected pesticide spectra, including (but not limited to) those analyzed as described in item 1 above.

The analytical sensitivities for limited mass monitoring are given in Table 1.

Table 1. Analytical sensitivities for limited mass monitoring.

Pesticide	Mass range monitored (amu)	Limit of detection[a] (ng)
Bromacil	205-207	20
Chlordane	94-105	<10
Dicofol	246-256	40
Diuron	185-200	5
Folpet	117-133	<15
Malathion	118-174	<10

[a]The limit of detection varies with the degree and type of contamination of the extract. For example, in the case of a heavily contaminated sample a low concentration may be detectable for a particular pesticide if the mass fragments of the contaminant do not lie within the mass range being monitored.

ANALYTICAL RESULTS

In all of the sample extracts, the pesticides listed above, if present, were at concentrations lower than our limits of detection. Table 2 shows the calculated upper limits to the concentration in the original samples, assuming complete extraction except where noted.

A summary of the results obtained by the LFE Environmental Analysis Laboratory is shown in Table 3. The greater sensitivity evinced in the data of Table 3 results from the use of electron-capture detection in the gas-chromatography analysis.

The LFE Environmental Analysis Laboratory reported that the sample extracts had heavy contamination peaks that masked the pesticide peaks. However, only one of their results is in disagreement with those of LLL; this is the high level of diuron reported in sample A. Using similar chromatographic conditions, the sample extract was repeatedly analyzed at LLL while monitoring the characteristic diuron mass fragments. None was detectable at the diuron chromatographic retention time, although a very considerable contaminant peak was present at this time. The high diuron concentration reported

Table 2. Calculated upper limits to pesticide concentrations in LLL storm-drain water.

Pesticide	Concentration (ppb) in sample						
	A[b]	B	C[c]	D[d]	E	F	G[e]
Bromacil	9,100	1.7	--	54	2.2	7	--
Chlordane	4,500	0.8	--	26	1.1	3.5	--
Dicofol	18,000	3.2	--	116	4.3	14	--
Diuron	2,300	0.4	--	16	0.5	2	--
Folpet	6,800	1.2	--	42	1.6	5	--
Malathion	4,500	0.8	--	26	1.1	3	--

[a]See pages 2 and 3 for description of samples.

[b]Concentration in sediment. The high limits here reflect the small sample (2.2 g) and the resultant low concentration factor.

[c]Blank for sample B.

[d]These results reflect the loss of half the sample extract.

[e]Blank for sample F.

(10,500 ppb in the extract) by the LFE Environmental Analysis Laboratory must be attributed principally to this unresolved background.

A summary of the results obtained by the LFE Environmental Analysis Laboratory is shown in Table 3. The greater sensitivity evident in the data of Table 3 results from the use of electron-capture detection in the gas-chromatography analysis.

Table 3. Pesticide concentrations in LLL storm-drain water.[a]

Pesticide	Concentration (ppb) in sample[b,c]						
	A[d]	B	C[e]	D	E	F	G
Bromacil	5,900	0.50	0.4	N.D.	--	--	--
Chlordane	270	--	--	0.5	--	0.2	--
Dicofol	--	--	0.03	0.5	0.14	--	--
Diuron	10,500	N.D.	N.D.	N.D.	N.D.	N.D.	N.D
Folpet	6,400	--	0.2	--	--	--	--
Malathion	--	0.03	--	1.3	--	--	--
Carbaryl	--	--	--	--	--	--	--
2,4-D	--	--	--	--	--	--	--

[a]Results obtained by the LFE Environmental Analysis Laboratory.

[b]See pages 2 and 3 for description of samples.

[c]N.D. = none detected.

[d]These results reflect the low concentration factor due to a small sample (2.2 g) as well as the high contaminant background in the sediment.

[e]This is a deionized water blank and thus gives some indication of the detection limit.

Two additional samples, consisting of known mixtures, were submitted to the LFE Environmental Analysis Laboratory. The results are presented in Table 4 to give an indication of the accuracy that can be expected under favorable conditions.

Table 4. Blind analysis of standard mixtures.

Pesticide	Known concentration (ng/µl)	LFE analysis (ng/µl)	Deviation (%)
	Sample x		
Chlordane	9.18	7.8	-15
Carbaryl	12.76	--	--
Bromacil	15.49	50	+223
Dicofol	21.04	20	-5
Malathion	31.06	34	+9
	Sample y		
Chlordane	36.74	58	+58
Carbaryl	51.04	--	--
Diuron	53.48	140	-162
Folpet	80.62	77	-4
2,4-D	79.81	170	+113

The rather erratic results on the uncontaminated mixed standard samples (Table 4) indicate the difficulty of optimizing gas-chromatography conditions for separating a diverse mixture of pesticides. Furthermore, electron-capture detection, though highly sensitive to molecular species containing electronegative atoms, is relatively nonspecific and thus more subject to interfering contaminants than is the mass spectrometer.

OTHER COMPOUNDS

A mass spectrum was obtained of each peak of the temperature-programmed gas chromatogram of each quarterly sample. These were inspected for ion fragments characteristic of the pesticide residues likely to be present. There were no fragments of the following m/e in any of the mass spectra:

201 amu (simazine)
Clusters at 290, 324, 358 amu (PCBs)
Clusters at 252, 286, 320 amu (chlorodioxins)
235 amu (DDT)
246 amu (DDE)
144 amu (carbaryl)

It will be noted that a number of the materials on the LLL list have not been discussed. Because of the changing pattern of pesticide use at LLL, several pesticides for which standards could not be obtained came into use. These include amitrole and amizine (these are not expected to be used again), benefin, and 2,4-D ester. Such pesticides as the carbamates, which are completely degraded in the environment in 4 to 8 weeks, were believed not to present an important residue problem. The simazine analyses are qualitative only because the poor solubility rendered the standards unreliable.

UNRESOLVED PROBLEMS

A number of additional unresolved problems may be pointed out. Some of these are to a degree common to all environmental pesticide analyses.

1. Analyses are for free pesticides and do not in general include degradation products or pesticides chemically bound to other species.

2. Efficiencies of recovery for the various pesticides through the extractions and cleanup are not known. Though this can be expected to vary from compound to compound and from one sample to another because of differences in sampling and handling, recoveries approaching 100% are possible.[4]

3. There are no quantitative data on the total quarterly or annual runoff at LLL, which precludes any evaluation of pesticide mass balance.

4. No analysis has been made of influent pesticides that may have been carried onto the site by air or groundwater from other sources.

CONCLUSION

Runoff-water samples for the first, third, and fourth quarters of 1975 were analyzed for pesticide residues at LLL and independently by the LFE Environmental Analysis Laboratories. For the compounds analyzed, upper limits to possible contamination were placed conservatively at the low parts-per-billion level. In addition, soil samples were also analyzed.

Future work will continue to include quarterly sampling and will be broadened in scope to include quantitative analysis of a larger number of compounds. A study of recovery efficiency is planned. Because of the high backgrounds on soil samples together with the uncertainties introduced by the cleanup procedures, there is little hope of evaluating the distribution of a complex mixture of pesticides among the aqueous and solid phases in a drainage sample. No further sampling of soil from the streambed is therefore contemplated.

REFERENCES

1. Hazards Control Progress Report No. 50, Lawrence Livermore Laboratory, Rept. UCRL-50007-75-1 (1975), p. 35.

2. J. F. Thompson, Ed., Analysis of Pesticide Residues in Human and Environmental Samples, U.S. Environmental Protection Agency, Washington, D.C. (1974).

3. G. Yip, J. Chromat. Sci. 13, 225 (1975).

4. J. W. Eichelberger and J. J. Lichtenberg, Envir. Sci. Technol. 5, 541 (1971).

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