

# **TENSION LYSIMETERS: MONITORING OF PESTICIDES IN SOIL WATER**

by

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## Abstract

The Pesticide Contamination Prevention Act (PCPA) of 1985 was added to the Food and Agricultural Code of the State of California effective January 1, 1986. The PCPA requires the California Department of Food and Agriculture (CDFA) to monitor soil and ground water for residues of pesticides determined to have the potential to pollute ground water resources. Monitoring practices currently employed by CDFA includes the collection of ground water samples from wells and the extraction of soil core samples from the soil profile. The latter process uses specially constructed equipment necessary in obtaining non-contaminated soil samples.

If as a result of legal agricultural use, a pesticide is recovered from depths greater than eight feet (or below the greatest depth of the soil microbial or root zones if either exceeds the eight foot depth), then the PCPA requires that the pesticide be evaluated as a potential threat to pollute ground water. In evaluating the potential threat to ground water, knowledge of the distribution of the pesticide residue is important. However, soil profile distribution as determined by whole soil extraction does not distinguish between residues dissolved in water and those adsorbed to soil particles. Pesticide residues dissolved in soil water are readily available for further transport in water from irrigation and rainfall drainage and therefore pose a greater threat to ground water than pesticides residues adsorbed onto soil solids.

Monitoring pesticide loads in soil water was the primary objective of the described study. Tension lysimeters were used to extract soil water samples from plots treated with eight pesticides. Drainage waters from six post-application irrigations were evaluated for residues. Procedures for the construction, use and installation of the tension lysimeters are documented.

Results indicate that soil water monitoring by tension lysimeters offers several advantages over whole soil extraction procedures. These advantages include savings in labor costs, supplies, equipment and the potential for repetitive use of the lysimeters over several seasons. A cost analysis is presented for a monitoring scenario that compares soil sampling procedures. Estimates suggest that use of lysimeters may cut the costs of soil monitoring projects in half. From a qualitative view, soil sampling strategies emphasizing the collection of soil water are more representative of actual pesticide loadings associated with leaching processes and are less destructive to experimental plots than drilling rigs. Soil water samples are less prone to exhibit analytical anomalies such as matrix interference problems and pesticide recoveries are often better than those associated with standard soil core samples. Statistically derived functions can be developed that describe the average loads of pesticides migrating past a set point in the soil such as the root zone depth and eight foot limits defined in the PCPA.

A comparison is made between the lysimeter study results and several pesticide leaching indices including Jury's Behavior

Assessment Model (BAM) and Rao's Attenuation Models for evaluating pesticide mobility. Spearman's  $r$  Tests of the resulting lysimeter rankings show a significant relation to those produced by the BAM using Specific Numerical Values (SNV) established by the CDFA. This significant correlation suggests that the methodologies employed by the CDFA in establishing SNV criteria has some validity as measured by the pesticide rankings developing from this study. A historical comparison between SNVs currently established by the CDFA and earlier attempts at assigning these values (within and outside the CDFA) show that those most closely associated with the empirical data presented here are the SNVs established by methods now in use by the CDFA.

Studies using tension lysimeters should be pursued for monitoring projects involving the PCPA. Tension lysimeters will not be successful in all situations, i.e. cracking clay soils. However, they should be of great benefit in most other soils especially those with a high sand content which are most often associated with incidences of groundwater contamination in California particularly in the San Joaquin Valley and the Santa Ana Basin.

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### Disclaimer

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## INTRODUCTION

Ground water contamination by pesticides has developed into a topic of major concern in California. Most incidences of contamination are from the San Joaquin Valley and specifically those areas on the eastern side of the Valley in association with mostly sandy soils formed from recent alluvial deposits. These areas are intensively cultivated to a wide-ranging spectrum of crops. Associated with these crops is an inseparable and diverse array of pests that is controlled through the use of pesticides to lessen their economic impact on agricultural productivity. Some of these pesticides have had complementary negative effects on the environment. In California, 21 pesticides have been positively identified in ground water samples (Brown et al., 1986; Ames et al., 1987; Cardozo et al., 1988). Although the sources of these contaminants have not necessarily been established (legal agricultural use; point vs non-point sources, etc), these pesticides are composed mainly of soil applied herbicides and nematicides/insecticides.

The Pesticide Contamination Prevention Act (PCPA) of 1985 (Connelly, 1985) has provided criteria to identify pesticides with a potential to pollute ground water and has mandated the monitoring of these pesticides contaminants in soil and ground water. Monitoring techniques employed by the Environmental Hazards Assessment Program (EHAP) have been limited to well water sampling and soil coring procedures which have been described in other in-house reports (Zalkin et al., 1984; Sava, 1986). Well

water monitoring has been fruitful in establishing spatial boundaries on the geographic extent of localized contaminated areas. Undisturbed soil core sampling methods utilizing the Mobile<sup>R</sup> drill rig have contributed to EHAP's sampling faculties enhancing the development of databases on pesticide contaminants and their distributions. These databases include the results of investigations conducted in areas of high use of specific pesticides, principally on active farms with well-documented histories of pesticide use (Duncan and Oshima, 1985; Marade and Segawa, 1988; Segawa et al., 1986; Troiano et al., 1987; Troiano and Segawa, 1987).

The incorporation of the PCPA in the Food and Agricultural Code has provided the impetus for increased sampling of soil and ground water. Given the large number of pesticides which are examined by the PCPA review process and the associated costs (manpower, laboratory fees, etc.), other procedures for screening pesticides for their potential as ground water contaminants need to be addressed. These procedures are intended to be complementary to field monitoring activities that include soil coring and well water monitoring. The first of these procedures involves the use of models to predict the potential migrations of compounds based on chemical and physical parameters inherent to a compound under investigation and on the characteristics of the media (soil) to which it is applied. A multitude of models exist and include PRZM (Carsel et al., 1984), Rao's (1985) Attenuation

Factor Model and the Jury et al. (1983, 1984a,b,c) Behavior Assessment Model.

The primary focus of this study is to evaluate an alternative approach to soil coring procedures for monitoring pesticide movement under field conditions. The study described emphasizes the monitoring and detection aspects of pesticides in the soil environment through the use of ceramic-tipped soil tension lysimeters. The major advantage for the use of tension lysimeters is that of monitoring field drainage waters, the principal agricultural component responsible for pesticide transport to ground water.

With the exception of the construction of the ceramic tips proper (clay mixtures, molding, firing, and testing), all facets of their assembly, installation, and their eventual linkage into a cohesive sampling system are discussed. A detailed description of the construction and installation of the tension lysimeters along with information on plot construction and irrigation is found in Appendix 1. The vacuum system which provided the necessary pressure drop relative to atmospheric conditions is also discussed therein. Information describing the costs involved in constructing the sampling system is included. A hypothetical monitoring project is developed in Appendix 2 to illustrate potential savings in labor, supplies and equipment that may be realized by the use of the techniques described.

## PROCEDURES

### Soil Water Sampling System

The procedures used in this portion of the study attempted to follow as closely as possible those suggested by Helling and Dragun (1981). Their protocol has been excerpted from an Association of Official Analytical Chemist symposium targeting the needs of the EPA for guidelines for the registration of pesticides and other toxic substances. Deviations from their protocol were adopted principally to minimize laboratory costs for analyses or to utilize existing plots which were available at the start of this project.

Tension lysimeters were installed in 24 non-cropped basins (6.1 m x 4.3 m dimensions). The plots received 6 consecutive irrigations (7.6 cm water application rates) at weekly intervals. Soil water samples were extracted intermittently from the plots over a 48-hour sampling period following each irrigation. The samples were later shipped to a contract laboratory in Sacramento for residue analysis. The drainage water sampling system consisted of four tension lysimeters installed at a 1.07 m depth within each plot. The four lysimeter sampling tubes were connected to a single collection vessel and a common vacuum supply system running under negative pressures of 400-500 KPa (304-380 mm Hg). The lysimeter-collection vessel assembly is shown in Figure 1.

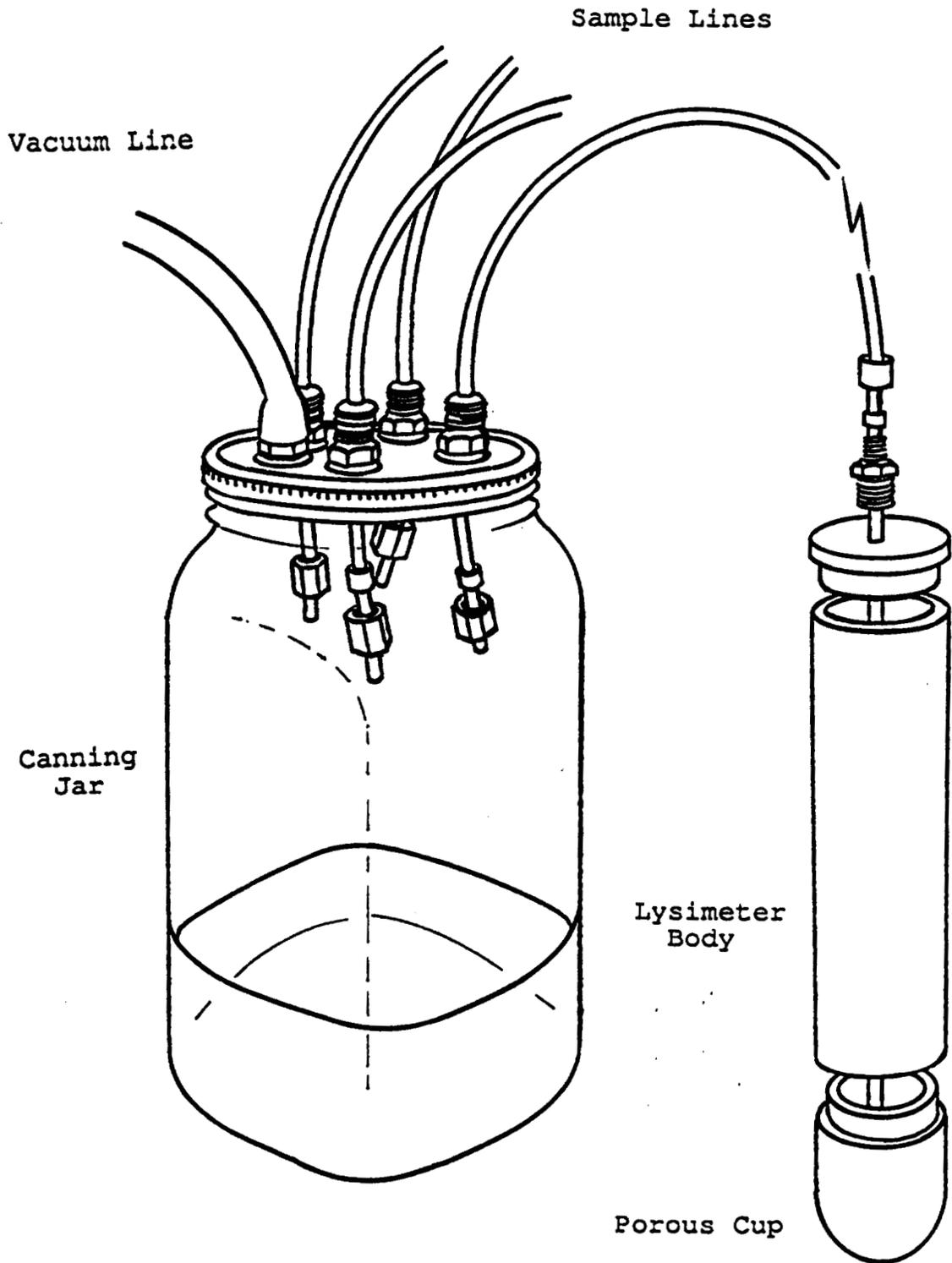


Figure 1. Tension lysimeter and sample collection assembly.

## Irrigation Practices

The frequency and amount of irrigation and rainfall water applied are critical factors that impact pesticide migration. These water inputs can be monitored closely in the field under experimental circumstances or they can be estimated from common meteorological records on rainfall and evapotranspiration. In the present study, 7.6 cm deep irrigations were applied to each basin at weekly intervals for 6 weeks (total water applied = 45.7 cm). This 45.7 cm total was selected as an intermediate level of water to that delivered by rainfall or used in evapotranspiration, especially in the Central Valley and Santa Ana Basins (Anonymous, 1986). Weekly irrigation intervals were chosen because this time span would ensure complete drainage of the plots between irrigations and to allow time for the processing of samples (splitting, labelling, etc.). The actual soil water sampling start time was five hours after irrigation. This delay was based on soil survey information identifying the plots as falling under a Hanford Series soil mapping unit with an associated percolation rate of 5.1-15.2 cm per hour (Knecht, 1971). At the maximum rate of percolation the water front would be expected to arrive at the lysimeter depth (1.07 m) in 7 hours. Percolation rates were monitored with a neutron probe in 6 of the 24 plots. Results from two of the plots suggested that the percolation rates were somewhat faster than 15.2 cm per hour. Accordingly, the start time of sampling was set to 6 hours post-irrigation to ensure that all draining waters would be sampled. All plots were

irrigated twice before the start of the experiment to ensure field capacity was reached within and between the plots.

Irrigation of all plots was accomplished within a 1 1/2 hour time span. Two cubic meters (7.6 cm depth equivalent) of water was delivered to each plot at each irrigation event. Irrigation commenced between 7:00 and 7:30 DST in the morning with the water sampling start-up time of 1:00 to 1:30 PM DST. Sampling was conducted for a period of 48 hours measured from the 1:00 PM DST start time. Sampling jars were checked periodically during the day. The collection jars were isolated from the vacuum source by use of a clamp across the latex tubing that connected the collection jar to the PVC manifold.

#### Pesticide Application

Eight candidate pesticides were selected based on several factors including the half-lives of the compounds, chemical classification, formulation and available historical information of associations as groundwater contaminants. The compounds included alachlor, simazine, atrazine, oxamyl, carbofuran, aldicarb, diazinon and malathion. Additional information on these compounds is listed in Table 1. The 24 basins were divided into three blocks of eight plots per block (see plot diagram, Figure 2). Each pesticide was randomly assigned to one basin within each block (three replicate treatments per pesticide). The rates of application for all pesticides were 13.0 grams of active ingredient per basin (equivalent to 5 Kg a.i. per hectare).

Table 1. Formulation information on pesticides used in study.

Common Name	Trade Name	Formulation	Manufacturer
atrazine	Aatrex 9-0 <sup>R</sup>	85.5% water misc. granule	Ciba-Geigy
alachlor	Lasso <sup>R</sup>	45% emulsifiable conc.	Monsanto
aldicarb	Temik <sup>R</sup>	10% granule	UnionCarbide
carbofuran	Furadan <sup>R</sup>	40% emulsifiable conc.	FMC Corp
simazine	Princep <sup>R</sup>	80% wettable powder	Ciba-Geigy
oxamyl	Oxamyl <sup>R</sup>	10% granule	E.I. DuPont
malathion	Malathion <sup>R</sup>	25% emulsifiable conc.	Ortho
diazinon	Spectracide <sup>R</sup>	25% emulsifiable conc.	Ciba-Geigy

# Pesticide Plot Layout

North →

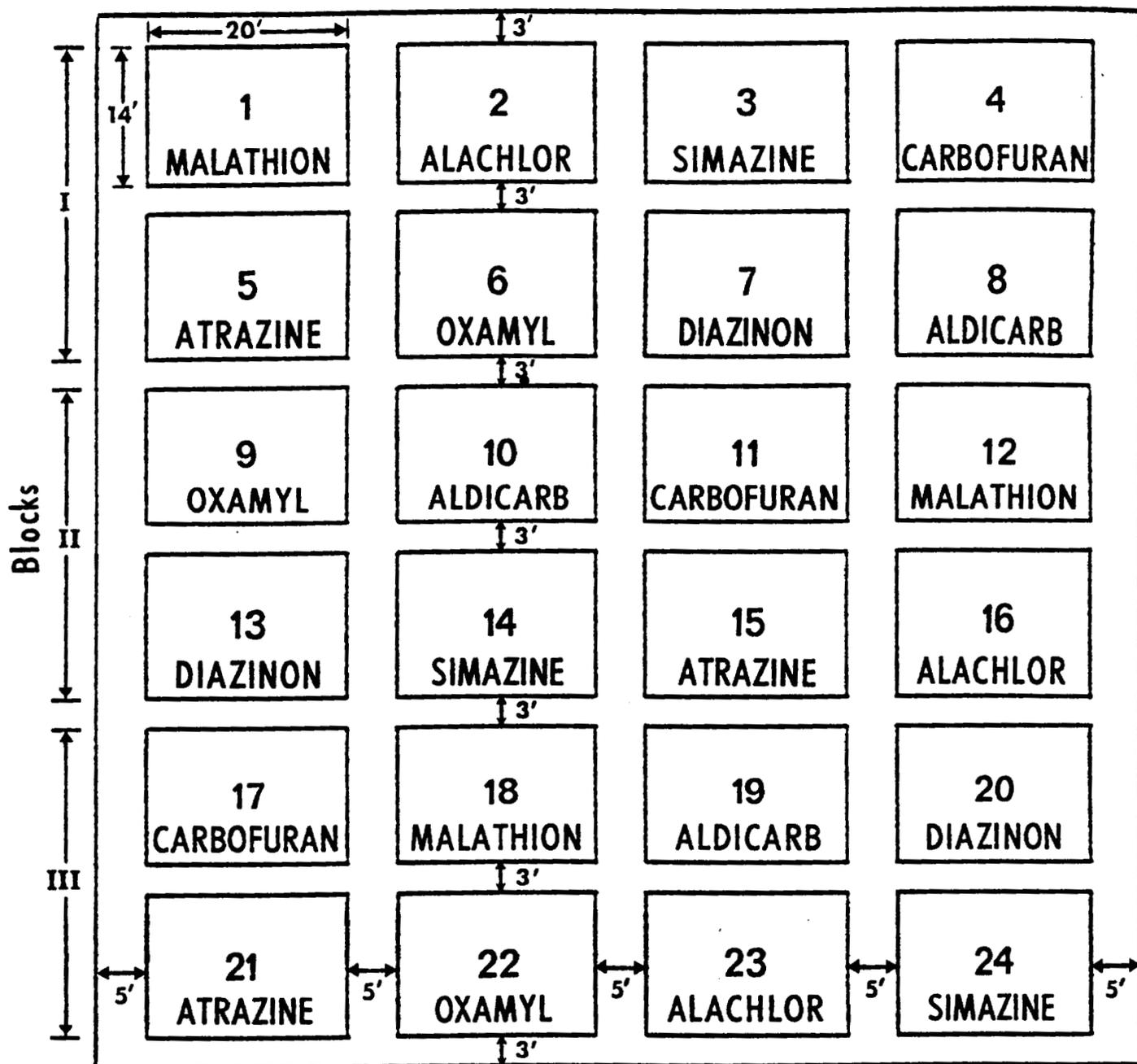


Figure 2

Atrazine was applied as a tracer to all 24 basins at the same rate. A potassium bromide tracer was also applied to each plot at a rate of 33.5 kgs/hectare of bromide. The tracers were used for comparative purposes as references for the remaining pesticides. Basins assigned the atrazine treatment received single aliquots of the compound.

Water miscible formulations were applied to the basins with a hand sprayer in 1.2 liters of water. The aldicarb, oxamyl and potassium bromide were applied in granular form with a hand crank spreader. All materials were applied using a serpentine technique across a plot followed by a similar procedure in a path perpendicular to the first. This was repeated until the loads were spent. All compounds were applied to the soil surface within a 2 1/2 hour period terminating at dusk. The following morning the compounds were rototilled into the basins to an approximate 3 in. depth. The basin floors were leveled off with bow rakes and the remainder of the day was spent in reassembling the soil water sampling system as previously described and in reinstalling the individual plot water distribution systems.

The first of six post-application irrigations was delivered the following morning. Soil water sampling started 5 hours after irrigation of the final plot. Clean two quart canning jars were mounted onto the sampler assembly (see Fig. 1). The assembled collection vessel was placed in a styrofoam ice chest and packed in ice immediately before sampling start time. Ice condition was checked periodically over the next 48 hours and repacked as

necessary. Sample collection was initiated by switching on a vacuum pump controlled by an electronic timer set to produce two equal interval (15 min.) on-off cycles per hour. Samples collected during this sampling period which approached the capacity of the jars were cutoff from the sampling process by means of a pinch clamp across the latex tubing connecting the jars to the vacuum manifold. At the end of 48 hours all sample jars were retrieved, labelled and transported to EHAP's Field 8C facility on the Citrus Experiment Station and placed in a cold box (36-38 F). Approximate sample volume data was estimated at the end of the experiment after retrieving unused liquid samples from the contract laboratory (see Appendix 3, Table A4.4). The samples were split when volumes were sufficient and transferred to one quart canning jars. Splitting of the sample involved filling a one quart jar to capacity which was earmarked for residue analysis. The remaining solution was also placed in a one quart jar and set aside for bromide analysis. Samples of less than one quart volume were used for pesticide analysis only. This procedure was used for each of the six irrigation/sampling periods.

### Soil Sampling

At the termination of the experiment soil samples were collected from each of the plots with Veihmeyer tubes to a depth of seven feet in one foot increments. A sampling site was selected within a two foot radius of each tension lysimeter position. Four equal depth sub-samples from each plot were combined in a one quart

canning jar and labelled. All sample jars were covered with aluminum foil and sealed with a ring and lid. The samples were later packed in dry ice and shipped to the contract laboratory in Sacramento for pesticide analysis. All samples (163 soil and 143 soil water) were analyzed for atrazine content and the appropriate companion pesticide. Bromide ion analysis on soil and soil water samples was conducted in EHAP'S lab facilities in Riverside as was soil texture analysis and pH. Soil texture analysis followed established EHAP procedures. Measurement of pH followed a technique described by Chapman and Pratt (1961) that utilizes a 2.5:1 water-soil suspension. An extract of this suspension recovered under vacuum through No. 2 Whatman filter paper was used for bromide analysis using a bromide ion probe (Orion<sup>R</sup>).

## RESULTS

### Laboratory Analysis and Quality Control

Residue levels of the various pesticides in the soil and liquid samples are presented in Appendices 3 and 4, respectively. Table A3.1 depicts soil values of atrazine determined for each depth with A3.2 showing the accompanying pesticide values for each plot as labelled. Values are placed corresponding to actual locations as shown in the plot diagram (Figure 2). Table A3.3 presents the bromide ion values determined for each of the 168 soil samples less a few missing values. Results of soil texture analysis are shown in Table A3.4. Tables A4.1, 2, and 3 of Appendix 4 display soil water sample values utilizing the order detailed above with the exception that concentrations found within each plot represent consecutive sampling periods (irrigations).

Several quality control problems were noted in the analyses performed by the contract laboratory, especially with regard to the handling of the soil samples. The soil samples were not homogenized prior to the extraction of a sub-sample to be used in residue analysis. Therefore, the degree to which the concentrations reported for each sample vary may be a reflection of the improper processing of each sample. A single data point reported may represent any portion of the one foot depth increment sample and any one of the four sub-samples taken from an individual plot. This scenario produces the worst case instance and has a realistically high probability of occurrence

since intact soil cores were discernable in sample jars retrieved from the contract laboratory. This potential effect on concentration variability may be somewhat dampened by the more uniform distribution of a pesticide after the six irrigations when the soil samples were collected. The contract laboratory reported significant matrix interference problems associated with the extraction procedures. This is most readily seen in soil and water concentrations shown for oxamyl (see Appendices, Tables A3.2 and A4.2). Reporting limits which are closely allied to the minimum detection limits ranged from <5 to <200 parts per billion (ppb). The reporting limits were markedly lower for malathion, diazinon, and aldicarb in soil water when compared to their counterparts in soil. The levels were 2.5 times lower in water (2 ppb) than in soil (5 ppb).

Recoveries from spiked samples reveal that additional problems were experienced in the laboratory with regard to the analytical procedures used for extraction and detection. Atrazine recoveries based on two spiked samples ranged from 54 to 128 percent. Recovery of atrazine varied between duplicate spikes and with the companion pesticide extracted. The precision of concentrations based on recoveries was not calculated due to insufficient spike replication.

Information on mean recoveries was ambiguous with respect to the media represented. This is readily seen in the percent recoveries of carbofuran and aldicarb presented in Table 2. Recoveries from soil water were 60% and 135% respectively for carbofuran and

Table 2. Recovery data reported by Enseco Laboratories.

Media	Pesticide	Spike 1 (ppb)	Spike 2 (ppb)	Spike Conc. (ppb)	Mean Recovery ( % )	Detection Limit (min.)
<u>Water</u>	malathion	8.4	---	10	84	2
	alachlor	11.0	11.0	10	110	5
	simazine	10.0	11.0	10	105	5
	carbofuran	4.0	8.0	10	60	5
	atrazine	----	----	--	---	-
	oxamyl	23.0	26.0	25	98	5
	diazinon	6.1	9.7	10	79	2
	aldicarb	73.0	62.0	50	135	2
<u>Soil</u>	malathion	180.0	190.0	200	92.5	5
	alachlor	78.0	230.0	200	77.0	5
	simazine	250.0	230.0	200	110.0	5
	carbofuran	220.0	350.0	200	131.0	5
	atrazine	-----	-----	---	-----	-
	oxamyl	-----	-----	---	-----	-
	diazinon	140.0	130.0	200	67.5	5
	aldicarb	23.0	11.0	50	34.0	5

---- denotes missing values

aldicarb. Extraction from soil samples had a decidedly opposite effect in that aldicarb recoveries were extremely low (34%) while carbofuran was overestimated (131%). These recoveries are estimated from 2 spiked samples each for soil and water. Water spikes used tap water for the matrix spike while the soil spikes used Hanford series soil samples collected from the field plots prior to the start of the experiment. There were problems referred to in contract laboratory reports as matrix interferences. This resulted in abnormal increases in the reporting limits for soil samples. Reporting limits as high as 200 ppb (oxamyl) were reported as developing from these interferences. Ten soil samples (6%) were reported with matrix inference problems when atrazine was the compound under investigation. Oxamyl values were questionable in eight of the 21 soil samples collected. Other compounds in this category listed by decreasing number of occurrences included carbofuran, diazinon and alachlor with 4, 1 and 1 problem soil samples, respectively. Soil water samples were relatively trouble free with only 3 data points reported with matrix interferences. These were manifest in two water samples potentially containing alachlor and one from a diazinon plot.

### Bromide Analysis

#### Soils

Bromide levels in the surface foot of soil at the termination of the experiment were approximately 2 times greater than background

samples taken prior to the application of potassium bromide. Water extractable bromide decreased with the depth of the soil from which samples were collected. This is partially attributed to the lighter soil textures found at greater depths within the soil profile which affects water retention.

The distribution of bromide ion concentrations of the soil profile after the final irrigation was modelled using linear regression. The mean bromide concentrations of the 24 plots was regressed on the seven - 1 foot depth increments.  $\text{Log}_e$  transformations of the bromide means were also tested. Data used in the regressions and the results of fitting the models are presented in Table 3 and Figure 3. The transformed bromide values were found to have higher coefficients of determination ( $r^2$  values) accounting for a greater proportion of the variability in the data. Individual plot concentrations of bromide ion were highly variable (see Table A3.3).

#### Soil Water

Analysis of the soil water collected using the ceramic samplers revealed a tendency for the mean bromide concentrations to increase with successive irrigations. These data and the resultant linear equation derived are shown in Table 4 and Figure 4. The values shown in Table A4.3 present the individual sample bromide ion concentrations by irrigation. In the majority of the plots (14) no distinct peaks in bromide concentrations were seen. In several instances bromide ion concentrations were still

Table 3. Mean soil bromide concentrations and sand content at various depths within the soil profile.

Soil Depth (ft)	Ave. Bromide Concentration (ppm)	Log <sub>e</sub> Bromide Concentration (ppm)	Sand Content ( % )
1	4.200	1.44	56.5
2	1.850	0.62	69.2
3	2.450	0.90	65.0
4	1.950	0.67	71.8
5	1.100	0.10	75.9
6	1.250	0.22	84.0
7	0.925	-0.08	88.5
[Bromide] = exp (-0.22[depth] + 1.43)			r <sup>2</sup> = 0.82*
[Bromide] = exp (-0.07[% sand] + 3.85)			r <sup>2</sup> = 0.91*
* - denotes significance at p<.05			

# Soil Bromide

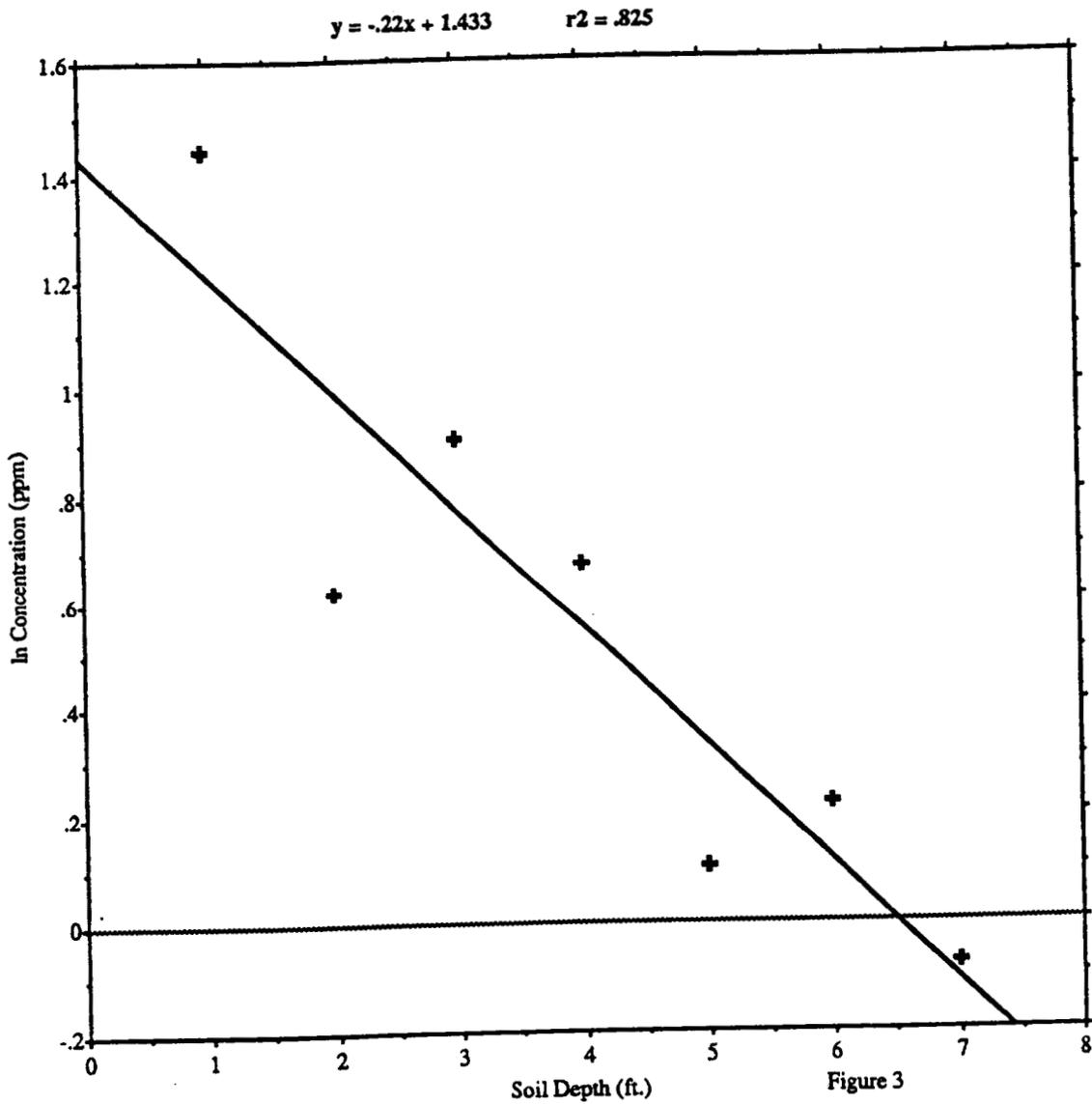


Figure 3. Mean distribution of bromide in soil profile.

Table 4. Mean bromide concentrations (ppm) in soil solutions over the six consecutive irrigations.

	Irrigation Number					
	1	2	3	4	5	6
Bromide Concentration (ppm)	4.95	7.27	9.15	9.08	12.93	14.36

# Soil Solution Bromide

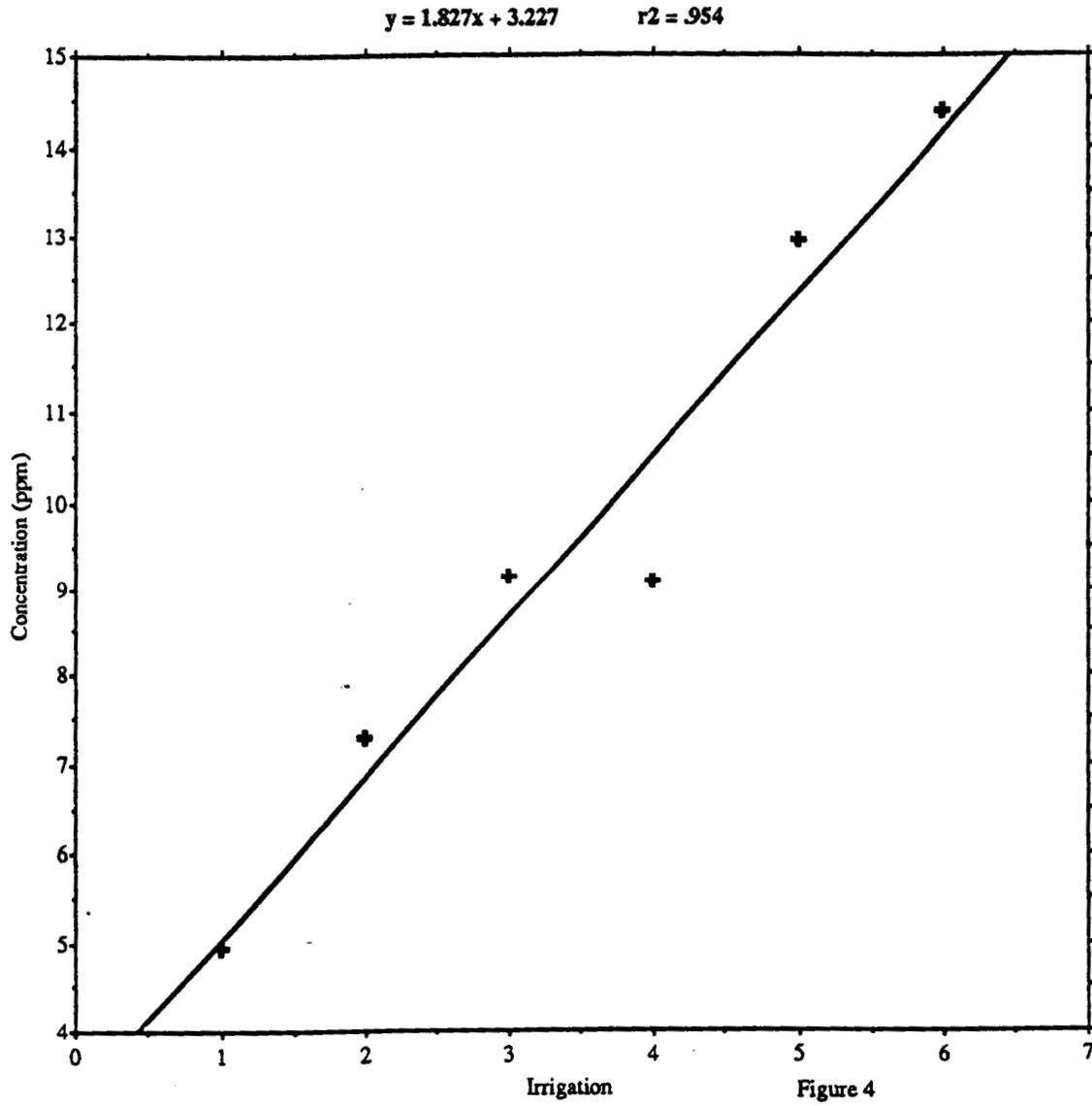


Figure 4. Mean distribution of bromide in soil water.

increasing at the end of the experiment. A few possibilities exist which may help explain this observation. First, there is evidence in existing literature on tension lysimeters that ceramic tips can alter solution constituents and must be cleaned before concentrations can be measured with confidence (Creasy and Dreiss, 1987; Grover and Lamborn, 1978; Neary and Tomassini, 1985). These studies have generally investigated inorganic ions including nitrate, bromide, and chloride. Second, since the potassium bromide was rototilled into the soil in its granular form, its limited distribution in the surface soil may have restricted its ability to move with the water front. The early irrigations had tendencies to infiltrate into the soil at a faster rate than later irrigations. These higher infiltration rates may have precluded the water from saturating the surface layer of soil diminishing its efficiency as a solvent for the available bromide crystals and affecting soil transport processes. The final and most plausible explanation for the variability in the bromide concentrations is the variability in soil tortuosity within the plots. This phenomenon and its effects on convective dispersion has been addressed by Butters et al. (1989). Their results are similar to those presented here, supporting the hypothesis the mean bromide concentration in soil water samples had yet to be reached given the net amount of water applied.

The first explanation implying that the affinity of ceramic samplers for bromide adsorption may be responsible for the

results observed is not considered to have much bearing in this case since the concentrations found in the extracted soil water samples at the first irrigation were substantially higher (mean = 5.6 +/- 4.2 ppm bromide) than bromide levels in irrigation water background samples taken at the beginning (1.61 ppm bromide) and at the end (1.45 ppm bromide) of the experiment. The first irrigation mean concentrations of bromide were also higher than that recorded from a composite sample consisting of soil water extracted from several plots during the testing of the sampling system. This composite sample was collected over the three pre-treatment irrigations and measured 1.78 ppm Br<sup>-</sup>.

## Pesticide Residues

### Soils

The soil concentrations of the pesticides covered a range of values. Table 5 depicts the average concentration of the three treatment replicates for each pesticide at each depth. Atrazine is an exception since the numbers corresponding to this compound are averaged over the 24 plots. Samples represented by reporting limits were treated as if they were zero values. Eighty-eight of the potential 163 soil atrazine values were below the reporting limits. One hundred twenty one of the remaining pesticide samples were also below their respective reporting limits. This resulted in a highly skewed (non-normal) distribution of the data. Transformation of the data was not a suitable solution for correction of this attribute. Statistical evaluation of the data

Table 5. Mean pesticide concentrations (ppb) in soil profile.

Pesticide	Soil Depth (ft)							Ave.
	1	2	3	4	5	6	7	
atrazine	344.18	36.38	34.84	22.83	4.19	3.69	6.52	64.66
carbofuran	34.00	22.00	27.00	6.67	1.67	N.D.*	N.D.	13.05
aldicarb	3.33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.48
diazinon	8.67	N.D.	N.D.	9.33	N.D.	N.D.	N.D.	2.57
alachlor	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
simazine	1.35	0.92	N.D.	N.D.	4.33	N.D.	N.D.	0.94
malathion	N.D.	N.D.	N.D.	N.D.	N.D.	1.97	10.00	1.71
oxamyl	6.03	N.D.	10.33	11.00	N.D.	N.D.	N.D.	3.91

\* - N.D. denotes no detection of pesticide

using Analysis of Variance was not appropriate. Regression Analysis was used to model the distribution of atrazine and carbofuran in the soil as was done previously with the bromide data.

Analysis of the atrazine data was similar to that of the bromide where the natural logarithm transformation of the atrazine data provided a better fit of the linear model. The carbofuran data contained "0" values which would require a constant value be added to all figures prior to transformation ( $\log_e$ ). This procedure was not appropriate given the low number (7) of points used to fit the model and unnecessary because of the relatively high coefficient of determination (84%) achieved with the linear regression of the untransformed data. In an effort to test for correlations between atrazine and soil texture, the pesticide data (see Table 5),  $\log_e$  transformed values for atrazine and untransformed for carbofuran, were regressed against the means in percent sand content for each depth shown in Table 3. The coefficients of determination ( $r^2$ ) for these regressions were markedly similar to those obtained in fitting the respective atrazine ( $\log_e$ ) and carbofuran data to soil depth. Figures 5 thru 8 graphically describe the results obtained for depth and percent sand content to atrazine and carbofuran values.

Soil concentrations of the remaining compounds were too scant to evaluate statistically. Malathion was peculiar in that residues in the soil were found only at the two greatest depths. However, these values were found to be completely related to occurrences

# Soil Atrazine

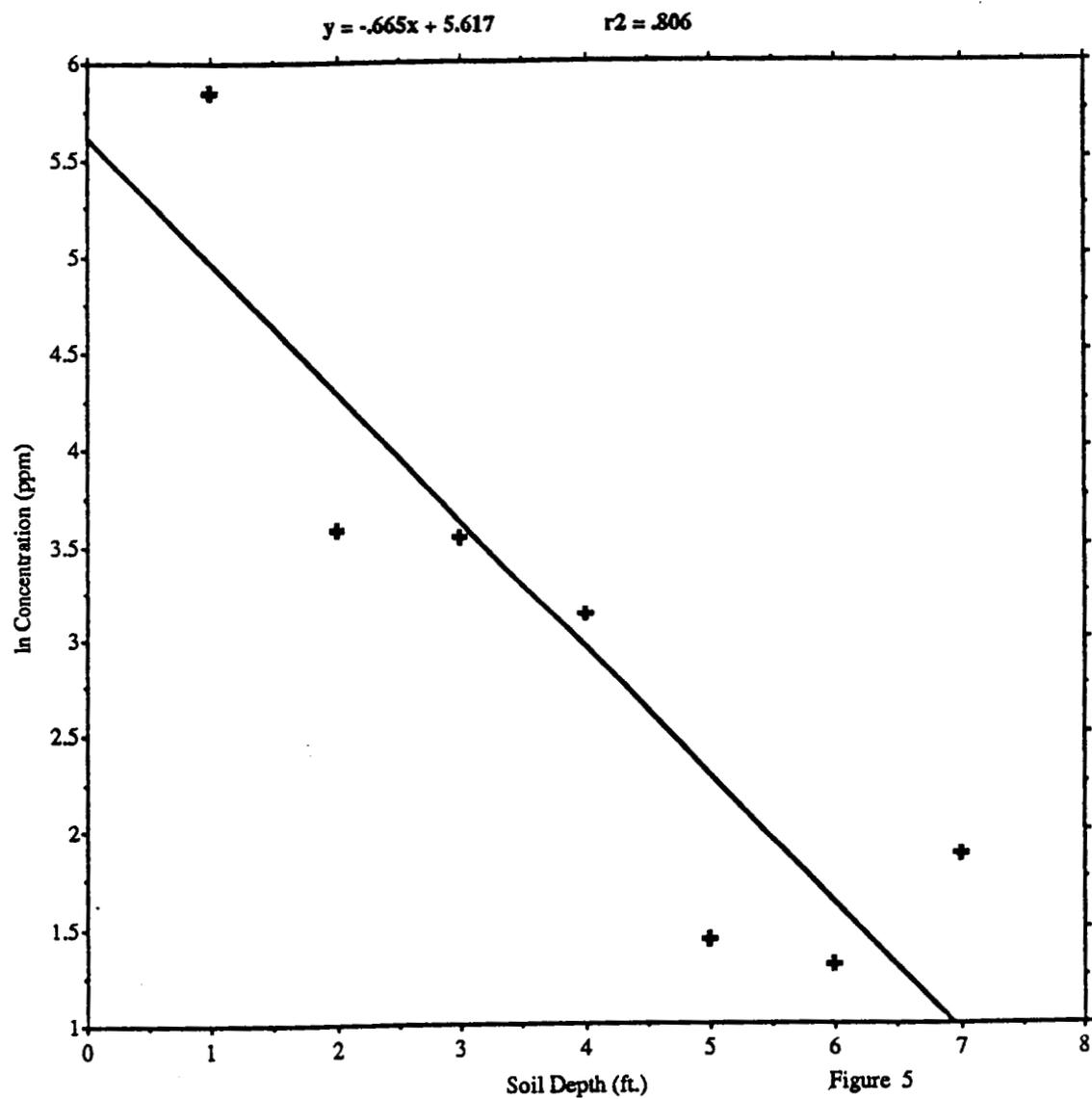


Figure 5. Mean distribution of atrazine in soil profile.

Soil Carbofuran

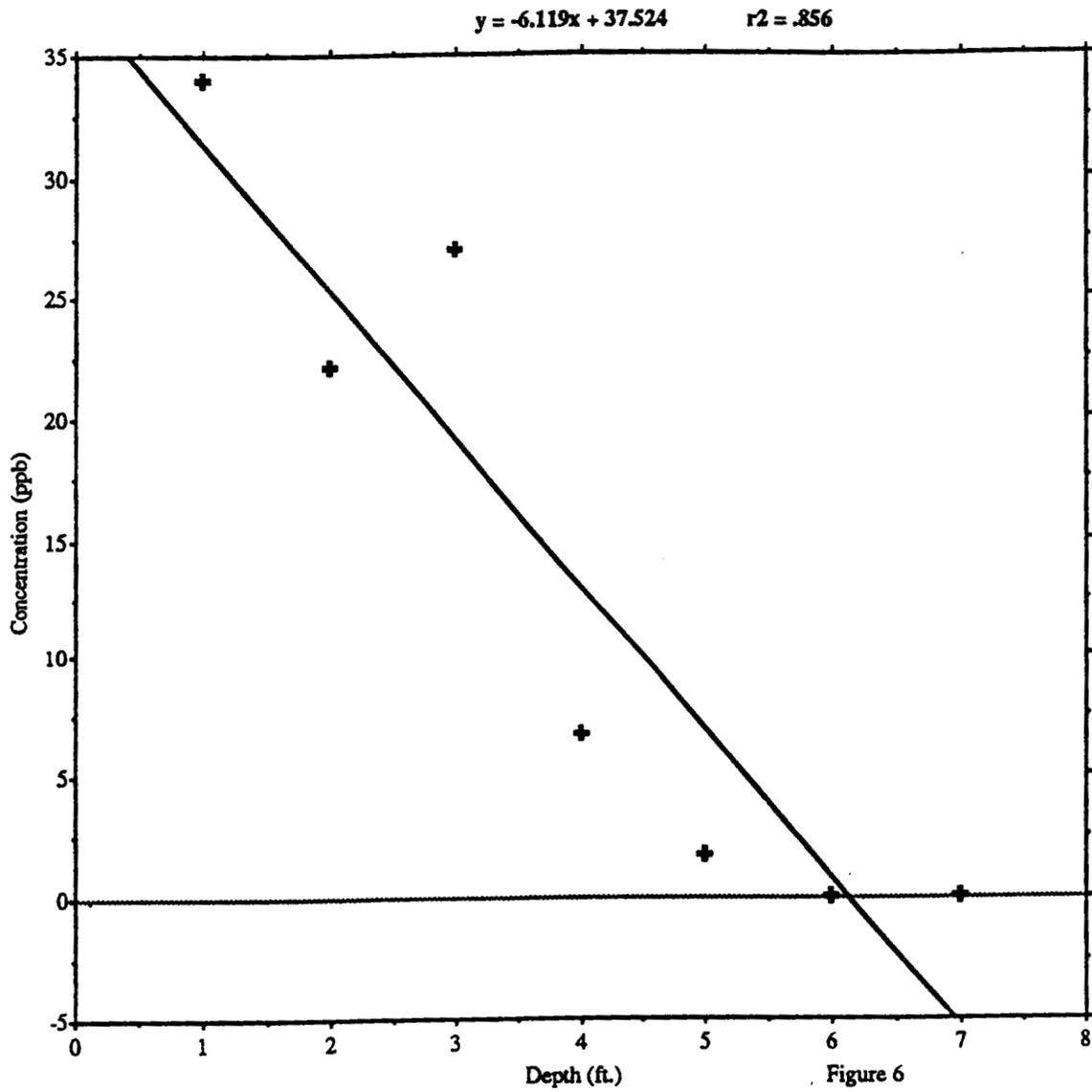


Figure 6. Mean distribution of carbofuran in soil profile.

Soil Atrazine

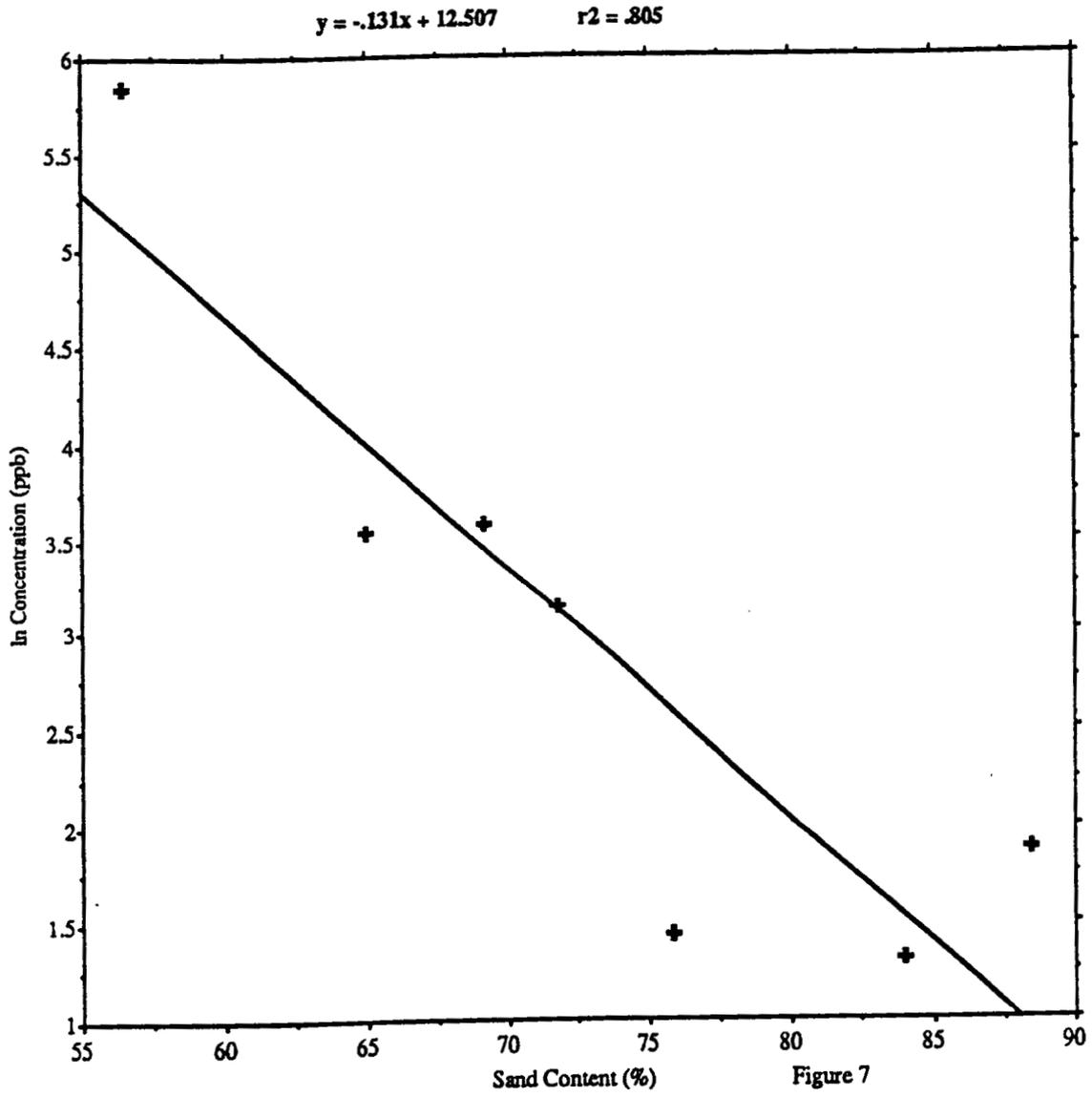


Figure 7. Correlation of mean atrazine levels with sand content.

# Soil Carbofuran

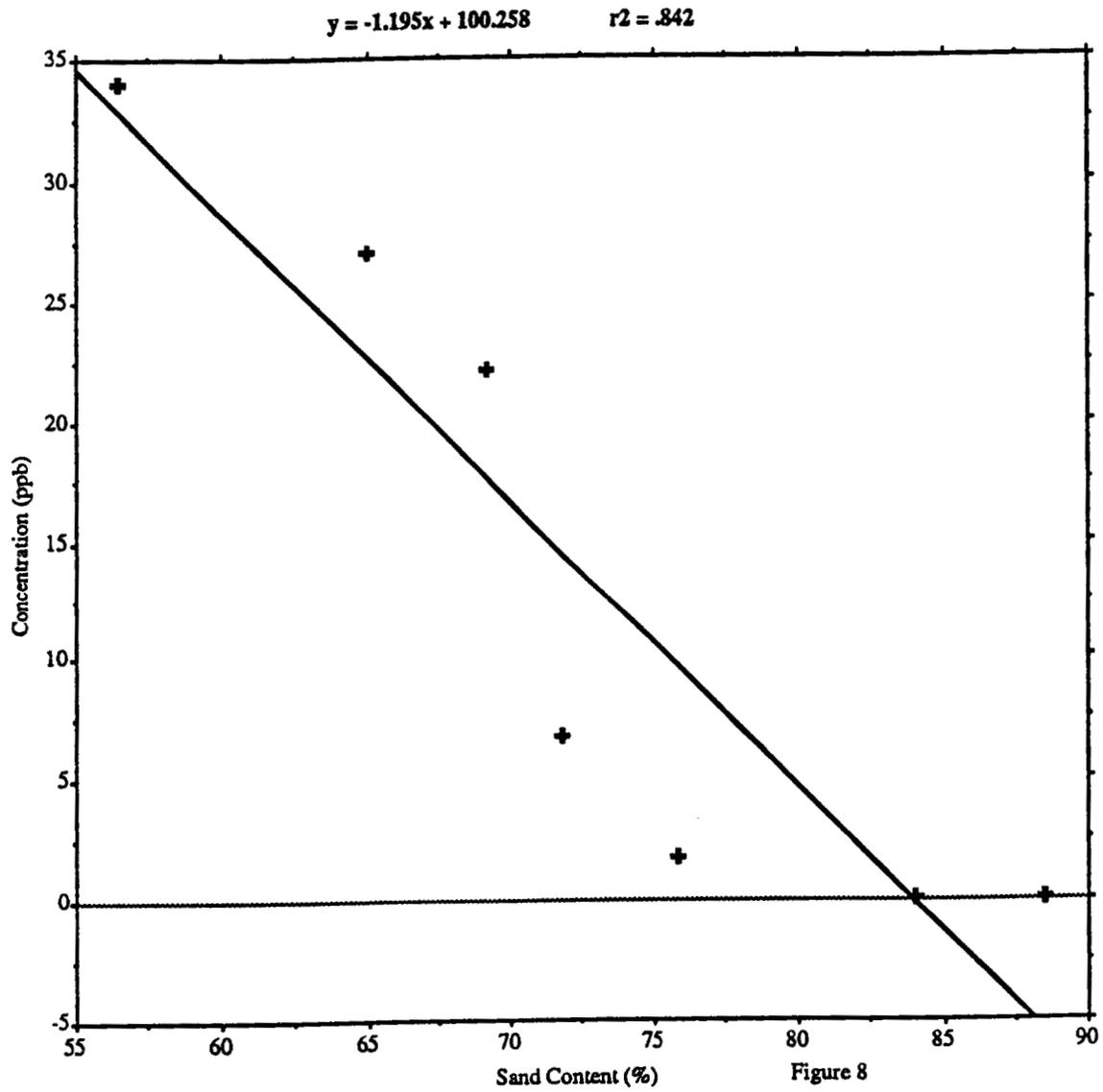


Figure 8. Correlation of mean carbofuran levels with sand content.

in one replicate only. None of the remaining samples proved positive for malathion. Alachlor was not detected in any soil samples. The remaining compounds were all detected in the surface foot of soil at mean concentrations ranging from 3.33 ppb (aldicarb) to 22.33 ppb (simazine). Of these, simazine was detected at the greatest class depth of 5 feet at an average concentration of 4.33 ppb. Oxamyl and diazinon were detected in the fourth soil increment sample at mean concentration of 11.00 and 9.33 ppb, respectively. Positive aldicarb findings were limited to 1 of 20 samples at a concentration of 10 ppb.

#### Soil Water

The soil water samples were processed for atrazine levels and the companion pesticide. The distributions of the data proved to be non-normal as with the soil samples. The data as a whole appeared to be more reliable since the problem of matrix interferences was subdued in comparison with the soil samples. Table 6 presents the mean concentrations of the eight pesticides used in the study over each of the six irrigation events. Tables A4.1 and A4.2 present the resultant data on atrazine and the other pesticides in water data accumulated during the course of this study. All of the pesticide compounds with the exception of malathion were detected in soil water. Diazinon was found in only 1 of 18 samples at a concentration of 0.2 ppb. This positive sample was collected at the first irrigation.

Table 6. Mean pesticide concentrations (ppb) in soil solution samples collected over the six irrigations.

Pesticide	Irrigation Number						AVE.
	1	2	3	4	5	6	
atrazine	7.28	5.48	7.49	12.86	13.15	14.72	10.16
carbofuran	47.00	9.33	27.33	48.33	30.00	34.67	32.78
aldicarb	N.D.*	3.63	5.93	0.70	N.D.	0.77	1.84
diazinon	0.07	N.D.	N.D.	N.D.	N.D.	N.D.	0.01
alachlor	0.27	N.D.	0.27	17.33	30.00	20.33	11.37
simazine	0.53	N.D.	N.D.	0.53	N.D.	N.D.	0.18
malathion	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
oxamyl	1.33	4.67	7.67	1.73	2.20	1.93	3.26

\* - denotes not detected

Simazine was also poorly represented in the samples with only two occurrences of identical 1.6 ppb concentrations obtained from the same replicated plot. Respective peak concentrations detected for oxamyl (7 positive samples) and alachlor (4 positive samples) in these two plots were 23 ppb and 90 ppb. In each case concentrations were noted as rising and falling within the 6 irrigations monitored. Both the oxamyl and alachlor peak concentrations occurred in the second irrigation sample subsequent to that in which the compound was first detected. Oxamyl was immediately detected in the sample taken after the first irrigation. The lone replicate testing positive for alachlor proved so at the third irrigation.

Aldicarb results were more interesting since two of the three replicates showed similar levels. Aldicarb was detected in all three replicates. In each of the three cases aldicarb was originally detected after the second irrigation with peak concentrations occurring after the third.

The levels of carbofuran in the independent replicate plots were highly variable. Though carbofuran was successfully detected in 19 of the 21 samples, concentrations within each replicate were markedly different. The first replicate had moderate levels of carbofuran starting with the first irrigation at 1.0 ppb and increasing to a peak concentration of 12 ppb at the fifth irrigation. The second replicate did not yield a positive carbofuran sample until the third irrigation. Concentrations were 6-8 times those of the first replicate ranging from 42.0-87.0

ppb. The only similarity between the two replicates was the distinguishable "hump" in the distribution of the values over successive irrigations. However, the first replicate plot would appear to be skewed to the right whereas the second is skewed to the left. The third replicate is notable because an unusually high level was seen after the first irrigation. The first sample registered the peak concentration for the plot at 140 ppb carbofuran. The remaining values were consistently higher when compared to those values recorded from other pesticide plots and ranged between 15.0-50.0 ppb.

Atrazine in soil water samples varied from none-detected to 140 ppb and had a mean level over the six irrigations and 24 plots of 10.2 ppb. Three of the 24 plots had no detectable levels of atrazine. Four additional plots had one detectable value. Twelve of the 24 plots had 4 or more positive samples over the course of the experiment. Little can be said about those plots with low numbers of positive samples. There were no apparent links between the atrazine values, the concentrations of the companion pesticides or the volumes of samples collected. The mean atrazine levels over the six irrigations for each of the three blocks in the experiment (see plot diagrams) were 2.93, 4.88, and 22.65 ppb for blocks 1,2, and 3, respectively. No reason is evident for the large gap between the first two blocks (plots 1-16) and the third (plots 17-24). The mean concentrations of atrazine for each irrigation taken over the 24 plots were regressed on the 6 irrigations and yielded the following equation:

$$[\text{Atrazine}] = 3.61 + .247X; \quad \text{where } X = \text{total H}_2\text{O applied (cm)}$$
$$r^2 = 0.83^* \quad * - \text{significant at } p < .05$$

This was significant at the 5% level of probability. Figure 9 depicts the mean levels of atrazine at each irrigation and the derived regression line.

# Soil Solution Atrazine

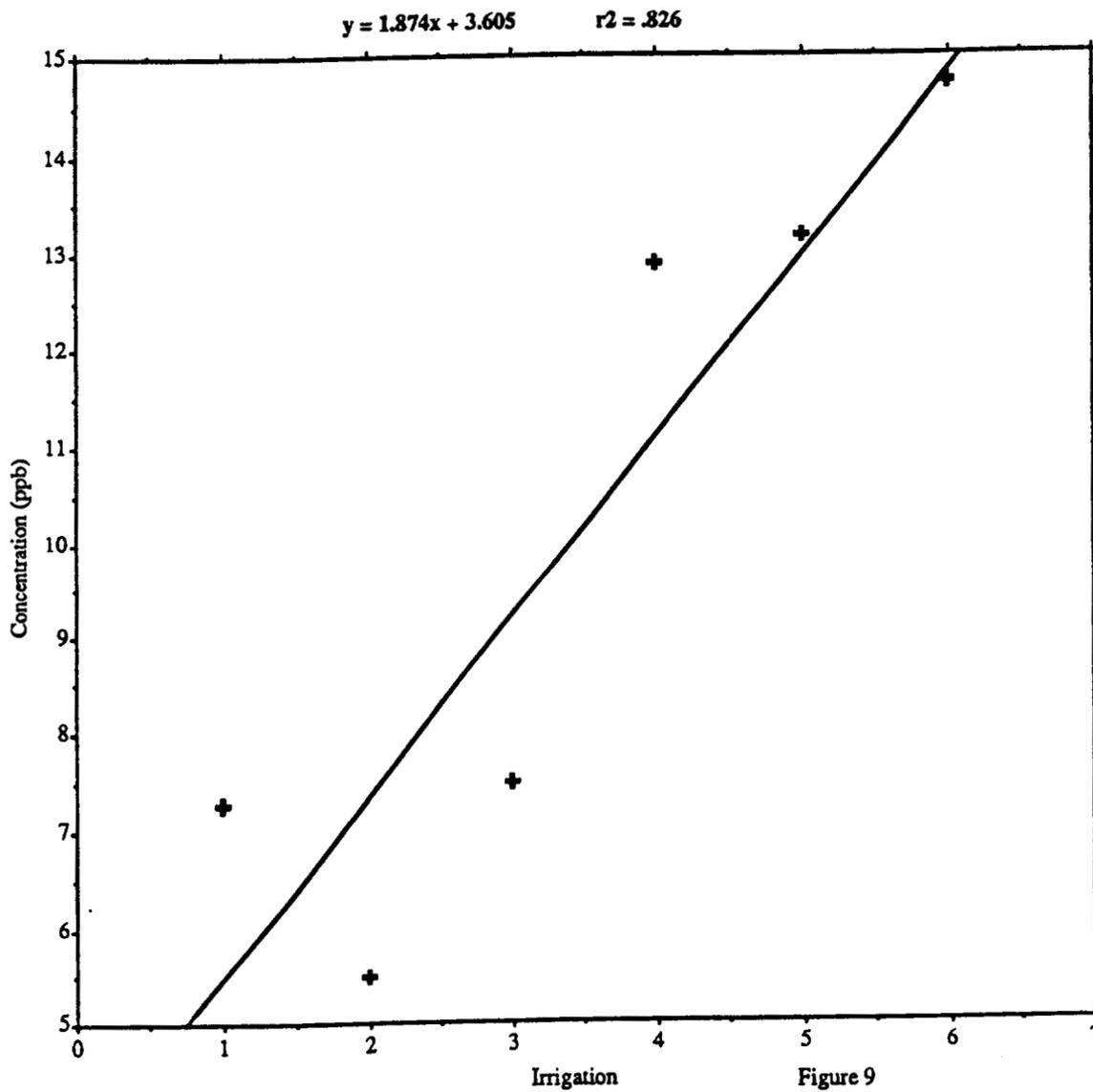


Figure 9. Mean concentrations of atrazine in soil water.

## DISCUSSION

The evaluation of the tension lysimeter is not complete without developing some method for assessing their success in this experiment. Tables 7 and 8 present data that address this facet of the experiment. The first table presents a summary of atrazine recovery from the soil profile, whether or not it was detected in solution, when it was first detected and the initial detection concentration. Soil detection events were assigned to two categories; 1) detection of the targeted compound at the ceramic tip depth (1.07 m) or shallower and 2) detection of the targeted compound at greater depths. The rationale inspiring this classification was that the tension lysimeter ceramic tips were located at the 1.07 m depth. The shallower depth category establishes the existence in the upper soil of a source of atrazine for the solution sampler. The second depth category in conjunction with the detection of pesticide in soil water is related to the success of the tension lysimeter in extracting the pesticide from the surrounding soil. The qualifying event that establishes the failure of a tension lysimeter is that circumstance where a pesticide is detected in the soil below the lysimeter coupled with the lack of detection in the soil water sample. The solutions collected via the ceramic samplers were found to have detectable levels of atrazine in 21 of 24 plots. In 10 of these 24 plots atrazine was detected at the initial irrigation with an average concentration of 15.9 ppb. One of the three plots where atrazine was not found in water samples (plot

Table 7. Variables used in rating performance of ceramic samplers for monitoring the movement of atrazine.

Plot Number	Soil Depth		Soil Solution	Irrigation Number <sup>W</sup>	Initial Conc. <sup>X</sup>
	≤1.07 m	>1.07 m			
1	+ <sup>Y</sup>	+	+	5	1.2
2	+	-	+	1	35.0
3	+	-	+	2	3.1
4	+	-	+	1	2.0
5	+	-	+	1	5.3
6	+	+	+	2	3.6
7	+	-	+	1	4.3
8	+	+	-	N.D. <sup>Z</sup>	N.D.
9	+	-	+	3	3.0
10	+	-	+	4	1.7
11	+	-	+	5	10.0
12	+	+	+	1	1.4
13	+	-	+	1	1.7
14	+	-	+	1	1.1
15	+	-	-	N.D.	N.D.
16	+	+	-	N.D.	N.D.
17	+	-	+	1	40.0
18	+	+	+	1	65.0
19	+	-	+	4	2.3
20	+	-	+	3	5.1
21	+	+	+	1	3.3
22	+	+	+	5	24.0
23	+	+	+	3	4.8
24	+	+	+	4	1.2

<sup>W</sup> - irrigation number at which atrazine was first detected.  
<sup>X</sup> - concentration at initial detection within plot.  
<sup>Y</sup> - +/- indicate presence or absence of pesticide.  
<sup>Z</sup> - not detected.

Table 8. Variables used in rating the performance of soil solution samplers for monitoring pesticides in irrigation water.

Pesticide	Rep.	Soil Detection		Solution Detection	Irrigation Number <sup>w</sup>	Initial Conc. <sup>x</sup>
		≤1.07 m	>1.07 m			
alachlor	1	-y	-	-	N.D. <sup>z</sup>	N.D.
	2	-	-	-	N.D.	N.D.
	3	-	-	+	4	0.8
simazine	1	+	-	-	N.D.	N.D.
	2	+	-	+	1	1.6
	3	+	+	-	N.D.	N.D.
carbofuran	1	+	-	+	1	6.67
	2	+	+	+	3	42.0
	3	+	-	+	1	140.0
atrazine	1	+	-	+	1	5.3
	2	+	-	-	N.D.	N.D.
	3	+	+	+	1	3.3
oxamyl	1	+	-	-	N.D.	N.D.
	2	+	-	+	1	4.0
	3	+	-	+	1	1.0
diazinon	1	-	-	-	N.D.	N.D.
	2	+	-	-	N.D.	N.D.
	3	+	-	+	1	0.2
aldicarb	1	-	-	+	2	2.3
	2	+	-	+	2	4.5
	3	-	-	+	2	4.1

w - represents irrigation number of first detection  
x - atrazine concentration at initial detection  
y - +/- indicate presence or absence of atrazine-positive samples  
z - not detected

no. 15) had no detectable atrazine below the tension lysimeter position within the soil profile and cannot be classified as a failure. Therefore, only 2 of the 24 plots can definitely be categorized as failures. This translates into a failure rate of 8.3% (2 of 24 plots).

A similar format is used to evaluate the utility of the tension lysimeters in monitoring the levels of the remaining pesticides (see Table 8). Because of the sparseness of the data, due partially to insufficient replication and analytical concerns, there is a general increase in the number (5) of no-contest plots where no serious evaluation can be made. Included in this category are those plots where no pesticide was detected at any level within the soil profile nor was it found to be in water samples. Of the remaining 19 plots, 13 succeeded in trapping the named pesticide in soil water. In the case of aldicarb the tension lysimeters cannot be considered as having failed since no parent compound was detected in the soil profile. Four additional plots had measurable levels in the upper strata but none below the tension lysimeter position. This leaves two plots which are definite failures and include the first malathion replicate and the third simazine replicate. This yields a failure rate of 10.5% (2 of 19 plots).

The apparent success of the tension lysimeter in trapping the pesticides concerned in this study is evident. However, the question remains as to what the concentrations detected represent. The levels noted may be undervalued in consideration

of the potential for the ceramic cup to adsorb some unknown quantity of pesticide. This effect has not been addressed for these particular pesticides as it has for certain anions as mentioned previously. It is the topic of a research project currently under investigation by EHAP. The results are to be published in a subsequent report.

There were no statistical links between measured soil variables and the concentrations noted in water samples. Soil variables evaluated included the texture of the soil at the surface-foot into which the pesticides were randomly incorporated and the sand fraction of the four-foot depth where the lysimeter was situated and soil pH. This inability in finding a soil attribute or combination of attributes which might help explain the relative movements of pesticides in soil or soil water may be a reflection of the low clay content found in most of the plots. Clay content may be a good index of soil pesticide activity in soils with low levels of organic matter.

Comparison of the pesticides tested in the experiment are tentative at best since the relationships between the soil water extracted and the actual soil water have not been quantified. A ranking of the leaching potential of the pesticides based on the average levels detected over the six irrigations would yield the following order:

carbofuran > alachlor > atrazine > oxamyl > aldicarb > simazine > diazinon > malathion.
--

This rank order is contrasted against rankings from model predictions published by Rao et al. (1985) and are shown in Table 9. Rao et al. compared the results of several simulation models including their Attenuation and Retardation Models, the Laskowski et al. (1982) LEACH and Volatility Models (VOLAT) and the Jury et al. (1983; 1984a,b,c) Behavior Assessment Models (BAM). A total of 41 pesticides were evaluated in Rao's study. The numbers presented in Table 9 represent the rank order of the pesticides incorporated in the tension lysimeter study relative to each other. The original rankings of each pesticide from among the original 41 pesticides are placed in parentheses. The pesticides are depicted in the order shown above from highest pesticide concentrations to lowest as collected via tension lysimeter. No obvious association between any of the models shown and the lysimeter data is evident. The Spearman Rank Correlation Coefficient (Siegel, 1956) was determined for the lysimeter ranking with the rankings developed by the models. There were no significant correlations detected between any of the rankings at the 5% level (see Table 9). However, the data used by Rao et al., including Koc and half-life values, are different from those found in Wilkerson and Kim's (1986) CDFA report, "The Pesticide Contamination Prevention Act: Setting Specific Numerical Values (SNV)", that developed a methodology for collecting and establishing these values in compliance with the PCPA. The SNV data may be more appropriate in developing models since it presents a method for selecting or deriving less biased values

Table 9. Comparison of lysimeter rankings to other indices.

Pesticide <sup>u</sup>	LYS <sup>v</sup>	Contamination Index <sup>t</sup>			Td <sup>z</sup>	LEACH	VOLAT
		RM <sup>w</sup>	AT <sup>x</sup>	Tc <sup>y</sup>			
carbofuran	1	3 (5)	1 (11)	3 (5)	4 (25)	5 (11)	8 (24)
alachlor	2	7 (20)	7 (31)	7 (20)	3 (24)	7 (20)	4 (13)
atrazine	3	6 (16)	4 (14)	6 (16)	6 (29)	4 (9)	5 (14)
oxamyl	4	1 (1)	6 (21)	1 (1)	8 (36)	1 (5)	3 (7)
aldicarb	5	2 (2)	2 (12)	2 (2)	1 (9)	3 (8)	7 (22)
simazine	6	5 (15)	3 (13)	5 (15)	7 (35)	2 (7)	2 (5)
diazinon	7	4 (13)	5 (16)	4 (13)	2 (14)	6 (12)	6 (16)
malathion	8	8 (31)	8 (41)	8 (31)	5 (27)	8 (29)	1 (3)
Spearman's r		.214	.381	.214	-.024	.143	-.524

P<sub>.05</sub> = .643

t - extracted from Rao et al., 1985

u - pesticides are listed relative to cumulative concentrations over 6 irrigations shown in Table 6.

v - Tension Lysimeter

w - Retardation Method                      x - Attenuation Method

y - Convection Travel Time                z - Vapor-Phase Diffusion

from similar data collected using unstandardized techniques found in the literature or reported by registrants.

Jury's Behavior Assessment Model (BAM) was selected for the purposes of comparing the Koc and half-life data sets that have appeared in the literature to the mean rankings of the pesticides from this study. The GWPOL program included in BAM uses both Koc and half-life data in its calculations to determine the time required for an organic compound to reach ground water. It also utilizes soil information that is relatively easy to collect and includes bulk density and organic carbon fraction. A copy of the BAM programs was obtained from Dr. William A. Jury (personal communications, 1989). The input variables to the GWPOL program consist of Koc, half-life, bulk density, organic carbon fraction, depth to ground water, depth of root zone, soil water content and annual drainage. Output from this program is presented in the form of three scenarios for a pesticide with known or assumed Koc and half-life values. Included are a low contamination scenario, a high leaching potential scenario and one in which the model user can specify the field conditions to be simulated. Table 10 lists the variables incorporated in the GWPOL program and the numerical values assigned to them in this study.

The GWPOL program was run for each of the pesticides using Koc and half-life values obtained from the following sources: 1) Table 2 from Rao (1985); 2) Jury's default values packaged with the GWPOL program; and 3) Wilkerson and Kim's Specific Numerical Values (SNV) as revised and reported by Johnson (1988). These

Table 10. Variables and variable settings used in GWPOL model.

Model Variable	Contamination Potential Scenario		
	Low	High	User Set
Bulk Density (g/cm <sup>3</sup> )	1.20	1.50	1.65
Water Content (cm <sup>3</sup> /cm <sup>3</sup> )	.500	.200	.200
Organic Carbon Fraction (g/g)	.030	.005	.005
Groundwater Depth (cm)	1000	300	100
Root Zone Depth (cm)	100	50	100
Annual Drainage (cm/year)	50	100	30

data are presented in Table 11. Some of the pesticides have identical values on the Rao index and the default GWPOL set (diazinon, malathion, simazine) because the numbers Rao used were originally tabulated by Jury et al. (1984b). Atrazine has a shorter half-life in the GWPOL default listings (64 days) than it had originally (71 days). These changes coupled with the SNV criteria are indicative of the processes under way in determining environmental fate constants for pesticides.

The GWPOL ranking using the SNV data has the closest association with the ranking developed empirically by monitoring of pesticides collected via the tension lysimeters (see Table 12). Comparison of the ranks for each pesticide reveals that in only one instance, that of oxamyl, was the discrepancy between ranks greater than two units. Simazine is 6th in both lysimeter and GWPOL rankings when SNV criteria are used. The remaining 6 pesticides were divided into equal groups whose ranks were off by one or two units. Spearman's  $r$  values were calculated in a test of the rankings. There was a significant correlation detected between the lysimeter- and SNV-generated rankings ( $p < .05$ ).

The GWPOL program results, measured in units of time (years to ground water), are depicted in Table 13 for each of the three contamination potential scenarios described earlier. It is evident that the user assigned scenario values are closely related to the high potential scenario results. This is not surprising since the high potential scenario presents the classic case of a sandy soil with low levels of organic carbon, etc. all

Table 11. Comparison of Koc and half-life values used in simulation with GWPOL.

Pesticide	<u>GWPOL</u> <sup>x</sup>		<u>Rao</u> <sup>y</sup>		<u>SNV</u>	
	Koc (cm <sup>3</sup> /g)	T <sup>1/2</sup> (days)	Koc (cm <sup>3</sup> /g)	T <sup>1/2</sup> (days)	Koc (cm <sup>3</sup> /g)	T <sup>1/2</sup> (days)
alachlor	120	18	190	7	150	18
aldicarb	36	70	10	28	79	14
atrazine	160	64	160	71	180	190
carbofuran	28	40	28	40	48	23
oxamyl	6	6	6	6	6	180
simazine	140	75	140	75	220	110
diazinon	85	32	85	32	1200	17
malathion	1800	1	1800	1	1000	1

x - Program default values  
y - Adapted from Jury et al. (1984b)

Table 12. GWPOL scenario rankings with select Koc and T<sup>1/2</sup> criteria.

Pesticide	LYS <sup>x</sup>	GWPOL Ranking								
		Default			SNV			Rao		
		Low	High	User	Low	High	User	Low	High	User
carbofuran	1	2	2	2	2	2	2	3	3	3
alachlor	2	5	5	5	4	4	4	7	7	7
atrazine	3	7	7	7	5	5	5	6	6	6
oxamyl	4	1	1	1	1	1	1	1	1	1
aldicarb	5	3	3	3	3	3	3	2	2	2
simazine	6	6	6	6	6	6	6	6	6	5
diazinon	7	4	4	4	8	8	8	4	4	4
malathion	8	8	8	8	7	7	7	8	8	8
Spearman's r		.429			.714*			.214		

\* - significant at p<.05  
x - Tension lysimeter rank

Table 13. GWPOL predictions of pesticide travel to groundwater.

Pesticide	GWPOL Prediction (yrs to groundwater)								
	<u>Default</u>			<u>SNV</u>			<u>Rao</u>		
	Low	High	User	Low	High	User	Low	High	User
carbofuran	30.2	1.2	1.4	44.6	1.7	2.0	30.2	1.2	1.4
alachlor	96.4	3.3	4.0	118.0	4.0	4.8	146.8	4.9	5.9
atrazine	125.2	4.2	5.1	139.6	4.6	5.6	125.2	4.2	5.1
oxamyl	14.3	0.7	0.8	14.3	0.7	0.8	14.3	0.7	0.8
aldicarb	35.9	1.4	1.7	66.9	2.4	2.8	17.2	0.8	0.9
simazine	110.8	3.8	4.5	168.4	5.6	6.7	110.8	3.8	4.5
diazinon	71.2	2.5	3.0	874.0	27.6	33.7	71.2	2.5	3.0
malathion	1306.0	41.1	50.2	730.0	23.1	28.2	1306.0	41.1	50.2

of which greatly influence pesticide migration. The Hanford series soil that composed the experimental plots are wide-spread throughout the Central Valley and the Santa Ana River Basin, areas where substantial problems with ground water toxicants have been encountered.

The utility of bromide and atrazine as tracers for other chemicals may be of significance for future monitoring studies. The information obtained on these two chemicals provides a tool for comparing additional compounds. The linear equations describing the concentrations of each chemical in water samples over the course of the experiment are virtually identical. Consideration should be given the fact that bromide is reported in units of parts per million (ppm) not parts per billion (ppb). Despite the 1000-fold difference in observed levels and a greater than 6-fold difference in application rates for bromide over atrazine, both compounds were on the average detected in soil water in a similar pattern. The relative amounts leaching through the soil are constant with respect to the time when a pesticide initially reaches a set depth in the soil. The concentrations demonstrated in the leaching process may be the result of rate controlling factors such as pesticide application rates and irrigation intensity. Brasino and Hoopes (1985) had similar responses in their Wisconsin study to those described here. They monitored a sandy potato field under irrigated conditions using tension lysimeters for applied bromide and aldicarb leachates. Their data, accumulated over 400+ days, show very similar trends

in solute movement early in the experiment. If anything, the present study was terminated too early.

The soil water sampling system as described was efficient in extracting liquids from soil in samples of sufficient volume to meet normal analytical needs. There are two potential drawbacks to using a system such as that described here in a monitoring program, though these were not critical to this investigation. First, there is a tendency for the four lysimeters in each plot to extract water from the soil at variable rates. This can result from improper installation, manifold leaks, differences in soil texture and/or variability amongst the ceramic tips proper. The problems associated with installation and lysimeter variability can be resolved by paying careful attention to installation procedures outlined by the manufacturer and by testing and grouping lysimeters by similarities in flow rates prior to installation. The second monitoring concern centers around the use of single tube lysimeters. In the normal sequence of a sampling event when the manifold is evacuated the sample flows up through the tubing and into the collection vessel. At the end of the sampling cycle, as air enters the system and equilibrates to atmospheric pressure, the sample remaining in the tubing is drawn back into the lysimeter potentially contaminating a subsequent sample. This could be of significance in a monitoring project and can be controlled by incorporating a second tube on the lysimeter attached to a second manifold which can be pressurized to extract residual samples at the termination of a sampling cycle.

Alternatively, the second manifold can be fitted with a normally-open solenoid valve. This would allow evacuation of both manifolds during the sampling cycle as well as allow air to enter the second manifold at the end of a sampling event effectively clearing the tension lysimeters.

Critical discussion has developed concerning the validity of the samples obtained via methods using various types of soil water samplers. Several variables have been investigated including extraction times, tension levels, and construction materials in relation to testing under field and laboratory conditions (Severson and Grigal, 1976; Silkworth and Grigal, 1981; Warrick and Amoozegar-Fard, 1977). The literature on tension lysimeters has recently been reviewed by Litaor (1988). One of the most comprehensive studies undertaken was conducted by Hansen and Harris (1975) who investigated the validity of samples collected with tension lysimeters. They suggest reducing variability by grouping samplers according to intake rate, using short sampling periods, maintaining constant tensions and by using uniform lysimeter lengths. All of these recommendations were adhered to in the course of this study with the exception of the grouping of lysimeters by intake rate. Under the more or less saturated conditions existing immediately following an irrigation event, there should be little distortion of flow fields in the immediate vicinity of the soil cup and greater yields of extracted sample are to be expected (Warrick and Amoozegar-Fard, 1977).

An EPA review written by Wilson (1980) on the subject of monitoring within the vadose zone concludes that solution samplers are the best overall technique available. Monitoring projects using tension lysimeters are now being conducted in California for measuring leachate levels and water quality in sewage-sludge spreading operations (Merry and Palmer, 1985). The use of tension lysimeters in monitoring for pesticides should be encouraged in the interests of economy and integrity of data.

## CONCLUSIONS

Additional studies are necessary for the tension lysimeters to be used with confidence. The system should be tested in several soils of the same type but that are physically separated. Since there is some concern as to their use in heavier, cracking clay soils (Vertisols and Vertic intergrades), they should also be tested in soils of different taxa. If lysimeter techniques are under consideration for use in pesticide monitoring programs, then each pesticide entering the evaluation process should have an adsorption study conducted to check for interactions between the ceramic matrix and the candidate compound.

Soil tension lysimeters possess several advantages in monitoring soil movement of pesticides when compared to the more typical soil coring practices. As may be surmised from the chemical analysis described previously, residue analysis is more reliable resulting in lower reporting limits with diminished matrix interference problems. Tension lysimeters have an extended service life (a season or longer). They cause minimal alterations to the soil or plot being monitored when compared to soil coring. Water samples collected are handled to a lesser extent than soil samples (coring, sample splitting, etc.) thereby preserving the integrity of the sample. Soil water sampling equipment is relatively inexpensive to purchase, install and maintain. Perhaps most relevant is the fact that the soil water itself is the objective of monitoring. It is generally recognized that the bulk of the transport of pesticides to ground water is occurring in

the liquid phase rather than in the solid phase. The tension lysimeters essentially monitor this water-soluble component of a contaminant in the soil. Since the PCPA requires the monitoring of soil and water for pesticide residues, the use of soil tension lysimeters provides an alternative soil monitoring mechanism to that of collecting undisturbed soil cores that EHAP currently employs. Information accumulated in this study (Appendix 2) supports the position that monitoring projects using tension lysimeters are very economical with savings of at least 58% over soil coring procedures. Tension lysimeters should work well at the minimum eight-foot depth action levels specified by the PCPA to trigger review of pesticides for ground water pollution potential and in studies generated by CDEA under its Ground Water Protection Plan.

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## Appendices

Appendix 1. Lysimeter Design and Plot Description.

Appendix 2. Cost Analysis

Appendix 3. Tables of Pesticide and Bromide Distributions within Soil Profile and Associated Soil Characteristics.

Appendix 4. Tables of Pesticide and Bromide Distributions in Soil Water and Approximate Volumes of Water Extracted.

## Appendix 1

Lysimeter Design and Plot Description

## TENSION LYSIMETER DESIGN AND CONSTRUCTION

Soil solution samplers, also referred to as soil tension lysimeters, have been used in agricultural research for many years. Most research efforts employing ceramic samplers have centered attention on water quality and nutrient status studies of soil waters and their respective effects on plant growth. The development of soil water samplers and the closely related soil tensiometer used in monitoring soil water status in irrigation management was largely the result of research conducted in the 1950s and 1960s. Ceramic-tipped samplers are the most commonly used type. Other materials are available and include porous Teflon<sup>R</sup> and fritted glass samplers. However, ceramics remain the most popular construction material. They offer several advantages not the least of which is economy. Pore sizes of ceramics may be "adjusted" to meet specific criteria by varying the proportions and types of clays used in the molding and firing of the finished product. These porosities will impact flow rates through the walls of the samplers and thereby affect sampling time. Pore size will also affect the efficiency of samplers in extracting water from soils of different textures.

Most soil tension lysimeters available through commercial firms essentially consist of 5 to 7 distinct parts. These parts include a ceramic tip glued to a section of PVC pipe, a plastic end cap which has one or sometimes two threaded holes for the mounting of one or two lengths of polyethylene tubing and appropriate fittings. The double-tube system has the advantage of producing

samples from greater depths than is possible with a single tube under vacuum since the second tube may be pressurized effectively "pushing" the sample to the surface. Adhesives used to cement the ceramic tip to the PVC tube are of a non-hardening epoxy type. The non-hardening characteristics are important because the coefficients of expansion of the ceramic tip and the PVC tube differ. When installed in soils exhibiting large seasonal temperature variations or if placed in contact with soils of a different temperature from that under which the lysimeters are assembled, potential leaks at the PVC-ceramic interface can occur. The non-hardening epoxy makes allowances for the expansions and contractions of the materials used. The polyethylene tubing conveys the sample liquid to the surface when the sampler is placed under vacuum. The sample is then trapped in a suitable container and may then be tested for soluble nutrients, salt levels, etc.

The samplers were built from basic materials to determine the sources of costs incurred in their construction and to identify problematic steps associated with their assembly and eventual use. Current price lists from SoilMoisture, Inc. quote lysimeters comparable to those used in this study at \$26.20. This does not include the costs of replacing the polyethylene tubing with that of Teflon<sup>R</sup> which is necessary in the collection of low concentration samples of organic compounds. Though ceramic tips can be made from "scratch" from cookbook methods, it is more expedient and efficient to purchase them ready-made. Sources for

raw materials (clays) are not dependable. In addition, ceramic tips available through commercial vendors are tested to conform to industry standards.

The plastic components that along with the ceramic tip constitute the body of the sampler were cut on a lathe. The tube portion was cut from nominal 1-1/2 in. Schedule 40 PVC pipe in 6-1/2 in. sections. Components of the tension lysimeter and dimensional specifications are shown in Figure 1 in the main body of text. A 3/8 in. hole was drilled in the center of the end cap and tapped to accommodate the 1/8 in. x 1/8 in. compression by male pipe thread (MPT) brass connector. The brass connector was bored out from the compression fitting end with a 3 millimeter drill, permitting a 1/8 in. diameter length of Teflon<sup>R</sup> tubing to be threaded through the opening and past the male pipe thread section of the fitting. The brass compression sleeve was discarded because it had the tendency of crimping and/or cutting the Teflon<sup>R</sup> tubing. It was replaced with an approximate 3/32 in. length of vinyl plastic tubing (1/8 in. I.D. x 1/16 in. wall thickness). This system provided an adequate sealing mechanism for this joint. Plastic fittings and sleeves (ferrules) are available as a substitute but their costs have not been verified. The end cap was cemented to the PVC tube with PVC glue. The ceramic tip was then attached using the recommended epoxy glue. A light coating of epoxy glue had previously been applied to the contact edge of the ceramic tip flange that fit into the tube. This is the procedure suggested by SoilMoisture<sup>R</sup> as an aid in

sealing the porous ceramic in this region, minimizing absorption of the glue and imparting greater security to the seal at this interface. The depth from the outside edge of the end cap to the inner wall of the ceramic tip was measured at 22.9 cm. The Teflon<sup>R</sup> tubing was threaded through the brass connector by this length to insure that the tube would reach to the bottom of the lysimeter. The tubing was then inserted into the lysimeter through the hole in the end cap. Occasionally the tubing would engage the flange of the ceramic tip, preventing its reaching the bottom. This was resolved by shaking the lysimeter or twisting the tubing free. A notch was cut at the extreme end of the tubing to avoid a potential seal from forming between the tube orifice and the ceramic wall, assuring a uniform vacuum within the lysimeter. It was important to place the tubing at the bottom of the sampler for two basic reasons. First, it must be below the PVC-ceramic joint in order to keep the sample liquid from contacting the PVC tube which may act as a sink for organic compounds in the collected sample. A second consequence of the tube's failure to reach the bottom of the lysimeter is that of trapping aliquots of samples from previous sampling periods (when the sample level falls below the tube orifice), potentially affecting sample concentrations. This problem is inherent in this system as described and will be addressed later. Teflon<sup>R</sup> tape was wrapped around the threads of the male end of the brass connector which was then screwed onto the end cap. The tension lysimeter was then tested for leakage by immersion in a water bath, pressurizing the sampler with air, followed by a visual

inspection for escaping air bubbles. Less than 10% of the lysimeters constructed with the procedures described had discernable signs of leakage. The problem tension lysimeter were fixed with the application of additional epoxy glue to the PVC-ceramic and/or end cap joints as necessary.

#### PLOT LAYOUT

Twenty four irrigation basins were located in Field 15c at the University of California, Riverside Citrus Experiment Station (UCRCES). Alfalfa had been grown several years in the plot area prior to this experiment. Records and personal communications disclosed no recent history of pesticide use on these plots with the exception of Round-up<sup>R</sup> (glyphosate) used for weed control along berms. Figure 2 presented earlier shows the layout of the plots used in these studies. All north-south oriented berms were removed. The plots were deep-chiseled and the berms reinstalled by the UCRCEs Agricultural Operations group. Twenty four plots were established in a 6 x 4 arrangement having basin floor dimensions of circa 6.1 m x 4.3 m Individual plots were separated from one another by earthen berms. The remaining berms from the original plots (east-west oriented) were ca. 0.3 m high x 1.5 m wide. The new berms were approximately 20.3 cm high by 0.9 m wide. Each plot had its own water delivery system (see Figure A1.1) consisting of a 3/4 in. water valve, a 3/4 in. water meter, and a 3.66 m length of garden hose attached to a rectangular 3/4 in. PVC structure terminating in PVC elbows at each corner. The elbows consisted of a 3 in. elbow with a 3/4 in. by 3 in. reducer

# Irrigation System

North →

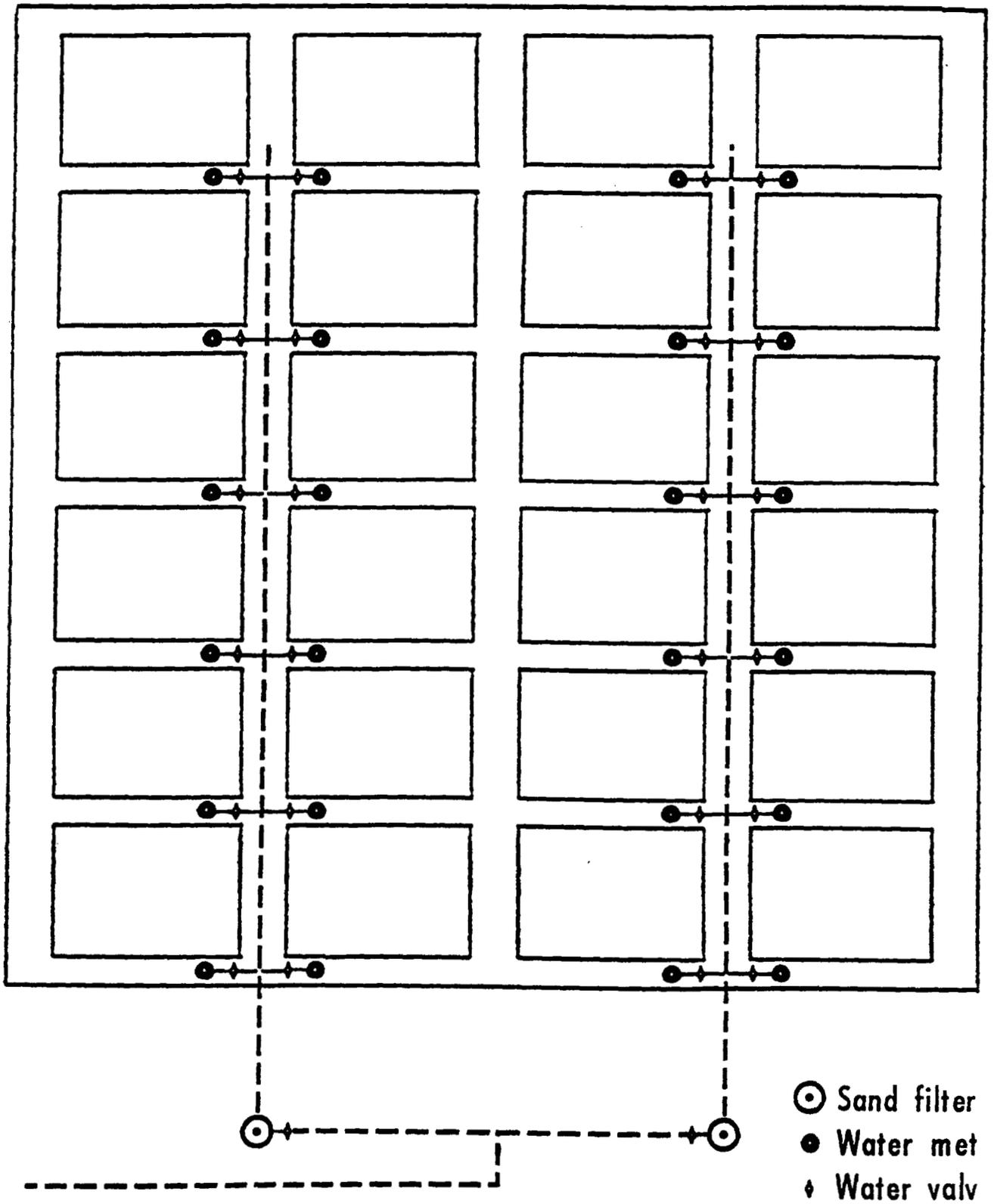


Figure A1.1

adapter. These fittings had the effect of lowering the terminal velocity of the water applied to the plots helping to minimize erosion damage in areas immediately surrounding the elbows. Irrigation water was supplied by a local canal. Water was delivered through 2 in. PVC pipe with an in-line sand filter. The pipe was further reduced to 1-1/2 in. pipe, followed by 1 in. pipe and final attachment to the water valves and meters. The plots were irrigated to test berm strengths and to aid the leveling of the basin floors.

#### TENSION LYSIMETER INSTALLATION

Four soil tension lysimeters were installed in each plot in a 1.83 m x 1.22 m pattern. Nylon lines were strung across the plots along these dimensions to align them as uniformly as possible. A six foot section of nominal 2 in. EMT conduit was pounded into the ground with a post driver to a depth of approximately four feet. Soil from outside the plots was sieved through a two millimeter (2 mm) screen to remove coarse fragments. A slurry was made with the screened soil by adding water and mixing. The slurry was made to a consistency that would flow freely from a beaker. Approximately 300 mls of the slurry was poured into the hole. A 2 m length of twine was tied snugly below the compression nut of the brass connector. The twine and Teflon<sup>R</sup> tubing were threaded through a five foot section of 3/4 in. Schedule 40 PVC pipe. A mark was placed on the pipe a distance of four feet as measured from the tip of the tension lysimeter. This served as a gauge for uniform depth in installation. By holding the twine

tightly through the gauging pipe, the sampler was held rigidly against the flat surface of the end of the pipe. This enabled the lysimeter and gauging pipe to function as a single unit when lowered into the slurry in the hole. The sampler was repeatedly raised and lowered into the slurry in attempting to establish a good contact between the soil:slurry:ceramic interfaces. A noticeable resistance to this "pumping" action developed as this contact was secured. The slurry was poured into the hole just prior to the installation of the lysimeter. This timing factor is critical to uniform installation because water from the slurry tends to flow into the surrounding soil. This results in the loss of plasticity in the soil slurry and poor surface contacts. This can effectively decrease the depth of the hole because the slurry tends to harden faster ending in the placement of the lysimeter on top of the slurry rather than within it. The gauging pipe was then removed. The final installation depth of the lysimeter as measured from the tip of the sampler was ca. 1.07 m.

The next step in the installation of the lysimeter involved the sealing of the hole. The proper functioning of the lysimeter with regard to the characteristics of the solution sampled depend on the adequate sealing of the hole, i.e. solution sampled should travel through undisturbed soil rather than along pathways determined by installation process. Once the gauging pipe was removed an additional 250 mls of soil slurry was poured into the hole. This was followed by a cap of approximately 400 mls of bentonite clay. Bentonite clay was mixed with screened soil

recovered from the coring procedure. The hole was filled level with the surface with the resulting mixture after tamping thoroughly during the filling process. Water was periodically added to enhance the settling process and as an aid in preventing irrigation from traveling through the disturbed portion of the soil or at interfaces with that part that remained undisturbed. As a final step, the Teflon<sup>R</sup> tube was threaded through a one foot section of 3/4 in. PVC pipe. This pipe was pressed into the soil at the point where the tubing broke the soil surface to a depth of circa 15 cm. This pipe was added to allow for splicing of the tubing with stainless steel couplings or heat shrinkable tubing in case the tubing should be damaged near the surface. It also protected the tubing from contact with the soil surface (causing possible contamination problems during pesticide application) since it could be coiled, wrapped in plastic bags and tied to the pipe off the ground.

#### SAMPLING SYSTEM DESIGN

A method for collecting of liquid samples extracted from the soil was developed. The mechanism used included three basic components: a sampling vessel, a vacuum manifold, and a sampling frequency timer. Prior to the first test of the sampling system no general knowledge about sample volumes or duration of extraction periods was available. Several variables such as soil texture and percolation rates can influence sample volumes. Because one liter or more is generally requested by the contract laboratory for analytical purposes, it became the target for

sample volume to be collected. In order to meet this goal, it was estimated that four soil tension lysimeters in each plot would be necessary. The estimation included consideration for events where one or possibly two lysimeters per plot might be inoperable for any reason. Since a main objective of this study was to determine the average concentration of pesticides in water flowing past the lysimeter in drainage water, the sampling procedure was greatly simplified by merging the samples collected from each of the four lysimeters in a plot into a common collection vessel. This consisted of a two quart (2 qt.) canning jar and its accompanying ring and lid. Five 9/32 in. holes were drilled in the lid. The holes were equally spaced around its perimeter so as not to interfere with the sealing ring. A 3/8 in. O.D. x 1/16 in. thickness O-ring was placed over the compression ends of five brass connectors. The coarse threads were then screwed into the five holes of the lid from the non-sealing side. These exhibited adequate sealing properties when torqued down finger tight plus a quarter turn. The four lysimeter tube lines were threaded through the brass connectors. The Teflon<sup>R</sup> lines extended about 1/4 in. past the brass nuts into the jar. The fifth brass connector was left open for the subsequent attachment of a vacuum line. The Teflon<sup>R</sup> lines were threaded through the outer side of the sealing ring prior to their being mounted on the lid. This was done for each of the 24 plots. The rings and lids were then screwed onto the jars to complete the collection system.

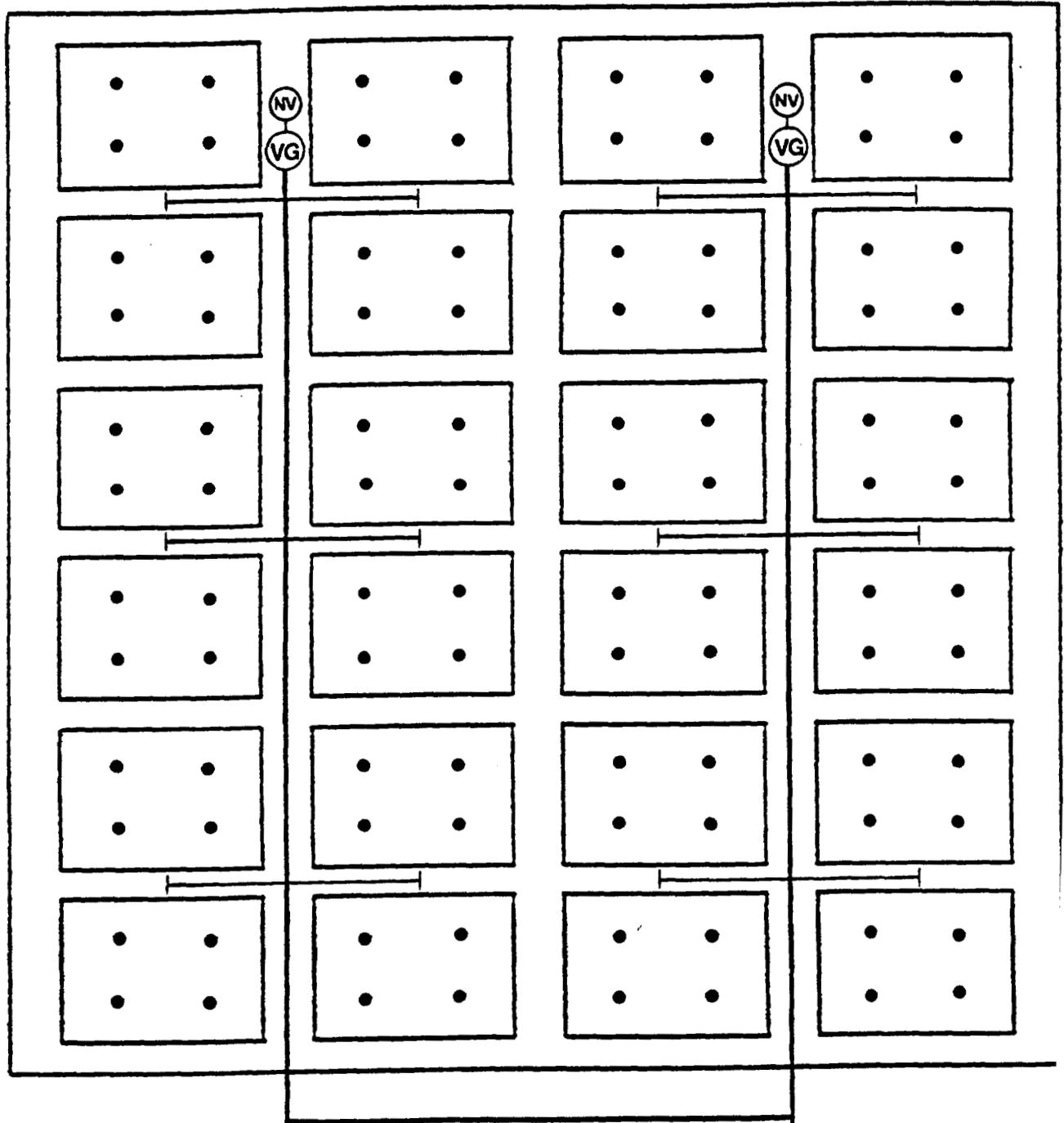
The vacuum system provides the necessary drop in pressure which allows water to flow from the soil into the lysimeter and up to the surface where it may be trapped. The system used in this experiment was composed of five basic units: a vacuum pump, a 3/4 in. PVC manifold, gauges, regulating valves, and a flexible hose link between the manifold and the collection jar. Vacuum was supplied to the system by an electric powered 1/8 HP Gast<sup>R</sup> Model DOA-101 pump that draws 4 Amperes at 60 Hertz (see Figure A1.2). The vacuum manifold consisted of 2 - 3/4 in. PVC lines running down the east-west berms alongside the main irrigation lines. These main manifold lines were tapped three times so that two adjacent east-west oriented plots on either side of a main line would be supplied with a vacuum source. The vacuum lines on the end of a run were terminated in a tee-shaped configuration and capped. The caps had been drilled and tapped to accept the male end of a brass connector. 1/2 in. O.D. x 1/8 in. wall thickness amber latex tubing was placed over the compression end of the brass connector on the terminal vacuum supply lines. The opposing end of the latex tubing was connected to the sampling jar. Clamping of the latex tubing at this point was not necessary. A pinch clamp was tied to the tubing and was used as a shutoff valve during sampling periods when a jar was filled with soil water preventing its backing up into the lysimeters or into the manifold lines. Each end of the main lines of the vacuum manifold was fitted with a tensiometer (vacuum) gauge and a needle valve, allowing for the monitoring and adjustment of the vacuum in the

lines which was maintained at between 400-500 KPa (304-380 mm Hg). The vacuum pump proper was also fit with a gauge and valve.

The frequency of drainage water sub-sampling was controlled by a Dayton 24-hour clock. The clocks trip switches were set to turn the vacuum pump on and off in 15 minute intervals (two 15 min. cycles per hour). The site was supplied with electricity (120 VAC) by underground cable with an outlet located at the far east end of the plot.

# Vacuum Manifold System

North →



- Sampler location
- (NV) Needle valve
- (VG) Vacuum gauge
- (VP) Vacuum pump
- (CI) Clock-24 hr. timer
- (AC) Electricity source



Figure A1.2

## Appendix 2

### Cost Analysis

## COST STUDY

A comparative cost study was conducted of the tension lysimeter system used in this study to the more commonly used soil coring procedures that the CDEA is presently using. The two methods are not directly comparable since different media or a combination of physical states are involved, i.e. whole soil vs soil liquid fraction. However, it is important to weigh the costs of the different methods because of resource constraints that may occur in the future affecting monitoring efforts. Table A2.1 presents a budget sheet of the monies expended in the development of the study site and the associated sampling system.

In order to compare the two methods a fictitious scenario representing a monitoring project will be assumed. The scenario will contain several elements normally encountered in real monitoring projects.

### Scenario

Pesticide X has been found and confirmed as a contaminant in several wells in an agricultural area in one of the State's southern counties. Pesticide X is used in various crops for the control of weeds. It is also used for roadside maintenance. There is no other known use in the vicinity. A monitoring project is to be developed to determine a) which use of the pesticide is most likely responsible for the contamination of ground water sources in the area and b) the seasonal effects of Pesticide X's use on the environment. A decision is made to conduct monitoring studies in two geographically separated areas of the State to include the

Table A2.1. Budget sheet listing expenditures incurred during construction of vacuum sampling system.

Item	Unit Price	Extension
<u>Samplers (per 100)</u>		
<u>Ceramic Tips</u>	6.99 ea	699.00
<u>PVC Bodies</u>		
1 1/2" SCH. 40 Pipe - 60 ft	.15/ft	9.00
1 1/2" PVC Round Stock - 88 in	.37/in	32.56
1/8" Teflon <sup>R</sup> Tubing - 1200 ft	.31/ft	372.00
Epoxy Glue	52.00/qt	26.00
Brass Fittings	.18 ea	18.00
<u>Machine Shop Labor (per sampler)</u>	3.15 ea	315.00
<u>Miscellaneous Labor</u>	6.49/hr	259.60
	Sub-Total (a)	1731.16
<u>Vacuum Manifold</u>		
Vacuum Pump (1/8 H.P.)	252.00 ea	252.00
Vacuum gauges - 3	7.53 ea	22.59
24 - Hour Timer	28.72 ea	28.72
Latex Rubber Tubing - 150 ft	.30/ft	45.00
Sch. 40 PVC 3/4" Pipe - 340 ft	.10/ft	34.00
Misc. PVC Fittings		25.00
O-Rings - 120	.12 ea	14.40
Brass Fittings - 144	.18 ea	25.92
Ice Chest, Styrofoam - 24	1.59 ea	38.16
Canning Jars, 2 Quart - 24	8.00/dz	16.00
<u>Misc. Labor Charges - 40 Hours</u>	6.49/hr	259.60
	Sub-Total (b)	761.39
	Total (a+b)	2492.55
	Tax	117.86
	Grand Total	2610.41

county in question and another county located in the lower San Joaquin Valley. Two sites will be selected within each county, one a roadside use situation and the other an orchard crop that uses minisprinkler irrigation methods. All projects will commence prior to the first seasonal application of Pesticide X and continue for a period of one year.

#### Soil Core Monitoring

Study of the seasonal aspects of the leaching of Pesticide X will require sampling each site 5 times including a background concentration study of the soil profile. The first step in field monitoring activities is to define the degree of soil contamination by the collection of background samples. Typical depths evaluated are on the order of twenty feet. A full characterization is necessary and the four sites will generate 36 soil samples each (CDFA drill rigs extract three samples of a 15.2 cm (6 in) segment length for each 50.8 cm (20 in) drilled which includes a 5.1 cm (2 in) section trapped in the bit that is discarded). This will yield a total of 144 soil samples (1 sampling period x 4 sites x 36 samples per site). Each of four subsequent field excursions during the one year sampling period will also produce the same number of samples though not all may be analyzed. For statistical purposes it is supposed that a minimum of 18 samples from each core will be extracted and processed for pesticide residues yielding an additional 288 soil samples (4 sampling periods x 4 sites x 18 samples per site). The minimum number of samples that will be processed will total 432

(144 background samples + 288 post-application samples) with a maximum of 720 (5 cores/site x 4 sites x 36 samples/core). Residue analysis costs are expected to run about \$150 per sample. Laboratory costs for the study will be between \$68,040 and \$113,400 including a 5% surcharge for quality control sample analysis.

A minimum of 5 persons are required to run the drill rig and process the samples with the tasks including drilling, washing the split barrel sampler, preparing the stainless steel sleeves, filling out chains-of-custody, weighing samples, etc. If the assumption is made that each county can efficiently be sampled in a 3.5 day period including travel time then 175 person-days will be expended in the collection of the samples (3.5 days per county x 2 counties x 5 persons per trip x 5 trips). At the current Environmental Hazard Scientist, Range B, Step I pay rate of 107.49 day equivalent this would total \$18,810.75 in labor costs. Per Diem charges per person for 3 full days at 82.00/day and 0.5 days claiming meals only will total 13,425.00 for the duration of the study.

The anticipated expenditures for this soil core study will be a minimum of \$100,275.75 and could rise to \$143,475.75 depending on the actual number of soil samples submitted for analyses (laboratory + salary + per diem totals). These costs do not include the accompanying transportation costs. Normally, two to three vehicles will be needed in the field in addition to the drill rig for the transport of augers, personnel and the delivery

of samples. Also not figured into these costs is the depreciation on equipment values of approximately \$100,000 for the drilling rig and vehicles.

#### Tension Lysimeter Monitoring

The first step in using the tension lysimeter for sampling soil water is to certify that the lysimeter itself is not interfering with the integrity of the sample collected, i.e. the ceramic tip is not appreciably affecting pesticide concentrations. This can be verified in the laboratory by passing low concentrations of pesticide of interest dissolved in water through the ceramic and noting the differences in concentration and whether or not an equilibrium is established. This will normally require up to 15 samples. Provided no significant problem is noted with residue entrapment the lysimeter can then be incorporated in a monitoring scheme.

Tension lysimeter installation will require 3.5 person-days per county. This will include one day for implanting of the lysimeters in the soil at both sites within a county. The lysimeters will be installed at an 2.54 m (8 ft) depth which according to the PCPA is the minimum depth at which pesticide residues can be considered a potential threat to ground water. Five lysimeters will be placed within a selected field site at a cost of \$26.00/lysimeter if purchased through a commercial vendor. Modifications to use Teflon<sup>R</sup> tubing lines would add \$8.00 to the cost. The remaining sampling system would include \$150.00

for a vacuum pump and a one hour timer clock (\$28.00). Generators to provide the power are already on hand. The vacuum system will be transportable between the two counties so that only two such systems will be required at any one time. Miscellaneous charges of \$50.00 to \$200.00 per site may be applicable for plastic tubing and associated fittings for building the sampling manifold. The initial investment in materials and supplies required to set up the lysimeter monitoring stations will total \$1086.00-\$1236.00.

The sampling strategy when using tension lysimeters will need to coincide with irrigation events and appropriately scheduled. An artificial irrigation prior to Pesticide X's application may be necessary in some soils to obtain sufficient soil water to do a background study for existing levels of Pesticide X. These samples would best be acquired during the installation period accruing an additional 1.5 person-days labor to each county. It is estimated that the remaining samples could be collected at a labor use of 3.5 person days/county. This is based on the fact that the duties assigned this employee will involve attaching clean jars to the system, packing the jars in ice, and starting the generator and vacuum pump. The samples will be collected, labelled and shipped to the analytical laboratories after a 48 hour sampling period or when irrigation drainage has ceased. The labor requirements for the seasonal sampling will be 28 person-days (3.5 person-days per county x 2 counties x 4 post-application sampling periods). With the addition of the labor for

installation (3.5 person-days per county) and background sampling (1.5 person-days per county) the total number of person-days will equal 38. At the equivalent pay rate of \$107.49 used earlier this amounts \$4084.62 in labor costs. Per Diem expenditures for the study would be \$2103.00.

Though soil distribution information is not an integral part of this monitoring scheme, it may yield data which may be of significance at some future date. During the installation of the tension lysimeters three soil samples will be collected from the displaced soil and will represent 1) the surface 30.5 cm (1 ft) of soil, 2) a composite sample of the next 2.13 m (7 ft) and 3) a sample of the 2.74 m (9 ft) increment. These increments would represent the region of expected high concentration of Pesticide X, an estimate of the potential availability of Pesticide X to be picked up by the tension lysimeter and finally a sample against which the lysimeter data can be contrasted to estimate the efficiency of the system. Soil samples would again be collected at the end of the study. The study would generate a total of 120 soil samples (2 sampling periods x 3 soil samples x 5 lysimeters x 2 sites per county x 2 counties).

The number of soil water samples generated by the study will be 100 (5 sampling periods including background x 5 lysimeters per site x 2 sites per county x 2 counties). The cost of the 220 samples (120 soil + 100 water) at \$150.00/sample will be \$34,650 including a 5% increment for Quality Control.

The grand total for completing the required monitoring will be \$41,923.62. This will yield a minimum savings of \$58,352.13 over the soil core process, yielding a minimum savings of more than 58% over the common soil core process. It should also be noted the lysimeter scenario includes soil sampling which may not be critical for this study and actually comprise over half of the samples collected.

The scenario presented is one not atypical of those common to CDEA. The costs above do not include costs for equipment, its maintenance and depreciation. Soil coring devices for the installation of the lysimeters can cost anywhere from \$100.00 (veihmeyer tubes) to ca. \$20,000.00 (Giddings Machine<sup>R</sup>). This is far less than the \$60,000.00 plus needed to purchase drilling rigs of the type necessary for environmental sampling. Coupled with the savings in labor and associated costs, use of tension lysimeters should be very beneficial to the CDEA's monitoring requirements associated with the PCPA or its developing Ground Water Protection Plan.

## Appendix 3

Tables of Pesticide and Bromide Distributions in  
Soil Profile and Associated Soil Characteristics

Table A3.1. Soil atrazine concentrations (ppb).

DEPTH	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	800	410	16	330
2	25	28	<5	18
3	<5	30	<5	12
4	30	<5	<5	<5
5	<5	<5	<5	<5
6	56	<5	<5	<5
7	17	<5	<5	<5
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	280	770	420	330
2	15	<200*	88	<5
3	<5	60	<5	<5
4	<5	80	<5	<5
5	<5	40	<5	<5
6	<5	<5	<5	<5
7	<5	48	<5	6.6
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	340	210	250	1200
2	32	16	49	58
3	210	<5	15	15
4	<50*	<5	<5	<5
5	<50*	<5	<5	<5
6	<200*	<5	<5	<5
7	<200*	<5	<5	25
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	250	50	68	20
2	150	29	<5	28
3	43	22	8.3	9.5
4	<10*	<5	<5	18
5	<5	<5	<5	<5
6	<10*	<5	<5	6.5
7	<5	<5	<25*	<5
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	220	220	240	130
2	36	18	53	11
3	8.0	23	22	18
4	<5	19	<5	<5
5	<5	14	<5	<5
6	<5	13	<5	<5
7	<10*	<5	<5	<5
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	1400	5.4	143	18
2	10	42	28	<5
3	35	58	6.8	<5
4	40	25*	<5	<5
5	34	<20*	<5	5.0
6	<5	5.7	5.3	<5
7	45	<5	<5	<5
	* samples with matrix interferences			

Table A3.2. Soil pesticide concentrations (ppb).

DEPTH	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	---	---	18	---
2	<2	<5	<5	18
3	<2	<5	<5	11
4	<2	<5	<5	<5
5	<2	<5	<5	<5
6	5.9	<5	<5	<5
7	30	<5	<5	<5
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	---	<50*	---	---
2	---	<50*	<2	<5
3	---	31	<2	<5
4	---	33	<2	<5
5	---	<5	<2	<5
6	---	<5	<2	<5
7	---	<5	<2	<5
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	12	10	35	<2
2	<20*	<5	24	<2
3	<20*	<5	35	<2
4	<20*	<5	20	<2
5	<20*	<5	5.0	<2
6	<20*	<5	<5	<2
7	<20*	<5	<5	<2
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	10	49	---	<5
2	<2	19	---	<5
3	<2	<5	---	<5
4	28	<5	---	<5
5	<2	<5	---	<5
6	<4*	<5	---	<5
7	<2	<5	---	<5
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	33	<2	<5	16
2	24	<2	<5	<2
3	36	<2	<5	<2
4	<10*	<2	<5	<2
5	<10*	<2	<5	<2
6	<10*	<2	<5	<2
7	<15*	<2	<5	<2
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	---	6.1	<50*	<5
2	---	<5	<5	6.0
3	---	<5	<5	<5
4	---	<5	<5	<5
5	---	<5	<5	13
6	---	<5	<5	<5
7	---	<5	<5	<5

\* matrix interferences      ---- missing data

Table A3.3. Soil bromide concentrations (ppm).

DEPTH	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	.88	2.80	1.32	8.75
2	.60	3.05	1.15	4.05
3	5.22	5.38	4.20	2.05
4	1.98	.78	3.25	1.02
5	.78	.55	1.12	.80
6	1.48	.68	1.00	.78
7	.90	.72	.92	2.40
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	1.32	8.85	2.12	9.05
2	1.75	1.28	2.38	2.32
3	3.88	1.55	2.78	.78
4	1.95	3.22	5.55	1.60
5	.68	2.18	1.80	1.30
6	.38*	.45	.98	1.68
7	1.08	.50	.58	1.40
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	.65	5.68	.92	10.70
2	2.68	.70	.40	3.60
3	2.72	3.20	4.28	2.85
4	2.20	2.28	2.00	1.82
5	1.75	1.68	1.78	.35*
6	.48	4.40	2.42	1.05
7	.30*	.78	.72	.82
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	.48	3.20	13.90	1.28
2	.92	1.57	2.88	1.85
3	1.05	.42	2.42	.78
4	.82	1.35	1.58	.80
5	.78	1.02	2.10	.10*
6	.48	.30*	1.58	3.05
7	.50	.20	1.62	.45
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	2.32	1.58	2.75	2.98
2	1.58	1.35	1.65	----
3	.28*	3.90	1.28	1.80
4	1.72	1.02	1.88	.68
5	.30*	.65	.75	1.22
6	.68	2.78	.90	.38*
7	1.02	.60	1.30	.52
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	1.32	1.70	3.35	.82
2	.98	1.02	4.88	.98
3	1.12	3.10	1.12	1.68
4	1.35	1.00	3.85	3.45
5	.98	2.85	.85	1.40
6	1.90	.75	1.42	.30*
7	.98	.85	.48	1.28
* Br <sup>-</sup> detection limits 0.4 ppm			---- missing data	

Table A3.4. Soil texture analysis results.

DEPTH	MALATHION			ALACHLOR			SIMAZINE			CARBOFURAN		
	SA*	SI*	CL*	SA	SI	CL	SA	SI	CL	SA	SI	CL
1	64	25	11	46	42	12	51	40	9	51	40	9
2	88	1	11	64	27	9	69	24	7	81	15	4
3	31	55	14	48	41	11	72	21	7	83	9	8
4	52	37	11	71	20	9	73	19	8	86	10	4
5	64	28	8	73	21	6	76	16	8	75	16	9
6	85	12	3	83	11	6	84	11	5	77	16	7
7	99	0	1	86	9	5	84	14	2	83	8	9
	ATRAZINE			OXAMYL			DIAZINON			ALDICARB		
1	72	24	4	39	37	24	43	46	11	46	39	15
2	64	26	10	55	34	11	78	20	2	58	36	8
3	37	51	12	87	4	9	75	18	7	70	20	10
4	70	21	9	73	19	8	71	26	3	75	18	7
5	67	24	9	75	0	25	80	14	6	78	18	4
6	80	13	7	89	8	3	85	8	7	87	9	4
7	90	6	4	51	43	6	89	5	6	88	8	4
	OXAMYL			ALDICARB			CARBOFURAN			MALATHION		
1	65	28	7	61	32	7	51	39	10	46	30	24
2	53	38	9	73	22	5	83	10	7	57	34	9
3	34	57	9	71	22	7	77	14	9	69	25	6
4	67	31	2	70	21	9	75	16	9	77	14	9
5	68	24	8	80	17	3	80	13	7	84	10	6
6	71	22	7	91	9	0	88	5	7	91	6	3
7	83	9	8	96	2	2	95	2	3	93	3	4
	DIAZINON			SIMAZINE			ATRAZINE			ALACHLOR		
1	64	29	7	69	24	7	49	42	9	49	41	10
2	57	35	8	73	23	4	74	19	7	80	12	8
3	48	43	9	67	27	6	60	33	7	84	6	10
4	68	26	6	70	23	7	77	18	5	78	15	7
5	71	22	7	72	19	9	83	13	4	85	11	4
6	78	14	8	83	11	6	93	3	4	93	4	3
7	86	10	4	88	5	7	98	1	1	93	3	4
	CARBOFURAN			MALATHION			ALDICARB			DIAZINON		
1	75	17	8	65	27	8	49	40	11	49	39	12
2	57	32	11	64	31	5	87	7	6	75	20	5
3	66	28	6	69	21	10	65	29	6	75	16	9
4	65	25	10	71	19	10	73	21	6	81	10	9
5	71	21	8	72	18	10	79	20	1	75	17	8
6	73	19	8	85	10	5	89	7	4	88	0	12
7	83	12	5	91	5	4	97	0	3	93	4	3
	ATRAZINE			OXAMYL			ALACHLOR			SIMAZINE		
1	71	22	7	73	19	8	61	29	10	48	42	10
2	47	43	10	71	20	9	87	8	5	66	23	11
3	59	30	11	66	26	8	71	20	9	75	16	9
4	69	22	9	64	25	11	77	17	6	71	21	8
5	73	22	5	80	15	5	81	14	5	79	16	5
6	66	26	8	78	15	7	91	2	7	89	4	7
7	86	9	5	82	12	6	95	2	3	95	2	3
	*SA - % SAND			*SI - % SILT			*CL - % CLAY					

Table A3.5. Soil profile pH values.

DEPTH	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	8.31	7.82	8.19	8.14
2	7.44	7.60	7.80	7.53
3	7.45	7.55	7.19	7.28
4	7.71	7.48	7.48	7.26
5	6.67	7.73	7.87	7.33
6	7.03	7.74	7.54	7.51
7	7.18	8.04	7.77	7.82
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	7.88	8.16	8.20	8.04
2	7.50	7.69	7.47	7.58
3	6.97	7.79	7.64	7.56
4	6.51	7.90	7.34	7.74
5	7.33	7.59	7.19	8.12
6	7.16	8.06	7.56	6.43
7	7.18	7.98	7.70	8.22
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	8.16	8.24	7.45	7.91
2	7.73	7.15	6.86	8.23
3	7.48	7.44	6.44	8.30
4	7.37	7.73	7.23	7.83
5	7.94	5.48	7.13	8.08
6	7.33	7.15	7.75	7.71
7	7.29	7.75	7.38	8.32
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	7.98	8.00	7.86	7.93
2	7.17	7.81	7.52	7.78
3	7.20	7.60	7.63	7.55
4	6.78	7.34	7.49	7.86
5	6.93	7.44	7.09	7.73
6	6.99	7.40	7.36	7.34
7	7.00	7.50	7.95	7.94
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	7.96	7.73	7.74	8.20
2	7.37	7.70	7.81	----
3	7.28	6.38	7.74	7.79
4	6.78	7.52	7.83	7.56
5	7.11	7.25	7.45	7.58
6	6.97	7.71	7.95	7.85
7	5.86	6.98	8.08	7.86
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	7.50	8.15	7.79	8.14
2	7.26	7.35	7.26	7.78
3	7.46	7.30	7.59	7.82
4	7.84	----	7.45	7.94
5	7.53	7.59	7.63	7.84
6	7.91	7.59	7.38	8.13
7	7.70	7.80	7.76	8.44
	---- missing data			

## Appendix 4

Tables of Pesticide and Bromide Distributions in Soil  
Water and Approximate Sample Volumes Extracted

Table A4.1. Atrazine concentrations (ppb) in soil solutions.

IRRIGATION	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	<1.0	35.0	----	2.0
2	<1.0	<1.0	3.1	<1.0
3	<1.0	<1.0	<1.0	<1.0
4	<1.0	<1.0	<1.0	<1.0
5	1.2	<1.0	<1.0	<1.0
6	<1.0	9.1	<1.0	<1.0
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	5.3	----	4.3	<1.0
2	2.5	3.6	<1.0	<1.0
3	4.1	<1.0	2.7	<1.0
4	8.9	2.0	2.9	<1.0
5	4.7	4.7	3.8	<1.0
6	7.7	10.0	7.6	<1.0
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	<1.0	<1.0	<1.0	1.4
2	<1.0	<1.0	<1.0	<1.0
3	3.0	<1.0	<1.0	1.0
4	5.9	1.7	<1.0	<1.0
5	3.4	9.5	10.0	4.5
6	4.7	18.0	10.0	13.0
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	1.7	1.1	<1.0	<1.0
2	<1.0	4.2	<1.0	<1.0
3	16.0	26.0	<1.0	<1.0
4	41.0	28.0	<1.0	<1.0
5	9.2	7.9	<1.0	<1.0
6	10.0	3.1	<1.0	<1.0
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	40.0	65.0	<1.0	<1.0
2	20.0	80.0	<1.0	<1.0
3	24.0	71.0	<1.0	5.1
4	42.0	40.0	2.3	8.9
5	6.0	55.0	25.0	7.5
6	21.0	37.0	29.0	2.0
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	3.3	<1.0	<1.0	<1.0
2	18.0	<1.0	<1.0	<1.0
3	22.0	<2.5	4.8	<1.0
4	3.7	<1.0	120.0	1.2
5	9.1	24.0	130.0	<1.0
6	15.0	16.0	140.0	<1.0
	---- denotes missing data			

Table A4.2. Pesticide concentrations (ppb) in soil solution.

IRRIGATION	MALATHION	ALACHLOR*	SIMAZINE	CARBOFURAN
1	<0.2	<1.0*	----	1.0
2	<0.2	<0.1	<1.0	4.0
3	<0.2	<0.1	<1.0	5.0
4	<0.2	<0.1	<1.0	8.0
5	<0.2	<0.1	<1.0	12.0
6	<0.2	<0.1	<1.0	10.0
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	5.3	----	<0.2	<1.0
2	2.5	<1.0	<0.2	2.3
3	4.1	<1.0	<0.2	<1.0
4	8.9	<1.5	<0.2	<1.0
5	4.7	<1.0	<0.2	<1.0
6	7.7	<1.0	<0.2	2.3
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	4.0	<1.0	<1.0	<0.2
2	14.0	4.5	<1.0	<0.2
3	23.0	8.0	42.0	<0.2
4	5.2	2.1	87.0	<0.2
5	6.6	<1.0	63.0	<0.2
6	4.8	<1.0	61.0	<0.2
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR*
1	<0.2	1.6	<1.0	<1.0*
2	<0.2	<1.0	<1.0	<0.1
3	<0.2	<1.0	<1.0	<0.1
4	<0.2	1.6	<1.0	<0.1
5	<0.2	<1.0	<1.0	<0.1
6	<0.2	<1.0	<1.0	<0.1
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	140.0	<0.2	<1.0	0.2
2	24.0	<0.2	4.1	<0.2
3	35.0	<0.2	9.8	<1.0*
4	50.0	<0.2	<1.0	<0.2
5	15.0	<0.2	<1.0	<0.2
6	33.0	<0.2	<1.0	<0.2
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	3.3	<1.0	<0.1	<1.0
2	18.0	<1.0	<0.1	<1.0
3	22.0	<2.5	0.8	<1.0
4	3.7	<1.0	52.0	<1.0
5	9.1	<1.0	90.0	<1.0
6	15.0	1.0	61.0	<1.0
	* matrix interferences		---- missing data	

Table A4.3. Bromide concentrations (ppm) in soil solution.

IRRIGATION	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	5.1	3.9	----	8.6
2	10.4	6.2	3.7	9.4
3	14.7	7.7	3.8	10.6
4	12.9	5.0	6.7	11.3
5	11.1	13.3	7.2	8.8
6	7.3	13.6	10.2	7.5
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	8.6	6.7	3.4	1.7
2	11.3	15.3	9.9	2.9
3	11.6	12.4	21.7	8.7
4	11.8	----	26.6	----
5	7.4	26.3	41.9	----
6	6.5	23.9	44.3	----
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	10.4	1.1	4.1	----
2	16.4	3.2	14.4	3.8
3	27.6	6.1	8.7	7.8
4	27.5	6.0	----	6.1
5	26.3	10.2	10.0	7.7
6	11.9	17.6	14.5	10.7
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	20.4	3.8	3.2	2.6
2	16.3	5.1	3.3	1.7
3	13.9	8.4	7.3	4.1
4	7.6	14.0	16.0	4.3
5	5.9	21.2	15.2	8.1
6	11.5	17.3	15.2	13.8
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	10.7	6.4	4.5	4.4
2	4.4	5.2	5.3	4.4
3	5.3	4.3	----	2.9
4	5.1	7.1	6.9	----
5	7.8	8.3	16.6	7.3
6	5.2	11.4	12.8	14.6
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	2.7	3.8	4.0	3.0
2	3.3	4.6	9.8	2.8
3	5.8	3.3	14.2	8.7
4	8.8	4.8	9.5	19.9
5	13.6	6.9	9.2	19.9
6	12.0	11.8	12.2	38.9
	---- denotes missing values			

Table A4.4. Approximate soil water sample volumes (mls).

IRRIGATION	MALATHION	ALACHLOR	SIMAZINE	CARBOFURAN
1	1020	<1000	----	1270
2	1790	<1000	<500	1620
3	1710	<1000	<500	1500
4	1790	<1000	<500	1270
5	1770	----	<500	1580
6	1620	----	<500	1670
	ATRAZINE	OXAMYL	DIAZINON	ALDICARB
1	1290	<1000	<1000	1320
2	1720	<1000	1210	<1000
3	1750	1100	1360	1200
4	1740	<1000	1110	<1000
5	1760	<1000	1620	<1000
6	1690	1150	1480	<1000
	OXAMYL	ALDICARB	CARBOFURAN	MALATHION
1	1630	1120	1160	<1000
2	1720	1220	1750	1290
3	1780	1530	1770	----
4	1780	1500	1790	1360
5	1680	1630	----	1280
6	1790	1570	1330	1110
	DIAZINON	SIMAZINE	ATRAZINE	ALACHLOR
1	1740	1590	1780	<1000
2	1740	1690	1710	----
3	1840	1660	1720	1400
4	1750	1610	1420	<1000
5	1640	1390	1470	1290
6	1750	1830	1110	1320
	CARBOFURAN	MALATHION	ALDICARB	DIAZINON
1	1810	1510	1330	1380
2	1780	1730	1370	1230
3	1740	1780	1380	----
4	1700	1550	----	----
5	1740	1820	1630	----
6	1760	1800	1490	----
	ATRAZINE	OXAMYL	ALACHLOR	SIMAZINE
1	1250	1200	----	1490
2	1780	1540	1160	1610
3	1780	1250	1170	1530
4	1390	----	1370	----
5	1710	1780	1520	----
6	1820	1770	1800	1070
		----		
		---- missing data		