13

BARD

FINAL REPORT

PROJECT No. I-95-79

Application of Pesticides Via Drip Irrigation Systems

B. Yaron, Z. Gerstl, W. Jury, W. Farmer,
W. Spencer

630.72

BAR

2nd copy

1983

USDA-ARS and Dept. of Soil
and Environmental Sciences
University of California
Riverside, CA., U. S. A.

April 1983

BARD
P.O.B. 6
Bet Dagan, ISRAEL

BARD No. of Proposal I-95-79

Title of Proposed Research

Application of Pesticides Via Drip Irrigation Systems

Name(s) of Investigator(s)

Principal Investigator: Dr. Bruno Yaron

Cooperating Investigator: Dr. Zev Gerstl (Israel)
Dr. William Jury; Dr. Walter Farmer, Dr. William
Spencer (U.S.A.)

Name and Address of Affiliated Institution(s)

Grantee Institution: Inst. of Soils and Water; Agric. Res. Org.; The
Volcani Center, Bet Dagan Israel

Cooperating Institution: USDA; ARS and Dept. of Soil and Environmental
Sci., UC Riverside, Riverside, CA

Project's starting date September 20, 1979

Type of Report: Initial   Comprehensive   Final X

Signature

Principal Investigator

Bruno Yaron

Institution's Authorizing Official

Zeev Gerstl

1) Trickle irrigation 2) Pesticides

630.72 : 631.7 : 632.915
BAR

2nd copy

APPLICATION OF PESTICIDES
VIA DRIP IRRIGATION SYSTEMS

by

Bruno Yaron and Zev Gerstl

Institute of Soils and Water
Agricultural Research Organization
Volcani Center
Bet Dagan, ISRAEL

and

William Jury, Walter Farmer, and William Spencer

Dept. of Soil and Environmental Sciences
University of California, Riverside

and USDA-ARS
Riverside, CA, USA

TABLE OF CONTENTS

	Page
Abstract	i
I. Introduction	1
II. Materials and Methods	3
1. Laboratory Studies - USA	3
2. Oxamyl Field Study - USA	7
3. Laboratory Studies - ISRAEL	8
4. Field Studies - ISRAEL	15
III. Theoretical Analysis	18
1. Dynamic Pesticide Adsorption Coefficient	18
2. Pesticide Movement From a Trickle Emitter	19
IV. Results and Discussion	32
1. Adsorption Studies - USA	32
2. Adsorption Studies - ISRAEL	33
3. Degradation Studies - ISRAEL	37
4. Laboratory Drip Irrigation Studies - ISRAEL	42
5. Laboratory Drop Irrigation Studies - USA	57
6. Field Experiments - ISRAEL	58
7. Field Experiments - USA	61
V. Model Simulations	63
VI. Evaluation of Objectives	66
VII. References	68
VIII. Tables	76
IX. Figures	103

ABSTRACT

The final report for the three-year study on application of pesticide via drip irrigation systems is reported herein. The interdisciplinary study consisted of laboratory and field experiments in Israel, laboratory and field experiments in the United States, and theoretical model development and simulation in the United States. A total of six soils were studied in Israel and three soils in the United States, all representative of arid conditions. Three chemicals, bromacil, devrinol (napropamide), and oxamyl were studied under simulated trickle irrigation systems in the laboratory and actual trickle irrigation systems in the field.

The Israeli studies consisted of concise laboratory measurements of adsorption coefficients, solubility and degradation rate coefficient for the chemicals under a variety of conditions and a round of laboratory simulated trickle irrigation experiments involving the application of water and chemical to soil contained in a cylindrical pail. The Israeli research culminated in a field study examining the movement of the herbicides under trickle irrigation to bare soil and to cropped soil.

The United States studies consisted of carefully controlled experiments in large cylindrical containers studying the influence of water evaporation on chemical movement and a supportive set of field measurements studying the spatial variability of the pesticide distribution coefficient. A co-sponsored experiment in the field looking at the persistence and mobility of oxamyl is also briefly reported.

A theoretical model using the method of characteristics was developed to predict the streamlines under evaporation-free and evaporation-aided trickle irrigation. The model is used in a series of scenario calculations to show the influence of water evaporation on pesticide movement.

I. INTRODUCTION

Increasing use of drip irrigation technology in crop production, primarily in semi-arid areas, offers a new approach for a safer and more efficient method of introducing pesticides into the soil environment. Application of a systemic pesticide-nematicide or an herbicide via drip irrigation minimizes or eliminates human exposure, non-target organism effect, and degradation of the environment. By applying it with the water it offers the opportunity for a more economical use of expensive chemicals. Furthermore, the pesticides could be applied when the crop is not water-stressed and thus be more able to absorb the chemical. Finally, the application occurs directly at the site to be protected.

Mobility and persistence of pesticides appear to be the limiting factors relative to their efficient use in drip irrigation systems. Some of the nematicide-insecticide systemics are not sufficiently mobile in highly adsorbing soils to provide pest control. Similarly, some herbicides might not move sufficiently in a lateral direction to control the weeds on the fringes of the wetted areas. Finally, both nematicides-insecticides and herbicides are degraded quite rapidly in the moist areas immediately adjacent to the drip emitters.

Because of the large and unexplored potential benefit in adapting pesticide application to drip irrigation systems, there exists a need to quantify the relationship between pesticide movement and relevant soil and environmental factors and, if possible, to develop a model capable of illustrating the effect of these parameters on movement. At a minimum, this quantification will require gathering information on

all parameters affecting pesticide transport and stability within the drip irrigation system such as adsorption on soil constituents and rate of degradation in soil at various moisture contents and temperatures.

The work contained in this report is part of an interdisciplinary study intended to investigate the problems associated with the application of pesticides in drip irrigation systems to insure effective pest control efficiency. While at the present time the application of pesticides via irrigation systems in Israel is severely limited due to the possible contamination of water sources from a sudden failure of the system, an intensive effort is currently underway to develop a reliable and economically feasible safety valve. Consequently, it is only a matter of time until these restrictions are removed making this area of research quite practical.

The research summarized in this report involved three years of experiments and analysis from the following objectives: 1) to determine the adsorption and degradation of pesticides by various soils as one parameter useful in predicting distribution of pesticides applied through drip irrigation systems, and to study the effect of soil moisture and soil temperature on these processes; 2) to study the effect of soil moisture content on the transport processes of soil-applied pesticides; 3) to develop and test a model to predict the distribution of pesticides in soil at various times following their application through drip irrigation systems.

In the sections which follow we present the results of the three-year study, concluding with an evaluation of the degree to which the objectives were met.

II. MATERIALS AND METHODS

1. Laboratory Studies - USA

a. Materials

The three pesticides used in this study were bromacil, oxamyl, and napropamide. For the Riverside laboratory studies, two area soils were selected: Pachappa sandy loam and Tujunga loamy sand. Samples taken for the laboratory study were obtained from the upper 30 cm of the soil profile. The Pachappa soil was air-dried, stones and plant residues removed, and the soil passed through a 2-mm sieve before use. The Tujunga soil used in the dynamic adsorption experiment was placed in soil cylinders in the field and tested in an undisturbed, natural state.

b. Procedures

Adsorption-desorption isotherms were obtained on Pachappa sandy loam at 20 and 30°C. Analytical methods were established for C-14 bromacil and napropamide by liquid scintillation analysis. Samples could be analyzed in aqueous solution, in soil or extracted into ethyl acetate. These methods were used to obtain adsorption-desorption isotherms on Pachappa soil using a 1:2 soil:solution ratio and a one-day equilibration time for adsorption and each successive desorption. Adsorption of bromacil on Pachappa was extremely low, even at 20°C so no studies were performed at 30°C.

The results obtained for bromacil and napropamide using liquid scintillation were confirmed by gas chromatograph analysis, using a Varian 3700 equipped with a thermionic specific detector. One-meter glass columns, packed with either 2.3% OV-17 on 100/120 gas chromatograph Q or 1.5% OV-17/1.95% QF-1 on 80/10 CHROM W were equally satisfactory for the analysis. Bromacil and napropamide were extracted into ethyl acetate before injection into the gas chromatograph.

Considerable time has been spent developing a simple method for handling the aqueous oxamyl samples. The reverse phase HPLC method using a C18 column and CH_3CN :buffered water mobile phase can be used for direct injection of some aqueous samples. Problems arose, however, after contact with certain soils at low concentration levels. It was preferable in any case to get the oxamyl out of aqueous solution and into an organic solvent which could be stored in the freezer and thereby slow down degradation. Success was attained using Waters' Sep-Pak C18 cartridges to sorb the oxamyl from aqueous solution and subsequent elution with CH_3OH .

Determination of the adsorption of oxamyl by soils is complicated by the fact that oxamyl is subject to rapid hydrolysis in the soil solution to the oxime. The HPLC method of Thean et al. (1978) was modified for use in the adsorption isotherm measurement to allow analysis of both the parent compound and its oxime. The analyses were performed on a Waters HPLC equipped with two 600 A pumps and a Model 440 U.V. detector. The column used was a 30-cm, 10-u, Microbondapac C18. The mobile phase was varied from 11 to 7% acetonitrile in phosphate buffer (1 g each $\text{K}_2\text{HOP}_4 + \text{KH}_2\text{PO}_4$ in 1 liter of water). The 11%

acetone nitrate mobile phase was preferred but had to be reduced to 7% as column performance deteriorated. The reduced level of acid to nitrate reduced pressure buildup in the column but also caused increased tension times for the sample.

Although an aqueous aliquot of the adsorption isotherm equilibrium solution could be analyzed directly via injection into the HPLC, it was preferable to remove the oxamyl from the aqueous environment thereby avoiding any further hydrolysis of the sample. Attempts to extract the oxamyl with ethyl acetate were unsuccessful because the ethyl acetate caused problems both with the C18 column and a micro-Bondapac-NH₂ column which was tried. Finally a method was developed for sample preparation using water C18 Sep-paks, essentially mini-C18 columns which were attached to a syringe. The Sep-paks were prewashed with 304 ml HC₃OH and 3X's with 4-5 ml deionized H₂O. Ten mg of sample were then put through the column and adsorbed oxamyl was eluted with CH₃OH. Problems were experienced with the variable recovery from the Sep-paks from lot to lot and also with volume and concentration of sample. Attempts to concentrate a low concentration sample by forcing a large volume of solution through the Sep-pak resulted in extremely low and variable recovery.

The Sep-paks were adequate for oxamyl samples in the aqueous concentration range from 0.5 to 50 ppm which was used for the sorption isotherm. Solutions initially containing 0.6 to 50 ppm oxamyl were equilibrated with Pachappa soil at a 1.2 soil:solution ratio at 10°C.

Dynamic Adsorption Coefficient Measurement. In order to estimate the influence of spatial variability of adsorption on transport under natural field conditions, 16 undisturbed soil cores were taken from the Tujunga soil at a spacing of 13.3 meters in a 4 x 4 square grid. Samples were taken by pushing 10-cm diameter cylindrical aluminum tubes to a depth of 15 cm in the soil and extracting the core by digging a hole around the sample. These undisturbed cores were returned to the laboratory and were subjected to a steady-state 20cm/day water flux rate while effluent from the bottom of the column was collected under gravity drainage. After steady state was reached, a concentrated pulse containing 500 ml of 15 meq/l calcium chloride and 50 ppm napropamide was added to the surface of the column, followed by continued steady-state water flow at 2 cm/day. Effluent samples were collected in the columns to observe the breakthrough time of the chloride and napropamide. From these measurements adsorption coefficients were calculated by the method explained in the theory section.

Trickle Irrigation Experiment. To study the influence of water evaporation on chloride and pesticide transport on trickle-irrigated soil, a large 60-cm diameter, 30-cm deep column was packed uniformly with air-dried Pachappa soil to a bulk density of 1.50. A single trickle emitter driven by a constant head device through a hypodermic needle was placed at the radial center of the surface located 1 cm above the soil.

In the first experiment, a wood cover was placed just above the soil surface to prevent any evaporation. Water was applied to the

column for three days at a steady rate of 3.5 l/day at which time a single concentrated pulse containing 500 ml of 15 meq/l CaCl_2 solution and 50 ppm napropamide was added to the emitter. When this was placed in the soil through the emitter, steady application of water was resumed at the surface for three more days at 3.5 l/day.

The procedure used for the experiment permitting water application was identical to the above, except that the soil cover was removed and an evaporation rate of approximately 0.5 cm/day was obtained by mounting three lamps moderated through a Variac at 1 m above the soil surface.

At the conclusion of the experiment the column was sectioned for analysis by using rings of various diameters and 2.5 cm depth. The rings -- 10, 15, 20, 25, and 30 cm in diameter -- were pushed into the soil and the material between the rings removed for analysis. Samples were split three ways and analyzed for napropamide, chloride, and water content. In this way, each sample represented a full average over a radial and depth increment, assuming cylindrical symmetry in the column. Evaporation rate was estimated as an average over the six days of the experiment by subtracting soil storage change from water applied.

2. Oxamyl Field Study -- USA

As part of a cooperative study, oxamyl was applied by flood irrigation at 1.0 kg/ha/month for nine months to a lemon grove near Thermal, California, between 5/7/81 and 1/11/82. The soil was sampled to a depth of 6 m on 1/25/82, 14 days after the last oxamyl application, and on 2/13/82, 35 days after the last application. The grove contained

five 1/4-acre plots receiving the 1.0 kg/ha treatment and five 1/4-acre plots which received no oxamyl. The purpose of this study was to determine whether oxamyl degraded rapidly enough to avoid leaching to great depths. Although partly outside the objectives of our proposal, it is included here as a secondary, indirect assessment of degradation of oxamyl and also of the influence of spatial variability on movement.

3. Laboratory Studies -- Israel

a. Materials

The chemicals studied were identical to those mentioned above in the USA discussion.

The soils studied, taken from different agricultural areas of Israel, are surface soils from the upper 10 cm of the soil profile. The soils were air dried, stones and plant residues removed and the soil passed through a 2 mm sieve before use. Their properties, determined by standard procedures, are given in Table 1a.

b. Procedures

The solubility of the herbicides in both water and 1-octanol was determined by placing an excess of analytical grade herbicide in glass tubes and adding 5 ml of the appropriate solvent. After 5 min of ultrasonic dispersion the test tubes were incubated at 55°C for 3 days and then for an additional 7 days at 25°C. At this time the solvent was either extracted (for water) or diluted (for 1-octanol) with ethyl acetate and the herbicide concentration determined by GLC.

The solubilities of oxamyl were not determined.

The partition of napropamide and bromacil between water and 1-octanol was determined by shaking aqueous solutions of ^{14}C -labeled herbicide with 1-octanol for 24 h and determining the final activity in both phases. This procedure was carried out for several initial concentrations of herbicide. The partition of oxamyl between water and 1-octanol was determined by depositing ^{14}C -labeled oxamyl on the walls of glass-stoppered centrifuge tubes and analytical grade 1-octanol (2 ml) was added. After 2 hours double-distilled water (51) was added and the tubes were shaken for 15 minutes, then centrifuged at 4000 rpm. An appropriate aliquot of the octanol layer was counted by a conventional liquid scintillation method. The remainder of the octanol was removed (including some water if necessary) and the water was transferred to a Corex centrifuge tube and centrifuged at 10,000 rpm for 15 minutes to separate any remaining octanol from the aqueous phase. An appropriate aliquot of the water was removed for oxamyl determination. The measurements were carried out in triplicate at three different oxamyl concentrations (equivalent to 100, 1,000, and 10,000 mg l^{-1} if all the oxamyl were to be found in the aqueous phase).

Adsorption isotherms were generated by adding 10 ml of ^{14}C labeled herbicide solutions to glass centrifuge tubes with glass stoppers containing 2-4 grams of soil for napropamide isotherms and 3-6 grams of soil for bromacil isotherms. After 24 h of shaking, the test tubes were centrifuged and the supernatant was analyzed for ^{14}C activity. Herbicide adsorption was determined by the change in solution concentration. Preliminary experiments showed that adsorption equilibrium was

attained after 2-3 hours and no degradation occurred during the adsorption experiments. Isotherms were run in duplicate at five initial concentrations.

Oxamyl adsorption isotherms were generated by adding ^{14}C -labeled solution (4 ml; initial concentration range 5-100 mg l^{-1}) to 4-8 grams of soil in glass centrifuge tubes. After 2 hours of shaking the test tubes were centrifuged and the clear supernatant was analyzed for ^{14}C -activity. Oxamyl adsorption was determined by the change in solution concentration. The short equilibration times were necessary to avoid decomposition.

Degradation of napropamide and bromacil was studied in Gilat and Neve Yaar soils. The variables were: temperature 5° , 25° , 35° and 50°C ; soil moisture content - 50% of field capacity, field capacity, and 133% of field capacity; and initial concentration - 16 and 4 $\mu\text{g/g}$. Field capacity of the Gilat soil was 16% and that of the Neve yaar soil was 30%. The air dry soils were mixed with the appropriate amount of formulated herbicide and wet to the desired moisture content with tap water. The soil was then placed in covered glass jars kept in desiccators with distilled water to prevent drying of the soil and maintained at the desired constant temperatures. At various intervals 2 g of soil were extracted for 2 h with water and ethyl acetate (5 ml of each), and the herbicide concentration in the organic layer determined by GLC, as described below, without any prior cleanup.

The degradation of oxamyl was studied as a function of soil type, soil moisture content, temperature and initial concentration. ^{14}C -labeled oxamyl solution to 0.005M CaCl_2 were prepared and applied

to the soils to give the required moisture content and initial concentration. The soils were incubated at the desired temperature in water filled desiccators to prevent changes in the soil moisture content. At various periods after the start of the incubation, samples were taken for analysis as described below.

The simulated drip irrigation system used for the bromacil and napropamide studies consisted of a plastic pail 35 cm high and with a 15 cm radius packed with soil to a uniform bulk density. The design was such that no water reached the walls of the pail. The solutions were applied with the aid of a peristaltic pump to the center of each pail. Samples were taken with the aid of a 1.5 cm diameter tube at intervals of 3 cm starting from the trickle source and with two depth increments of 3 cm, followed by four increments of 6 cm each. This procedure was carried out along two diameters of the pail with the corresponding samples on each diameter being combined to provide two samples for each point. Formulated herbicides were used for these experiments.

For the oxamyl studies plastic buckets with a 17 cm radius were filled with the Bet Dagan I soil to a height of 33 cm and bulk density of $1.3 \text{ g}^3 \text{ cm}^3$. The buckets, the bottoms of which were perforated and covered by a screen, were kept in a constant temperature room at $22 \pm 2^\circ \text{C}$ and the oxamyl solution was applied directly to the centre of the buckets. Evaporation from an open water source was measured daily and averaged $1.32 \text{ mm}^{-1} \text{ day}$ for the duration of all the experiments.

The following treatments were conducted on the Bet Dagan I soil and sampled after 24 hours:

- (A) 1800 ml of a herbicide solution containing 50 ppm (a.i.) of both bromacil and napropamide was added to the soil;
- (B) 900 ml of a 100 ppm herbicide solution was added to the soil;
- (C) 900 ml of tap water was applied, followed 24 h later by 900 ml of a 100 ppm herbicide solution;
- (D) 900 ml of a 100 ppm herbicide solution was applied followed 24 h later by 900 ml of tap water.

The buckets were covered after each addition to prevent evaporation. All applications were at the rate of 4 l/h. In addition to the above treatments, a series of buckets were given treatment (B) and kept uncovered in a glasshouse. Half of the buckets were watered weekly and half-twice weekly. The amount of water evaporated was determined by weight loss. After one week the weekly treatment was sampled.

The remaining buckets were sampled after 5 weeks. In none of the above treatments did the applied water reach either the sides or the bottom of the buckets thus preventing any possible side or wall effect on the water or pesticide distribution.

A second set of experiments consisted of applying 900 ml of 100 ppm (a.i.) herbicide solution at 4 l/h and 1.5 l/h to four soils with sampling after 24 h.

A third set of pails of each soil were prepared as above and kept in a glasshouse with irrigation every few days to make up evaporative losses as determined by weighing the pails. After several weeks the pails were sampled and the water content and herbicide distribution were determined. The Mivtachim, Bet Dagan I, Gilat, Bet Dagan II and

Neve Ya'ar soils were packed to bulk densities of 1.6, 1.3, 1.3, 1.3 and 1.1 g/cc, respectively. All soils were sieved to the fraction finer than 0.5 mm except for the Neve Ya'ar soil for which the 1-2 mm size fraction was used.

In the oxamyl studies the buckets were irrigated for 2 days with tap water (300 ml) and left for 48 hours before initiation of the treatments which were as follows:

Ninety mg of ^{14}C -labeled oxamyl was applied in tap water (300 ml) on the first day, followed by five daily applications of 300 ml tap water (pulse);

Thirty mg of ^{14}C -labeled oxamyl in tap water (300 ml) was applied to the bucket on each of days 1, 3 and 5, and oxamyl free tap water (300 ml) on days 2, 4 and 6 (split application);

Fifteen mg of ^{14}C -labeled oxamyl in tap water (300 ml) was applied daily for 6 days (continuous).

After the 6th day of solution application the buckets were left for 48 hours before sampling. Samples were taken with the aid of a 1.5 cm diameter tube at intervals of 3 cm starting from the trickle source, with two depth increments of 3 cm followed by four increments of 5 cm. This procedure was carried out along two diameters of the bucket, with corresponding samples on each side of the point source being combined to provide two samples for each point.

Analysis of the samples included oxamyl determination as described below and soil moisture content.

c. Analytical Methods

^{14}C -labeled compounds used in the above studies were counted in a Packard Prias liquid scintillation counter. Unlabeled herbicides were determined in a Tracor 560 gas chromatograph equipped with an N-P sensitive detector and a 3% OV-17 column, 2 meters in length. The conditions were: H_2 -3.1 ml/min; N_2 -20 ml/min; air-40 ml/min; inlet 255°C ; column 250°C ; and detector 260°C .

Soil samples were extracted for oxamyl by a slightly modified procedure of Smelt et al. (1979). Between 2 and 5 grams of soil were weighed into glass stoppered centrifuge tubes and extracted with acetone (10 ml) for 2 hours. After centrifugation a portion of the clear supernatant was quantitatively transferred to a second test tube with a calibrated pitette and CHCl_3 (10 ml) was added, followed by anhydrous Na_2SO_4 . The dried solution was transferred to a round-bottomed flask (50 ml) as were the subsequent CHCl_3 washings of the test tube and Na_2SO_4 . The volume of the organic solvents was reduced on a rotary evaporator while heating the flask to 40°C . The remaining few ml of solvent were evaporated under a stream of air. The residue was taken up in the eluting solvent which was ethyl acetate (1 ml) containing water ($25 \text{ g kg}^{-1}\text{s}$). The extract was applied to the top of a silica gel column (1 cm i.d.) for clean-up. The column was slurry packed with 4 g of silica gel (63-200 μm) and preconditioned with 10 ml of the eluting solvent. After introduction of the sample, the flask was washed with the eluting solvent (0.5 ml) which was subsequently applied to the silica gel column and followed by further eluting

solvent (50 ml). The first 17 ml was discarded and the 17-50 ml fraction was collected for oxamyl determination. This fraction was concentrated to several ml on a rotary evaporator and the volume was recorded. One-half ml was then taken for ^{14}C -activity determination. Recovery by this method averaged 99.2% with a range of 96-101%, based on duplicate extractions from four soils.

4. Field Studies - Israel

a. Field description

The experiment was performed at the Bet Dagan Experiment Station. Properties of the soils for three depth increments are given in Table 1b.

Experimental

Two experiments were conducted during the summer of 1981. The first experiment consisted of 19 plots measuring 5.5 m x 12 meters. Each plot consisted of five laterals of 10 drippers spaced 1 meter apart with 1 meter between laterals. The treatments, run in triplicate plots, included:

- I: Cropped control; no herbicide application;
- II: Herbicide applied to bare field; daily irrigation at 2 l/h;
- III: Herbicide applied to cropped field; weekly irrigation at 4 l/h;
- IV: Herbicide applied to cropped field; daily irrigation at 4 l/h;

V: Herbicide applied to cropped field; in a split application (5 applications), daily irrigation at 4 l/h;

VI: Herbicide applied to bare field; daily irrigation at 4 l/h.

The herbicide applied to cropped plots was Devrinol 2-E at the rate of 4 kg (a.i.)/ha. The plots were planted with tomato (*Lycopersicon esculentum*) cultivar 1684 one week before herbicide application. The uncropped plots received, in addition to Devrinol, Hyvar-X at the rate of 4 kg (a.i.)/ha. Soil samples were taken at various intervals after the herbicide application from around individual drippers and analyzed for moisture and herbicide content.

The second experiment consisted of 5 laterals of 5 drippers each with each dripper spaced 3 m apart to prevent any possible overlap of the wetted zone. Two of the laterals were run at 4 l/h with one line receiving daily and the second weekly irrigations. The third line was irrigated daily at 2 l/h.

Daily irrigation at the rate of 12 l/dripper day was begun two weeks prior to the herbicide application. The herbicide solution contained 300 mg/l active ingredients of both bromacil and napropamide. On August 4, 1982, 12 l/dripper of the herbicide solution was applied to the bare field. Upon completion of the herbicide application one lateral of 4 l/h drippers was immediately irrigated with another 60 l/dripper. This line was then irrigated at weekly intervals at a rate of 72 l/dripper. The remaining two laterals, one of 4 l/h and one of 2 l/h, were irrigated daily with 12 l/dripper.

At various intervals after the herbicide application soil samples were taken from around individual drippers for moisture and herbicide

content. Samples were taken from directly beneath the emitter and at various distances from and depths from the emitter. The samples were kept frozen until analysis (approximately 1 week). One half the sample was taken for moisture content determination and the other for herbicide extraction as described previously.

III. THEORETICAL ANALYSIS

1. Dynamic measurement of adsorption coefficient

If one assumes that the distribution coefficient K_D is constant, then the total concentration C_T of a pesticide in soil may be written as

$$C_T = \rho_b C_S + \theta C_L = (\rho_b K_D + \theta) C_L \quad (1)$$

where C_L is concentration in solution, ρ_b is bulk density and θ is water content. In the absence of appreciable degradation the mass continuity equation for a chemical may be written as:

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_S}{\partial z} = 0 \quad (2)$$

where J_S is the mass flux.

Of, if we neglect diffusion and dispersion, and assume steady water flow

$$\frac{\partial C_T}{\partial t} + J_W \frac{\partial C_L}{\partial z} = 0 \quad (3)$$

or finally

$$\frac{\partial C_L}{\partial t} + V_S \frac{\partial C_L}{\partial z} = 0 \quad (4)$$

where $V_S = J_W / (\rho_b K_D + \theta)$ is the solute velocity. If a chemical pulse of pesticide and chloride is added to a soil column of length L in

which water is flowing at J_w , the travel time ratio of the chloride breakthrough to the pesticide breakthrough is

$$t_p/t_c = 1 + \rho_b K_D / \theta \quad (5)$$

2. Pesticide movement from a trickle emitter

The model makes four assumptions about solute transport from a trickle emitter

- 1) Water flow from the emitter is steady
- 2) The hydraulic conductivity K -matric potential head h (cm) relation is given by Eq. (6)

$$K(h) = K_0 \exp(\alpha h) \quad (6)$$

- 3) Solute transport occurs by piston flow Eq. (4) along the water streamlines
- 4) Water evaporation rate E is either zero (Case 1) or is equal to a constant E_0 over the soil surface (Case 2)

CASE 1: $E = 0$

The steady-state water flow from the emitter is described by

$$\nabla \cdot K(h) \nabla H = 0 \quad (7)$$

with a flow rate Q cm³/sec at the origin ($\rho=0$, $z=0$).

In cylindrical coordinates, using the relation in Eq. (6), Eq. (7) becomes

$$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \phi}{\partial \rho} \right) + \frac{\partial^2 \phi}{\partial z^2} = \alpha \frac{\partial \phi}{\partial z} \quad (8)$$

where

$$\phi = \int_{-\infty}^h K(h) dh = \frac{K(h)}{\alpha} \quad (9)$$

is the Kirchhoff variable (Philip, 1969)

The solution to Eq. (9) for a point source at $\rho = z = 0$ and no flow across $z = 0$, $\rho \neq 0$ (i.e. no evaporation) is given by Philip (1971).

$$\bar{\phi}(Z, R) = 2 \left[\frac{e^{Z-P}}{P} - e^{2Z} \int_Z^{\infty} \frac{e^{-(Z'+P)}}{P} dZ' \right] \quad (10)$$

where

$$\bar{\phi} = 8\pi\phi/\alpha Q; \quad R = \alpha\rho/2; \quad Z = \alpha z/2; \quad P = \sqrt{R^2 + Z^2}$$

Philip (1971) also points out that the stream function $\psi(R, Z)$ for this problem is given by

$$\psi(\rho, z) = \frac{\alpha Q}{8\pi} \left[\frac{z}{\sqrt{z^2 + \rho^2}} \exp \left[+ \frac{\alpha}{2} (z - \sqrt{\rho^2 + z^2}) \right] \right] \quad (11)$$

or

$$\frac{\bar{\psi}}{\psi} = \frac{8\pi\psi}{\alpha Q} = \frac{Z}{P} e^{Z-P} \quad (12)$$

All points (ρ, z) satisfying $\psi(\rho, z) = A = \text{constant}$ are streamlines, which in this model (see eq. 4) are the solute flow paths. We therefore have only to parameterize these curves to generate our solution.

The solutions to $\bar{\psi}(R, Z) = A$ fit well to the polynomial

$$Z = \sum_{j=1}^6 a_j^A R^j \quad (13)$$

unless $A < .02$.

The dimensionless volume $V = \alpha^3 v/8$ swept out by revolving the polynomial equation (13) about the Z axis ($R = 0$) is given by

$$V_A(Z) = \int_0^Z \pi R^2 dZ(R) \quad (14)$$

$$= \pi \sum_{j=1}^6 \frac{R^j}{(j+2)} a_j^A R^{j+2} \quad (15)$$

The total volume of water entering per unit time between two adjacent stream tubes A_N and A_M is $Q(A_N - A_M)$. The soil volume which is filled between these two streamtubes is given by

$$\frac{8\bar{\theta}}{\alpha^3} [V_{A_N}(Z(R)) - V_{A_M}(Z(R))] = \frac{8\bar{\theta}}{\alpha^3} \delta V \quad (16)$$

where $\bar{\theta}$ is the average volumetric water content in the soil.

Thus, in a time t , a volume of water $Qt\delta A$ enters the soil between the two streamlines and moves solute by piston flow to a depth $Z(R)$ which satisfies the equation

$$Qt\Delta A = \frac{8\bar{\theta}}{\alpha^3} \delta V(Z) \quad (17)$$

To find the correct depth Z for each A , we must calculate $t_A(Z)$ curves for each streamline A . We first define a dimensionless time

$$T = \frac{Q\alpha^3 t}{8\bar{\theta}} \quad (18)$$

$$\text{so that } T(Z) = \delta V(Z)/\delta A \quad (19)$$

We have fit this relationship to the function

$$\ln Z = \sum_{J=1}^6 b_J (\ln T)^{J-1} \quad (20)$$

for a sequence of values of T . The streamtubes are formed from adjacent streamlines differing by $\delta A = .01$.

Equations (13) and (20) together specify the transport problem. The model generates solutions according to the following sequence of calculations:

- 1) Obtain or estimate K_o , α , $\bar{\theta}$ for the soil
- 2) Read in Q
- 3) Solve $\bar{\psi}(Z, R) = A$ for a series of values Z_i , $i = 1, \dots, N$ between 0 and $Z_{\max}$ where $Z_{\max}$ is the maximum depth of interest in the problem. For a given Z_i and A_j , the value R_i satisfying $\bar{\psi}(Z_i, R_i) = A_j$ is obtained by the Newton-Raphson method. A total of 40 values of A between 0 and 1 are used in this report. (Twenty stream tubes δA).

4) The N values (Z_i, R_i) $i = 1, \dots, N$ for a given A are fit to the polynomial Eq. (8) by standard polynomial regression methods (Himmelblau, 1980). The values of a_j^A for each A are stored.

5) The series of (Z_i, R_i) values are associated with a T_i time as follows:

- i) δV is calculated for a given R_i and δA by Eq. 15 and 16.
  - ii) $T_i(Z_i)$ is obtained by Eq. (19).
  - iii) The series (T_i, Z_i) are fit to the expression in Eq. (20) by nonlinear regression. The coefficients b_j are stored for each A .
- 6) A time t is entered and a T calculated by Eq. (18).
- 7) Twenty values of Z_j are calculated from $J = 1 \dots 20$ for each stream tube A_j are calculated from the appropriate Eq. (20).
- 8) Twenty values of R_j are calculated from Z_j and the appropriate Eq. (13) by the Newton-Raphson method.
- 9) The twenty values of (Z_j, R_j) are plotted to form the solute front at t .
- 10) A solute pulse may be represented by two fronts separated by Δt . Pesticide adsorption is modeled using the time calculated by Eq. (5).

The two limiting streamlines $A = 0$ and $A = 1$ are obtained by special methods.

$A = 1$ corresponds to $R = 0$. Water moving along this streamline has the velocity

$$v_z = \frac{\alpha^2 Q}{8\pi \bar{\theta}} \left[\frac{(z+1)}{z^2} \right] \quad (21)$$

so that

$$t(z) = \frac{2}{\alpha} \int_0^z \frac{dz}{v_z} = 1 \frac{6\pi \bar{\theta}}{\alpha^3 Q} (a^2/2 - z + \ln(1+z)) \quad (22)$$

or

$$T(Z) = 2\pi \left(\frac{Z^2}{2} - Z - \ln(1+Z) \right) \quad (23)$$

The $A = 0$ line corresponds to $Z = 0$. Water moving along this streamline has the velocity

$$v_R = \frac{2Q}{8\pi \bar{\theta}} \left[\frac{e^{-R}}{R^2} \right] \quad (24)$$

or

$$T(R) = 2\pi(R^2 - 2 + 2)e^R \quad (25)$$

CASE 2: EVAPORATION

For this problem we will allow a pond of ~~radius~~ R_1 to form on the surface. Outside of this radius we set up an evaporation rate $E_0(\rho)$.

The upper boundary condition is therefore given by (assuming positive z down)

$$-K(h) \left[\frac{\partial h}{\partial z} - 1 \right] = Q/\pi R_1^2 \quad 0 < \rho < R_1 \quad (26)$$

$$= -E_o(\rho) \quad \rho > R_1$$

Together with

$$\frac{\partial h}{\partial \rho} = 0 \text{ at } \rho = 0 \quad 0 < z < z_1$$

$$\frac{\partial h}{\partial \rho} = 0 \text{ at } \rho = R_2 \quad 0 < z < z_1 \quad (27)$$

$$\frac{\partial h}{\partial z} = 0 \text{ at } z = \infty \quad 0 < \rho < R_2$$

The finite value R_2 is chosen large enough to give realistic answers to the infinite problem.

The following conditions will be imposed on $E_o(\rho)$.

- i) $\frac{\partial E_o}{\partial \rho} < 0$ (decreases away from source)
- ii) $E_o(\rho) = 0$ if $\rho > R_2$

$$\text{iii) } \int_{R_1}^{R_2} 2\pi r E_o(\rho) d\rho = W \leq Q$$

Solution: If we again use Eq's. (6) and (9), then Eq. (26) becomes

$$-\frac{\partial \phi}{\partial z} + \alpha \phi = F(\rho) \quad \text{at } z = 0 \quad (28)$$

The stream function ψ is defined in cylindrical coordinates as
(Philip, 1971)

$$-\frac{1}{\rho} \frac{\partial \psi}{\partial \rho} = -\frac{\partial \phi}{\partial z} + \alpha \phi = J_z \quad (29)$$

$$\frac{1}{\rho} \frac{\partial \psi}{\partial z} = -\frac{\partial \phi}{\partial \rho} = J_\rho \quad (30)$$

Note that $\psi(\rho, z)$ satisfies the equation

$$\frac{\partial^2 \psi}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial \psi}{\partial \rho} + \frac{\partial^2 \psi}{\partial z^2} - \alpha \frac{\partial \psi}{\partial z} = 0 \quad (31)$$

which may be verified by plugging in Eq's. (29-30).

It is advantageous to define new dimensionless variables $y = \rho/R_2$;
 $x = z/R_2$; $S = 2\pi\psi/Q$; $\gamma = R_2\alpha$ so that Eq. (31) becomes

$$\frac{\partial^2 S}{\partial y^2} - \frac{1}{y} \frac{\partial S}{\partial y} + \frac{\partial^2 S}{\partial x^2} - \frac{\partial S}{\partial x} = 0 \quad (32)$$

The boundary conditions on ϕ transform to those on ψ using Eq. (29-30),
with the result

$$S(y, 0) = S(0, 0) - y^2/2\xi^2 \quad 0 < y < \xi \quad (33)$$

$$= S(\xi, 0) + \frac{2\pi R_2^2}{Q} \int_{\xi}^y y E_0(R_2 y) dy \quad \xi < y < 1$$

where $\xi = R_1/R_2$

Now the flow rate between $\rho = 0$ and R_1 is by definition

$$Q = \int_0^{R_1} 2\pi r J_z dr = 2\pi(\psi(0,0) - \psi(R_1,0)) \quad (34)$$

So, if we set $S(0,0) = 1$ then $S(\xi,0) = 0$ and Eq. (33) becomes

$$S(y,0) = 1 + y^2/\xi^2 \quad 0 < y < \xi \quad (35)$$

$$= \frac{2\pi R_2^2}{Q} \int_{\xi}^y y E_{dy} \quad \xi < y < 1$$

At $y = 0$ and $y = 1$ S will be constant, since $\partial\psi/\partial z = 0$. Thus, assuming that the asymptotic streamlines join

$$s(0,x) = 1 \quad (36)$$

$$s(1,x) = 1 \quad (37)$$

Finally, at $z = \infty$ we transform the gravity flow condition $\partial h/\partial z = 0$ to

$$S(y,\infty) = 1 - \frac{2\pi\alpha R_2^2}{Q} \int_0^y y\phi(\infty,y) dy \quad (38)$$

In general, the value of $\phi(\infty,y)$ is not known. However, it is reasonable to assume that if no deep drainage occurs

$$\lim_{\eta \rightarrow \infty} \phi(\eta,y) = 0$$

and replace Eq. (38) with

$$S(y, \infty) = 1 \quad (39)$$

Equations 22-28 will now be solved by separation of variables. Let

$$S(y, x) = Y(y)X(x) + 1.$$

Then Eq. (32) gives

$$\frac{d^2 X}{dx^2} - \gamma \frac{dX}{dx} - \omega^2 X = 0 \quad (40)$$

and

$$\frac{d^2 y}{dy^2} - \frac{1}{y} \frac{dy}{dy} + \omega^2 Y = 0 \quad (41)$$

where $\omega = \text{constant}$

The solution $X(x)$ which satisfies (see Eq. 39) $X(\infty) = 0$ is

$$X(x) = a \exp \left[\frac{\gamma x}{2} (1-f) \right] \quad (42)$$

$$\text{where } f = \sqrt{1 + 4\omega^2/\gamma^2}$$

The solution $Y(y)$ which satisfies (see Eq. 36) $Y(0) = 0$ is (Churchill, 1963)

$$Y(y) = b y J_1(\omega y) \quad (43)$$

where $J_1(x)$ is the integral Bessel function for $N = 1$. The second condition $Y(1) = 0$ is satisfied by requiring $J_1(\omega) = 0$ or $\omega = r_N$; $N = 1, 2, \dots$ the roots of J_1 . Thus, the general solution $S(y, x)$ is

$$S(y, x) = 1 + y \sum_{N=1}^{\infty} A_N J_1(r_N y) \exp \left[\frac{\gamma x}{2} (1 - f_N) \right] \quad (44)$$

The surface condition Eq. (35) is used to evaluate A_n , as:
(Churchill, 1963)

$$A_N = \frac{\int_0^1 [S(y,0) - 1] J_1(r_N y) dy}{\int_0^1 y J_1^2(r_N y) dy} \quad (45)$$

A convenient model form for $E_o(\rho)$ is

$$E_o(\rho) = C e^{-b\rho/\rho} \quad (46)$$

which if $W = Q$ gives

$$E_o(y) = \frac{Q}{2\pi R_2^2} \frac{\beta e^{-\beta y}}{(e^{-\beta \xi} - e^{-\beta})} \quad (47)$$

where $\xi = bR_2$ is a shape factor. Thus, the upper boundary condition Eq. (35) for $S(y,0)$ becomes

$$\begin{aligned} S(y,0) &= 1 - y^2/\xi^2 & 0 < y < \xi \\ &= (e^{-\beta \xi} - e^{-\beta y})/(e^{-\beta \xi} - e^{-\beta}) & \xi < y < 1 \end{aligned} \quad (48)$$

where, to avoid an unrealistic boundary at $y = 1$, the parameter β should be large, i.e. $\beta > 3$. Then, approximately

$$S(y,0) \sim 1 - e^{-\beta(y-\xi)} \quad \xi < y < 1 \quad (49)$$

If Eq. (49) is valid, then A_N becomes simply

$$A_N = \frac{2}{r_N^2 P_N^2(r_N)} - \frac{1}{\xi^2} \int_0^\xi y^2 J_1(r_N y) dy - \int_\xi^1 e^{-\beta(y-\xi)} J_1(r_N y) dy \quad (50)$$

where $P_N(x) = dJ_1(x)/dx$.

Thus, the coefficients in Eq. (44) are functions of the parameters ξ and β , and the dimensionless streamlines are functions of ξ , β and γ .

Calculation of A_N , $N = 1, \dots, 50$ was carried out by quadrature integration of Eq. (50) for several combinations of ξ and β .

The solute transport model was developed from this as follows:

- i) $S(y, x)$ values were calculated for a dense grid of points in the x, y plane and stored.
- ii) The (x, y) coordinates of points satisfying $S(y, x) = A$ were obtained by interpolation.
- iii) These points were fit by regression to orthogonal polynomials satisfying the equation, which after some simplification, reduce to

$$C_N = \frac{2R_2^2}{X_N^2 R_1^2 I_N^2} \left\{ \int_0^\xi y^2 J_1(X_N y) dy + \xi^2 \int_\xi^1 \frac{(e^{-\beta y} - e^{-\beta})}{(e^{-\beta \xi} - e^{-\beta})} J_1(X_N y) dy \right\} \quad (51)$$

where $\xi = R_1/R_2$, $\beta = R_2 B$ and $I_N = \left(\frac{dJ_1(x)}{dx} \right)_{x=x_N}$

Thus, the C_N are functions of the parameters ξ , β , R_2 and the corresponding streamlines are functions of ξ , β , R_2 , α .

Note however that $\bar{\psi}(y,z)$ has C_N which depend only on ξ, β

$$y^A = \sum_{J=1}^N a_J^A P_J(X^A) \quad (52)$$

The coefficients a_J^A were stored for each streamline value A and $A - .01$ as before. Polynomial functions relating travel time within a stream tube to the coordinate location R within the tube were obtained by regression.

IV. RESULTS AND DISCUSSION

1. Adsorption Studies -- USA

Figure 1 presents the adsorption-desorption isotherm obtained at 20 C at a 1:2 soil:solution ratio for bromacil on Pachappa sandy loam. Adsorption on this soil was extremely small, even at 20 C, from which we concluded that bromacil would move freely and could be approximated by chloride. For this reason, no analysis was made on bromacil on Pachappa at 30 C. Figures 2 and 3 present adsorption of napropamide on Pachappa at 20 and 30 C, respectively. The approximate K_D values obtained from the adsorption isotherm are very similar to the Bet Dagan soil #1, given in Table 2. Also notable on Figures 2 and 3 are the lack of temperature dependence of the adsorption isotherm. These two curves would be essentially interchangeable in the range between 20 and 30 C. Desorption effects are non-negligible but not as severe as have been observed in other circumstances. Desorption effects could significantly hamper the modeling assumptions, however.

Table 3 presents equilibrium solution concentrations of oxamyl and its oxime on Pachappa sandy loam at 10 C after various equilibration periods. As was the case with bromacil, adsorption of oxamyl is so slight as to be neglectable, even at the low temperature of 10 C. For this reason the mobility of oxamyl was expected to be comparable to that of chloride in soils where anionic effects are negligible.

Figure 4 presents a typical breakthrough curve for chloride and napropamide from the dynamic adsorption coefficient studies. For these studies we chose the 50% breakthrough point as the common index and the

ratio was obtained from Eq. (5). Table 4 presents the 16 K_D values (ml/g) for the sites in the dynamic study, together with the mean and standard deviation. The extremely high variability seems to be characteristic of all field-scale processes and could significantly hamper efforts to model transport under natural conditions (Jury and Collins, 1982). The extent of this variability is further illustrated in figure 5 which gives a frequency diagram for the 16 K_D values, together with a normal distribution fit through the data. Although use of the mean value could significantly hamper simulation using a deterministic model assuming uniform soil properties, information such as that furnished on Figure 5 could be useful if a stochastic transport model can be developed (Jury and Collins, 1982; Jury and Elabd, 1982).

2. Adsorption Studies -- Israel

Adsorption Isotherms: The adsorption isotherms were determined on soils characteristic of Israeli agriculture which were rather low in organic matter (<2.00%) but which contained a rather large range of clay contents. The isotherms of all three pesticides were linear in all the soils studied and no better fit was found for the Freundlich equation. Adsorption was single valued and no hysteresis was observed in desorption studies.

The adsorption coefficients and the calculated K_{OC} values (the adsorption per unit weight of organic carbon) are presented in Table 2. Correlation of the K_d values with the soil clay content for both napropamide ($r^2 = 0.634$) and bromacil ($r^2 = 0.738$) was rather poor.

The correlation of K_d with the soil organic matter content was, on the other hand, quite significant for both bromacil ($r^2 = 0.987$) and napropamide ($r^2 = 0.937$). Since first proposed by Goring (1962), the role of organic matter as the main soil component responsible for the adsorption of pesticides has been widely accepted and numerous published reports have provided supportive data (Bailey and White, 1970; Briggs, 1973, 1981; Hamaker and Thompson, 1972). Despite the low level of organic matter in the soils studied, our results also emphasize the importance of this soil constituent in pesticide adsorption. A close look at the data in Table 2 reveals that for all of these compounds studied the K_{OC} values in the Mivtachim soils are somewhat greater than those in the other soils. Hassett et al. (1981) presented results for the sorption of 1-naphthol which showed that when the % Organic Carbon/% Montmorillonite Ratio of soils was below a certain value hydrophobic sorption was no longer the controlling mechanism of sorption. Similar results were found for acetophenone by Khan et al. (1979). No data is available as to the montmorillonite content of the soils used; however with the possible exception of the Shefer soil, it is the main component of the clay fraction in Israeli soils, (Banin and Amiel, 1969). The ratio % Organic Matter/% Clay for the Mivtachim soil is lower than in all the other soils indicating that the extremely low organic matter content cannot control the sorption process and so the clay fraction can contribute significantly to the overall sorption. While the soil organic matter is of major importance in the adsorption of bromacil and napropamide by soils, other soil components may contribute significantly to adsorption in certain cases (Bailey et al., 1968; Van Bladel and

Moreale, 1974; Bowman and Sans, 1977). In the present study oxamyl adsorption is slightly better correlated to clay content ($r^2 = 0.953$) than it is to organic matter content ($r^2 = 0.893$); thus, the adsorption due to clays, but attributed to organic matter, will result in higher K_{OC} values. Singhal et al. (1978) reported on oxamyl adsorption by montmorillonites. Their proposed mechanism of adsorption of oxamyl involves either protonation or coordination of the exchangeable clay cations to the carbonyl of the amide group. The initial slopes of their adsorption isotherms give K_d values on the order of 300 ml g^{-1} which would explain the good correlation of oxamyl adsorption with soil clay content reported above. It should also be born in mind that the soils studied here are relatively low in organic matter. This would enable other factors, such as clay content, to exert their influence on adsorption. In soils with higher organic matter contents these contributions may be masked.

Several attempts have been made recently to correlate the K_{OC} of organic compounds with easily measured properties of these chemicals such as their aqueous solubility or their partition between water and an organic solvent, usually 1-octanol (K_{OW}). Briggs (1973), Chiou et al. (1979) and Karickhoff et al. (1979) have proposed using the K_{OW} of a compound to predict its adsorption, while others (Chiou et al. , 1979; Felsot and Dahm, 1979) have used the compounds aqueous solubility for the same purpose. The aqueous solubility of bromacil was found to be 1064 ppm (4.08 mmole/l) at 25°C which is slightly higher than the usually reported value of 815 ppm (Pease and Deye, 1967); however, it should be pointed out that the aqueous solubility reported by manu-

facturers does quite often differ from that determined in the laboratory (Bowman and Sans, 1979). Using our value for bromacil solubility to estimate the K_{OC} results in values ranging from 59 -- based on the equations of Felsot and Dahm (1979), to 556 -- based on the equation of Karickhoff et al. (1979), the actual value calculated from the isotherms is 24 ± 9 (Table 2). For napropamide the determined solubility was 69 ppm ($254 \mu\text{mole/l}$) at 25°C , nearly identical to the reported value of 73 ppm (Patchett et al. , 1976). The determined K_{OC} value of 336 ± 68 compares favorably with that of 263 calculated from the equation of Felsot and Dahm (1979) but not with the value of 2497 based on the equation of Karickhoff et al. (1979). This range of nearly one order of magnitude in the estimated K_{OC} indicates that the use of aqueous solubility alone may not adequately describe a pesticide's behavior in the soil. A more reliable estimate of K_{OC} may be obtained by a compound's octanol-water partition coefficient, K_{OW} . The K_{OW} of bromacil and napropamide were determined by equilibration of aqueous solutions of the herbicide with octanol as well as by determining their solubility in octanol and computing the ratio of their solubilities while for oxamyl only the first method was used. By the first method the K_{OW} values obtained for bromacil napropamide and oxamyl were 70, 1201 and 0.37 respectively, while the second method gave values of 85 and 3116 for bromacil and napropamide respectively. The difference in the values for bromacil is well within the range of experimental error and similar to the reported value of 105 (Metcalf and Lu, 1981), but for napropamide it seems that the very slight solubility of octanol in water result in lower K_{OW} values for the

equilibration method. This would be true in particular for compounds with a low water and high octanol solubility, such as napropamide. Ellgehausen et al. (1981) reported K_{OW} values for seven compounds determined by both methods in which the ratio of solubilities was greater than the experimentally determined value. Since most data in the literature are determined by equilibration methods and not by solubility ratios, the former values will be used from here on. Several authors have proposed relationships between the K_{OC} of pesticides and other organic compounds to their K_{OC} (Briggs, 1973, 1981; Chiou et al., 1979; Karickhoff et al., 1979; Mingelgrin and Gerstl, 1983). In each case a different relationship was found between K_{OC} and K_{OW} . For bromacil the range of calculated K_{OC} values is rather narrow, 45-65 but all overestimate adsorption. The range of K_{OW} values for napropamide 292-767, which includes all but one of the determined values (Table 2). The K_{OC} range based on the measured K_{OW} of oxamyl values is 0.22-4.1 which is considerably lower than expected although still within an order of magnitude of the measured value which is within the claims of most of the cited references. The use of K_{OW} , therefore, may be preferable to that of aqueous solubility in calculating K_{OC} values.

3. Degradation Studies -- Israel

The degradation of napropamide and bromacil in the two soils studied at several moisture contents, temperatures and initial concentrations followed first order kinetics. The half lives ($T_{1/2}$) of napro-

napropamide under the various experimental conditions are presented in Tables 5 and 6, and of bromacil in Tables 7 and 8. With the exception of the napropamide samples incubated at 5°C, and of the bromacil sample at 8% moisture content in the Gilat soil, the correlation coefficients were reasonably high. At 5°C the degradation was so slow that accurate calculation of the rate constants presented difficulties, as was the case for the fairly dry Gilat soil.

The half-life of napropamide for all the conditions studied ranges from 17-1643 days; however, considering only the conditions likely to occur under irrigated agriculture (25-35°C; field capacity and 133% of field capacity) the range narrows to 34-201 days. For field soils the range of napropamide half-lives has been reported to be between 54 and 266 days depending on the soil, moisture content and assay method (Hurle, 1977; Patchett et al., 1976; Walker, 1974) in good agreement with the present results. Similarly, the total range of bromacil half-life was 14-1494 days, while for likely irrigated conditions the range reduces to 85-758 days which compares favorably with published data (Leistra et al., 1975; Wolf and Martin, 1974; Zimdahl et al., 1970).

The effect of temperature on the decomposition of napropamide did not follow the Arrhenius relationship over the entire temperature range studied. In general, the rate leveled off between 35°C and 50°C for soils kept at field capacity. However, for the Neve Ya'ar soil at 133% of field capacity the Arrhenius relationship was followed. For bromacil this relationship was not followed in either the Gilat or Neve Ya'ar soil. Bromilow et al. (1980) also noted that the decomposition

of oxamyl and aldicarb at several temperatures did not follow the Arrhenius relationship in the temperature range of 5-15°C. The rate of napropamide degradation, unlike that of bromacil, did not change from 35°C-50°C. Since napropamide decomposition is microbial in nature (Patchett et al., 1976) the leveling off of the decomposition rate at 50°C in the present study may be due to a decrease in microbial activity. At 50°C the moisture content at field capacity in the Neve Ya'ar soil might not have been enough to sustain the microbial population while at 133% of field capacity the greater amount of available water resulted in increased microbial activity and hence in an increase in the degradation rate.

Napropamide and bromacil degradation generally decreased as the soil moisture content decreased as has been found to be the case for several other pesticides (Bromilow et al., 1980; Roberts and Stoyelin, 1976; Walker, 1978). This is to be expected for a microbial process, since microbial activity also decreases with decreasing moisture content (Alexander, 1964). Walker (1974, 1978) proposed a relationship between the half-life of a pesticide in soil and the soil moisture content which takes the form of $T = aM^{-b}$, where T is the half-life of the pesticide at the moisture content, M, and a and b are constants. No relationship was found between the empirical constants calculated from the present study and any of the experimental parameters; nor are the constants a and b similar to those found by Walker (1974, 1978). They do, however, fit the napropamide data fairly well, enabling use of the equation for predicting napropamide degradation in these soils at other moisture contents within the range of moisture contents studied.

Napropamide and bromacil degradation in both soils appears to be concentration dependent, as at an initial concentration of 4 ug/g the half-lives are considerably shorter than at 16 ug/g with the exceptions of napropamide in the Neve Ya'ar soil at field capacity and bromacil at 50% of field capacity in the Gilat soil. Similar results have been reported for atrazine and picloram (Hamaker, 1972). One possible explanation for such a dependence may be that while the degradation of both herbicides is a microbiological process, the compounds are degraded "passively" by the existing microbial population without inducing enzymatic changes in the soil microorganisms to utilize effectively the carbon in the herbicides for growth (Hiltbold, 1974). Thus, since the nature and activity of a soil's microbial population is determined by soil chemical, physical and environmental conditions, pesticide treatment will not influence the microbial activity and pesticide metabolism is incidental to that of other natural substrates. If such is the case, then the pesticide concentration will, to a large extent, determine its degradation rate by the existing microbial population.

The degradation of oxamyl in soils differs significantly from that of the two herbicides studied. The degradation of oxamyl in all cases studied could be described by first-order kinetics, as seen from the results of Tables 9 and 10.

The effect of soil moisture content is readily apparent. As the water content increases, so does the reaction rate. At about 60% field capacity (field capacity of the Bet Dagan soil is 12%), the rate levels off. The effect of moisture content on oxamyl decomposition may result from its effect on microbial activity. As the soil dries out it can

support a smaller microbial population and hence a decrease in decomposition of organic molecules such as oxamyl. Similar results have been noted for the variety of pesticides in soils. (Smelt et al., 1979; Odrigawitch et al., 1982; Roberts and Stoydin, 1976). The results of Table 8 for four additional soils at field capacity and one at 60% field capacity bear out these results. In all cases a half-life of 4 days is obtained, indicating that under conditions of uniform soil moisture tension the microbial activity in these soils is fairly similar, with little effect being exerted by the soil colloids. It should be pointed out that the results of Table 8 are based on only one replicated sampling date so that these data should be viewed only as rough estimates of the true degradation rate. They do, however, substantiate, the fact that at, or near, field capacity the degradation of oxamyl in Israeli soils will be rapid and to a large extent independent of soil type. This lack of sensitivity to soil type is most probably due to the uniformly high pH of the Israeli soils used in this study. Oxamyl is more stable under acidic to neutral conditions and less so at higher pH values. Smelt et al. (1979) also observed that in two acidic soils the half-life of oxamyl at field capacity was quite similar and considerably greater than that found in two slightly alkaline mineral soils.

The effect of temperature on oxamyl decomposition is quite pronounced and follows the Arrhenius relationship with an activation energy of $16.5 \text{ KCalmole}^{-1}$ which is typical of soil degradation reactions (Hamaker, 1972). The range of temperature studied was chosen to cover the range of soil temperatures which may be expected to occur in

Israeli soils during the growing season. If oxamyl is applied to soil in the late spring or early summer it will disappear quite rapidly even in dry soils, so that it may be necessary to apply higher rates to achieve adequate insect control. Bromilow et al. (1980) did not observe the same temperature effect described above; rather, between 10 and 15°C, little or no increase was observed in oxamyl decomposition. In their study the soil was held at 10% moisture content which, for the sandy soil used, is close to field capacity, so that one would expect a temperature effect as soil moisture is not limiting. The lack of this effect might indicate a change in the microbial population or dynamics at lower temperatures; however, not enough data are available to elucidate the apparent discrepancy in the results.

A slightly greater half-life is observed for oxamyl at 50 mg⁻¹kg than at 5 mg⁻¹kg (Table 9). This has been noted previously for oxamyl and other compounds as well (Hamaker, 1972). The difference in reaction rates, however, is rather small.

4. Laboratory Drip Irrigation Studies -- Israel

Pesticide distribution in soils when applied from a simulated point source were studied in three sets of experiments. The following discussion will deal with each set separately and will be summarized in the final section.

a. Bromacil and Napropamide in a Hamra soil

Immediate Distribution

The distribution of the herbicides 24 h after they were applied in 1800 ml of irrigation water to an initially dry soil is presented in Fig. 6. The distribution of bromacil generally coincided with that of the water and was nearly uniform in the wetted soil volume. The fact that the bromacil front lagged slightly behind the wetting front is to be expected for a compound only slightly adsorbed by the soil.

A completely different picture is found for the distribution of napropamide. From Fig. 6 it can be seen that a very sharp concentration gradient was formed with the highest concentration occurring around the emitter. The isoconcentration lines are not symmetrical in the horizontal and vertical directions. This type of distribution is to be expected, considering the relatively high adsorption of napropamide by the soil. According to Brandt et al. (1971) and Bresler et al. (1971) the application of water from a trickle source at a high discharge rate results in a water saturated entry zone with an initial stage of ponding on the soil surface. The ponded area slowly increases with continued irrigation. Hence, napropamide will move laterally more easily in the ponded water before it is adsorbed by the soil. This can cause the high concentration zones for napropamide to be wider and shallower than the low concentration zones.

Application of the same amount of herbicides in 900 ml of irrigation water (instead of 1800 ml) resulted in a smaller and shallower zone of high moisture content (Fig. 7). The distribution of the herbicides was similarly altered with both napropamide and bromacil

distributions assuming the same shape as that of the water. Since the initial concentration was twice that of the previous treatment, the soil concentration of bromacil - which is only slightly adsorbed - was nearly twice as high.

The effect of initial moisture content on the distribution of the herbicides is shown in Fig. 8. The moisture distribution obtained by adding 900 ml herbicide solution to the soil which 24 h previously had received 900 ml of water, was similar to that in treatment A. However, the herbicide distribution was intermediate between that of treatments A and B. Both the vertical and horizontal distribution of bromacil and napropamide were affected by the initial soil moisture content. In the case of bromacil three concentration zones can be defined for treatments B and C. However, the high concentration zone was narrower and deeper for the initially moist soil. The low concentration zone was deeper but did not advance horizontally past the limit reached in the initially dry soil (treatment B). For napropamide the high concentration zone (50-100 mg/g) in treatment C was shallower but wider, while the highest concentration zone (200-300 mg/g) immediately under the emitter was absent. An increase in the depth of the lowest concentration zone was seen but, unlike bromacil, its largest movement was retarded.

The main effect of high initial moisture content on bromacil seems to be the dilution of the incoming herbicide solutions as bromacil is only slightly adsorbed by the soil. Napropamide, on the other hand, was found to be slightly more mobile in treatment C and this may be explained by adsorption kinetics. If the soil water is divided into a mobile and immobile phase (e.g. Van Genuchten et al. 1976), then the

adsorption will depend on the rate of transfer of the adsorbed compound from the mobile to the immobile phase. In a moist soil it is possible to obtain greater mobility of a compound if its rate of transfer to the immobile phase (and hence its adsorption) is slower than the movement of the mobile phase. In our case this is quite feasible considering the fast application rate (41/h) and this explains the absence of a zone of high concentration.

Redistribution with Time

Once a herbicide is introduced into the soil via the irrigation water it will be redistributed if irrigation continues. Several situations were selected and the results are herewith presented and discussed.

Irrigation Immediately after Initial Application. Fig. 9 presents the distribution of water, bromacil and napropamide following the addition of 900 ml water 24 h after the soil had received treatment B. The moisture profile was quite similar to that in treatment A with only a slightly difference in the upper layer and a slightly greater gradation of moisture contents near the wetting front.

As might be expected, bromacil was completely leached from the region of the emitter and was redistributed toward the edges of the wetted front. Comparison with the initial distribution (Fig. 7) emphasizes bromacil's high mobility in soils. Less drastic, but still significant, was the effect of additional irrigation on the distribution of napropamide. The two high concentration zones were smaller than in

treatment B; the 20-50 ug/g zone increased, as did the least concentrated zone, mainly in the vertical direction. Despite the fact that in both cases the additional irrigation resulted in displacement of the chemical in the soil, in the case of the slightly adsorbed bromacil the concentration gradient from the emitter was considerably altered, whereas in the case of napropamide the area around the emitter remained highly concentrated due to its strong adsorption.

Redistribution after Successive Irrigations

When left uncovered for one week those buckets which received treatment B lost 28% of the applied water due to evaporation, mainly from the upper 15 cm of soil. The resulting redistribution of water and herbicides is shown in Fig. 10. As can be seen the bromacil moved upwards with the soil water increasing in concentration in the top 10 cm of soil. Napropamide was also slightly mobile and its concentration immediately under the emitter increased to more than 200 ug/g. The concentration of napropamide in the zone spreading laterally to 3 cm and to a depth of 9 cm increased from 50-100 ug/g to 100-200 ug/g while the remaining profile was basically undisturbed. The lateral area from 7 to 11 cm was devoid of napropamide whereas in treatment B this zone contained 1-5 ug/g devrinol. Since napropamide was not found to degrade during this period of time it seems possible that at these low napropamide concentrations fixation occurred upon drying, so that napropamide was not recovered. At such low concentration hysteresis was observed by Wu et al. (1975) for the desorption of napropamide

which would tend to support our assumption. Losses due to volatilization might also be a factor: however, no information exists on the volatility of napropamide in soils.

By addition of the water lost by evaporation the distribution of the herbicides was significantly altered (Fig. 11). Bromacil was almost completely leached from the emitter zone and only a small zone of high concentration remained near the soil surface. Napropamide was also leached but the only noticeable effect was in the zone adjacent to the emitter.

Irrigation was continued for a total of 5 weeks by adding the water lost by evaporation either once or twice a week. The bromacil distribution (Fig. 12) for the weekly irrigation treatment exhibits a highly leached zone around and under the emitter and a small zone of concentration on the soil surface near the wetting front due to the alternate wetting and evaporation cycles. This effect was less pronounced in the twice weekly irrigation (Fig. 13) where the leached zone was rather small and the concentrated zone was deeper and closer to the emitter. This difference appears to be the result of the increased number of evaporation cycles undergone by this treatment. Evaporation was greatest during the first few days following irrigation after which the rate of evaporation decreased upon the drying out of the soil surface. This means that whereas the amount of water added at each application of the twice weekly treatment was about two-thirds that of the weekly irrigation, redistribution occurred more often and not necessarily at a lesser intensity. Bromacil was leached during the twice-weekly application because of the smaller quantity of irrigation water but it had

nearly the same chance to redistribute upon evaporation as the weekly treatment. Napropamide behaved in the same manner (Fig. 12 and 13) but again due to its adsorption the changes are less pronounced.

b. Bromacil and Napropamide in soils of varying texture.

These experiments were designed to gain a better insight into some of the complex processes not accounted for by existing models such as simultaneous water and solute movement after several irrigation cycles with evaporation.

Water Distribution in the Soil

The water distribution in the various soils 24 h after application at a rate of 4 l/h is shown in Figures 14-17A. The water content of the soils immediately around the emitter increased with the clay content of the soils. The average soil moisture content of the sandy Mivtachim soil is 7% while that of the heavier Neve Ya'ar is 43% (Fig. 16). Furthermore, it may be noted that as the soils increase in clay content the relative volume around the emitter which is at this average soil moisture content (field capacity) decreases.

One would expect, based on published calculations (Bresler et al., 1971; Warrick, 1974), that for the sandy Mivtachim soil the water movement would be deeper and radially much narrower than for the heavier soils because of the relatively greater influence of the gravitational head in the sand. That this was not so may be attributed to the fact that at the application rate of 4 l/h, and with a bulk density of 1.6 g/cc, the infiltration capacity of the soil was exceeded, resulting in ponding of the applied water as described previously. The application

of water from a trickle source can result in a water saturated entry zone and ponding on the soil surface within the immediate vicinity of the emitter if the soils infiltration capacity is exceeded. This ponded area slowly increases with continued irrigation. At higher application rates one may expect larger ponded areas than at lower application rates so that in the former case there will be greater lateral movement and in the latter case greater vertical movement. This is further demonstrated by the results in Figures 18-21 which depict the soil water content distribution 24 h after application at 1.5 l/h. In all cases, except for the Mivtachim soil, the wetted zones were narrower and deeper, as would be expected if one takes into account that at the slower application rate the size of the saturated zone is smaller.

Continued irrigation of the pots for several weeks at twice-weekly intervals was based on weighing the pots and adding the water lost by evaporation, with a dripper at 4 l/h. After several cycles of wetting and drying the moisture content distribution of the soils was only slightly altered. In the Mivtachim soil the added water went to expand the wetted volume of soil. After the initial irrigation with 900 ml water, the depth reached by the infiltrating water was only 18 cm while in the successively irrigated soil the wetting depth was 23 cm. In this case the drainage of the additional irrigation water was quite rapid, allowing penetration to depth before considerable evaporation could occur. In the Bet Dagan I soil the 10-15% zone narrowed, as did the entire wetted zone, but increased in depth from 13 to 17 cm. A narrowing of the wetted zone was also observed in the Bet Dagan II soil

while in the Gilat and Beg Dagan II soils the wetted depth was also considerably decreased. It appears that in the Bet Dagan I soil, as in the sandy Mivtachim soil, the added water moved mainly vertically resulting in drying out of the soil at the outer edges of the wetted zone. In the heavier Gilat and Bet Dagan II soils infiltration and drainage were considerably slower than in the lighter soils, so that evaporation from the soil surface was more of a factor causing greater upward flow of water from deeper depths in the soil.

Herbicide Distribution in the Soil

The distribution of napropamide and bromacil in the different soils under the various treatments are presented in Figures 14-17B and 14-17C respectively. As previously reported, adsorption of napropamide varied from a K_d of 0.27 ml/g for the sandy Mivtachim soil to 2.96 ml/g for the heavier Bet Dagan II soil while for bromacil the range in K_d values was 0.03-0.32 ml/g for the same soils. The effect of adsorption is readily evident in the retardation of napropamide's penetration into the soil volume and its concentration in the area around the emitter. Even in the sandy Mivtachim soil napropamide movement lagged considerably behind that of the soil water (Figure 14). As the soil's clay and organic matter contents increase so does the retardation effect. In the Mivtachim and Bet Dagan I soils some traces of napropamide can be found in nearly the entire soil volume even though the major portion is concentrated around the emitter. In the Gilat and Bet Dagan II soils only half of the wetted soil volume contained napropamide due to its higher adsorption on these soils.

Bromacil, on the other hand, was found to be distributed in a pattern similar to that of the soil water with less concentration around the emitter and more movement into the wetted soil volume even in the heavy Bet Dagan II soil. This difference in mobility is expected for compounds of such different adsorption and is similar to the case of nitrate and phosphate movement described by Bar-Yosef and Sheikholislami (1976).

The effect of flow rate on the distribution of the herbicides (Figures 18-21) was quite pronounced. In the Mivtachim soil napropamide was more highly concentrated around the emitter at 1.5 l/h than at 4 l/h even though the soil volume in which it could be found was slightly smaller. This may indicate that adsorption kinetics, and not only batch K_d values, is of importance. This may also be the case for bromacil in the Mivtachim and Bet Dagan I soils. In general, at the slower application rate the herbicide distribution was narrower and deeper than at the higher rate. In several cases the effect on herbicide distribution was more pronounced than on water distribution. For example, in the Bet Dagan II soil at 4 l/h napropamide was found at a distance of 9 cm from the emitter and at a depth of 10-11 cm. In the same soil at 1.5 l/h, the herbicide could be found only 6 cm from the emitter but at a depth of 16 cm. During the 24 h following application of the herbicide solution the redistribution of water was primarily that of herbicide free water since a significant portion of the herbicides had been adsorbed. Subsequent movement of the herbicides, in the absence of continued irrigation, will be primarily by diffusion which is extremely slow even for the slightly adsorbed bromacil.

Once a compound is applied to the soil, irrigation will redistribute the chemical. Continued irrigation of the pots for several weeks at twice-weekly intervals considerably altered the chemicals' distribution in soils by increasing the volume of soil in which the herbicide could be found (Figures 22-25).

In the sandy Mivtachim soil a small herbicide free zone developed around the emitter as the napropamide was leached by the successive irrigations. Some of the herbicide was concentrated at the soil surface between 5 and 12 cm from the emitter most probably due to its upward movement with the evaporating water. Further highly concentrated zones were found at a depth of 13-20 cm directly beneath the emitter. The bulk of the material, however, was leached into the soil volume wetted by the additional irrigations.

In the slightly heavier Bet Dagan I soil most of the napropamide was leached out of the emitter zone and concentrated concentrically from about 3-7 cm from the emitter to 4-10 cm beneath the emitter. This distribution is nearly identical to that presented previously for the same soil. It should be noted that after 24 h napropamide was observed at 12 cm from the emitter but not after several cycles of wetting and drying. Degradation may be ruled out as the source of the chemical's disappearance from the degradation data which showed that at these low water contents one can expect a half-life of several months. It is possible that some of the herbicide was lost by volatilization or photodecomposition but no information exists for these processes in regard to napropamide. It is more likely that the chemical underwent fixation upon drying, as observed by Moyer et al. (1972) for other

sizes which greatly reduced the rate of water movement to the surface from the deeper soil layers.

Soil Structure Effect

Recent work (Thomas and Phillips, 1979) has shown that the flow of water through macropores is important in salt movement through soils. Similar results are observed for the behavior of napropamide and bromacil. The effect of soil structure can be discerned from the results (Figure 26) of the Neve Ya'ar soil where the 1-2 mm size fraction was used. In the Neve Ya'ar soil the radial distribution of soil water is not observed. Because of its extremely high clay content (70%) and >0.5 mm fraction resulted in considerable swelling and an exceedingly large saturated zone with very slow infiltration. Under these conditions the lateral movement of the water quickly reached the walls of the container resulting in vertical flow. When the 1-2 mm size fraction was used little ponding was observed and rapid percolation of the applied water through the macropores occurred due to the large contribution of the gravitational potential. Under such conditions the interior of the soil aggregates are not immediately wet as the bulk of the applied water does not immediately enter the micropores of the soil aggregates. After the cessation of infiltration the movement of the soil water will be primarily in response to the matric potential gradient thereby giving a more radial distribution.

Despite the rapid percolation of the applied solution, napropamide is still highly concentrated around the emitter as would be expected for a K_d of 2.54 ml/g and the general direction of movement was vertical and not horizontal. This is a direct result of the flow of water through

the macropores, as discussed previously, allowing rapid percolation of the herbicide solution. Since the interior of the soil aggregates are not wet immediately the effective K_d for napropamide in the soil was considerably reduced. It is quite likely, therefore, that under actual field conditions, where soil structure provides both macro- and micro-pores, the movement of highly adsorbed compounds differs from predictions based on disturbed soil experiments. Bromacil movement in the Neve Ya'ar soil was less affected than was napropamide movement in that the chemical could be found in the total wetted soil volume. It should also be mentioned that despite its relatively low K_d it was still found at a concentration of 130 ug/g in the vicinity of the emitter.

c. Oxamyl Distribution in Soil after Point Source Application

The results described till now deal with compounds which did not undergo significant degradation during the course of the experiments. Oxamyl, on the other hand, presents us with a case of rapid decomposition with little or no adsorption.

The results presented previously indicate that application of oxamyl to soils of pH >7 under irrigated conditions prevalent in Israel and the Southwestern U.S. will lead to a rather rapid decline in oxamyl concentrations. Since oxamyl is only weakly adsorbed by the soil colloids it will move readily in soils (Leistra et al., 1980) and can easily be applied by drip irrigation. The results of applying oxamyl to the soil from a simulated drip system are presented in Figure 27 and Tables 11-13. The amount of oxamyl applied (90 mg active ingredients/pail) is equivalent to 0.9 kg ha^{-1} which is within the range of

recommended rates for field use (Martin and Worthing, 1977). The soil moisture content distribution pattern in Figure 27 is typical of the three treatments (which all had the same irrigation regime) and is similar to that observed for drip irrigation systems in both field and laboratory studies (Jury and Earl, 1977; Bresler et al., 1971). Water movement was primarily vertical, due to the sandy texture of the soil. For heavier soils one could expect a greater degree of horizontal water movement and shallower penetration (Bresler et al., 1971).

Although not determined, oxamyl can be assumed to have been nearly uniformly distributed in the soil immediately after application. This is based on the low K_d in Bet Dagan soil ($0.08 \text{ ml}^{-1} \text{ g}$) which is similar to that of bromacil ($0.10 \text{ ml}^{-1} \text{ g}$) which, when applied to an initial moist soil was found to have a uniform distribution pattern. The three application treatments of oxamyl resulted in different spatial distribution patterns. When oxamyl was applied in one concentrated pulse and subsequently leached for 5 days, a rather large oxamyl free zone was formed, with the bulk of the compound found between 18 and 24 cm depth and 9-12 from the application point (Table 9). Very low concentrations were found at the edge of the wetted zone 15 cm from the emitter, testifying to oxamyl's high mobility in soils. It is interesting to note the uppermost soil layer. This buildup is similar to that noted for bromacil and napropamide and is a result of oxamyl's upward translocation with the soil water as evaporation proceeds.

By dividing oxamyl application into three portions (split application) a different concentration profile is obtained (Table 12). Again, the area around the emitter has been leached but to a much lesser

extent, as only one leaching occurred subsequent to the last oxamyl application. Oxamyl is found in reasonable concentrations between 6 and 24 cm below and up to 9 cm from the emitter. Under such a system of application the only area which would be leached free of oxamyl is the emitter zone itself and even here one would be able to find acceptable oxamyl concentrations after its application but prior to the succeeding irrigation. In this case also one may note the accumulation of oxamyl in the top soil layer at a 9-cm distance from the source.

The most uniform distribution of oxamyl was achieved by its continuous application (Table 13). In this case oxamyl was present in high concentration to a depth of 24 cm and to 9 cm lateral distance. A slight build-up in oxamyl concentration is noted for the upper soil layer at a 9 cm lateral distance. It is interesting that the oxamyl concentration below the 30 cm depth was greater than that of the soil layer immediately above. This higher concentration of oxamyl occurs because at this depth the soil moisture content is rather low (2-3%) so that decomposition of oxamyl proceeds rather slowly. In the 24-30 cm layer immediately above, the soil moisture content was considerably higher, so that degradation proceeded at a much greater rate.

5. Laboratory Drip Irrigation Studies--USA

Table 14 presents volumetric water content measured at the end of the laboratory pesticide trickle irrigation experiments for the case of no evaporation and evaporation. Since the water regimes were comparable in the two experiments the different water contents can be taken as an

indication of the influence of evaporation on the process. Clearly, regions adjacent to the emitter are much wetter in the absence of evaporation and, furthermore, the water content directly adjacent to the emitter is wetter when no evaporation is present.

Tables 15 and 16 present the chloride and pesticide concentrations at the end of the experiment with and without evaporation. Notable is the significant increase in lateral movement to the soil surface obtained under natural evaporative conditions for both pesticide and chloride. Leaching is comparable directly below the emitter in both cases. This would indicate that models which do not take evaporation into account, such as the trickle irrigation models of Philip (1971), Warrick (1973), Raats (1975), Brandt et al. (1971), or Bresler (1976) will not do a realistic job in modeling the chemical velocities and flow paths under natural conditions.

6. Field Experiments--Israel

The distribution of bromacil, napropamide and soil moisture content for the various treatments of the second field experiment are presented in Tables 17-24. Although the distribution of the two compounds around the emitter was to be determined immediately after application it may be assumed from the previously reported laboratory results for these compounds that napropamide was highly concentrated around the emitter while bromacil was nearly evenly distributed in the wetted soil volume. This will be true even in the case of an initially moist soil. The soil moisture content after 1 week is rather uniform to a depth of 60

cm and a distance of 30 cm. Below 60 cm the moisture content is slightly higher most probably due to the higher clay content of this layer. Past 30 cm from the dripper the surface layers are drier but this difference is not notable below 40 cm. After 28 and 42 days the moisture contents, especially in the upper layers, increase and even at 70 cm from the emitter the soil is relatively wet.

The movement of napropamide under continued daily irrigation at 4 l/h can be followed by comparing the second columns for each lateral distance. Even after one week we find that napropamide is concentrated around the emitter although sizeable concentrations are found at a depth of one meter and a radial distance of 40 cm due to structural effects and surface pondings. The distribution after 28 days shows reduced but still high, concentrations around the emitter. On the soil surface at 30 cm from the emitter a considerable amount of napropamide has built up due to the upward movement of evaporating water. Hurle (1977) reported that at concentrations of less than 1 mg/kg napropamide was a highly effective herbicide thus under the present conditions adequate week control could be achieved for at least several weeks. After 6 weeks nearly no napropamide is to be found in the soil profile due only in part to degradation since degradation during this period would account for only about 25% of the original applied dose. Loss of napropamide from the surface horizons is indicated and may be expected considering its vapor pressure and the climatic conditions prevailing during the experiment (Jury et al. 1983). The disappearance of napropamide in the lower profile is due primarily to leaching.

The behavior of napropamide with weekly irrigations differs slightly from that of daily irrigations. After one week we find a somewhat higher herbicide concentration below 40 cm and at distances of 20-50 cm from the emitter. This difference results from the initial application of the herbicide. Under weekly irrigation herbicide application was immediately followed by continued irrigation thereby leaching the material further into the soil and preventing, to a certain extent, its upward movement with the evaporating soil water. This trend continues and after several weeks the weekly irrigated plot still has a higher herbicide concentration in the lower portion of the profile.

The effect of flow rate is also observed by noting that a 2 l/h napropamide is more highly concentrated in the 10-60 cm depths between 0-20 cm from the emitter since at this irrigation rate a smaller saturated zone is formed restricting lateral and favoring vertical flow. After 6 weeks, however, these differences disappear due to leaching and volatilization losses.

Bromacil too behaves in the field as it did in the simulated studies. Even after 1 week of daily irrigation it is concentrated in a band ranging from 10-60 cm directly beneath the emitter to 20-50 cm from the emitter on the soil surface. Upon continued irrigation bromacil is leached out of the lower soil depths and concentrates on the soil surface where it undergoes less of loss due to vaporization than napropamide because of its lower vapor pressure. The effects of irrigation frequency and rate on bromacil distribution are similar to those described previously for napropamide.

The effect of a growing crop on pesticide distribution is two-fold. As it grows the developing crop canopy decreases the evaporative loss of water. In addition, the developing root system removes water from the profile and forms potential gradients within the soil which result in soil water movement. Neither of these two effects has been adequately described although some work has been done in modeling these effects (Jury and Earl, 1977). Under a growing crop the water distribution will be significantly different from a bare field (Earl and Jury 1977) and so too the distribution of agrochemicals applied to the soil. One difficulty in studying systems with growing crops is that the root system will result in numerous changes in the soil structure by forming larger pores for soil water movement as a result of the wetting and drying cycles which accompany irrigation and rainfalls. Thus, the natural variability of soils is compounded by the effects of the growing crop as can be seen by the data in Table 20 which provides the means and standard deviation of three replicates for the identical treatment. These data highlight the difficulty on analyzing field data with a growing crop. For the sake of brevity the full data for the first experiment will not be presented, however, it is possible to discern the same trends as were observed for the previously described experiment.

7. Field Experiment -- USA

Table 25 presents residue analysis on 50-g samples of soil taken at various soil depths for oxamyl 14 and 35 days after cessation of

application. Table 26 gives the corresponding soil moisture contents at 14 and 35 days. The texture of these soil samples ranged between sand, sandy loam, silt loam, loamy sand, and loam, and therefore have a high affinity for transporting chemicals. The fact that oxamyl was below detection limit at all depths in virtually all cases would indicate that it degrades rapidly enough so that its extremely high mobility does not present a pollution hazard. Therefore, its effectiveness at control seems to be the only parameter governing its use, at least in the lemon grove setting.

V. MODEL SIMULATIONS

Because of the extreme variability found in the field setting and because even under controlled laboratory circumstances data lacked symmetry, the purpose of the model simulations are for scenario analysis to determine the influence of soil type and evaporation rate on transport. A qualitative comparison with the USA evaporation and no evaporation will be made at the end of this report.

Figure 28 shows the model hydraulic conductivity matric potential head functions used to represent ideal sand, silt and clay properties for which the Roman numeral alpha parameter was 0.03, 0.01, 0.05, respectively. These model functions in this form are necessary for the linearized model used in the analysis based on the earlier work of Philip (1971). They may qualitatively represent idealized soil behavior in limited ranges.

Figure 29 represents streamlines for the zero evaporation case representing lines of constant streamline or equivalently of solute flow paths for the convective model. These are plots of Eq. (13). They represent chemical flow lines emerging from a single point at the center because the model of Philip (1971) does not allow for a puddle to form at the soil surface under the emitter. Therefore, the somewhat unrealistic spherical profile is reached which allows substantial lateral movement to take place in the absence of evaporation. Figure 30 plots 0.25, 0.5 and 0.75 streamlines for the prototype sand and clay soils, respectively. As expected, more downward movement occurs with the sandy soil. These streamline values represent the fraction of the total flow occurring between the plane parallel to the surface and the

herbicides. Wu et al. (1975) observed that at very low concentrations hysteresis occurred in the adsorption-desorption of napropamide which tends to support this assumption.

In the heavier Gilat and Bet Dagan II soils the most highly concentrated zone was still found around the emitter, even though these soils were leached with nearly the same amount of water as the Mivtachim soil. This zone is now much larger and has an average concentration of 20-50 ug/g as compared with >200 ug/g after only 24 h. In the heavier soils the movement of the herbicide was more horizontal than vertical, following the water distribution pattern in these soils (Bresler et al., 1971).

The behavior pattern of bromacil in the various soils studied is similar in that it too was leached out of the emitter zone but to a greater extent than napropamide. In the Mivtachim soil bromacil was concentrated at the soil surface on the fringe of the wetted area. This is due to its upward movement with evaporating water and its outward leaching with continued irrigation. In the Bet Dagan I soil the wetting-drying cycles give a more complicated picture. The herbicide-free zone is slightly smaller and bromacil is concentrated not only at the upper boundary of the wetted volume but also to depth, leaving a zone of very low (<5% mg/g) bromacil concentration above, as was observed previously for the same soil. A similar pattern was observed in the Gilat soil. In the Bet Dagan II soil the herbicide was nearly radially concentrated at 9 cm from the emitter with a highly concentrated zone 9-10 cm beneath the emitter. In this soil the evaporative effects were less than on the lighter soils due to the smaller pore

tube bounded by the line. Thus for the clay soil, a relatively large fraction of the flow goes off at an angle nearly parallel to the soil surface. This could create substantial lateral movement.

Figure 31 gives frontal lines for two 2, 4, 6, 8, and 10 days after application of a chemical pulse, represented as a single line, neglecting diffusion and dispersion. Shown in the figure are the prototype sand and clay calculations which differ only slightly within this time frame. As mentioned before, the rather symmetrical pattern in the radial and vertical directions is largely due to all water originating at a point on the soil surface and is unrealistic for soils which form a substantial puddle on the soil surface during trickle irrigation. As mentioned by Jury and Earl (1977) substantial water can be transported laterally above the soil surface by this mechanism. However, also pointed out by Jury and Earl (1977), the extent of this ponding is not predictable from a measurement of hydraulic conductivity which was assumed by Brandt et al. (1971), since the hydraulic conductivity appears to decrease continuously with time, either due to microbial activity or to plugging of the soil surface by soil colloids.

Evaporation Case

Figure 32 presents streamlines calculated for the case $R_2/R_1 = 4$ and when evaporation equals water application rate. These lines were calculated from Eq. (52). It is interesting to compare Figs. 29 and 32 to see the solute flow paths. Obviously, the ultimate destination of all chemicals applied to the soil surface in this scenario is the evaporative surface adjacent to the emitter. This somewhat artificial

situation was created by requiring that no deep drainage occur at large depth and that evaporation rate equal water application rate. Nevertheless, it is clear that a chemical transport model must include evaporation in order to assess the ability to apply the chemicals between the emitters. Figure 33 presents chemical frontlines at various times after application of a chemical pulse to the situation where evaporation occurred. This somewhat asymmetric pattern compared to Figure 31 is a manifestation both of enhanced lateral movement due to water ponded on the soil surface and due to lateral transport toward the evaporation site.

Simulation of Laboratory Experiment

As mentioned earlier, many simplifying assumptions of this model or any other model currently in use preclude its use in a complex, multi-dimensional situation. The extent to which these simple models describe the behavior can be seen by looking at Figure 34 which replots the laboratory data together with appropriate simulations of chemical frontlines obtained with the two models. Although qualitative agreement is obtained, it is obvious that many of the features are imperfectly modeled.

VI. EVALUATION OF OBJECTIVES

After three years of experimentation and analysis, we feel that much has been learned about the transport of bromacil, oxamyl and napropamide under trickle irrigation application. With the variety of soils we looked at, all appropriate to arid zones, we found that bromacil and oxamyl adsorbed negligibly in all cases. Therefore, for these chemicals knowledge of the water flow transport path would be sufficient to determine their movement. Degradation studies were conducted under laboratory conditions for bromacil and napropamide and under laboratory and field conditions for oxamyl. The half-lives of napropamide and bromacil are long enough to be moderately persistent when applied under trickle irrigation, whereas, oxamyl would be expected to disappear quite rapidly. In all cases the measured half-lives are short enough so that prolonged persistence in the environment is not expected.

The influence of soil moisture and soil temperature were studied, both in Israel and in the United States. The temperature dependence of adsorption seems to be moderate in the thermal ranges expected to be encountered, except near the surface, and the moisture content dependence was consistent with pre-conceived notions.

The modeling effort did not result in the ability to simulate the chemical processes but yielded substantial information about the importance of various parameters in describing transport. Most notably, we determined that it seems essential, should a model be developed for trickle irrigation systems, to include evaporation at the surface as

part of the boundary conditions. To date, no other model, except for the one described herein, makes an attempt to do such. It seems particularly critical for herbicide chemicals to be able to describe the transport processes toward the area in between the emitters where weed control is needed.

It should be emphasized that the chemicals selected in these experiments were picked for their ease in experimentation. Although they are used commercially, we do not mean to imply that we consider them the most important or most useful chemicals to apply under trickle irrigation systems. Rather, from the range of mobility, persistence, and solubility covered by the three chemicals, we hope to have provided information relevant to a spectrum of other chemicals potentially applicable to trickle irrigation systems as well. In this sense, it may be considered that we have selected prototypes for transport studies rather than chemicals selected for their commercial effectiveness.

VII. REFERENCES

1. Alexander, M. (1964) Introduction to Soil Microbiology. J. Wiley and Sons, New York, N.Y.
2. Bailey, C. W. and J. L. White (1970) Factors influencing the adsorption, desorption and movement of pesticide in soils. Residues Rev. 32:29-92.
3. Bailey, C. W., J. L. White and T. Rothberg (1968) Adsorption of organic herbicides by montmorillonite: role of pH and chemical character of adsorbate. Soil Sci. Soc. Amer. Proc. 32:222-234.
4. Banin, A. and A. Amiel (1969) A correlative study of the chemical and physical properties of a group of natural soils of Israel. Geoderma 3:185-198.
5. Bar-Yosef, B. and M. R. Sheikholislami (1976) Distribution of water and ions in soils irrigated and fertilized from a trickle source. Soil Sci. Soc. Amer. J. 40:575-582.
6. Bowman, B. T. and W. W. Sans (1979) The aqueous solubility of twenty-seven insecticides and related compounds. J. Environ. Sci. Health B14:625-634.
7. Brandt, A., E. Bresler, N. Diner, I. Ben-Asher, J. Heller and D. Goldberg (1971) Infiltration from a trickle source. I. Mathematical models. Soil Sci. Soc. Amer. Proc. 35:675-682.
8. Bresler, E. (1975) Two dimensional transport of solutes during nonstudy infiltration from a trickle source. Soil Sci. Soc. Amer. Proc. 39:604-613.

9. Bresler, E., J. Heller, N. Diner, I. Ben-Asher, A. Brandt, and JD. Goldberg (1971) Infiltration from a trickle source. II. Experimental data and theoretical predictions. Soil Sci. Soc. Amer. Proc. 35:683-689.
10. Briggs, G. G. (1973) A simple relationship between soil adsorption of organic chemicals and their octanol/water partition coefficients. Proc. 7th British Insecticide and Fungicide Conf. pp. 83-86.
11. Briggs, G. G. (1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors, and the parachor. J. Agric. Food Chem. 29:1050-1059.
12. Bromilow, R. H., R. J. Baker, M. A. H. Freeman and K. Gorog (1980) The degradation of aldicarb and oxamyl in soil. Pestic. Sci. 11: 371-378.
13. Chiou, C. T., L. J. Peters and V. H. Freed (1979) A physical concept of soil-water equilibria for non-ionic compounds. Science 206:8310832.
14. Churchill, R. V. (1963) Fourier Series and Boundary Value Problems. McGraw-Hill, New York.
15. Earl, K. D. and W. A. Jury (1977) Water movement in bare and cropped soil under isolated trickle emitters. II. Analysis of cropped soil experiments. Soil Sci. Soc. Amer. J. 41:856-861.
16. Ellgehausen, H., C. d'Houdt and R. Fuerer (1981) Reversed phase chromatography as a general method for determining octan-1-ol water partition coefficients. Pestic. Sci. 12:219-227.

17. Felsot, A. and P. A. Dahm (1979) Sorption of organophosphorus and carbamate insecticides by soil. *J. Agric. Good Chem.* 27:557-563.
18. Goring, C. A. I. (1962) Control of nitrification by 2-chloro-6-(trichloromethyl) pyridine. *Soil Sci.* 93:211-218.
19. Hamaker, J. JW. (1972) Decomposition: Quantitative Aspects. In: C. A. I. Goring and J. W. Hamaker (eds.) *Organic Chemicals in the Soil Environment.* pp. 253-340. Marcel Dekker Inc., New York, N.Y.
20. Hamaker, J. W. and J. M. Thompson (1972) Adsorption. In: C. A. I. Goring and J. W. Hamaker (eds.) *Organic Chemicals in the Soil Environment.* pp. 49-144. Marcel Dekker Inc., New York, N.Y.
21. Hassett, J. J., W. L. Banwart, S. G. Wood and J. C. Means. (1981) Sorption of a-naphthol: Implications concerning the limits of hydrophobic sorption. *J. Soil Sci. Soc. Am.* 45:38-42.
22. Hiltbold, A. E. (1974) Persistence of Pesticides in Soil. In: W. D. Guenzi (ed.) *Pesticides in Soil and Water.* pp. 67-98. Soil Science Society of America, Madison, Wisc.
23. Himmelblau, D. (1970) Process analysis by statistical methods. Sterling Swift Publ. Co., Manchaca, TX.
24. Hurle, K. (1977) Ein vergleich von biotests mit chemischanalytischen methoden zum nachweis von atrazin, 2,4-D, DNOC und napropamid im boden. *Weed Research* 17:25-32.
25. Jury, W. A. and Hesham El Abd. (1982) Problems in predicting chemical transport in soil. Proc: Special symposium "Current and needed research in aquifer protection". Amer. Soc. Civ. Eng. April 22-26, 1982.

26. Jury, W. A. and Tim Collins. (1982) Stochastic vs. deterministic models for solute movement in the field. Proc: Symposium on unsaturated flow modeling. Battelle, WA, March 23-24, 1982.
27. Jury, W. A. and R. D. Earl (1977) Water movement in bare and cropped soil under isolated trickle emitters. I. Analysis of Soil Sci. Soc. Amer. J. 41:852-856.
28. Jury, W. A., W. F. Spencer and W. J. Farmer (1983) Use of models for assessing relative volatility, mobility and persistence of pesticides and other trace organics in soil systems. In: J. Saxena (ed.) Hazard Assessment of Chemicals, Vol. 2. Academic Press, N.Y.
29. Karickhoff, S. W., O. S. Brown and T. A. Scott (1979) Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.
30. Khan, A., J. J. Hassett, W. L. Banwart, J. C. Means and S. G. Wood (1979) Sorption of acetophenone by sediments and soils. Soil Sci. 128:297-302.
31. Leistra, M., R. H. Bromilow, and J.J.T.I. Boesten (1980) Pestic. Sci. 11:379-388.
32. Leistra, M., J. H. Smelt, and R. Zandvoort (1975) Persistence and mobility of bromacil in orchard soils. Weed Res. 15:243-247.
33. Martin, H. and C. R. Worthing (1977) Pesticide Manual. British Crop Protection Council. pp. 394.
34. Metcalf, R. L. and P. Y. Lu (1981) Partition coefficients as measures of bioaccumulation potential for organic compounds. U.S. Environmental Agency Report (In press).

35. Mingelgrin, U. and Z. Gerstl (1982) Reevaluation of partitioning as a mechanism of nonionic chemical adsorption in soils. J. Environ. Qual. 12:1-11.
36. Moyer, J. R., R. B. McKercher and R. J. Hance (1972) Desorption of some herbicides from montmorillonite and peat. Can. J. Soil Sci. 52:439-447.
37. Obrigawitch, T., R. G. Wilson, A. R. Martin and F. W. Roeth (1982) The influence of temperature, moisture, and prior EPTC application on the degradation of EPTC in soils. Weed Sci. 30:175-181.
38. Patchett, G. G., D. J. Brookman and J. E. Rodebush (1976) Devrinol. In: G. Zweig (ed.) Analytical Methods for Pesticides and Plant Growth Regulators. Vol. VII. pp. 347-358. Academic Press, New York.
39. Philip, J. R. (1969) Theory of infiltration. Adv. Hydrosci. 5:215-296.
40. Philip, J. R. (1971) General theorem on steady infiltration from surface sources with application to point and line sources. Soil Sci. Soc. Amer. Proc. 35:867-871.
41. Raats, P.A.C. (1971) Steady infiltration from point sources, cavities, and basins. Soil Sci. Soc. Amer. Proc. 35:689-694.
42. Roberts, T. R. and G. Stoydin (1976) Degradation of the insecticide SD 8280, 2-chloro-P- (2,4-dichlorophenyl) vinyl dimethyl phosphate in soils. Pestic. Sci. 7:145-149.

43. Singhal, J. P., S. Khan and O. P. Bansal (1978) Adsorption of oxamyl on montmorillonites. Aust. J. Chem. 31:2151-2156.
44. Smelt, J. H., A. Dekker and M. Leistra (1979) Effect of soil moisture conditions on the conversion rate of oxamyl. Neth. J. Agric. Sci. 27:191-198.
45. Thean, J. E., W. G. Fong, D. R. Young and T. L. Stephens (1978) J. Assoc. Offic. Analy. Chem. 61:15-17.
46. Thomas, G. W. and R. E. Phillips (1979) Consequences of water movement in macropores. J. Environ. Qual. 8:149-152.
47. Van Bladel, R. and A. Moreale (1974) Adsorption of fenwron and monwron by two montmorillonite clays. Soil Sci. Soc. Amer. Proc. 38:244-249.
48. Van Genuchten, MTh. and P. J. Wienega (1976) Mass transfer studies in sorbing porous media. I. Analytical Solutions. Soil Sci. Soc. Amer. Proc. 40:473-480.
49. Walker, A. (1974) A simulation model for prediction of herbicide persistence. J. Environ. Qual. 3:396-401.
50. Walker, A. (1978) Simulation of the persistence of eight soil-applied herbicides. Weed Res. 18:305-313.
51. Warrick, A. W. (1974) Time dependent linearized infiltration. I. Point sources. Soil Sci. Soc. Amer. Proc. 38:383-386.
52. Wolf, D. C. and J. P. Martin (1974) Microbial degradation of 2-carbon-14 bromacil and terbacil. Soil Sci. Soc. Amer. Proc. 38:921-925.

53. Wu, C. H., N. Buehring, J. M. Davidson and P. W. Santelmann (1975)
Napropamide adsorption, desorption and movement in soils. Weed Sci.
23:454-457.
54. Zimdahl, R. L., V H. Freed, M. L. Montgomery and W. R. Furtick
(1970) The degradation of triazine and uracil herbicides in soil.
Weed Res. 10:18-26.

List of publications resulting from BARD project I-95-79b to date.

1. Saltzman, S., Z. Gerstl, and B. Yaron (1981) Factors to be considered in the application of pesticides via drip irrigation. In: Colloque Franco-Israelien. "Les phenomenes de transport de l'eau et des solutes et l'irrigation", Avignon, France pp. 71-82.
2. Gerstl, Z., S. Saltzman, L. Kliger and B. Yaron (1981) Distribution of herbicides in soil in a simulated drip irrigation system. Irrigation Sci. 2:155-166.
3. Gerstl, Z. and B. Yaron (1982) Behavior of bromacil and napropamide in soils. I. Adsorption and Degradation. Soil Sci. Soc. Amer. J. (accepted for publication).
4. Gerstl, Z. and B. Yaron (1982) Behavior of bromacil and napropamide in soils. II. Distribution after application from a point source. Soil Sci. Soc. Amer. J. (accepted for publication).
5. Gerstl, Z. (1982) Adsorption, decomposition and movement of oxamyl in soil. Pestic. Sci. (accepted for publication).
6. Yaron, B. and Z. Gerstl (1982) Herbicide residues in soils following point source application. Fifth IUPAC Congress of Pesticide Chemistry. Kyoto, Japan.

Table 1. Properties of the soils used for a) studying the behavior of napropamide, bromacil and oxamyl in laboratory studies and b) field studies.

-a-

Soil	% Clay	% OC	% CaCO ₃	pH ¹
Mivtachim	7.5	0.06	3.5	8.5
Bet Dagan	13.7	0.40	2.3	7.9
Gilat	23.1	0.55	12.9	7.8
Shefer	70.0	0.72	0.2	7.2
Neve Ya'ar	70.0	1.18	8.9	7.7

¹
Measured in a saturated soil paste.

-b-

Depth	% Clay	% OC	K _d (Nap)	K _d (Bro)
0-20	26.3	0.95	2.3	0.26
20-60	28.1	0.62	1.4	0.20
60-100	37.5	0.47	3.4	0.30

Table 2. Adsorption coefficients for napropamide, bromacil and oxamyl on several Israeli soils.

Soil	Napropamide		Bromacil		Oxamyl	
	K_d (mL/g)	K_{OC}	K_d (mL/g)	K_{OC}	K_d (mL/g)	K_{OC}
Mivtachim	0.27 ($r^2 = .89$)	450	0.03 ($r^2 = 0.93$)	50	0.05 ($r^2 = 0.989$)	78.1
Bet Dagan I	1.40 ($r^2 = 1.00$)	350	0.10 ($r^2 = 0.99$)	25	0.08 ($r^2 = 0.997$)	20.3
Gilat	1.92 ($r^2 = 0.98$)	349	0.16 ($r^2 = 1.00$)	29	0.15 ($r^2 = 0.997$)	27.2
Bet Dagan II	2.96 ($r^2 = 1.00$)	293	0.32 ($r^2 = 0.99$)	32	--	--
Shefer	2.35 ($r^2 = 1.00$)	326	0.24 ($r^2 = 0.98$)	33	0.26 ($r^2 = 0.996$)	36.3
Neve Ya'ar	2.94 ($r^2 = 0.99$)	249	0.39 ($r^2 = 1.99$)	33	0.31 ($r^2 = 0.995$)	26.3

Table 3. Equilibrium solution concentrations of oxamyl and its oxime
in adsorption studies with 1:2 soil solution ratio of Pachappa
sandy loam at 10 C after various equilibration periods.

Oxamyl			Oxime		
Initial	1 hr	1 day	Initial	1 hr	1 day
----- g/ml -----			----- g/ml -----		
0.63	0.55	0.58	0.08	0.06	0.16
0.68	0.54	0.57	0.10	0.06	0.15
1.08	1.04	0.93	0.07	0.15	0.17
1.07	1.00	0.91	0.11	0.12	0.17
2.04	1.95	1.81	0.10	0.19	0.22
1.99	1.95	1.75	0.11	0.17	0.26
5.00	4.35	4.43	--	0.14	0.49
5.10	4.42	4.47	--	0.14	0.48
10.4	9.90	8.90	--	--	0.95
10.6	9.80	8.80	--	0.02	0.91
20.8	19.0	17.7	--	0.2	1.73
20.9	19.3	17.7	--	0.4	1.74
50.8	50.1	43.9	--	0.2	3.96
51.3	49.4	43.9	--	0.1	4.00

Table 4. Dynamic K_D values (ml/g) measured in undisturbed field cores.

Column No.	K_D	Column No.	K_D
A1	2.29	C1	2.52
A2	1.85	C2	1.41
A3	1.53	C3	1.37
A4	1.85	C4	2.75
B1	3.82	D1	1.94
B2	2.14	D2	0.41
B3	1.80	D3	1.96
B4	1.68	D4	1.54
Mean = 1.93			
Variance = .53			

Table 5. Half-life (days) of napropamide as affected by temperature in Neve Ya'ar and Gilat soils ($C_0 = 16 \mu\text{g/g}$).

MOISTURE CONTENT (%)	Neve Ya'ar		Gilat
	30	40	15
Temp. ($^{\circ}\text{C}$)			
2	1643 ($r=0.82$)	485 ($r=0.80$)	617 ($r=0.73$)
25	151 ($r=0.99$)	150 ($r=0.99$)	201 ($r=0.99$)
35	61 ($r=0.99$)	93 ($r=0.96$)	76 ($r=0.99$)
50	55 ($r=0.54$)	17 ($r=0.96$)	86 ($r=0.99$)

Table 6. Half-life (days) of napropramide in Neve Ya'ar and Gilat soils at 25°C as affected by moisture content and initial concentration.

Moisture Content (%)	Neve Ya'ar		Moisture Content (%)	Gilat	
	$C_0 = 16 \mu\text{g/g}$	$C_0 = 4 \mu\text{g/g}$		$C_0 = 16 \mu\text{g/g}$	$C_0 = 4 \mu\text{g/g}$
	$T_{1/2}$	$T_{1/2}$		$T_{1/2}$	$T_{1/2}$
15	923 (r= .89)	507 (r= .95)	8	436 (r= .93)	217 (r= .99)
30	151 (r= .99)	180 (r= .99)	16	201 (r= .99)	117 (r= .99)
40	150 (r= .99)	108 (r= .99)	21	156 (r= .93)	34 (r= .97)

Table 7. Half-life (days) of bromacil as affected by temperature in Neve Ya'ar and Gilat soils at field capacity and an initial concentration of 16 $\mu\text{g/g}$.

Temp. ($^{\circ}\text{C}$)	Neve Ya'ar	Gilat
	$T_{1/2}$	$T_{1/2}$
5	677 (r= .87)	1033 (r= .95)
25	758 (r= .88)	421 (r= .98)
35	233 (r= .99)	340 (r= .99)
50	14 (r= .93)	32 (r= .99)

Table 8. Half-life (days) of bromacil in Neve Ya'ar and Gilat soils at 25°C as affected by moisture content and initial concentration.

Moisture Content (%)	Neve Ya'ar		Moisture Content (%)	Gilat	
	$C_0 = 16 \mu\text{g/g}$	$C_0 = 4 \mu\text{g/g}$		$C_0 = 16 \mu\text{g/g}$	$C_0 = 4 \mu\text{g/g}$
	$T_{1/2}$	$T_{1/2}$		$T_{1/2}$	$T_{1/2}$
15	650 (r= .83)	233 (r= .96)	8	1044 (r= .96)	1494 (r= .42)
30	758 (r= .88)	138 (r= .97)	16	421 (r= .98)	213 (r= .94)
40	372 (r= .96)	85 (r= .94)	21	310 (r= .98)	191 (r= .92)

Table 9. Oxamyl decomposition in the Bet Dagan soil as a function of soil moisture content, temperature and initial concentration.

Soil Moisture Content (%)	Temperature (°C)	Initial Oxamyl concentration (mg/kg ⁻¹)	(days ⁻¹)	t 1/2 (days)
3.5	25	5	0.052 _± .004	13.3
5.5	15	5	0.021 _± .001	32.7
5.5	25	5	0.079 _± .006	8.8
5.5	35	5	0.182 _± .013	3.8
5.5	25	50	0.062 _± .004	11.1
7.1	25	5	0.139 _± .010	5.0
10.4	25	5	0.158 _± .009	4.4
16.6	25	5	0.168 _± .006	4.2

Table 10. Oxamyl decomposition in four Israeli soils at field capacity
(25°C; 5 mg oxamyl kg⁻¹).

Soil	Moisture Content %	K (days ⁻¹)	t _{1/2} (days)
Mivtachim	6.5	0.17	4.1
Bet Dagan	10.4	0.158	4.4
Gilat	14.4	0.23	3.1
Shefer	33.2	0.22	3.2
Neve Ya'ar*	32.5	0.11	6.5
Neve Ya'ar	52.8	0.13	5.2

* 60% field capacity

Table 11. Distribution of oxamyl (mg kg^{-1}) in Bet Dagan soil 8 days after application of a single concentrated pulse (300 ml of 300 mg l^{-1}) followed by daily irrigation with 300 ml tap water at 4 l h^{-1} .

Depth (cm)	Lateral distance from emitter (cm)					
	0	3	6	9	12	15
0-3	0	0	0.3	6.3	4.1	0
3-6	0	0	0.1	1.6	3.6	0.8
6-12	0	0	0.1	2.2	5.3	0.7
12-18	0	0	0.1	1.3	3.4	0.2
18-24	1.5	1.6	2.5	2.0	0.9	0
24-30	0.8	0.8	0.4	0.2	0.3	0
30-35	0	0	0	- *	-	-

* not sampled

Table 12. Distribution of oxamyl (mg kg^{-1}) in Bet Dagan soil 8 days after applying 300 ml of a 100 mg l^{-1} oxamyl solution on days 1, 3, and 5 and application of 300 ml of tap water on days 2, 4, and 6. Irrigation was at 4 l h^{-1} .

Depth (cm)	Lateral distance from emitter (cm)					
	0	3	6	9	12	15
0-3	0	0.1	0.9	5.2	0.9	0
3-6	0.1	0.2	2.7	2.3	0.9	0
6-12	0.4	1.2	3.5	2.0	0.7	0
12-18	3.7	5.0	2.4	1.6	0.3	0
18-24	2.5	2.6	2.0	1.3	0.1	0
24-30	0.9	0.9	0.4	0.3	0	0
30-35	0	0	0	- *	-	-

* not sampled

Table 13. Distribution of oxamyl (mg kg^{-1}) in Bet Dagan soil 8 days after applying 300 ml of a 50 mg l^{-1} oxamyl solution for 6 consecutive days at 4 l h^{-1} .

Depth (cm)	Lateral distance from emitter (cm)					
	0	3	6	9	12	15
0-3	3.8	3.6	3.6	5.5	0.8	0
3-6	3.5	3.8	3.7	3.2	0.8	0
6-12	3.0	4.1	3.9	2.3	0.3	0
12-18	3.0	4.0	4.2	2.7	0.2	0
18-24	5.4	4.3	4.7	1.7	0.1	0
24-30	0.4	0.3	0.6	0.6	0	0
30-35	1.1	1.3	1.3	- *	-	-

* not sampled

Table 14. Volumetric Water Content in Pesticide Trickle Experiments

Vertical Distance (cm)	Radial Distance (cm)						
	0-5	5-7.5	7.5-10	10-12.5	12.5-15	15-20	20-30
A. No Evaporation							
0-2.5	.290	.273	.259	.243	.223		
2.5-5	.267	.264	.256	.244	.220		
5-7.5	.275	.253	.254	.244	.231		
7.5-10	.279	.265	.258	.247	.235		
10-12.5	.252	.243	.236	.231	.219		
12.5-15	.243	.238	.231	.232	.216		
15-17.5	.211	.230	.220	.223	.212		
17.5-20	.220	.220	.213	.210	.202		
20-22.5	.218	.212	.208	.203	.197		
22.5-25	.218	.212	.208	.203	.197		
B. With Evaporation							
0-2.5	.232	.201	.195	.180	.166	.144	.137
2.5-5	.206	.196	.186	.179	.169	.144	.137
5-7.5	.192	.181	.178	.170	.168	.155	.149
7.5-10	.184	.179	.174	.172	.169	.155	.149
10-12.5	.184	.174	.172	.169	.169	.173	.165
12.5-15	.186	.173	.174	.177	.172	.173	.165
15-17.5	.194	.185	.189	.188	.187	.187	.193
17.5-20	.198	.189	.188	.194	.189	.187	.193
20-22.5	.206	.208	.210	.206	.209	.209	.203
22.5-25	.206	.208	.210	.206	.209	.209	.203

Table 15. Chloride Concentration (meq/l) in Pesticide Trickle Experiments

Vertical Distance Z (cm)	Radial Distance R (cm)				
	0-5	5-7.5	7.5-10	10-12.5	12.5-15
A. No Evaporation					
0-2.5	1.14	.98	1.10	1.11	1.16
2.5-5	1.24	.98	.96	.99	1.10
5-7.5	.99	.94	.81	.79	.95
7.5-10	.89	.83	.89	.89	.90
10-12.5	.87	1.10	1.04	.91	1.11
12.5-15	1.01	.81	.86	.95	1.64
15-17.5	.94	.77	1.02	1.54	4.71
17.5-20	.78	1.6	3.80	6.77	6.58
20-22.5	4.08	5.73	6.33	4.01	1.36
B. Evaporation					
0-2.5	2.67	2.57	5.17	17.84	34.62
2.5-5	3.78	2.58	1.87	1.92	2.76
5-7.5	2.02	2.07	1.71	1.68	1.73
7.5-10	1.84	1.77	1.73	1.97	1.79
10-12.5	2.01	1.97	1.71	.172	1.67
12.5-15	1.92	1.78	1.66	1.44	1.71
15-17.5	1.84	1.55	1.28	1.29	2.26
17.5-20	1.36	1.49	1.68	2.72	5.07

Table 16. Pesticide Concentration (meq/gm) in Trickle Experiments

Vertical Distance Z (cm)	Radial Distance R (cm)				
	0-5	5-7.5	7.5-10	10-12.5	12.5-15
A. No Evaporation					
0-2.5	1.11	5.03	3.19	1.27	0.08
2.5-5	.92	4.91	4.79	.66	0.00
5-7.5	7.19	2.29	3.11	.04	0.00
7.5-10	5.55	2.70	0.07	0	0.00
10-12.5	0	0.03	0.00	0.05	0.00
B. Evaporation					
0-2.5	4.07	3.07	1.16	6.34	2.77
2.5-5	0.50	1.40	2.45	4.23	2.39
5-7.5	1.19	2.84	3.54	3.33	0
7.5-10	2.29	5.82	3.08	1.02	.09
10-12.5	5.25	2.10	2.34	.32	.01
12.5-15	2.02	.99	0	0	0
15-17.5	0.43	0	0	.01	0

Table 17. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving daily irrigation at the rate of 4 l/h. Time of sampling was 7 days after herbicide application.

Depth (cm)	Radial Distance (cm)																				
	0			10			20			30			40			50			70		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B			
0-5	16.9	103	0.9	16.4	30	1.0	16.3	55	15	15.7	22	4.9	13.5	21	6.5	13.0	0.3	6.8	3.1	0	0
5-10	14.8	83	1.5	15.9	71	1.1	15.5	11	9.5	15.6	14	2.4	14.8	15	5.0	13.1	0	4.2	3.7	0	0
10-20	15.4	49	5.5	14.8	30	3.0	15.4	4.7	12.5	15.8	0.8	4.9	14.1	1.7	4.8	13.1	0	4.5	14.2	0	0
20-40	15.3	7.8	6.7	15.4	5.7	9.7	14.7	3.7	8.6	15.7	0.5	8.3	14.5	0.3	2.7	12.7	0	2.4	-	0	0
40-60	16.6	4.2	3.5	17.5	1.2	5.7	16.3	3.2	7.0	18.0	1.4	5.1	16.8	0.9	2.1	17.5	0	0	17.5	0.2	0
60-80	18.2	1.7	1.1	19.0	0.6	2.4	16.8	1.4	1.2	16.6	0.4	1.2	17.2	0.5	0.7	16.5	0.2	0.1	14.0	0.1	0.1
80-100	18.3	3.9	1.5	17.1	3.4	1.6	18.2	0.3	0.6	15.8	0.3	1.5	17.4	0.3	0.4	16.5	0	0.1	-	-	-

Table 18. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving daily irrigation at the rate of 4 l/h. Time of sampling was 28 days after herbicide application.

Depth (cm)	Radial Distance (cm)											
	0			10			20			30		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B
0-5	20.4	6.0	0.2	20.8	4.3	0.3	19.8	5.4	0.8	19.2	27.2	15.7
										14.6	2.0	17.0
										9.1	1.1	3.8
5-10	17.4	6.2	0.4	19.1	5.4	0.2	19.1	4.1	0.3	19.2	7.7	1.7
										17.1	0.9	5.9
										15.8	1.4	0.6
10-20	17.9	3.1	0.5	17.5	3.3	0.3	15.3	2.4	0.1	19.0	2.5	0.9
										16.9	3.1	6.0
										15.2	0.6	0.2
20-40	17.7	1.1	1.6	18.5	2.1	1.1	18.4	1.7	0.5	19.0	1.6	0.7
										17.0	2.2	1.3
										15.7	0.4	0.2
40-60	19.6	0.4	3.9	19.5	0.5	1.8	18.3	1.4	0.9	18.2	0.9	2.4
										16.9	0.3	0.8
										17.3	0.1	0.3
60-80	18.5	0.4	2.8	20.0	0.4	1.1	19.8	0.9	1.5	19.2	1.1	2.2
										18.1	0.4	1.9
										20.4	0.2	0.4
80-100	19.2	0.1	1.0	20.7	0.3	1.6	20.3	0.6	0.9	18.0	1.1	0.9
										18.3	0.2	1.0
										16.1	0.2	0.5
										15.6	0	0.5
										10.1	0.2	0.2
										12.1	0	0.2
										16.1	0.2	0.1
										16.2	0	0.2
										17.0	0	0.6
										15.6	0	0.5

Table 19. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving daily irrigation at the rate of 4 l/h. Time of sampling was 42 days after herbicide application.

Depth (cm)	Radial Distance (cm)																	
	0			10			20			30			40			50		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B
0-5	19.9	0.4	0	21.2	0.2	0	18.9	1.2	2.3	15.3	0.1	1.8	11.5	0	0.8	11.3	0	0.2
5-10	18.0	0.1	0	17.4	0.1	0	18.0	0.4	0.3	12.5	0	0.1	14.5	0	0.1	12.6	0	0.4
10-20	18.0	0.5	0	16.1	0.2	<0.1	15.2	0.9	1.2	15.2	0.1	0.2	15.5	0	<0.1	11.6	0	0.2
20-40	18.4	0.5	0	18.5	0.1	0	15.7	<0.1	0	15.1	<0.1	<0.1	15.7	0	0.3	16.5	<0.1	0.2
40-60	18.2	<0.1	0	17.5	<0.1	<0.1	16.1	<0.1	0	17.4	0	<0.1	16.6	0	0	16.7	0	0.3
60-80	18.8	<0.1	0	18.9	0	0	18.4	<0.1	<0.1	15.8	0	0.1	17.3	0	<0.1	17.5	0	0.2
80-100	17.8	<0.1	0	18.9	0	0	19.0	0	0.3	19.3	0	0.3	17.1	0	0.3	16.8	0	0.2

Table 20. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving weekly irrigation at the rate of 4 l/h. Time of sampling was 7 days after herbicide application.

Depth (cm)	Radial Distance (cm)														
	0			10			20			30			40		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B
0-5	16.7	400	0.8	18.6	52	2.1	17.0	47	3.6	16.4	6.9	16.3			
5-10	17.2	105	1.9	18.9	46	1.7	17.4	32	2.8	15.5	16.0	4.7	15.0	1.2	4.3
10-20	16.6	38	3.0	17.7	24	2.7	17.6	16	1.4	17.7	11.0	7.1	13.3	0.3	4.3
20-40	13.6	6.2	2.8	14.7	10.2	3.0	14.4	8.5	3.3	15.5	6.0	2.8	13.6	3.1	1.4
40-60	18.5	7.3	2.3	18.1	2.7	1.8	17.7	1.3	2.1	17.0	3.3	3.3	15.6	1.4	1.9
60-80	16.4	9.1	2.6	16.1	1.8	1.3	16.6	1.8	7.0	17.7	1.4	3.8	13.7	2.5	2.6
80-100	17.0	8.8	1.6	16.5	1.9	1.0	15.0	1.1	0.6	15.7	0.8	2.7	16.5	0.7	0.9
100-120	17.1	4.5	1.4										13.7	0.5	0.5

100-120 17.1 4.5 1.4

Table 21. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving weekly irrigation at the rate of 4 l/h. Time of sampling was 21 days after herbicide application.

Depth (cm)	Radial Distance (cm)																	
	0			10			20			30			40			50		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B
0-5	18.2	8.6	0.1	17.1	5.5	0.2	15.8	21.7	1.9	15.2	19.6	8.3	10.7	2.4	10.2	8.9	0.1	0.2
5-10	20.0	5.3	0	18.5	7.3	0.1	17.6	17.3	0.6	16.8	23.2	5.9	13.8	1.1	3.2	9.1	0	0
10-20	17.1	7.6	0.2	17.5	8.1	0.3	14.8	11.7	1.3	15.6	6.9	2.2	12.6	0.2	3.0	12.4	0.1	0
20-40	15.7	4.6	0.1	16.5	5.9	0.2	17.1	6.2	0.5	15.7	8.2	0.9	13.5	0.3	0.9	13.5	0	1.1
40-60	18.4	12.2	1.7	17.9	2.4	0.8	17.5	3.0	1.0	16.4	1.5	1.7	18.4	1.5	1.4	15.8	0	0.9
60-80	17.3	5.3	1.2	18.1	1.5	1.2	16.8	6.2	1.5	18.0	2.6	1.5	16.9	0.4	1.3	16.2	0.1	0.8
80-100	18.6	2.8	0.6	16.6	2.0	1.2	17.4	3.1	0.5	17.8	3.1	1.6	11.1	0.3	1.7	16.3	0.3	0.4

Table 23. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving daily irrigation at the rate of 2 l/h. Time of sampling was 7 days after herbicide application.

Depth (cm)	Radial Distance (cm)																	
	0			10			20			30			40			50		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B
0-5	22.1	18	0.3	19.7	17	8.6	19.1	15	17.3	17.1	0.3	10.8	14.2	0	0.1	11.2	0.2	0.2
5-10	19.8	19	0.1	17.7	26	1.3	18.0	30	5.2	17.1	0.3	11.0	14.1	1.5	1.1	11.5	0.2	0.2
10-20	18.5	55	0.4	14.9	29	0.8	16.7	30	1.6	16.4	0.6	7.5	15.0	0	0	13.9	0	0
20-40	17.5	31	0.5	17.2	21	1.1	16.2	5.7	5.8	15.4	0.1	8.0	13.8	0	0.1	10.1	0	0
40-60	18.9	2.8	6.7	17.3	4.7	4.6	17.6	1.2	10.3	17.9	0	0.4	17.7	0	0.2	15.4	0.2	0
60-80	17.1	1.4	1.2	19.5	4.9	5.8	17.8	0.7	1.8	18.2	0	1.7	17.9	0	0.7	17.1	0.2	0
80-100	17.8	1.4	1.5	19.0	1.7	1.0	18.5	2.2	2.5	17.4	0	0	16.2	0.1	0.2	16.6	0.2	0

Table 24. Distribution of soil moisture content (%), napropamide (mg kg^{-1}), and bromacil (mg kg^{-1}) around an isolated dripper receiving daily irrigation at the rate of 2 l/h. Time of sampling was 42 days after herbicide application.

Depth (cm)	Radial Distance (cm)																				
	0			10			20			30			40			50			70		
	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B	PW	N	B
0-5	21.1	0.1	<0.1	20.0	0.2	<0.1	18.9	1.0	1.0	17.6	0.8	1.3	14.6	0.4	1.1	10.0	0	0.4	6.3	0	0
5-10	18.8	0.2	0	18.4	<0.1	<0.1	17.6	0.2	0.3	11.7	0.5	0.2	14.8	0	0.3	13.2	0	0.4	9.1	0	0
10-20	17.0	0.3	0	17.1	<0.1	0	15.3	0.1	0	13.9	0.3	0.1	15.0	0	0.2	15.3	<0.1	0.4	8.6	0	<0.1
20-40	16.4	0.4	0	16.7	0.1	0	16.1	0.2	0.1	16.1	0.3	0.2	13.9	0.1	0	14.9	0.4	0.8	10.5	0	<0.1
40-60	16.5	0.2	0	16.5	0	0.2	18.1	0.4	0.1	17.9	0.3	0	16.5	0.1	0.1	16.3	0.5	0	17.0	<0.1	0.1
60-80	18.2	0.4	<0.1	18.4	0.3	0	17.6	0.2	<0.1	18.1	0.7	0.2	18.3	<0.1	<0.1	22.2	<0.1	0.1	17.3	0	0.2
80-100	17.3	0	0	17.4	<0.1	0.1	18.4	0.2	<0.1	17.6	<0.1	<0.1	17.9	0	0.2	17.4	0	0	15.8	<0.1	0.1

Table 25. Average and standard deviation of soil moisture content (%) and napropamide (mg kg^{-1}) from three replicated cropped plots, irrigated daily at 4 lh^{-1} and sampled 8 days after herbicide application.

Depth (cm)	Radial Distance (cm)											
	0			10			20			30		
	Pw	N		Pw	N		Pw	N		Pw	N	
0-5	20.1 $\pm$ 0.6	7.0 $\pm$ 1.1		19.0 $\pm$ 0.9	14.1 $\pm$ 11.5		16.4 $\pm$ 1.1	22.7 $\pm$ 32.4		12.8 $\pm$ 1.4	0.3 $\pm$ 0.3	
5-10	19.4 $\pm$ 1.2	10.4 $\pm$ 8.5		19.3 $\pm$ 1.1	8.8 $\pm$ 1.6		18.2 $\pm$ 2.0	10.7 $\pm$ 14.3				
10-20	18.9 $\pm$ 0.6	9.4 $\pm$ 3.7		19.7 $\pm$ 1.1	5.2 $\pm$ 2.6		19.4 $\pm$ 2.2	3.3 $\pm$ 3.5		14.9 $\pm$ 3.3	0.0 $\pm$ 0.0	
20-40	18.9 $\pm$ 2.3	5.2 $\pm$ 0.8		18.2 $\pm$ 2.2	3.3 $\pm$ 2.2		17.6 $\pm$ 1.5	0.9 $\pm$ 0.9		16.1 $\pm$ 1.9	0.4 $\pm$ 0.3	
40-60	20.4 $\pm$ 2.1	1.8 $\pm$ 1.0		18.4 $\pm$ 2.0	2.5 $\pm$ 2.8		19.9 $\pm$ 2.1	0.5 $\pm$ 0.6				

Table 27. Soil moisture content by depth.

Soil Depth	Soil Moisture Content (%)											
	14 Days						35 Days					
	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>Ave.</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>Ave.</u>
0-4"	11	7	14	6	4	8.4	12	15	9	12	9	11.4
4-8"	7	7	8	7	6	7.0	13	15	6	8	11	10.6
8-12"	23	15	8	7	6	11.8	16	15	18	8	11	13.6
1-2'	13	19	10	10	9	12.2	11	8	10	13	12	10.8
2-3'	6	13	1	1	2	5.2	8	6	6	9	8	7.4
3-4'	10	3	4	4	5	5.6	8	7	11	9	13	9.6
5-6'	6	2	2	2	7	4.4	5	5	4	8	8	6.0
7-8'	9	3	5	5	10	6.2	10	8	3	11	5	7.4
9-10'	9	5	1	1	11	5.8	14	8	2	10	10	8.8
13-14'	6	7	5	5	6	5.4	17	6	2	7	5	7.4
25-26'	7	10	4	4	11	8.0	12	9	5	6	8	8.0
19-20'	9	8	3	3	8	6.8	10	9	4	7	9	7.8

Figure 1. Adsorption-desorption isotherm for bromacil at 20°C.

Figure 2. Adsorption-desorption isotherm for napropamide at 20°C.

Figure 3. Adsorption-desorption isotherm for napropamide at 30°C.

BRIDGEMAN FOR
COLUMBIA

Figure 4. Dynamic breakthrough curve for Cl^- and devrinol (napropamide).

Figure 5. Frequency distribution for dynamic K_D values.

Figure 6. Distribution of a) water, b) devalinol and c) bromacil 24 hr after application of 1800 ml of a 50 ppm herbicide solution to a hamra soil at 4L/hr (Treatment A).

Figure 7. Distribution of a) water, b) devrinol and c) bromacil 24 hr after application of 900 ml of a 100 ppm herbicide solution to a hamra soil at 4L/hr (Treatment B).

Figure 8. Distribution of a) water, b) devrinol and c) bromacil 24 hr after application of 900 ml of a 100 ppm herbicide solution to an initially moist soil (Treatment C).

Fig. 9. Distribution of a) water, b) devrinol and c) bromacil 24 hr after

Figure 9. Distribution of a) water, b) devrinol and c) bromacil 24 hr after Treatment B was leached by 900 ml tap water (Treatment D).

Fig. 10. a, b, c = 1

Figure 10. Distribution of a) water, b) devrinol and c) bromacil 1 week after application of 900 ml of a 100 ppm herbicide solution and kept under evaporative conditions for 1 week and prior to irrigation.

Fig. 12. Distribution of a) water, b) devrinol, and c) bromacil 5 weeks after application of 900 ml of a 100 ppm herbicide solution and kept under evaporative conditions. Evaporation losses were made up by weekly irrigations.

Figure 12. Distribution of a) water, b) devrinol, and c) bromacil 5 weeks after application of 900 ml of a 100 ppm herbicide solution and kept under evaporative conditions. Evaporation losses were made up by weekly irrigations.

11g. 1000g to 2-3

Figure 13. Distribution of a) water, b) devrinol and c) bromacil 5 weeks after application of 900 ml of a 100 ppm herbicide solution and kept under evaporative conditions. Evaporation losses were made up by biweekly irrigations.

MOISTURE CONTENT (%)

HERBICIDE CONCENTRATION ($\mu\text{g/g}$)

Figure 14. Laboratory drip irrigation, water content and chemical concentrations.
See text for details.

MOISTURE CONTENT (%)

HERBICIDE CONCENTRATION ($\mu\text{g/g}$)

Figure 15. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

Figure 16. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

Figure 17. Laboratory drip irrigation water content and chemical concentrations. See text for details.

Figure 18. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

MOISTURE CONTENT (%)

HERBICIDE CONCENTRATION ($\mu\text{g/g}$)

Figure 19. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

MOISTURE CONTENT (%)

HERBICIDE CONCENTRATION ($\mu\text{g/g}$)

Figure 20. Laboratory drip irrigation water content and chemical concentrations. See text for details.

Figure 21. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

Figure 22. Laboratory drip irrigation water content and chemical concentrations. See text for details.

Figure 23. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

Figure 24. Laboratory drip irrigation water content and chemical concentrations. See text for details.

MOISTURE CONTENT (%)

HERBICIDE CONCENTRATION ($\mu\text{g/g}$)

Figure 25. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

MOISTURE CONTENT (%)

HERBICIDE CONCENTRATION ($\mu\text{g/g}$)

Figure 26. Laboratory drip irrigation water content and chemical concentrations.
See text for details.

Figure 27. Water content in simulated drip experiment using oxamy1.

23

Figure 28. Canonical $K(h) = K_0 \exp(\gamma h)$ relations for three soil types used in model simulations.

Figure 29. Streamlines for $E = 0$ case.

Figure 30. 0.25, 0.50, 0.75 streamlines for sand and clay soils ($E = 0$).

Figure 31. Simulated solute front for two soils ($E = 0$).

Figure 32. Streamlines for $E = \text{const}$ case.

Figure 33. Simulated solute front ($E = \text{const.}$).

RADIAL DISTANCE IN 2.5 CM INCREMENT

VERTICAL DISTANCE IN 2.5 CM INCREMENTS

Figure 34. Experimental and simulated napropamide concentrations in laboratory experiments.