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Control of Nonfumigant Nematicide Distribution and Activity in Irrigated Soils

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W.F. Spencer**

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Title

CONTROL OF NON-FUMIGANT NEMATOCIDE DISTRIBUTION
AND ACTIVITY IN IRRIGATED SOILS

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PART I

STUDIES IN U.S.

OBJECTIVES OF PROJECT

The United States investigators were charged in the BARD project with developing an environmental fate model for the prediction of pesticide movement through the natural environment which took into account the effect of temperature. In addition, the predictions of the model were to be subjected to experiment test and the implications both of the model predictions and of the presence or absence of agreement under natural field conditions were to be discussed.

There were three BARD sponsored investigations conducted at UC Riverside during the lifetime of the BARD project which addressed the above objectives. These investigations were as follows:

1. Development of a temperature-dependent pesticide transport/screening model

At the time of initiation of the BARD project, the US investigators (Jury, Spencer, Farmer) had just developed a multi-media pesticide transport/screening model which provided a complete environmental fate description for pesticides in ideal scenarios as a function of basic so-called chemical benchmark properties (organic carbon partition coefficient, environmental half-life, Henry's constant). The information from this screening model was published during the lifetime of the BARD project (Jury et al., 1983; Jury et al., 1984a,b,c). Under BARD sponsorship, a Ph.D. dissertation was written at the University of California, Riverside in which the model was reformulated to include dependence on temperature, laboratory volatilization cell experiments were run under different temperatures, and guidelines were developed for pesticide simulation under varying thermal environments (Streile, 1984).

2. Field scale pesticide transport and spatial variability experiment

Under BARD sponsorship, a comprehensive 1.4 hectare field experiment on bare soil was conducted in which the pesticide napropamide was applied and leached into the soil under two weeks of periodic irrigation. At the conclusion of this time, soil core samples were taken and the pesticide transport and variability characterized as a function of the pesticide and soil properties. This study was the logical next step in the development of a field transport model in that it provided a link between the theoretical model and the real-world complexity introduced by spatial variability. It produced a second Ph.D. thesis (Elabd, 1984).

3. Field test of screening model predictions

Under BARD sponsorship, a field study in which several pesticides were applied simultaneously was conducted in order to validate the assumptions of the screening model, thus providing a direct link between the screening model behavior assessment prediction and behavior under real-world environments. Use of several pesticides with dramatically different environmental fate properties provided a spectrum of information from which various compounds could be extrapolated. It resulted in a Master of Science thesis (Clendening, 1985).

RESULTS OF INVESTIGATION

A. Transport and Loss of Pesticides under Varying Temperature Conditions

The pre-existing isothermal behavior assessment model of Jury et al. (1983) makes the following assumptions:

1. Pesticide resides in dissolved, gaseous, and adsorbed phases.

The total concentration of the pesticide C_T may be written as

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

where C_S is adsorbed concentration ($\mu\text{g/g}$), C_L is dissolved concentration ($\mu\text{g/cm}^3$ solution), C_G is gaseous concentration ($\mu\text{g/cm}^3$ air), ρ_b is bulk density, θ is volumetric water content and a is volumetric air content.

2. The following linear equilibrium partition relationships are assumed to be valid in the soil:

Henry's Law:

$$C_G = K_H C_L \quad (2)$$

where K_H is the dimensionless form of Henry's constant.

Linear adsorption isotherm:

$$C_S = K_D C_L = f_{oc} K_{oc} C_L \quad (3)$$

where K_D is the distribution coefficient, K_{oc} is organic carbon partition coefficient and f_{oc} is organic carbon fraction.

3. Transport through the soil is assumed to occur by gaseous diffusion and by liquid diffusion and convection. The gaseous diffusion flux is written as

$$J_G = -D_G \frac{\partial C_G}{\partial z} = -\xi_g(a) D_G^{\text{air}} \frac{\partial C_G}{\partial z} \quad (4)$$

where D_G^{air} is binary gaseous diffusion coefficient in free air, D_G is gaseous diffusion coefficient in soil, and $\xi_g(a)$ is the tortuosity coefficient given by the Millington and Quirk model as

$$\xi_g(a) = a^{10/3} / \phi^2 \quad (5)$$

where ϕ soil porosity.

The liquid diffusion flux is given similarly by

$$J_{LD} = -D_L \frac{\partial C_L}{\partial Z} = -\xi_L(\theta) D_L^{\text{water}} \frac{\partial C_L}{\partial Z} \quad (6)$$

where D_L^{water} is the liquid binary diffusion coefficient in pure water, and D_L is the liquid diffusion coefficient in soil, where C_L is the tortuosity coefficient for liquid diffusion given in the Millington and Quirk model as

$$\xi_L(\theta) = \theta^{10/3} / \phi^2 \quad (7)$$

Liquid convection is given in the model as the product of the liquid water flux J_W and the dissolved concentration

$$J_{LC} = +C_L J_W \quad (8)$$

Thus the total solute flux is the sum of the three fluxes or

$$J_S = -D_G \frac{\partial C_G}{\partial Z} - D_L \frac{\partial C_L}{\partial Z} + C_L J_W \quad (9)$$

By using the two partitioning coefficients in equations (2) and (3) together with the definition of the total concentration in equation (1) the solute flux J_S may be rewritten as a function of the total concentration as follows

$$J_S = -D_E \frac{\partial C_T}{\partial Z} + V_E C_T \quad (10)$$

where D_E is the effective diffusion coefficient, equal to

$$D_E = (K_H D_G + D_L) / R_L \quad (11)$$

where R_L is the liquid/total partition coefficient, equal to

$$R_L = (\rho_b K_D + \theta + a / K_H) \quad (12)$$

Similarly, the effective velocity of the solute V_E is given by

$$V_E = J_W / R_L \quad (13)$$

4. The chemical is assumed to undergo a first order biochemical degradation described by an effective rate coefficient μ_E so that within a confined element of soil equation (14) is valid.

$$\left(\frac{dC_T}{dt}\right)_{el} = -\mu_E C_T \quad (14)$$

5. The chemical in soil is assumed to obey the mass balance conservation law

$$\frac{\partial C_T}{\partial t} + \frac{\partial J_S}{\partial z} = \mu_E C_T = 0 \quad (15)$$

In the original screening model papers (Jury et al., 1983; 1984a,b,c) the authors developed an analytical solution to equations (10) and (15) for chemical initially incorporated at a uniform concentration in a subsurface zone between the soil surface and an arbitrary finite depth. The upper boundary condition to the atmosphere was expressed as vapor diffusion through a stagnant boundary layer whose thickness was defined by assuming that water vapor moved through the boundary layer as well, thus allowing measured water evaporation rate to define the properties of the layer. The mathematical description of this boundary condition is given in equation (16)

$$J_S(0,t) = hC_G(0,t) = H_E C_T(0,t) \quad (16)$$

where h is the transfer coefficient through the boundary layer and $H_E = h/R_L$. This scenario was deemed general enough to allow a classification of organic chemicals into different categories based on how the compound partitioned between volatilization losses, degradation losses, leaching losses and persistence within the surface layer.

In the dissertation study described below, this model was extended to cover different temperatures by deriving theoretical relationships for

the temperature dependence of each of the parameters in the model described in equations (1) - (16). A thorough discussion of each of these equations and their implications is given by Streile (1984). The most important of these derived results are given below.

A. Temperature dependence of the Henry's constant

$$K_H(T) = K_H(T_1) \exp\left\{-\frac{(\Delta H_{\text{vap}} - \Delta H_{\text{dis}})}{R} \left[\frac{1}{T} - \frac{1}{T_1}\right]\right\} \quad (17)$$

where ΔH_{vap} is the partial molar enthalpy of vaporization from a pure substance, ΔH_{dis} is the partial molar enthalpy of dissociation from solid into aqueous form and R is the universal gas constant.

B. Distribution coefficient

$$K_D(T) = K_D(T_1) \exp\left\{-\frac{\Delta H_{\text{ads}}}{R} \left[\frac{1}{T} - \frac{1}{T_1}\right]\right\} \quad (18)$$

where ΔH_{ads} is the partial molar enthalpy of adsorption.

C. Biodegradation rate coefficient

$$\mu(T) = \mu(T_1) \exp\left\{-\frac{\Delta E_a}{R} \left[\frac{1}{T} - \frac{1}{T_1}\right]\right\} \quad (19)$$

where ΔE_a is the partial molar activation energy for the reaction.

Streile (1984) used these temperature dependent expressions in the screening model of Jury et al. (1983) to study the influence of temperature on volatilization, degradation and leaching. The experimental description is given below.

Materials and Methods

The soil used in this study was Pachappa sandy loam, a fine loamy mixed thermic, mollic haploxeralf taken from the Ap horizon of a field

plot of the United States Salinity Laboratory in Riverside County. The Pachappa series is well drained, formed predominantly on alluvial fans and consists primarily of granitic materials. The soil sample used was passed through a 2.5 mm sieve before packing.

Two pesticides, lindane and napropamide, were used in the experimental studies. Lindane is hexachlorocyclohexane, γ isomer. It is an insecticidal neurotoxicant used in a great variety of situations including seed treatment. Napropamide is N,N-diethyl-2(1-naphtholenyloxy)-propionamide and is commonly referred to as devrinol. It is an herbicide used primarily for the control of grasses and broadleaf weeds in vineyards, orchards, and on direct seeded tomatoes, strawberries and tobacco. These chemicals were chosen because of their contrasting benchmark properties and because between them they encompass a range of chemical properties possessed by many pesticides. Benchmark properties for the two compounds which have been gathered from the literature are given in Table 1 along with respective references. Adsorption measurements for the compounds fitted to different adsorption models at the two temperatures are given in Table 2. From these equations and the temperature range spans, temperature-dependent partition coefficients for the two compounds were derived as given in Table 3.

Volatilization Cell Experiments

Vapor loss experiments were carried in a constant temperature incubator with soil packed into volatilization cells constructed as described and illustrated in Spencer et al. (1979) and as shown in Figure 1. Each cell is rectangular and for this study, made up of six de-mountable sections which are held together with eight threaded bolts and hex nuts.

Table 1. Benchmark pesticide properties, as a function of temperature, gathered from the literature, along with references

Pesticide	Property	Temperature	Value	Reference
Lindane	p^{sat}	20°C	3.26×10^{-5} mm Hg	Spencer and Cliath (1970)
		30°C	12.82×10^{-5} mm Hg	
		40°C	45.6×10^{-5} mm Hg	
Lindane	C_1^{sat}	25°C	$7.3 \mu\text{g}/\text{cm}^3$	Gunther et al. (1968)
		35°C	$12.0 \mu\text{g}/\text{cm}^3$	
		45°C	$14.0 \mu\text{g}/\text{cm}^3$	
Napropamide	p^{sat}	25°C	4×10^{-6} mm Hg	WSSA (1974)
		50°C	100×10^{-6} mm Hg	
Napropamide	C^{sat}	25°C	$73.0 \mu\text{g}/\text{cm}^3$	WSSA (1974)

Table 2. Parameters of three types of adsorption equations found by least squares regression of adsorption data from experiments at two temperatures (regression r^2 included)

Pesticide	Type of Adsorption Equation	20°C			30°C		
		K_D	1/n	r^2	K_D	1/n	r^2
Lindane	linear	3.243		0.995	2.409		0.995
	linear through origin	3.294		0.996	2.428		0.996
	Freundlich	4.453	0.968	0.999	3.697	0.942	0.992
	linear through origin (range of experiment)*	3.803		0.999	2.673		0.989
Napropamide	linear	1.190		0.999	1.072		1.000
	linear through origin	1.185		0.999	1.085		0.999
	Freundlich	1.331	0.946	0.998	1.305	0.932	0.999
	linear through origin (range of experiment)*	1.185		0.999	1.085		0.999

*Using only the data points which coincide with the range of C_1 values encountered in the volatilization experiments

Table 3. Equations expressing the temperature dependence of benchmark pesticide properties

Pesticide	Equation
Lindane	$C_v^{sat}(T) = (1.6331 \times 10^{17}/T) \exp(-12178/T)$ $C_l^{sat}(T) = (1.2226 \times 10^5) \exp(-2970/T)$ $K_H(T) = (1.3358 \times 10^{12}) \exp(-9308/T)$ $K_D(T) = (8.6816 \times 10^{-5}) \exp(3134/T)$ $\mu(T) = (1.0109 \times 10^3) \exp(-3699/T)$
Napropamide	$C_v^{sat}(T) = (2.0258 \times 10^{16}/T) \exp(-12406/T)$ $C_l^{sat}(T) = (6.2806 \times 10^4/T) \exp(-2013/T)*$ $K_H(T) = (3.2255 \times 10^{11}/T) \exp(-10393/T)$ $K_D(T) = (8.1828 \times 10^{-2}) \exp(783.7/T)$ $\mu(T) = (1.6350 \times 10^8) \exp(-7690/T)$

*Calculated from one data point, assuming that $\Delta H_{dis} = 16.736$ kJ/mol (4 kcal/mol)

Fig. 1. Schematic diagram of the volatilization cells (modified from Spencer et al., 1979).

The four internal sections form a chamber into which pesticide-treated soil is packed. The chamber is 10 cm long by 3 cm wide and approximately 10 cm deep. The bottom section contains a continuation of the soil chamber through half of its depth and is packed with untreated soil. It also contains three porous ceramic tubes running the length of the chamber through which water for evaporation can enter the soil. The upper section contains an air space 2 mm deep and 3 cm wide, and has a port on either end to allow air inflow and outflow. For an air flow rate of 1 dm³ per minute through the cell, across the soil surface, a windspeed of 1 km/hr is achieved. This flow rate changes the air above the evaporating surface approximately 167 times per minute. The air chamber extends 7.5 cm in front of and beyond the soil surface to allow the air to spread out before reaching the soil and to assure laminar flow. Each cell section has a groove cut in its lower face for placement of a rubber O-ring to assure a positive seal between sections when they are tightened together. In addition, the uppermost soil chamber suction has a groove in its upper face as well, to provide a positive seal with the top section. The top section and the first soil section were made of aluminum to minimize the pesticide adsorption in these areas of most critical activity. The remaining sections were constructed of plexiglas.

Constant Temperature Incubator and Air Flow System

These volatilization cells were included as part of a closed air flow system in a constant temperature incubator (Convion, model I24) which was assembled in a manner similar to that of Spencer et al. (1979) and shown below in Figure 2. Air flowed into the system through a filter and was subsequently split between two flowpaths. One path was direct

Fig. 2.

Schematic diagram of the air flow system in the constant temperature incubator (modified from Spencer et al., 1979)

and the other was through a series of distilled water filled spargers. As the figure illustrates, the filter and the spargers were the only component parts not inside the incubator. Bypass valves located along the flowpaths could be adjusted so that the air reaching the main manifold could be of any relative humidity. Relative humidity at the manifold was adjusted to approximately 50% and the air flow to each cell was adjusted to 1 dm³/min using needle valves and ballrotammeters positioned directly after the manifold. For cells in which pesticide volatilization without water flow was to be studied, the air was then bubbled through water to increase the relative humidity to 100% before being blown across the soil surface. The volatilized pesticides were carried from the air space above the soil surface by the flowing air and trapped in polyurethane foam plugs mounted in the two-piece glass vapor traps attached to the outflow port of the volatilization cell.

Water Inflow System

Water inflow to the bottom of the volatilization cells was from a burette used as a Mariotte bottle which would maintain soil matric potential at the ceramic tubes at $H = -30$ cm of water. Water evaporation rates were measured by monitoring water loss from the burette. All tubing was glass and all connectors were teflon to minimize the chance of pesticide adsorption (see Fig. 3).

Soil Preparation and Fortification

The soil used was first prepared by autoclaving for one hour at 125°C and 15 psig twice at four day intervals. Then a prechosen mass of pesticide was added to approximately 800 gms of air-dry soil by atomizing it in 50 ml of hexane onto soil in a large glass carboy. Sufficient

Fig. 3. Schematic diagram of the constant head water inflow apparatus.

pesticide was added to achieve a concentration of $10 \mu\text{g}/\text{cm}^3$ when the appropriate mass of soil was packed in the chambers to a bulk density of $1.45 \text{ gm}/\text{cm}^3$. For the high temperature napropamide experiment, the initial soil concentration was increased to $40 \mu\text{g}/\text{cm}^3$ since samples from the previous run were close to the detection limits of the analytical equipment. After atomization the solvent was allowed to evaporate by placing the soil in a vented fume hood for three hours. During this time the soil was intermittently mixed to expose new surfaces to evaporation. After solvent evaporation the soil was mixed for one hour in an Eberhart reciprocating shaker to assure uniform pesticide distribution and thereafter stored in sealed glass jars in the constant temperature incubator until chamber packing.

Experimental Conditions and Monitoring

Two separate runs of four volatilization cells each were conducted, one at 20°C and one at 35°C . For each run, two of the cells contained lindane-treated soils and two contained napropamide-treated soils. For each pesticide one had air of 50% relative humidity passing across the soil surface to induce water flow while the other had air of 100% relative humidity passing over the soil surface to prevent water flow. Burette readings for water flux determinations were taken once per day. Plugs in the vapor traps were changed periodically at intervals chosen in an attempt to collect a similar easily analyzable amount of pesticide in each plug. Subsamples of the treated soil used to pack the chambers were analyzed for pesticide content at the time that the run was initiated to determine the initial concentration for each soil. The remainder of the treated soil was kept in the incubator in sealed glass jars for the

duration of the run and at the run's termination, further subsamples were analyzed for final pesticide concentration to determine the extent of degradation which had occurred.

At the end of each run the four cells were disassembled section-by-section and subsamples of soil were taken for water content and final total pesticide concentration profiles. The soil was divided into six depth intervals for water content profiles, and eight depth intervals for pesticide concentration profiles. A summary of the experimental conditions for the four studies are given in Table 4.

Analytical Procedures

The resulting samples were analyzed by gas chromatography either directly or after dilution to an appropriate concentration. Lindane was analyzed on a Varian 3700 gas chromatograph equipped with an electron capture detector. Napropamide was analyzed on two different gas chromatographs using two different columns. The first unit was a Tracor 2,2,2-GC equipped with Tracor 702 nitrogen phosphorus detector. The second unit was a Varian 3700 GC equipped with a thermal thermionics specific detector.

Results

Volatilization Flux

Figure 4 illustrates the effect of varying the relative humidity of the air passing over the soil surface for the experiments at 20°C. In Figure 5 the corresponding results for the experiments conducted at 35°C. At the lower temperature the volatilization flux is greater when the water evaporation is also occurring. The effect seems to be more pronounced for devrinol. At the higher temperature, however, the effect of

Table 4. Measured values of relative humidity of the air stream over the soil surface (RH), water flux (J_w), average volumetric water content (θ), average bulk density (ρ_b), average total porosity (P_T), initial total soil pesticide concentration (C_{T0}), and degradation half life ($t_{1/2}$ for each volatilization cell.

	Lindane		Napropamide	
	20°C			
RH	1.0	0.45	1.0	0.45
J _w (cm/day)	-0.010	-0.193	-0.013	-0.194
θ	0.40	0.40	0.39	0.40
ρ _b (g/cm ³)	1.43	1.44	1.42	1.43
P _T	0.46	0.46	0.46	0.46
C _{T0} (μg/cm ³)	10.42	10.11	9.56	9.64
t _{1/2} (days) ¹	207	207	1047	1047
	35°C			
RH	1.0	0.40	1.0	0.40
J _w (cm/day)	-0.016	-0.674	-0.033	-0.696
θ	0.37	0.38	0.36	0.37
ρ _b (g/cm ³)	1.45	1.46	1.48	1.51
P _T	0.45	0.45	0.44	0.43
C _{T0} (μg/cm ³)	10.20	10.27	38.64	39.35
t _{1/2} (days) ¹	112	112	292	292

¹measured from treated soil kept in separate glass jars in the incubator during experiment.

Fig. 4. Scaled volatilization flux vs. time data for the experiments at 20°C: comparison of two ambient air relative humidities (two water fluxes).

Fig. 5. Scaled volatilization flux vs. time data for the experiments at 35°C: comparison of two ambient air relative humidities (two water fluxes)

varying water flux seems to be almost the same for the two chemicals. By direct comparison one sees that the amount of volatilization is greater in all cases for lindane than for devrinol. In addition the shape of the flux versus time relation is quite different for the two chemicals. The lindane flux always starts out high and then decreases with time while the devrinol flux either increases with time or remains more or less stable. Figure 6 shows a replot of the two chemicals for the case of no water evaporation when the temperature is varied. As seen, little difference exists for the lindane but a substantial increase in volatilization has occurred with the devrinol. The effect is even more pronounced under conditions where water evaporation is present as is shown in the next figure (Fig. 7).

Comparison of Theory and Experiment

All curves presented in the figures of this section were drawn by using the appropriate pesticide property values from Table 3 and the appropriate experimental conditions from Table 4 as input parameters to the temperature adjusted behavior assessment model of Jury et al., 1983. There is no direct calibration obtained on the experimental data. Figures 8-11 show plots of the four lindane evaporation fluxes together with the model predictions and Figures 12-15 plot the corresponding devrinol fluxes and predictions. As shown in the figures, the model adequately reproduces all volatilization fluxes including the large observed differences at different temperatures.

Figures 16-19 and 20-23 show the corresponding predicted and measured values for final concentration in the soil. The agreement in this case between the model curves and the data is not nearly as good as

Figure 6 Scaled volatilization flux vs. time data for the experiments where $J_w = 0$ (RH = 1): comparison of behavior at two temperatures

Fig. 7. Scaled volatilization flux vs. time data for the experiments where $J_w \neq 0$ (RH < 1): comparison of behavior at two temperatures.

Fig. 8. Comparison of volatilization flux vs. time data with the flux curve predicted by the model for lindane, $T = 20^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 9. Comparison of volatilization flux vs. time data with the flux curve predicted by the model for lindane, $T = 20^{\circ}\text{C}$, $\text{RH} = 45\%$ ($J_w \neq 0$).

Fig. 10. Comparison of volatilization flux vs. time data with the flux curve predicted by the model for lindane, $T = 35^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 11 Comparison of volatilization flux vs. time data with the flux curve predicted by the model for lindane, $T = 35^{\circ}\text{C}$, $\text{RH} = 40\%$ ($J_w \neq 0$).

Fig. 12. Comparison of volatilization flux vs. time data with the flux curve predicted by the model for devrinol, $T = 20^\circ\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 13. Comparison of volatilization flux vs. time data with flux curve predicted by the model for devrinol, $T = 20^{\circ}\text{C}$, $\text{RH} = 45\%$ ($J_w \neq 0$).

Fig. 14. Comparison of volatilization flux vs. time data with flux curve predicted by the model for devrinol, $T = 35^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 15. Comparison of volatilization flux vs. time data with the flux curve predicted by the model for devrinol, $T = 35^{\circ}\text{C}$, $\text{RH} = 40\%$ ($J_w \neq 0$).

Fig. 16. Comparison of final soil pesticide concentration vs. depth data with the concentration profile predicted by the model for lindane, $T = 20^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 17. Comparison of final total pesticide concentration vs. depth data with the concentration profile predicted by the model for lindane, $T = 20^{\circ}\text{C}$, $\text{RH} = 45\%$ ($J_w \neq 0$).

Fig. 18. Comparison of final soil pesticide concentration vs. depth data with the concentration profile predicted by the model for lindane, $T = 35^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 19. Comparison of final soil pesticide concentration vs. depth data with the concentration profile predicted by the model for lindane, $T = 35^{\circ}\text{C}$, $\text{RH} = 40\%$ ($J_w \neq 0$).

Fig. 20. Comparison of final total soil pesticide concentration vs. depth data with the concentration profile predicted by the model for devrinol, $T = 20^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 21. Comparison of final soil pesticide concentration vs. depth data with the concentration profile predicted by the model for devrinol, $T = 20^{\circ}\text{C}$, $\text{RH} = 45\%$ ($J_w \neq 0$) (the surface data point is off scale at $z = 0.42$ cm, $C_{Tf}/C_{T0} = 4.35$).

Fig. 22. Comparison of final total soil pesticide concentration vs. depth data with the concentration profile predicted by the model for devrinol, $T = 35^{\circ}\text{C}$, $\text{RH} = 100\%$ ($J_w \approx 0$).

Fig. 23. Comparison of final soil pesticide concentration vs. depth data with the concentration profile predicted by the model for devrinol, $T = 35^{\circ}\text{C}$, $\text{RH} = 40\%$ ($J_w \neq 0$) (the surface data point is off scale at $z = 0.42$ cm, $C_{Tf}/C_{T0} = 4.35$ cm).

it was in the case of the flux comparisons. There are several possible explanations. There is always some possibility of sample loss during the processing or storage procedures. However, considerable efforts were made in this experiment to avoid loss during these stages. The data for the lindane cells come closest to supporting the sample loss theory since almost all of the data points lie below the model curve while retaining more or less the same shape as the curve. However, the same cannot be said for the napropamide data. The napropamide data seems to be below the model curve for the greater depths and above the model curve for the shallower depths. This could possibly be explained by error in the pesticide input parameters and would have been closer in agreement had the value of K_D been decreased (Streile, 1984). Tables 5 and 6 show the final mass balance analyses for the data and the model for the two experiments. Degradation is not measured directly in the experiments and instead is lumped as part of the percentage unaccounted for by subtracting volatilization and final storage from the amount initially applied. The mass balance estimates support the contention that sample was lost in the lindane experiment but not in the napropamide experiment.

Use of Model in Temperature Varying Environments

A numerical model was developed which used the temperature varying coefficients described in Equations 17 through 19 together with the mass balance equation 15 and flux equation 10. The purpose of this numerical model was to simulate pesticide transport under temperature varying conditions and compare the prediction of volatilization and mobility with that of an isothermal screening model operating at a single temperature. Several conclusions were drawn from this theoretical study.

Table 5. Measured (data) and predicted (model) mass balances for lindane 20°C and 35°C.

Mass Balance Component (%)	$J_w \approx 0$		$J_w \neq 0$	
	data	model	data	model
	RH = 1.0		RH = 0.45	
	20°C			
Volatilized	13.4	8.4	24.4	18.6
Remaining in Soil	38.4	76.1	33.0	66.8
Degraded*	--	15.5	--	14.6
Unaccounted fort	48.2	--	42.6	--
	RH = 1.0		RH = 0.40	
	35°C			
Volatilized	13.8	10.2	39.5	50.3
Remaining in Soil	22.8	74.8	18.7	38.1
Degraded*	--	15.0	--	11.6
Unaccounted fort	63.4	--	41.8	--

* Calculated from the model as the difference between the total mass added initially and the sum of the predicted volatilization loss and the predicted mass remaining in the soil.

† Calculated as the difference between the total mass added initially and the sum of the experimentally measured volatilization and mass remaining in the soil, but not necessarily all lost by degradation.

Table 5. Measured (data) and predicted (model) mass balances for napropamide at 20°C and 35°C.

Mass Balance Component (%)	$J_w \approx 0$		$J_w \neq 0$	
	data	model	data	model
	RH = 1.0		RH = 0.45	
	20°C			
Volatilized	1.07	1.08	6.40	6.49
Remaining in Soil	106	95.5	71.3	90.4
Degraded*	--	3.42	--	3.11
Unaccounted fort	-7.07	--	22.3	--
	RH = 1.0		RH = 0.40	
	35°C			
Volatilized	7.12	4.43	38.2	66.3
Remaining in Soil	79.6	89.1	39.9	30.7
Degraded*	--	6.47	--	3.00
Unaccounted fort	13.3	--	21.9	--

* Calculated from the model as the difference between the total mass added initially and the sum of the predicted volatilization loss and the predicted mass remaining in the soil.

† Calculated as the difference between the total mass added initially and the sum of the experimentally measured volatilization and mass remaining in the soil, but not necessarily all lost by degradation.

- o The numerical model using the temperature dependent coefficient ran extremely slowly even on a high-speed computer.
- o Predictions of the model were very similar to those of the isothermal model which possesses an analytic solution, provided that a temperature close to that of the average surface temperature was used to predict volatilization and close to that of the average subsurface soil temperature was used to predict leaching.

These two discoveries lead us to recommend use of the isothermal model with a surface-weighted temperature when volatilization is important and use of an isothermal model neglecting temperature variations when deep soil leaching is included.

This phase of the BARD research left us with a transport/screening model whose predictions have been verified as a function of temperature in laboratory environments. We moved to the field environment for the next stage of the study and conducted a foundational experiment designed to study the spatial variability of pesticide movement. The description of this experiment and its results are given in the next section.

B. Spatial Variability of Pesticide Movement Under Field Conditions

This section presents the results of a comprehensive study of the spatial variability of pesticide adsorption over a 0.64 ha sandy field using three different methods for assessing the adsorption coefficient:

1) Batch adsorption measurements, 2) comparison of pesticide and chloride leaching through undisturbed soil columns, and 3) direct observation of the downward movement of the simultaneously applied chloride and pesticide pulse measured by soil cores.

Materials and Methods

Field Experiment

The field study was conducted on the inner 0.64 ha of a 1.44 ha field of bare Tujunga loamy sand (mixed thermic typic xerosperments) located in Etiwanda, California. Initially the field was leached with 30 cm of high quality water to remove dissolved salts from the surface layer. The plot was divided into a 6 x 6 grid for sampling. Prior to the experiment two sets of samples were taken from the study area. First a set of 36 "undisturbed" soil cores was taken by slowly pounding 10 cm diameter columns into the soil to a depth of 15 cm. This set of 36 columns was used for both partition coefficient and bulk density determination. Second, a set of 36 disturbed soil samples were taken from the sides of the holes formed after taking the undisturbed soil cores. This set was used for the adsorption isotherm determination by the batch equilibrium method.

After these samples were taken the sprinkler system was removed from the field to assure uniform application of the pesticide. Napropamide was applied using a self-propelled herbicide sprayer with a 4.26 meter boom that had a spraying coverage 6.1 meters in width. The solution applied to the surface consisted of 3.63 kg of the pesticide as an emulsifiable concentrate mixed with 300 gallons of irrigation water which was sprayed onto a 1 ha area that included the 0.64 ha study area. Immediately after the pesticide application, the sprinkler system was reinstalled and a 3 cm pulse of saline water containing 15 meq/l chloride was applied to the field through the irrigation system. After the chloride pulse was added, high quality water was used for irrigation

through the end of the experiment, a period of two weeks. After 23 cm of net applied water was applied, a soil sampling of the entire field took place. Thirty-six soil cores were taken to a depth of 300 cm divided into 10 cm increments, bagged and kept refrigerated prior to analysis.

Analytical Methods

Chloride was obtained from saturation extracts by analysis with an Aminco analytical chloride titrator. Organic carbon was determined by the Walklee-Black procedure (Allison et al., 1965). Napropamide was extracted with 50 ml of 5% aqueous hexane acetone solution and measured by gas chromatography.

Dynamic Column Experiments

The 36 undisturbed soil columns together with four additional repacked columns were returned to the laboratory and irrigated using a 30 cm long, 24 gauge hypodermic stainless steel tube at a constant flow rate of approximately 4 cm/day. When steady state water flow was set up in each column, a pulse of concentrated calcium chloride and napropamide was applied to the surface and analyzed in the drainage water until all of the effluent had passed through the system.

Batch Adsorption Determination

Batch adsorption was determined on 10 gram soil subsamples which were mixed with 10 ml of initial solution and placed in 50 ml teflon centrifuge tubes. The tubes were first capped with a rubber screw-in stopper and lined with 1 ml teflon sheets and were then mounted on reciprocatory shakers in constant temperature incubators for 24 hours. After the incubation period the samples were placed in a refrigerated centrifuge for 20 minutes. A 1 ml volume of the supernatant solution

was mixed with 20 mls of the scintillation solution in a 25 ml glass vial. The vials were capped and placed in a scintillation counter. A refrigerated Beckman liquid scintillation system was used and each sample was counted 3 times for 20 minutes. Adsorption isotherm experiments were performed using C-¹⁴ labeled napropamide at initial solution concentrations of 1, 3, 7, 20 and 45 ppm.

Results

Batch Equilibrium Experiments

Each of the 36 batch equilibrium isotherms were fitted to linear and nonlinear Freundlich models over the range of concentrations studied. Figure 24 shows the adsorption isotherms plotted for the entire field on a single graph.

Soil Column Experiments

The method of estimation of the adsorption coefficient for the soil column experiments was as follows. Breakthrough curves for both chloride and napropamide were measured in the outflow concentrations of the columns as, for example, in Fig. 25. Each of the breakthrough curves was fitted to the two parameter convection-dispersion model

$$D_E \frac{\partial^2 C}{\partial Z^2} - V_E \frac{\partial C}{\partial Z} = \frac{\partial C}{\partial t} \quad (20)$$

for a narrow pulse input. The ratios of the effective velocities V_E obtained for the chloride and napropamide, respectively are equal to

$$\frac{(V_E)_{Cl}}{(V_E)_{nap}} = 1 + \rho_b K_D / \theta \quad (21)$$

(Elabd et al., 1986; Elabd, 1984). Thus by simultaneously measuring bulk

Fig. 24. Adsorption isotherms for the 36 field locations, with points at different concentrations connected for each site.

density, water content and outflow concentration, dynamic adsorption distribution coefficients could be obtained.

When fitted by the method of moments (Jury and Sposito, 1985), parameter estimates for the convection-dispersion model are obtained irrespective of the degree of agreement between the model and the data. Although for many of the outflow experiments both the chloride and the napropamide pulses behaved in a manner which could be described well by the model (see Fig. 25) in a larger number of cases the napropamide behaved in manner which was not well described by the model (see Fig. 26). Nonetheless, the method of moments simply calculates the average velocity of the center of mass of the entire pesticide and calculates and effective average distribution coefficient for the two curves together. Table 7 contains a summary of the average distribution coefficient and standard deviation of the distribution coefficient obtained by the two methods together with the correlation coefficients between them. As seen in this table, although the two methods predicted somewhat similar means and variances, they were largely uncorrelated. The only explanation for this phenomena is that the dynamic column experiments, which measured adsorption coefficients greater than the batch method a good period of the time, were in fact measuring a combination of an adsorption and a desorption coefficient. This is one weakness of the column flow-through method when used with soil pulses.

Field Results

Figure 26 shows concentration-depth curves for the napropamide measured in the soil cores from the field experiment with the figure in the lower right hand corner representing the mean value for the entire

Fig. 25. Concentration of napropamide and chloride versus drainage for undisturbed soil, columns A0 and C3

Fig. 26. Naproamide concentration in 19 field locations and the resulting average versus soil depth.

Table 7. Adsorption distribution coefficients and their spatial variability.

	Mean	Standard Deviation	CV (%)
	cm ³ /g	cm ³ /g	
K _D batch	2.01	0.63	31
K _D equilibrium	1.91	0.49	26
r = -0.21 N = 36			

field. There are several striking features of the soil coring results from the field experiment. First, virtually every soil core shows pronounced deep movement of part of the pesticide added to the soil surface. Second, the area averaged curve shows a secondary maximum at approximately 90 cm in the soil which is consistent with a chromatographic separation of two different species or of strongly rate-limited transport of part of the pesticide profile. At the time this experiment was performed three hypotheses were generated to account for these observations.

1. A portion of the surface-applied pesticide was caught in soil macropores and transported to great depths in the soil without adsorbing substantially.

2. Part of the dissolved pesticide in solution formed a solution complex with dissolved humic or fulvic acids which subsequently moved without adsorbing through the soil pore space.

3. Part of the dissolved pesticide attached to suspended colloidal material in the soil solution which transported through the coarse-textured sandy material of the field soil. It was not possible to distinguish between these explanations in the field study.

Some indication of the degree to which the pesticide acted as though it was not adsorbed is shown in Fig. 27. This figure shows the field-averaged pesticide concentration as a solid histogram together with a smooth curve which represents the predicted pesticide profile obtained by mapping the measured chloride distribution onto the pesticide curve by dividing the depth of chloride location by the retardation factor R , (approximately 10 for this compound). Thus, the measured average chloride curve ($C_{Cl}(Z)$ (normalized to unit area), is transformed into a

predicted curve $C_p(Z)$ by

$$C_p(Z) = RC_{C1}(Z/R) \quad (22)$$

Equation 22 is obtained by assuming linear, equilibrium adsorption with each stream tube (Elabd, 1984). As is seen from Fig. 27, much of the deep movement is simply not consistent with adsorption as measured in the laboratory for this compound.

The failure of the equilibrium adsorption model to describe the field-averaged pesticide movement has substantial implications for transport modeling. It implies that either the hydrologic description must be increased in complexity to describe macropore transport or that the solution chemistry description must be made more concise to take into account formation of complexes. In either case, traditional laboratory indices of adsorption obtained by batch or flow-through methods are not likely to provide information about this type of transport under field conditions. However, the deep transport of pesticide occurs for only a fraction of the applied mass. Table 8 shows the percent of the total mass which was found in the top 10 cm of 19 field locations. On average, 76% of all the mass recovered was obtained in this shallow increment which is consistent with predicted location given equilibrium adsorption. Thus, penetration of pesticide to great depths occurs for only a fraction (in this case 24%) of the applied pesticide mass. Behavior of the bulk of pesticide applied conforms to standard modeling principles.

C. Field Test of Screening Model Prediction

Much of the effort of our research group over the previous three years was dedicated to developing a general transport/screening model

Fig. 27. Average field relative napropamide concentration versus soil depth. The solid curve is the chloride average relative concentration versus the partition coefficient R_{cde} /chloride depth.

Table 8. Percent of the total mass found in the top ten centimeters in nineteen field locations.

Location	P ₁₀	Location	P ₁₀
A0	52	B0	66
A1	56	B1	53
D1	84	F1	73
A2	58	B2	90
C2	73	D2	97
F2	84	A3	6
B3	77	C3	94
D3	89	A4	83
B4	73	C4	81
A5	89	MEAN	76

which would predict the relative behavior of pesticides and other organic compounds in the real environment. The first field scale experiment discussed above revealed a propensity for deep movement not consistent with equilibrium adsorption principles. Therefore, it became important to determine the degree to which the screening model could predict relative behavior irrespective of its ability to predict the absolute transport of a given compound. If the screening model produced a relative ranking system which could, for example, identify marker compounds whose behavior could represent entire classes of organic chemical, then a relatively small amount of in situ field experimental information could be used to make decisions about the environmental suitability or agricultural suitability of a large class of compounds with similar environmental fate characteristics. To this end, we designed the following field experiment.

Materials and Methods

All experiments were performed on the Etiwanda field site discussed in the previous section. In the first set of field studies, eight randomly located 1 m x 1 m plots, hereafter labeled E1-E8 were chosen for the first study. The plots were first cleared of a sorghum crop that had been growing on the field. Subsequently the soil was pre-irrigated several times to ensure a moist initial state. At the initiation of the experiment, four of the plots, E5-E8, were given an application of approximately 2 liters of a solution containing three pesticides and bromide applied by a hand-operated sprayer. The plots received multiple applications of the pesticide solution in the spray pattern to attempt an even application. The sprayer was weighed before and after each plot was

sprayed to determine the amount of pesticide solution applied. Table 9 shows the three pesticides used together with their benchmark properties.

Immediately following the pesticide application wood boxes with the dimensions of 1.2 x 1.2 x 0.05 m were used to cover the plots to prevent water evaporation and pesticide volatilization. The inside areas of boxes were lined aluminum foil to prevent pesticide adsorption to the wood. The plots were left to equilibrate for 72 hours.

Three days later the remaining four plots (E1-E4) were sprayed with the pesticide solution in the same manner as the first group of plots. Immediately following the pesticide application to these plots, the wooden boxes were removed from the previous plots and sprinkler irrigation commenced on all eight plots. Irrigation collection cups were placed at the four corners of each plot to monitor the amount of water applied within. The plots were irrigated until approximately 10 cm of water had been applied. In between irrigations the plots were covered by the aluminum-lined wood boxes. At the conclusion of this irrigation phase one single soil core was taken at the approximate center of each plot to a depth of 200 cm by a Giddings hydraulic rig. Subsamples were taken at 10 cm intervals within this core and were placed in glass canning jars lined with aluminum foil. Additional samples were taken at each depth increment and placed in plastic bags for bromide analysis and water content determination.

The experiment was repeated on six additional 1 m x 1 m plots (called M1-M6) with extra water applied to the plots to ensure deeper leaching. The solution containing the four chemicals, prepared as in the first study, was applied in the same fashion as previously. As before,

Table 9. Benchmark properties of the pesticides used in the field experiment.

Properties	Prometryn	Napropamide	Bromacil
molecular weight*	241.1	271.4	261.1
mobility class†	2	3	4
solubility			
water (mg·l ⁻¹)	48	73	815
acetone (g·l ⁻¹)	soluble	1,000	165
half life (T ^{1/2} days)†	60	70	350
K _H (Henry's constant)†	5.6 x 10 ⁻⁷	7.9 x 10 ⁻⁷	3.7 x 10 ⁻⁸
decomposition temperature (°C)*	118 - 120	74.8	158

half of the plots were allowed to equilibrate for 72 hours before irrigation commenced. In this study, the daily irrigations continued until each plot had received approximately 18 cm of net applied water. At the conclusion of this time, one core was removed from the center of each plot to a sampling depth of 300 cm and subsampled at 10 cm increments as previously described.

Analytical Procedures

Soil saturation extracts were prepared from the field samples by standard methods. The extracts were measured for bromide using an Orion Research 901 Microprocessor Ion Analyzer equipped with a bromide electrode.

The pesticides were extracted with acidified acetone and analyzed by gas chromatography.

Results

Three of the field plots (E2, E3 and M1) were not used in the calculations for various reasons relating to unregulated ponding on the plots or contamination during the extraction procedures. The other 11 plots were used to make the following analyses.

Measured concentrations of prometryn, napropamide, bromacil and bromide vs. soil depths for a relative representative field plots are shown in Fig. 28. In virtually all of the field plots there were two distinct peaks for prometryn and napropamide. The E plots which received approximately 10 cm of net applied water had the deep peak for prometryn centered at about 60 cm and the deep peak for napropamide at about 70 cm. The M plots which received approximately 18 cm of water had the second

Fig. 28. Concentrations of prometryn, napropamide, bromacil and bromide for field plots E6 ($I = 10$ cm, sampling depth, 200 cm).

peak for prometryn centered between 70 and 100 cm and the second peak for napropamide between 90 and 110 cm. The bromacil curve did not split and the peak was located between 50 to 100 cm for the E plots and 75 to 110 cm for the M plots. In general, the bromacil and secondary peaks for prometryn and napropamide in the M plots were found approximately 25 cm deeper than in the E plots.

This behavior is illustrated in greater detail in Fig. 29-32 which shows the relative concentration of each chemical recovered for the 11 field plots.

It is evident from the summary diagrams above that both of the strongly adsorbed compounds showed the same phenomena of partial non-adsorption as did the previous field study. The degree to which such behavior could not be predicted by a linear equilibrium adsorption model is shown in the next figures (Fig. 33-38) which, as above, map the observed bromide distribution onto the pesticide distribution by dividing by the partition coefficient (see eq. 23).

It is clear from these figures that the average bromacil concentration was predicted satisfactorily in the plot studies, whereas the other compounds were partly predictable and partly unpredictable. Table 10 summarizes the literature adsorption parameters for these three compounds showing the range in expected pesticide mobility as a function of site specific conditions. For example, depending on the studies cited, the napropamide and prometryn are either significantly different in their adsorption or quite similar. Thus the screening model prediction for their behavior depends on the precise choice of adsorption coefficients used.

Fig. 29. Relative concentrations of prometryn for all field plots.

Fig. 30 Relative concentrations of napropamide for all field plots.

Fig. 31. Relative concentrations of bromacil for all field plots.

Fig. 32. Relative concentrations of bromide for all field plots.

Fig. 33. Predicted and measured concentrations of prometryn for E field plots ($R = 12.5$, $I = 10$ cm).

Fig. 34. Predicted and measured concentrations of prometryn for M field plots ($R = 12.5$, $I = 18$ cm).

Fig. 35. Predicted and measured concentrations of napropamide for E field plots ($R = 10.6$, $I = 10$ cm).

Fig. 36. Predicted and measured concentrations of napropamide for M field plots ($R = 10.6$, $I = 18$ cm).

Fig. 37. Predicted and measured concentrations of bromacil for E field plots ($R = 2.2$, $I = 10$ cm).

Fig. 38. Predicted and measured concentrations of bromacil for M field plots ($R = 2.2$, $I = 18$ cm).

Table 10. Adsorption parameters for chemicals in field experiments.

Chemical	K_d	K_{oc}	R	Number of Soils or Replicates	Reference
	- ($\text{cm}^3 \cdot \text{g}^{-1}$) -				
Prometryn	4.86	810	24.1	1 replicate	Kenaga 1980
	2.50	518	12.4	102 replicates	Hamaker et al. 1972
	3.68	614	18.5	38 replicates	Rao & Davidson 1980
Napropamide	2.01	335+	10.6	36 replicates	Elabd 1984
	0.28-2.96	249-450		36 replicates	Gerstl & Yaron 1983
Bromacil	0.25	41	2.2	7 soils	Corwin 1985
	0.20	34	2.0	6 soils	Gerstl et al. 1981
	0.42	72	3.1	2 soils	Rao & Davidson 1980

With these limitations in mind cumulative probability distributions were constructed for each of the average plots showing the sample probability for penetration below a given depth as indicated in Fig. 39 and 40. Although the individual details are quite chaotic, the figures roughly show that the relative order of penetration (prometryn: napropamide:bromacil:bromide) is exactly as predicted from the partition coefficients (18:11:2.3:1).

DISCUSSION AND SIGNIFICANCE OF FINDINGS

The multi-phase theoretical and experimental investigation discussed above has revealed several extremely important characteristics of field-applied pesticides which must be taken into account in any transport model which hopes to achieve a realistic description of environmental fate of organic chemicals. Relative to the original BARD objectives, we have reached consensus on several important simplifications of thermally varying chemical transport which could potentially simplify the description of such processes in the natural state.

The transport/screening model of Jury et al. (1983) contains a realistic description of transport thorough idealized media under conditions where both the liquid/vapor and liquid/adsorbed phases partition linearly to equilibrium at all times during transport. Although this is likely not to be strictly correct during transport through natural soils with structural voids and substantial dead end pore space, a sophisticated theoretical description of transport through these more complex media quickly finds itself at odds with our capacity to measure the large number of rate parameters which emerge from such a description.

Fig. 39. Cumulative probability for prometryn, napropamide, bromacil and bromide for E plots.

Fig. 40. Cumulative probability for prometryn, napropamide, bromacil and bromide for M plots.

As an alternative we propose use of the more idealized model as a screening tool to develop similarities between different chemicals thereby lessening the amount of experimental work which must be conducted. At the same time, the above mentioned experiments and theory have shown that the screening model performs at different temperatures adequately in isothermal media using adjusted values for the benchmark properties, and compares favorably with a complex theoretical model taking into account time varying temperatures but substituting an average temperature for the process. This average temperature, which should be biased toward the surface temperature when volatilization is important and biased toward the subsurface temperature when leaching is important, allows one to decouple from the thermally varying regime and use actual constants for the parameters which would otherwise be variable functions of temperature.

Our repeated observations of an apparently non-adsorbing component of two strongly adsorbed pesticides has substantial environmental implications. The field data we have assembled on this should provoke considerable discussion in academic circles and will ultimately lead to widespread experimentation which should allow more rigorous hypotheses to be generated. Some of this work is currently under development in our own laboratories.

Despite the overwhelming complexity of the field regime, the screening model behaved satisfactorily as a tool for describing the relative behavior of four different dissolved compounds applied simultaneously to field plots. Thus, despite an inability to model the leading edge except by assuming it is nonadsorbed and moves as rapidly as

bromide, we were able with the screening model to account satisfactorily for the trailing edge, or adsorbed portion, of the peaks as well as to indicate the relative order of penetration of the four compounds averaged over the fields in the two experiments. Given the extreme spatial variability of the transport/adsorption process, this achievement is encouraging.

SUMMARY AND CONCLUSIONS

From the theoretical and experimental research sponsored by BARD, the USA investigators have shown the following:

1. The transport screening model of Jury et al. (1983) satisfactorily described napropamide and lindane volatilization from controlled cells at two temperatures, using chemical benchmark properties and an isothermal model.
2. Comparison with a numerical model which described pesticide transport and loss under thermally varying conditions revealed that the screening model could match the predictions of the numerical model when a single average temperature was used. This temperature should be close to the average surface temperature when volatilization is simulated and close to the average subsurface temperature when leaching is simulated.
3. A field scale study of spatial variability over 1.4 ha showed that the batch equilibrium adsorption coefficient had approximately a 30% coefficient of variation between replicates. Comparable means and variances were achieved with a dynamic soil column experiment on 36 undisturbed cores, but the individual values showed little correlation with the batch measurements taken nearby. It was tentatively concluded

that the apparent agreement was fortuitous and that the portion of the laboratory experimental values which had higher adsorption than the corresponding batch studies were caused by a combination of adsorption and desorption effects on the pulse simultaneously.

4. A 1.4 ha field study of napropamide movement revealed that approximately 20% of the field applied pesticide migrated to depths far in excess of those which could be reached by an equilibrium adsorption process. This leading edge movement was unpredictable given any current or proposed transport model and will ultimately require either an improved hydrologic description which takes into account macropore movement or an improved chemical description which allows solution complexing of pesticide with dissolved organic material or particulate matter.

5. A field study on 1 meter square plots of the relative movement of three pesticides and a water tracer showed the same deep penetration for a portion of the application of the two strongly adsorbed pesticides. Despite this complexity the screening model predictions of relative movement were matched by the field averaged pulse penetration from the plot experiments.

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PART II

STUDIES IN ISRAEL

OBJECTIVES

The studies in Israel were carried out with the aim of finding experimental parameters describing the nonfumigant pesticides behavior under variable environmental conditions. The pesticides considered in the research were bromacil, napropamide, etraprop and nemacur. Each pesticide was selected as a function of the problem to be studied. For the soil nonhomogeneity case the bromacil and napropamide was experimented. The effect of temperature fluctation on the persistence of pesticide was studied using ethroprop and the bioactivity of the pesticide affected by the soil moisture fluctuation under an irrigated nectarine growth was defined by using the nemacur nematocide.

Various experimental techniques were selected as a function of the research requirement. The effect of soil aggregation on the leaching of herbicides was studied on undistrubed cores under controlled environmental conditions. The effect of temperature fluctuation on the nematocide degradation was studied in laboratory and their bioactivity was determined in outdoor large containers, under irrigated nectarine.

The diversity in the experimental procedures and in the research approach used give us the possibility of obtaining broad information on the behavior of non-fumigant pesticides distribution and activity under fluctuated environmental conditions in irrigated soils.

RESULTS

B. PERSISTENCE OF ETHROPROP IN SOILS AS AFFECTED BY THE FLUCTUATION
OF TEMPERATURE AND MOISTURE CONTENT

INTRODUCTION

In the irrigated agriculture the nematocides introduced to the soil are subjected to changes in the ambient temperature and soil moisture content. The existing information describes the nematicide persistence and activity in soils mainly at constant temperature and soil water content.

A laboratory study was performed in order to determine the effect of the changes in the ambient temperature and moisture content on the persistence of Mocap (ethroprop), a nonfumigant nematocide in soils. Comparative studies on the behavior of Mocap under constant ambient conditions was simultaneously performed.

MATERIALS AND METHODS

The soils used in the experiments were:

Gilat - a loessial sierozem with 15% clay content, 0.5 OM and 15% FC;

Bet Dagan - a sandy Mediterranean, Red soil with 8% clay content, 0.8 OM and 12% FC;

Neve Ya'ar - a clay grumusol with 40% clay content, 1.7 OM and 55% FC.

The nematocide used was Mocap or ethroprop.

The laboratory studies consist of incubation experiments at 3 temperatures (15, 25 and 35°C) and 3 soil moisture contents (FC, 0.6 x FC and 0.3 x FC). The nematocide was applied to the soil and kept at controlled constant or variable environmental conditions during a 60 day

period. The variable conditions used in the experiment are described below.

P

	0-15	15-40	40-60	
Treat.I				T = 25°
Treat.II		15°C	35°C	
		19%	19%	
Treat.III		25%	25°C	
		12%	19%	
Treat.IV		15%	35°C	
		12%	19%	
	MC = 19%			

Samples were taken periodically and extracted with 1:1 water/ethylacetate aliquotes of the organic solvent were taken and C¹⁴ activity determined by LSC.

All the experiments were carried out in triplicate.

RESULTS AND DISCUSSION

1. Effect of moisture and temperature: constant conditions

The laboratory studies have concentrated to date on ethroprop (Mocap). Three soils characterized by different mineralogy, organic matter content and mechanical composition (Gilat, Neve Ya'ar and Bet Dagan) were used in the experiment. In order to reproduce natural conditions - where environmental factors like temperature and soil moisture content are fluctuating, - range of values were selected for incubation experiments.

The incubation experiments were used to test the persistence of nematocides in soils at three temperatures and three moisture contents. The results of the above experiment are summarized in Tables 1-4. The combined effect of moisture and temperature on the persistence of the mocap may be seen in Table 1. At each temperature the half-life of the compound decreased with the decrease of the soil moisture content.

The type of soil has a major effect in defining the persistence of mocap. The half-life of the compound varies from 365 days, in the Gilat soil at 15°C and 7.1% soil moisture content at 6.2 days in the Neve Ya'ar soil at 35°C and 55% soil moisture content.

Table 2 is a summary of the effect of temperature on degradation at constant moisture content as calculated from the Arrhenius equation. The effect of moisture content on degradation at constant temperature is presented in Table 3. The constants A and B are from the equation of Walker (1976) $T_{1.2} = AM^{-B}$ where $T_{1.2}$ is the half-life (Table 1) and M is the soil moisture content. The data from Tables 2 and 3 were used to compute coefficients (Table 4) which will enable prediction of ethroprop

degradation under conditions of varying moisture contents and temperatures.

Table 1

Table 1: First-order degradation rate constants (K) at several temperatures and moisture contents in three soils.

Treat- ment *	Soil	Temp. (°C)	P _w (%)	K (day ⁻¹)	T _{1/2} (days)	r ²
1	Gilat	15	19.1	0.0124	56	0.964
2	"	15	11.3	0.0060	116	0.901
3	"	15	7.1	0.0019	365	0.846
4	"	25	19.2	0.0229	30	0.992
5	"	25	9.8	0.0107	65	0.942
6	"	25	5.8	0.0091	76	0.796
7	"	35	18.0	0.0505	14	0.973
8	"	35	11.6	0.0234	30	0.948
9	"	35	7.7	0.0168	41	0.916
10	Neve Yaar	15	55.4	0.0290	24	0.996
11	"	15	33.1	0.0186	37	0.994
12	"	15	18.5	0.0056	124	0.899
13	"	25	57.1	0.0752	9.2	0.984
14	"	25	35.0	0.0489	14	0.964
15	"	25	19.7	0.0162	43	0.958
16	"	35	55.6	0.1127	6.2	0.978
17	"	35	33.3	0.0946	7.3	0.987
18	"	35	20.9	0.0313	22	0.986
19	Bet Dagan	15	11.8	0.0186	37	0.995
20	"	15	8.0	0.0116	60	0.977
21	"	15	5.3	0.0062	112	0.956
22	"	25	12.6	0.0493	14	0.975
23	"	25	6.9	0.0333	21	0.930
24	"	25	4.5	0.0210	33	0.889
25	"	35	12.6	0.0832	8.3	0.994
26	"	35	7.6	0.0596	12	0.978
27	"	35	6.1	0.0367	19	0.982

* Treatments: Each soil was incubated with Mocap at three temperatures and at each temperature at three moisture contents for a total of nine treatments/soil. Each treatment was run in triplicate.

Table 2

Table 2: Effect of temperature on degradation at constant moisture content.

Soil	P _w (%)	Ea (Kcale/mole)	r ²
Gilat	FC	5.54	0.995
	0.6FC	5.37	0.993
	0.3FC	8.60	0.940
Neve Yaar	FC	5.36	0.949
	0.6FC	6.42	0.988
	0.3FC	6.80	0.982
Bet Dagan	FC	5.92	0.971
	0.6FC	6.46	0.973
	0.3FC	7.02	0.956

Table 3

Table 3: Effect of moisture content on degradation at constant temperature.

Soil	Temperature (°C)	A	B	r^2
Gilat	15	13379	1.885	0.974
	25	333	0.787	0.920
	35	635	1.305	0.959
Neve Yaar	15	9255	1.513	0.951
	25	3021	1.456	0.960
	35	942	1.291	0.831
Bet Dagan	15	1088	1.375	0.996
	25	108	0.814	0.979
	35	113	1.047	0.893

Table 4

Table 4: Coefficients for the calculation of degradation of ethroprop
under varying conditions of temperature and moisture content.¹

	α	β	γ
Gilat	16.10	1.326	-7493
Neve Yaar	15.93	1.420	-7129
Bet Dagan	19.07	1.079	-7444

¹
$$K(T,M) = \exp \left(\alpha + \beta \ln M + \frac{\gamma}{T} \right)$$

2. Effect of fluctuation of moisture content and temperature

The effect of fluctuation of moisture content and temperature on ethroprop persistence was studied in the Gilat soil. During their incubation, the soil samples with soil nematocide, were projected to 3 stages of temperature and moisture content. The fitted results of the various experiments at constant conditions were used in predicting the expected Mocap residues. The resulted obtained are given in Table 5 and in Graphs 1-4. Figure 1 shows the Mocap residues in soil during 60 days of incubation when both the soil moisture and the temperature were kept at constant levels. It may be observed that the decrease in the nematicide content of the soil is linear and the degradation curve show a first order reaction pattern. Experiment results were observed.

The effect of the fluctuation of the temperature on the Mocap residues are presented in Figure 2. The moisture content was kept constant all along the experiment. The degradation pattern with time exhibited three distinct first-order reaction-type curves, each one characterizing a different incubation temperature. Good agreement between calculated and measured degradation was observed. The fluctuation of the soil moisture content (Fig. 3) has less effect on the slope of the degradation curve. We can observe 3 distinct phases but the difference between the slope of each phase is smaller than in the case of the temperature fluctuation. When both moisture and temperature are fluctuating the mocap residues measured in the Gilat soils present three distinct degradation stages, each one being represented by a single order reaction type.

TABLE : KINETICS OF MOCAP DEGRADATION UNDER CONSTANT AND VARYING CONDITIONS.

TREATMENT	TIME (DAYS)											
	0	3	7	10	15	18	22	29	40	47	52	56
I	8310	7281	6522	5683	4865	4841	4376	3654	3031	2284	2186	1921
II	8310	7256	6545	5731	6041	6058	5775	5247	4924	3357	2880	2331
III	8310	7836	6525	6659	6026	5511	5453	4578	4273	3399	3196	2845
IV	8310	7772	6997	6101	5825	6057	5948	5560	4854	3676	2947	2645

I CONSTANT TEMPERATURE AND MOISTURE CONTENT
 II CONSTANT MOISTURE CONTENT; VARIABLE TEMPERATURE
 III CONSTANT TEMPERATURE; VARIABLE MOISTURE CONTENT
 IV VARIABLE MOISTURE CONSTANT AND TEMPERATURE

Table 5

MOCAP RESIDUES – CONSTANT CONDITIONS

PREDICTED & MEASURED MOCAP RESIDUES

VARYING TEMPERATURE & CONSTANT MC

PREDICTED & MEASURED MOCAP RESIDUES

VARYING MC & CONSTANT TEMPERATURE

PREDICTED & MEASURED MOCAP RESIDUES

VARYING MC & TEMPERATURE

C. EFFECT OF FENAMIPHOS ON THE NEMATODES ACTIVITY IN AN IRRIGATED
NECTARINE GROWTH

Netcarine, Amygdalus persica v. nectarina. cv. Early sungrand seedlings, grafted on peach understock (cv. Baladi), were planted in round containers (1 m diameter) mounted in the soil (1.5 m depth). The containers were disinfected prior to planting with methyl bromide (500 kg./hectare) and then were aerated and washed thoroughly to remove the bromide residues. Two weeks after planting, half of the seedlings were inoculated with the root-knot nematode, Meloidogyne javanica, by introducing 5000-6000 second-stage juveniles in the vicinity of the roots.

Nutritional treatments were accomplished by treating each plant, weekly, with 28 ml. of a 7.5-3-6.5 commercial liquid fertilizer (Fertilizers & Chemicals Ltd., Haifa, Israel), in 30 L water. The irrigation was performed by a drip irrigation system: 4 drippers were located around the seedlings, in each container, supplying 4.5 L water/hour. Fenamiphos (Nemacur 10%, granulate, Bayer A.6.), 10g/plant, was applied monthly from April to August, each year. Nematode infection level was evaluated twice a year: in winter (October or November) and at the beginning of summer (April or May). Tomato seedlings were reared in soil samples taken from infected and non-infected containers, near the root-zone, in 0.75 L pots. These tests were run in a temperature-controlled greenhouse. Thirty days after planting, root-knot index (galling on a 0-5 scale) was evaluated. Stem thickness was measured every two months, each year. Evaluation of flush, blooming and fruit yields were performed each year.

In the first year, flush and consequently fruit yields, were negligible. The second winter was cold enough to yield good harvest, while the third year winter was relatively warm, thus fruit yields decreased significantly. Generally, no thinning was made after ripening in order to examine the tree reaction in fruit load situation.

The findings described here are average results from a three year period: 1984-86.

RESULTS

Root-knot indices were relatively high within all infected non-treated plants (between 3.5-4) and fenamiphos treatments reduced them, in the summer, to 2.5-3.0; however, in winter, no differences were found in root indices between fenamiphos-treated or untreated plants.

Stem thickness increased mainly in the non-inoculated plants, although fenamiphos delayed the development of nectarine seedlings in the first year (Fig. 1). Nematode-infected plants, both fenamiphos-treated and non-treated, revealed lower increase in this parameter through the whole experiment (Fig. 1). Generally the prominent increase in stem thickness was recorded in summer (April - September). This may explain why that parameter was influenced significantly, by nematode infection: In that season, the conditions for the development of the root-knot nematode, populations are optimal (high temperatures and appearance of young roots).

Fruit yields are presented in Fig. 2. Fenamiphos treatments, in 1985, lowered the fruit yields of both nematode-inoculated and non-inoculated

trees by 41%. However, in 1986, where the total harvest was very poor, fenamiphos-treated plants gave the highest yields (results are not shown).

The average weight of a single fruit (AWSF) was also influenced by the presence of both nematodes and fenamiphos (Fig. 3). While fruit yield decreased in the presence of fenamiphos, AWSF was the same for treated and untreated plants, but nematode inoculation significantly decreased this parameter, especially in the presence of fenamiphos (Fig. 3).

Fenamiphos&nema—inoculated nectarine

Fig.1 Stem thickness measurements

Fenamiphos&nema-inoculated Nectarine

Fig.2 Total fruit yield in 1985

Fenamiphos&nema-inoculated Nectarine

Fig.3 Average weight of a single fruit

SUMMARY AND CONCLUSIONS

From the research sponsored by BARD the Israeli investigators have shown the following:

1. In structured clay soils a greater proportion of pesticides is leached from initially dry cores than from prewet cores. The preferential flow of water down cracks and channels between soil aggregates led to a short travel time and apparently low volume of soil water participating in the pesticide transport.
2. The disappearance of Mocap from the soil under constant temperature and soil moisture content is linear, fitting a first order reaction. Fluctuation of the temperature and of the soil moisture affect the mocap residues in soil and the pattern of degradation. The linear degradation characterize the constant conditions is changed in a fractured curve with distinct linear stages each one representing a different level of temperature and soil moisture content .
3. Changes in the temperature and soil moisture content affects the nematocide bioactivity in soil and indirectly the nematodes effect on irrigated nectarine trees.

PART III.

Appendix

BEHAVIOR OF HERBICIDES IN IRRIGATED SOILS: A STATE-OF-THE-ART REVIEW

BY THE JOINT US-ISRAELI TEAM

PUBLICATIONS UNDER BARD CONTRACT

A. Student Dissertations and Degrees

Three students, two Ph.D. and one Master of Science, matriculated under partial funding from BARD. The dissertation titles and degrees are given below.

1. Clendening, L. Denise. 1985. Evaluation of mobility screening parameters under field conditions, Master of Science Dissertation, University of California, Riverside. 86 pages.
2. Elabd, Hesham. 1984. Spatial variability of the pesticide distribution coefficient. Ph.D. Dissertation, University of California, Riverside. 100 pages.
3. Streile, Gary. 1984. The effect of temperature on pesticide phase partitioning, transport and volatilization from soil. Ph.D. Dissertation, University of California, Riverside. 152 pages.

B. Professional Manuscripts

The following professional manuscripts were published from the BARD research done at the University of California, Riverside.

1. Jury, W. A. and H. Elabd. 1984. Field scale movement of non-adsorbing and adsorbing chemicals applied to the soil surface. pp. 203-202. Proceedings of Symposium "Characterization and Monitoring of the Vadose Zone". National Water Well Association, Las Vegas, NV.
2. Jury, W. A., H. Elabd and M. Resketo. 1986. Field study of napropamide movement through unsaturated soil. Water Resour. Res. 22:749-755.
3. Jury, W. A., H. Elabd L. D. Clendening and M. Resketo. 1986. Evaluation of pesticide transport screening models under field conditions. In ACS Symposium Series 315 "Evaluation of Pesticides in Groundwater". Willa Garner, Ed.
4. Yaron, B., Gerstl, Z. and Spencer, W.F. (1985) Behavior of herbicides in irrigated soils. Adv. Soil Sci. 3: 121-211.
5. White, R.E., Dyson, J.S., Gerstl, Z. and B. Yaron (1986) Leaching of herbicides through undisturbed cases of structural clay soil. Soil Sci Soc. Am. J. 50: 277-283.