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BARD

FINAL REPORT

PROJECT NO. I-744-84

Combined Application of Liquid Fertilizers and Pesticides Through Irrigation Systems

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BARD project No. 307-000-000 *15-744-84*

Title

Combined application of liquid fertilizers and pesticides through
irrigation systems.

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Project's starting date: 11.85

Type of Report: 1st Annual 2nd Annual Final X

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הספריה המדעית
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$\frac{630.72}{\text{BAR/SAL}}$: 631.8 : 631.7 : 632.95
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Table of Contents

Page

I. Objectives

II. Description of the research results.....	1
1. The physical compatibility of selected pesticides and liquid fertilizers.....	1
1.A. Tank-mix compatibility studies.....	1
1.B. Estimation of the physical compatibility between emulsifiable concentrate formulations (EC) and liquid fertilizers.....	7
2. Soil behavior of pesticides, as affected by the presence of fertilizers.....	29
2.A. Adsorption and mobility of pesticides.....	29
2.B. Persistence of pesticides.....	38
3. The effect of pesticides and environmental stress on ammonium oxidation in soil.....	44
3.A. CO ₂ - nitrification relationships.....	44
3.B. The effect of pesticides on ammonium oxidation in the Hamra soil.....	52
3.C. Ammonium oxidation in the Tifton loamy sand soil..	60
4. The combined effect of herbicides and nitrogen source on plants.....	63
4.A. Metolachlor.....	63
4.B. EPTC.....	89
5. Fertigation and chemigation - field and greenhouse experiments.....	106
5.A. Drip irrigation.....	106
5.B. Sprinkler irrigation.....	138
6. References.....	152
III. Description of cooperation.....	156
IV. Evaluation of the research achievements.....	157
V. List of publications	

Abstract

The aim of this research was to study the parameters needed and to develop the required technology for the elaboration of integrated fertigation-chemigation management programs, in order to increase the efficiency of both fertilizers and pesticides, and lower the production cost.

In the framework of this project a rapid test to estimate the compatibility between emulsifiable concentrate formulations and liquid fertilizers has been developed. Under the experimental conditions used, the presence of nutrient solutions did not affect the adsorption, mobility and persistence of pesticides. However, pesticides might inhibit such important biological processes, as ammonium oxidation. In some cases, the effect of pesticides and environmental stress on nitrification was synergistic. A remarkable inhibitory effect of subtoxic concentrations of the herbicides metolachlor and EPTC on the growth of cucumber plants have been observed.

One of the problems related to chemigation by drip irrigation in sandy soils, might be the undesirable movement of agrichemicals out from the rooting zone of young plants. The efficiency of herbicides and nematicides combinations applied by sprinkler irrigation was equal or better than that obtained by conventional application.

The main achievement of this research is its contribution to a better understanding of the mutual effect of fertilizers and pesticides in soil and plant, and of the factors affecting the efficiency of agrichemicals applied through irrigation systems.

I. Objectives of the research

1. To study the physical and chemical compatibility of selected pesticides and fluid fertilizers.

2. To study the effect of soil-applied pesticides on the nutrient status in soils, and on the nutrient uptake by plants under combined fertigation-chemigation, as compared to conventional fertilization and pesticide application.

3. To check the effect of fertilizers on soil behavior of pesticides.

4. To develop the required technology for the combined application of fertilizers and pesticide along with irrigation by both sprinkler and drip irrigation systems.

5. To optimize the fertilization and pesticide application level by taking into account their relationship when applied in combination through irrigation systems.

6. To assess the soil and groundwater pollution hazard by nitrates and pesticides in the fertigation-chemigation program proposed.

The work done in the framework of the project addressed all these objectives, except for the last one. This objective was not achieved because of the lack of enough data to assess the pollution hazard.

II. Description of the research results

1. The physical compatibility of selected pesticide and liquid fertilizers

The combined application of crop protection chemicals and fertilizers is a time-, labor- and energy-saving technique (Martens et al., 1978; Sander et al., 1987). The manufacture of combined formulations, attempted in the past rather unsuccessfully (Jacob, 1954), has been replaced by the "tank mix" practice. This procedure has become more convenient with the increasing use of liquid fertilizers. Combining liquid fertilizers and pesticides in the tank, just before use, allows for versatility in the preparation of the mixtures and avoids eventual problems arising from their storage (Lindner, 1973).

One of the main requirements for pesticide-fertilizer combinations is to form homogeneous and stable mixtures, in order to provide a uniform distribution and avoid blockage of the application equipment (Petty et al., 1971). However, pesticide formulations which are manufactured to form stable suspensions or emulsions upon dilution with water, may behave differently when mixed with liquid fertilizers. The presence of fertilizers could affect the ease of homogenization and stability of the mixtures, resulting in phase separation and hence, in non-uniform application and eventual damage to the application equipment.

1.A. Tank-mix compatibility studies

Laboratory studies of the compatibility of pesticide formulations with fertilizers are generally carried out by two kinds of tests: testing under static conditions which enables the assessment of the nature of incompatibility, and testing under dynamic conditions simulating agitation

in the spraying equipment. These tests were used in order to check the tank-mix compatibility of selected pesticides with several liquid fertilizers. The pesticide formulations tested are listed in Table 1. The liquid fertilizers checked are shown in Table 2.

The physical compatibility was tested according to the procedure proposed by Shell Development Comp., the Biological Sciences Research Center, Modesto, California. By this procedure the stability of fertilizer-pesticide mixtures up to 24 h, with or without agitation, is determined, and the probability of damage to the application equipment is assessed by sieving. In addition, the homogeneity of the mixtures was checked by determining the pesticide concentration in several samples from each experimental vessel. Pesticide concentration was determined by extracting aliquots from the mixtures with ethyl acetate and analysis by gas-chromatography.

The pesticides checked can be divided into two groups, according to the type of formulation: wettable powders (atrazine, diuron, terbutryn) and emulsifiable concentrates (chlorpyrifos, metalochlor and trifluralin). Although each pesticide-fertilizer mixture had specific compatibility problems, some common features were observed for each group.

Wettable powders. When diluted with liquid fertilizers instead of water, rapid sedimentation occurred with all the mixtures. However, the mixtures were easily resuspendable, indicating that they could still be rehomogenized after being left in the tank for up to 24 h. All the sediments formed upon standing passed through the 50, 100 and 325 - mesh screens, which indicates that, if efficient agitation is provided, clogging of the spray equipment will probably not occur. An exception was

terbutryn-fertilizer 4-8-12 mixture which formed screen residues, only partially passing through the 325-mesh screen.

The dynamic test showed that with all the mixtures a good suspension (similar to that in the water carrier) can be maintained. In the terbutryn-fertilizer 4-8-12 mixture a very fast, almost instantaneous settling was observed when agitation ceased.

As shown by the chemical analyses, in all the mixtures pesticide concentration did not significantly change 24 h after mixing.

Emulsifiable concentrates. The use of fluid fertilizers as diluents for chlorpyrifos and metolachlor resulted in evident difficulties in homogenizing the mixtures. Phase separation was observed in all the mixtures standing for 4 h without agitation. Rehomogenization of the mixtures was difficult, mainly after 24 h of standing without agitation. However, rehomogenization was easier in the mixtures with the fertilizer urea-ammonium nitrate.

The dynamic test indicated that if continuous agitation is provided, no phase separation occurred. But, if agitation ceased, fast phase separation took place, mainly in the mixtures with ammonium nitrate.

Table 1: Pesticides used in the tank-mix compatibility study

Common name	Formulation	Uses	Manufacturer
Atrazine	Wettable powder	Pre-emergence herbicide	Agan, Israel
Chlorpyrifos	Emulsifiable concentrate	Insecticide	Makteshim, Israel
Diuron	Wettable powder	General weed control and pre-emergence herbicide	Agan, Israel
Metolachlor	Emulsifiable concentrate	Germination inhibitor herbicide	Ciba-Geigy, Switzerland
Terbutryn	Wettable powder	Pre- and post-emergence herbicide	Agan, Israel
Trifluralin	Emulsifiable concentrate	Pre-emergence herbicide	Agan, Israel

Table 2: Liquid fertilizers used in the tank-mix compatibility study

Fertilizer	Composition	pH	Uses
Ammonium nitrate	9% N-NH ₄ + 9% N-NO ₃	6.8	All kinds of irrigation systems
Urea-ammonium nitrate (Uran)	18.4% N-NH ₂ + 4.8% N-NH ₄ + 4.8% N-NO ₃	6.9	All kinds of irrigation systems
Fertilizer 16-8-0	3.5% N-NH ₄ + 12.5% N-NH ₂ + 8% P ₂ O ₅	6.8	Not recommended for drip irrigation
Fertilizer 4-8-12	4% N-NH ₂ + 8% P ₂ O ₅ + 12% K ₂ O	1.15	All kinds of irrigation systems

1.B. Estimation of the physical compatibility between emulsifiable concentrate formulations (EC) and liquid fertilizers

The four EC formulations selected for this study belong to different chemical classes and uses and were manufactured in different countries (Table 3). Since these products are already applied, in some cases, through irrigation systems, they could be used eventually in mixtures with liquid fertilizers. The liquid fertilizers used (Table 4) are from the most widespread nitrogen and mixed nutrient fertilizers applied through irrigation systems. The fertilizer solutions were prepared in the laboratory from chemically pure substances, in absolute and relative concentrations similar to those of the commercial products. In addition, a 1N KCl solution was used. A range of dilutions (1:2, 1:5, 1:10, 1:16, 1:20, and 1:25) was prepared for each fertilizer, and the electrical conductivity of these and of the undiluted fertilizers was measured. For the KCl solutions the dilutions were 3:4, 1:1, 1:4 and 1:10 and the respective electrical conductivities were 73.2, 57.5, 32.1, 13.6 and for the undiluted solution 105.4 dS m⁻¹.

The experiments were carried out in 50 mL glass tubes with I.D. 2 cm. Thirty mL of each fertilizer solution was mixed manually with 0.3 mL of each of the pesticide formulations, by inverting the tubes 30 times. The height of the liquid in the tube was 11.5 cm. The mixtures were kept at room temperature ($24 \pm 2^{\circ}\text{C}$) and sampled at 2 and 24 h after preparation, each time before and immediately after remixing. Sampling was done by pipetting 1 mL of the mixture at 3 cm from the top level, except for the EPTC-containing mixtures, which were sampled at 3 cm from the bottom of the tubes. (In these mixtures no sedimentation but creaming occurred, upon

standing.) The samples were diluted with a 25% w/v NaCl solution up to a convenient concentration, and their optical density was determined by measuring light absorbance at 550 nm. Preliminary experiments showed that the turbidity of emulsions diluted with 25% w/v NaCl was constant for several hours. For each mixture, serial dilutions were prepared from an emulsion with known concentration. In such dilutions a linear relationship between turbidity and the concentration of the dispersed phase was obtained. The relative concentration of the EC in a mixture was estimated from the plot of turbidity against concentration. All the tests were replicated three times; the standard error was, in all cases, less than 2%.

In addition to the spectrophotometric measurements, the stability of the emulsions and the nature of the separating phase were visually estimated.

The effect of the concentration and nature of liquid fertilizers on the emulsion stability of the EC formulations studied was estimated by using the electrical conductivity of the solutions as a common parameter, and by checking the relationship between the emulsion stability and this parameter for each EC-fertilizer mixture. A nephelometric technique together with visual observations were used as a qualitative test to assess the emulsion stability. All the mixtures were grouped into stability classes according to the concentration of the dispersed phase in the depleted portion of the emulsion after a predetermined time, and the reversibility of flocculation upon remixing. The emulsions in which more than 70% of the dispersed phase remained in suspension for at least 2 h without mixing, were considered highly stable; moderately stable when flocculation and sedimentation were observed after 2 h of standing, but the flocculation was reversible; poorly stable when irreversible oil separation or coalescence occurred.

Chlorpyrifos-fertilizer mixtures

Visual observations of chlorpyrifos-fertilizer mixtures, immediately after preparation, showed that this formulation readily formed a milky, homogeneous, dispersed phase in water and in all the fertilizer solutions, up to concentrations equivalent to approx. 50 dS m^{-1} . At higher salt concentrations poor dispersion was noted, and almost no dispersion could be obtained in the systems with more than 100 dS m^{-1} .

The relationship between the concentration of chlorpyrifos in the depleted portion of the mixtures and the electrical conductivity of fertilizer solutions at 2 h after preparation, is shown in Fig. 1. This relationship was generally similar for all the fertilizer solutions. High emulsion stability was observed in the salt concentration range equivalent to about $30\text{--}50 \text{ dS m}^{-1}$. In the low electrical conductivity range (up to $25\text{--}30 \text{ dS m}^{-1}$) the emulsions were moderately stable; although fast flocculation and sedimentation occurred, the separating phase was homogeneous, without oil separation. This indicates that the systems were still emulsions and with continuous agitation, no coarsening process would occur. As compared to all the other EC checked, which formed stable emulsions at low salt concentrations, this is uncommon behavior. Its understanding would require complementary studies including microscopic observations and measurements of droplet size distribution, which is beyond the aim of this work. The mixtures with electrical conductivity higher than 50 dS m^{-1} were unstable; coalescence and separation of the oily phase were observed, immediately after preparation.

In addition to the liquid fertilizers tested, the effect of KCl solutions on the stability of chlorpyrifos was determined in a

concentration range equivalent to 14-105 dS m⁻¹. The data obtained (Fig.1) show that the relationship between the emulsion stability and electrical conductivity was similar to that observed for the liquid fertilizers checked.

The ease of resuspension of chlorpyrifos was checked by determining the concentration of the dispersed phase immediately after remixing the mixtures prepared 2 h before (Table 5). Although the concentration of the dispersed phase increased upon remixing, the dispersion was not substantially improved; this indicates that the coarsening process in such mixtures was not reversible by the standard manual mixing.

Ageing of the stable and moderately stable emulsions for 24 h resulted in a decrease in the concentration of the dispersed phase (Table 5). The decrease was approx. 30% in the moderately stable emulsions but in most cases the settled material was easily resuspended. In the high stability range ageing did not affect the stability of most mixtures. Still, a drastic phase separation, approx. 80% settling, occurred in the AN- and AN-K-containing mixtures, at salt concentrations equivalent to about 40 dS m⁻¹. However, these mixtures could be easily rehomogenized by remixing.

Metolachlor - fertilizer mixtures

The metolachlor formulation tested readily dispersed in all the fertilizer solutions, except the concentrated ones, usually with electrical conductivity higher than 100 dS m⁻¹, in which very poor or no dispersion could be obtained.

The relationship between the stability of the emulsions and the electrical conductivity of the fertilizer solutions, measured at 2 h after

preparation, is shown in Fig. 2. Except for the U-AN-P-K-containing mixtures, the stability of the emulsions was high at low salt concentrations. The electrical conductivity at which a strong decrease in the concentration of the dispersed phase occurred was $60-70 \text{ dS m}^{-1}$ for AN and AN-K, and higher than 100 dS m^{-1} in the U-AN fertilizer. The emulsion stability of metolachlor in U-AN fertilizer, even at high salt concentrations, is probably due to the presence of urea which, in combination with ionic salts, may reduce the surface tension and increase the water activity (Lindner, 1973).

In the mixtures containing AN, the emulsions were moderately stable up to $90-100 \text{ dS m}^{-1}$; at this salt concentration, gross flocculation and sedimentation were observed, but no coalescence occurred.

The emulsions of metolachlor in the mixed U-AN-P-K fertilizer were less stable than in the other fertilizer solutions, even at low salt concentrations. Since for the preparation of this fertilizer, di-ammonium hydrogen phosphate was used as the P-source, the pH of these solutions was slightly alkaline (pH 7.6-7.8). The adjustment of the pH to approx. 5 or, alternatively, the use of mono-ammonium dihydrogen phosphate or potassium dihydrogen phosphate for the preparation of the solutions, improved the stability of the emulsions (Table 6). At acidic pH the stability of metolachlor in the U-AN-P-K fertilizer was similar to that obtained in the other fertilizer solutions.

The stability of metolachlor emulsions in KCl solutions was high at low salt concentrations, up to approx. 60 dS m^{-1} , moderate at 75 dS m^{-1} and poor at electrical conductivities higher than 100 dS m^{-1} (Fig. 2). This

behavior was similar to that of the other metolachlor - fertilizer mixtures, except for those prepared with the U-AN fertilizer.

The remixing of the emulsions at 2 h after their preparation did not significantly change the concentration of the dispersed phase, except for the moderately stable metolachlor-AN mixture at 93 dS m^{-1} . In this mixture 70% of the suspended material settled, but it was easily re-emulsified (Table 7).

Significant changes in the concentration of the dispersed phase occurred upon ageing the U-AN, AN-K and U-AN-P-K-containing mixtures for 24 h. The decrease in concentration was between 20% and 50%, mainly in the highly stable emulsions, but the settled material could be easily remixed (Table 7). This indicates the need for continuous agitation of metolachlor-liquid fertilizer mixtures in order to prevent sedimentation.

EPTC - fertilizer mixtures

Visual observations of EPTC - fertilizer mixtures immediately after preparation showed that homogeneous, milky dispersions could be obtained only at low salt concentrations, up to approx. 40 dS m^{-1} . At higher concentrations the mixtures were opalescent and either flocculation or oil separation were observed. Since the density of this EC is lower than unity the separating phase was lighter than the bulk and separated by creaming.

The relationship between the relative concentration of the dispersed phase and the electrical conductivity of the mixtures was similar for all the fertilizer solutions, except for the slightly alkaline, P-containing fertilizer (Fig. 3). In the low electrical conductivity range, up to about 35 dS m^{-1} , all the emulsions were highly stable, but moderately stable in the U-AN-P-K fertilizer.

With all the fertilizers at concentrations equivalent to 35-45 dS m⁻¹, the emulsions were moderately stable; the dispersed phase flocculated and separated in an easily redispersible layer (Table 8). The flocculation was reversible not only at 2 h after preparation, but even in the mixtures standing for 24 h. This indicates that with proper continuous agitation the homogeneity of such mixtures could be maintained. At fertilizer concentrations higher than 45 dS m⁻¹ the dispersion was poor, and oil separation and coalescence of the oil droplets were observed in the samples standing for 2 h. This phase separation could not be reversed by remixing.

EPTC emulsions in the U-AN-P-K fertilizer were only moderately stable in the low concentration range. However, high emulsion stability was obtained by acidifying the mixtures to pH 5. In the mixtures prepared with KCl, the relationship between the emulsion stability and the electrical conductivity was similar to that obtained for all the fertilizers (Fig. 3).

Fenamiphos - fertilizer mixtures

Homogeneous, milky emulsions were obtained upon mixing fenamiphos with all the liquid fertilizer solutions, except for the concentrated fertilizers, and the 1:2 dilutions with AN and U-AN-P-K. These mixtures were opalescent, and rapid oil separation could be observed.

Turbidity measurements carried out at 2 h after the preparation of the mixtures showed that with all the fertilizers, except U-AN-P-K, the relationship between emulsion stability and electrical conductivity was similar (Fig. 4). As compared with the other EC formulations checked, stability of fenamiphos emulsions was the least affected by the presence of salts. In all the mixtures the suspension stability was high at conductivities up to 100-120 dS m⁻¹, except for the U-AN-P-K solutions.

With this fertilizer, irreversible oil separation was observed at a concentration equivalent to 85 dS m^{-1} . High emulsion stability was obtained in a 1M KCl solution, having an EC of 105 dS m^{-1} .

The highly stable emulsions were not affected by ageing for 24 h (Table 9). In a single, moderately stable mixture (AN-K at 117 dS m^{-1}), flocculation and sedimentation occurred after 24 h; however, the sediment was easily resuspendable following remixing.

The effect of electrolytes on the potential energy of interactions of the particles in an emulsion is very complex. However, it is generally accepted that this is mainly an electrostatic effect, related to the concentration and valence of the electrolyte (Hiemenez, 1986; Adamson, 1976). The nature of the ion, related to its radius and polarizing power, is a second-order effect (Hiemenez, 1986). With stabilized EC formulations, the effect of electrolytes is even more complex.

The conductivity of electrolyte solutions, which is a measure of the total electrical charge in solution, is a function of the concentration, of the ion charge and its mobility. The relationship between this parameter and the stability of EC formulations was checked, in an attempt to find a common property of the fertilizer solutions affecting the emulsion stability. This approach is based on a simplified model of the effect of electrolytes on emulsion stability, and, therefore, it was used as a qualitative test of this effect.

The data presented in this work show that for each EC formulation, the relationship between the emulsion stability and the electrical conductivity of all the fertilizer solutions was fairly similar. (This was true for slightly acidic and acidic solutions; while the emulsion stability was

lower in alkaline reaction conditions.) The relationships obtained show that for each formulation there is a critical electrical conductivity range, above which irreversible destabilization occurs. In many cases, in a narrow conductivity range, slightly higher than the critical range, the emulsions were moderately stable. From the above observations results that the stability of a specific EC in the most commonly used liquid fertilizers could be estimated from its stability at different concentrations of a single salt solution. KCl, as a test solution, yielded satisfactory results.

The emulsion stability was assessed by turbidimetric measurements of the depleted portion of the mixtures, at predetermined times, and by visual observations. Despite the semi-empirical nature of nephelometry applied to emulsion stability measurements, satisfactory results may be obtained for dilute emulsions which are re-emulsifiable after the standing period (Hill, 1989). These conditions were fulfilled only in the highly stable emulsions and in part of the moderately stable ones, while for the rest the reported results are probably excessively high (Hill, 1989). However, the turbidity data were considered as a qualitative measure of concentration and were used accordingly.

Flocculation, coagulation and coalescence of EC by salts may be reversible or irreversible. In the first case, the initial concentration can be restored by remixing, while in the second case, remixing has no significant effect. The concentration of the emulsions in the EC-salt mixtures and the reversibility of flocculation upon remixing were the criteria used to group the mixtures into stability classes.

In conclusion, in the EC-liquid fertilizer mixtures tested, the relationships between the emulsion stability and electrical conductivity of different fertilizer solutions were fairly similar for each formulation. A critical conductivity range, below which the emulsions were highly or moderately stable and above which irreversible destabilization or no emulsification occurred, was also specific for each formulation.

The correlations observed suggest that the effect of different liquid fertilizers on the emulsion stability of a specific EC formulation could be estimated from the effect of only one salt solution. With a simple analytical technique to check the concentration of the dispersed phase, this could be a rapid qualitative test to estimate the compatibility between EC formulations and liquid fertilizers. This test must be limited to slightly acidic and acidic solutions.

Table 3 - Pesticide formulations tested

Chemical name	Active compound	Use	Formulation	Density (d ₄ ²²)	Manufacturer
Chlorpyrifos	O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate	Insecticide	EC 480 gL ⁻¹	1.111	Makhteshim, Israel
Metolachlor	2-chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)acet-O-toluidide	Soil-herbicide	EC 960 gL ⁻¹	1.148	Ciba-Geigy AG Basel, Switzerland
EPTC	S-ethyl dipropylthiocarbamate	Soil-herbicide	EC 770 gL ⁻¹	0.948	Stauffer Chemical Co., Westport, CT, USA
Fenamiphos	Ethyl 4-methylthio-m-tolyl isopropylphosphoramidate	Nematicide	EC 400 gL ⁻¹	1.088	Bayer AG Leverkusen, FRG

Table 4 - Fertilizer solutions tested

Fertilizer	Concentration (g L ⁻¹)	Electrical conductivity (dS m ⁻¹)	pH
Ammonium nitrate 18-0-0 (AN)	514.2	310.3	4.60
Urea-ammonium nitrate 32-0-0 (U-AN)	783.0	150.0	6.30
Ammonium nitrate-potassium chloride 8-0-4 (AN-K)	305.4	256.0	5.30
Urea-ammonium nitrate-diammonium hydrogen orthophosphate-potassium- chloride 8-2-4 (UAN-P-K)	316.2	174.0	7.75
Potassium chloride 1M (KCl)	74.6	105.4	5.10

Table 5- Stability of chlorpyrifos in liquid fertilizers
(% in the dispersed phase)

Fertilizer	Electrical conductivity dS m ⁻¹	Time (h)			
		2		24	
		n.r. ^{x)}	r. ^{x)}	n.r.	r
AN	<0.01	16.0	18.9	9.4	23.4
	26.9	58.2	64.3	55.7	66.8
	32.7	98.0	98.4	96.7	98.8
	39.0	70.9	84.4	13.9	100.0
	57.5	9.4	18.0	9.4	19.3
	93.4	6.6	17.2 ^{xx)}	6.1	20.5
	179.5	6.6	n.e.	4.9	n.e.
	310.3	4.1	n.e.	2.0	n.e.
U-AN	20.8	19.7	27.0	18.9	29.5
	24.8	42.2	48.0	37.3	47.5
	29.4	77.8	82.8	75.8	79.1
	43.4	97.9	100.0	62.7	100.0
	69.1	11.9	22.9	9.4	17.6
	122.7	11.5	n.e.	n.e.	n.e.
	150.0	11.1	n.e.	n.e.	n.e.
AN-K	17.8	23.6	32.2	18.5	32.4
	22.0	34.5	46.0	26.9	41.2
	26.1	83.3	93.7	60.9	68.5
	39.0	69.0	78.2	17.2	100.0
	66.8	12.6	n.e.	5.8	n.e.
	117.6	8.6	n.e.	4.2	n.e.
	256.0	9.2	n.e.	4.0	n.e.
U-AN-P-K	13.0	24.3	36.4	24.3	42.9
	16.9	26.4	41.4	27.9	46.5
	19.9	28.6	41.4	31.4	50.7
	29.6	82.1	100.0	83.6	100.0
	48.8	22.1	28.6	10.0	n.e.
	85.3	28.6	n.e.	12.9	n.e.
	174.0	29.3	n.e.	28.6	n.e.

x) n.r. = not remixed; r = remixed

xx) n.e. = no emulsification

Table 6- Stability of metolachlor in U-AN-P-K as affected by pH and the P-source (% in the dispersed phase at 2 h after mixing)

Electrical conductivity (dS/m)	P source / pH		
	$(\text{NH}_4)_2\text{HPO}_4$ 7.6-7.8	$\text{NH}_4\text{H}_2\text{PO}_4$ 4.3-4.5	KH_2PO_4 4.5-4.6
12.0-13.6	59.1	76.4	72.0
13.8-16.9	69.6	87.4	78.0
18.0-19.9	68.3	90.0	94.4
26.6-29.6	82.6	95.9	96.7
44.7-48.8	97.4	100.0	96.3

Table 7 - Stability of metolachlor in liquid fertilizers
(% in the dispersed phase)

Fertilizer	Electrical conductivity (dS m ⁻¹)	Time (h)			
		2		24	
		n.r. ^{x)}	r ^{x)}	n.r.	r
AN	<0.01	95.0	98.6	95.6	98.3
	26.9	97.4	98.6	93.9	99.6
	32.7	98.3	99.6	95.6	99.1
	39.0	97.8	99.6	90.9	97.4
	57.5	100.0	100.0	100.0	100.0
	93.4	30.0	97.0	3.9	88.7
	179.5	11.4	13.0	9.3	7.6
	310.3	6.5	n.e. ^{xx}	n.e.	n.e.
U-AN	20.8	76.6	78.7	39.9	61.8
	24.8	86.5	86.9	52.8	75.3
	29.4	91.4	92.2	67.4	84.3
	43.4	93.9	93.9	77.5	87.6
	69.1	96.7	97.6	89.3	95.5
	122.7	98.3	98.3	96.2	98.9
	150.0	50.8	51.2	21.3	23.0
AN-K	17.8	83.6	84.0	60.1	75.3
	22.0	85.2	86.9	53.4	73.0
	26.1	85.2	86.9	47.2	74.2
	39.0	93.0	93.0	76.4	89.3
	66.8	96.7	96.7	89.9	95.5
	117.6	27.1	28.8	3.3	14.7
	256.0	14.3	16.4	5.1	9.0
U-AN-P-K	13.0	59.1	61.7	28.7	65.6
	16.9	69.6	74.3	33.9	84.8
	19.9	68.3	73.5	40.0	85.6
	29.6	82.6	84.3	62.6	86.9
	48.8	97.4	98.3	93.5	99.6
	85.3	9.5	11.9	1.6	14.1
	174.0	26.5	n.e.	21.7	n.e.

x) n.r. = not remixed; r = remixed

xx) n.e. = no emulsification

Table 8 - Stability of EPTC in liquid fertilizers
(% in the dispersed phase)

Fertilizer	Electrical conductivity (dS/m)	Time (h)			
		2		24	
		n.r. x)	r. x)	n.r.	r.
AN	<0.01	83.8	83.8	71.5	82.8
	26.9	95.0	91.1	96.1	96.0
	32.7	86.1	100.0	89.9	95.0
	39.0	35.8	90.5	4.5	89.9
	57.5	14.0	20.7	4.5	n.e.
	93.4	11.8	19.0	4.5	n.e.
	179.5	10.1	n.e. xx	3.4	n.e.
	310.3	7.3	n.e.	1.1	n.e.
U-AN	20.8	95.3	96.1	75.0	88.2
	24.8	88.4	90.1	91.9	92.0
	29.4	99.4	100.0	90.7	100.0
	33.4	39.0	80.2	11.0	82.0
	69.1	19.2	n.e.	3.5	n.e.
	122.7	19.2	n.e.	5.2	n.e.
	150.0	22.7	n.e.	14.5	n.e.
AN-K	17.8	84.4	83.8	95.8	100.0
	22.0	94.8	100.0	95.3	98.9
	26.1	93.5	88.3	98.9	100.0
	39.0	13.6	100.0	3.2	100.0
	66.8	11.7	n.e.	3.2	n.e.
	117.6	7.8	n.e.	4.2	n.e.
	256.0	4.5	n.e.	2.6	n.e.
U-AN-P-K	13.0	54.9	57.5	49.7	62.1
	16.9	54.9	56.2	45.1	57.5
	19.9	52.9	55.6	41.2	50.9
	29.6	52.2	88.2	63.4	88.2
	48.8	11.1	n.e.	6.5	n.e.
	85.3	16.3	n.e.	10.4	n.e.
	174.0	26.8	n.e.	22.0	n.e.

x) n.r. = not remixed; r = remixed
xx) n.e. = no emulsification

Table 9- Stability of fenamiphos in liquid fertilizers
(% in the dispersed phase)

Fertilizer	Electrical conductivity (dS/m)	Time (h)			
		2		24	
		n.r. ^{x)}	r. ^{x)}	n.r.	r.
AN	<0.01	89.7	93.8	93.3	94.3
	26.9	89.7	93.8	82.0	88.7
	32.7	92.3	97.4	88.1	91.8
	39.0	94.3	100.0	91.2	97.9
	57.5	96.4	97.9	92.3	95.9
	93.4	99.5	100.0	100.0	100.0
	179.5	31.9	n.e. ^{xx)}	23.2	n.e.
	310.3	6.2	n.e.	1.0	n.e.
U-AN	20.8	92.8	95.9	91.2	94.8
	24.8	92.3	96.4	93.3	97.9
	29.4	93.3	96.4	94.3	97.9
	43.4	88.6	99.5	97.4	100.0
	69.1	100.0	100.0	100.0	100.0
	122.7	100.0	100.0	100.0	100.0
	150.0	26.8	n.e.	27.3	n.e.
AN-K	17.8	94.3	95.4	93.3	100.0
	22.0	91.2	36.4	90.7	97.9
	26.1	95.9	97.4	89.2	89.7
	39.0	93.3	98.5	94.3	100.0
	66.8	100.0	100.0	100.0	100.0
	117.6	100.0	100.0	14.3	100.0
	256.0	10.3	n.e.	1.5	n.e.
U-AN-P-K	13.0	82.2	86.1	90.2	93.8
	16.9	83.0	87.6	90.7	93.8
	19.9	87.6	86.6	91.7	95.5
	29.6	88.1	94.3	95.4	100.0
	48.8	93.3	98.5	100.0	100.0
	85.3	30.9	n.e.	3.1	n.e.
	174.0	17.5	n.e.	17.5	n.e.

^{x)} n.r. = not remixed; r = remixed
^{xx)} n.e. = no emulsification

Figure Legends

Fig. 1. The effect of the electric conductivity of fertilizer solutions on the emulsion stability of chloropyrifos.

Fig. 2. The effect of the electrical conductivity of fertilizer solutions on the emulsion stability of metolachlor.

Fig. 3. The effect of the electrical conductivity of fertilizer solutions on the emulsion stability of EPTC.

Fig. 4. The effect of the electrical conductivity of fertilizer solutions on the stability of fenamiphos.

Figure 1

המכון למחקר
למדינת ישראל
בית-דגן

Figure 2

Figure 3

Figure 4

-bard2

2. Soil behavior of pesticides, as affected by the presence of fertilizers.

2.A. Adsorption and mobility of pesticides

The pesticides used in this study were described in Table 3. In all the experiments, nonformulated, technical grade pesticides were used. The pesticides were spiked with ^{14}C -labeled material. Three fertilizers (U-AN, 32-0-0; AN-K, 8-0-4; U-AN-P-K, 8-2-4) were compared with distilled water (as the control) for each pesticide. The fertilizers were diluted during testing to concentrations appropriate to field chemigation situations. The pesticide/fertilizer combinations were studied with three soils (Table 10).

Radioactive pesticides were analyzed by thin-layer chromatography (TLC) or high performance liquid chromatography, then purified as necessary before further use.

The batch method was used to measure adsorption. Air-dry soil was shaken with pesticide solutions, by using a 1:5 soil:solution ratio, for 24 h at 20°C . The time was selected after conducting an initial time-of-equilibration study for each pesticide. Radioactivity in the residual solution was measured by standard liquid scintillation counting techniques and the results expressed by the log transformed Freundlich adsorption isotherm,

$$\log x/m = \log K + 1/n \log C_e$$

where x/m is the mass of adsorbed pesticide (ug) per gram of soil, C_e is the equilibrium solution concentration of pesticide (ug/ml), K is the Freundlich adsorption constant, and $1/n$ is an exponential fitting constant.

Each pesticide was tested at five initial concentrations. With metolachlor and fenamiphos, three concentrations of each fertilizer were used for the Maryland and Georgia soils. Only a single concentration (200 ppm) of fertilizer was used in testing the Israeli soil. In all cases, four replications for any specific treatment were used.

The statistical evaluation of the adsorption data is presented in Tables 11-14. The results obtained show that there is no definite effect of fertilizer, up to the highest tested concentration, on pesticide adsorption. For chlorpyrifos, the average K values were 56.77, 24.62 and 9.26 for Maryland, Georgia and Israel soils, respectively. EPTC was less adsorbed, with overall average K values of 1.67, 0.88 and 0.23 for Maryland, Georgia and Israel soils, respectively. The $1/n$ term was generally near 1.0, implying linear adsorption. The order of adsorption is chlorpyrifos > fenamiphos > metolachlor > EPTC.

The mobility study was carried out by soil thin-layer chromatography (soil TLC). For soil TLC, duplicate applications of each [^{14}C] pesticide were made to each soil plate (i.e. 8 spots per plate). Results are generally based on three TLC plates. The developing solution was either water or one of the three fertilizer solutions, run at 200 ppm. A filter paper wick was attached along the bottom of each plate before leaching; this alleviated soil sloughing that was a problem for the sandy loam soils. A second special problem was that EPTC was almost completely lost by volatilization during TLC plate air drying after leaching and before exposure to X-ray film. This was solved by freezing the wet plate immediately after the wetting front has reached 10 cm, then conducting

autoradiography in a freezer. A sandwich technique, used for some plates during leaching, was unnecessary.

The results of the soil TLC leaching experiments are shown in Table 15. Certain generalizations are immediately apparent. The order of mobility among pesticides in EPTC > metolachlor > fenamiphos > chlorpyrifos. All chemicals tend to leach within soils in the order Hamra (Israel) > Tifton (Georgia) > Hatboro (Maryland). There seems to be no evidence that 200 ppm of the three fertilizers has affected leaching of any pesticide, so this is consistent with observations based on batch adsorption measurements. Possible pesticide metabolites sometimes appeared on the autoradiograms.

Table 10: Soils tested in the adsorption and mobility studies

Soil series	Soil subgroup	Sample location	Soil texture
Hatboro	Typic Fluvaquents	Beltsville, Maryland (USA)	silt
Tifton	Plinthic Paleudults	Tifton, Georgia (USA)	ls
Sandy hamra	Rhodoxeralfs	Bet Dagan (Israel)	sl

Table 11: Chlorpyriphos adsorption as affected by fertilizers and soils.

Fertilizer	Intercept (K)				1/n			
Treatment	Log(K)	SE LOG(K)	Cl	K	1/n	Se 1/n	Cl	
Hatboro Sil (Maryland)								
0	1.7722	0.0448	0.0934	59.1834	0.9693	0.0254	0.0530	
N 200	1.7579	0.0528	0.1101	57.2625	0.9700	0.0302	0.0630	
NK 200	1.7152	0.0358	0.0746	51.9003	0.9591	0.0207	0.0433	
NPK 200	1.7318	0.0588	0.1232	53.9250	0.9408	0.0330	0.0691	
Tifton LS (Georgia)								
0	1.3607	0.0577	0.1211	22.9462	0.9170	0.0399	0.0838	
N 200	1.4407	0.0536	0.1122	27.5880	0.9814	0.0373	0.0781	
NK 200	1.4207	0.0890	0.1863	26.3421	0.9697	0.0612	0.1281	
NPK 200	1.3971	0.0905	0.1902	24.9523	0.9270	0.0623	0.1309	
Sandy Hamra (Israel)								
0	0.9461	0.0089	0.0186	8.8333	1.0307	0.0087	0.0183	
N 200	1.0101	0.0237	0.0501	10.2360	1.0839	0.0225	0.0475	
NK 200	1.0803	0.0207	0.0436	12.0298	1.0529	0.0186	0.0390	
NPK 200	0.8344	0.0721	0.1509	6.8289	0.8858	0.0694	0.1453	

Table 12: Metolachlor adsorption as affected by fertilizers and soils
(Statistical analysis).

Fertilizer	Intercept (K)				1/n		
Treatment	Log (K)	SE Log(K)	CI	K	1/n	SE 1/n	CI
Hatboro Sil (Maryland)							
Average 0	0.3253	0.0122	0.0260	2.1149	0.9494	0.0137	0.0292
N 0	0.2943	0.0096	0.0207	1.9694	0.9626	0.0108	0.0233
N 100	0.3599	0.0251	0.0534	2.2905	0.9854	0.0287	0.0611
N 200	0.3259	0.0172	0.0366	2.1176	0.9346	0.0193	0.0411
N1000	0.3834	0.0169	0.0361	2.4177	0.9351	0.0191	0.0406
NK 0	0.3411	0.0158	0.0337	2.1931	0.9357	0.0178	0.0378
NK 100	0.3378	0.0143	0.0305	2.1768	0.9318	0.0161	0.0342
NK 200	0.3503	0.0094	0.0201	2.2400	0.9468	0.0106	0.0226
NK1000	0.3655	0.0122	0.0260	2.3202	0.9742	0.0139	0.0295
NPK 0	0.3405	0.0111	0.0236	2.1902	0.9501	0.0125	0.0266
NPK 100	0.3759	0.0159	0.0339	2.3761	0.9130	0.0178	0.0378
NPK 200	0.3352	0.0122	0.0259	2.1637	0.9249	0.0136	0.0290
NPK1000	0.3757	0.0105	0.0225	2.3750	0.9234	0.0114	0.0244
Tifton LS (Georgia)							
Average 0	-0.0016	0.0297	0.0632	0.9964	0.9362	0.0327	0.0697
N 0	0.0172	0.0354	0.0755	1.0403	0.9728	0.0393	0.0838
N 100	0.0569	0.0361	0.0769	1.1400	0.9359	0.0400	0.0851
N 200	0.0378	0.0361	0.0774	1.0909	0.9073	0.0398	0.0853
N 1000	0.0182	0.0220	0.0469	1.0427	0.8111	0.0238	0.0507
NK 0	0.0505	0.0254	0.0540	1.1234	0.9117	0.0279	0.0595
NK 100	0.0494	0.0316	0.0674	1.1205	0.8546	0.0345	0.0736
NK 200	0.0167	0.0334	0.0712	1.0391	0.9044	0.0367	0.0783
NK 1000	0.0143	0.0440	0.0937	1.0334	0.9197	0.0485	0.1034
NPK 0	-0.0724	0.0282	0.0601	0.8464	0.9242	0.0310	0.0660
NPK 100	-0.0080	0.0389	0.0830	0.9817	0.9868	0.0434	0.0924
NPK 200	-0.0401	0.0368	0.0790	0.9118	0.9388	0.0399	0.0855
NPK 1000	-0.0199	0.0398	0.0849	0.9551	0.8748	0.0435	0.0927
Sandy Hamra (Israel)							
0	-0.2782	0.0358	0.0752	0.5270	1.0229	0.0394	0.0828
N 200	-0.2963	0.0323	0.0678	0.5054	1.0105	0.0351	0.0738
NK 200	-0.3067	0.0150	0.0319	0.4935	0.9828	0.0167	0.0356
NPK 200	-0.3306	0.0129	0.0271	0.4670	1.0177	0.0144	0.0303

Table 13: EPTC adsorption as affected by fertilizers and soils.

Fertilizer		Intercept (K)				1/n		
Treatment	LOG(K)	SE LOG(K)	Cl	K	1/n	SE 1/n	Cl	
Hatboro Sil (Maryland)								
0	0.2110	0.0183	0.0388	1.6256	0.9279	0.0163	0.0345	
N 200	0.2245	0.0430	0.0900	1.6768	0.9529	0.0411	0.0860	
NK 200	0.2406	0.0235	0.0499	1.7400	0.9556	0.0232	0.0492	
NPK 200	0.2408	0.0147	0.0309	1.7409	0.9135	0.0138	0.0290	
Tifton LS (Georgia)								
0	-0.0929	0.0326	0.0690	0.8073	0.9036	0.0274	0.0581	
N 200	-0.0346	0.0233	0.0494	0.9235	0.8760	0.0191	0.0405	
NK 200	0.0014	0.0221	0.0472	1.0032	0.8937	0.0189	0.0403	
NPK 200	-0.0190	0.0170	0.0358	0.9572	0.8763	0.0146	0.0307	
Sandy Hamra (Israel)								
0	-0.5970	0.0683	0.1475	0.2529	1.0141	0.0629	0.1360	
N 200	-0.7045	0.0467	0.0978	0.1975	1.0785	0.0398	0.0833	
NK 200	-0.6288	0.0535	0.1128	0.2351	0.9694	0.0476	0.1005	
NPK 200	-0.6648	0.0628	0.1331	0.2164	1.0298	0.0550	0.1165	

Table 14: Fenamiphos adsorption as affected by fertilizers and soils
(Statistical analysis).

Fertilizer		Intercept (K)				1/n		
Treatment		Log(K)	SE Log(K)	CI	K	1/n	SE 1/n	CI
Hattboro Sil (Maryland)								
Average 0		0.4412	0.0073	0.0154	2.7621	0.9030	0.0067	0.0141
N	0	0.4563	0.0074	0.0155	2.8598	0.9148	0.0069	0.0145
N	100	0.4531	0.0087	0.0182	2.8388	0.9106	0.0081	0.0169
N	200	0.4628	0.0058	0.0121	2.9030	0.9067	0.0054	0.0113
N	1000	0.4949	0.0236	0.0493	3.1253	0.8564	0.0219	0.0457
NK	0	0.4342	0.0067	0.0140	2.7179	0.9029	0.0061	0.0128
NK	100	0.4480	0.0110	0.0232	2.8056	0.9062	0.0098	0.0206
NK	200	0.4249	0.0118	0.0251	2.6601	0.9255	0.0102	0.0218
NK	1000	0.4508	0.0075	0.0156	2.8233	0.9116	0.0068	0.0142
NPK	0	0.4331	0.0079	0.0166	2.7111	0.8912	0.0072	0.0150
NPK	100	0.4435	0.0055	0.0114	2.7766	0.9016	0.0054	0.0112
NPK	200	0.4499	0.0073	0.0153	2.8180	0.8949	0.0068	0.0142
NPK	1000	0.4584	0.0073	0.0152	2.8739	0.8952	0.0068	0.0141
Tifton LS (Georgia)								
Average 0		0.1153	0.0236	0.0496	1.3041	0.7781	0.0216	0.0453
N	0	0.1069	0.0242	0.0513	1.2791	0.8259	0.0242	0.0513
N	100	0.1763	0.0312	0.0669	1.5007	0.7584	0.0262	0.0561
N	200	0.1439	0.0290	0.0618	1.3928	0.7987	0.0253	0.0538
N	1000	0.1143	0.0152	0.0320	1.3011	0.7932	0.0130	0.0273
NK	0	0.1193	0.0244	0.0511	1.3161	0.7673	0.0213	0.0445
NK	100	0.1113	0.0262	0.0555	1.2921	0.7869	0.0218	0.0462
NK	200	0.1796	0.0286	0.0604	1.5120	0.7341	0.0272	0.0573
NK	1000	0.0618	0.0167	0.0349	1.1529	0.7985	0.0145	0.0302
NPK	0	0.1197	0.0223	0.0465	1.3174	0.7412	0.0193	0.0402
NPK	100	0.1383	0.0207	0.0432	1.3750	0.7390	0.0179	0.0374
NPK	200	0.1313	0.0250	0.0521	1.3531	0.7300	0.0216	0.0450
NPK	1000	0.1138	0.0229	0.0479	1.2997	0.7372	0.0198	0.0413
Sandy Hamra (Israel)								
	0	-0.2379	0.0266	0.0555	0.5783	0.9767	0.0229	0.0477
N	200	-0.3470	0.0322	0.0671	0.4498	1.0398	0.0277	0.0577
NK	200	-0.3196	0.0161	0.0335	0.4791	1.0523	0.0139	0.0289
NPK	200	-0.3209	0.0213	0.0444	0.4777	1.0379	0.0183	0.0382

Table 15 Soil TLC leaching of chlorpyrifos, EPTC, fenamiphos, and metolachlor as influenced by soils and fertilizer solutions.

Soil	Leaching solution	R_f of pesticide			
		Chlorpyrifos	EPTC	Fenamiphos	Metolachlor
Hatboro	Water	0.03	0.41	0.33	0.27
	200 N	0.02	0.43	0.26	0.38
	200 NK	0.03	0.41	0.27	0.33
	200 NPK	0.02	0.39	0.28	0.28
	X $\pm$ SD	0.02 ± 0.01	0.41 ± 0.08	0.28 ± 0.11	0.31 ± 0.07
Tifton	Water	0.04	0.48	0.31	0.48
Hamra	Water	0.44	0.97	0.55	0.76
	200 N	0.31	0.92	0.61	0.79
	200 NK	0.34	>0.5	0.61	0.79
	200 NPK	0.38	1.00	0.62	0.81
	X $\pm$ SD	0.37 $\pm 0.$	>0.85 $\pm 0.$	0.60 $\pm 0.$	0.79 $\pm 0.$

2.B. Persistence of pesticides

The soil used in this study was the Hamra soil from Bet Dagan, Israel. This soil has the following characteristics: particle size distribution 85% sand, 4% silt, 11% clay; organic matter content 0.6%; pH 8.15; water retention capacity 7.9% at 1/3 atm. The N-mineral content was 2-5 ppm $\text{NH}_4\text{-N}$, and 5-10 ppm $(\text{NO}_3^- + \text{NO}_2^-)\text{-N}$. Sampling was done from the upper 20 cm of an uncultivated field. The soil was air-dried, ground, passed through a 2-mm sieve, and stored in the laboratory in a closed container.

Four soil-applied crop protection chemicals, covering a broad range of uses and properties, were studied (Table 3). All the pesticides were commercial formulations, and were applied to soil as water emulsions.

The incubation experiments were carried out in closed 720-mL glass jars, in a dark, temperature-controlled room at, 27°C. Each jar contained 40 g soil, to which an appropriate volume of water, or $(\text{NH}_4)_2\text{SO}_4$ solution with or without pesticide was added, to give a moisture content equivalent to 80% field capacity. The added NH_4^+ was in all cases 100 ppm $\text{NH}_4^+\text{-N}$; the initial concentrations of pesticides in soil were 1, 10 and 100 ppm, and in some cases 5 and 50 ppm. The solutions were incorporated into the soil by manual mixing.

After various periods of time, triplicate samples from each jar were analyzed for pesticide content. A sample of 3 g soil was dispersed in 5 mL deionized water by shaking in a Vortex, and extracted with 5 mL ethyl acetate by mechanical shaking. The supernatant was separated by centrifugation and analyzed by gas-chromatography, with a Tracor 560 gas chromatograph. For chlorpyrifos and metolachlor an EC detector was used; the column (2.5 m x 2 mm i.d.) was packed with 4% OV-101 on Gas-Chrom Q

80-100 mesh. The chromatograms were carried out isothermally. The oven, inlet and detector temperatures were 200, 220 and 350°C respectively for chlorpyrifos, and 220, 240 and 350°C for metolachlor. For fenamiphos and EPTC analysis a NP detector was used; the column (1.5 m x 2 mm i.d.) was packed with 3% OV-17 on Gas-Chrom Q 80-100 mesh. The column, inlet and detector temperatures were 200, 220, and 250° C, respectively, for fenamiphos, and 130, 180 and 250° C for EPTC. For all the pesticides, the recovery was between 89% and 102%.

The relative amounts of pesticide extractable after 14 and 35 days of incubation are shown in Table 16, except for EPTC. This product having a high vapor pressure, was not found in the soil extract after a few days of incubation, even at the high concentrations tested. (At 50 ppm initial concentration, only 50% could be recovered after one day of incubation.)

The data in Table 16 show that for chlorpyrifos and fenamiphos the persistence increased as the initial concentration increased. The reduced degradation rate at high initial concentrations may result either from a limitation in the number of free reaction sites in soil, or from toxic effects on microorganisms, and/or enzymes inhibition (Hurle and Walker, 1980). The persistence of metolachlor was less affected by the initial concentration, mainly at 10 and 100 ppm; at these concentrations the degradaton rate was almost proportional to the initial concentration.

Comparatively, metolachlor was the most persistent at the low application rates (1 and 10 ppm) and fenamiphos was the most persistent at the high application dose. This suggests a possible toxic effect of this pesticide on the microflora capable to degrade it.

The application in the $(\text{NH}_4)_2\text{SO}_4$ solution did not significantly affect the persistence of chlorpyrifos, but slightly increased the persistence of metolachlor, especially at the initial low concentrations (1-10 ppm). At these concentrations the persistence of fenamiphos was also much higher in the presence of $(\text{NH}_4)_2\text{SO}_4$ than when applied in water. This increased persistence is possibly due to the decrease in pH following the application of $(\text{NH}_4)_2\text{SO}_4$, which decreases the rate of the alkaline hydrolysis of this compound. Such possible effects of salts on the persistence of pesticides must be considered, mainly in the case of simultaneous applications of pesticides and liquid fertilizers.

The kinetics of pesticide disappearance, as shown in Fig. 5 for chlorpyrifos, is characterized by an initially sharp drop in concentration. In the first 3 days of incubation the amounts of extractable chlorpyrifos decreased by 58%, 38%, and 20% at the initial concentrations of 1, 10, and 100 ppm, respectively. The disappearance rate was much slower after one week of incubation. This behavior can be described by the "two compartment" model suggested by Hamaker and Goring (1976) in which pesticides are considered to be in both an available and an unavailable fraction, the first being subject to degradation. The initial rapid disappearance may be explained by the fact that the freshly added compound is more available for degradation. At the same time, the extractability decreases because of the diffusion and adsorption of the pesticides at less available sites.

For EPTC, as for most thiocarbamate pesticides, volatility is a major factor which determines its persistence in soil. Kaufman (1974) showed that plant bioassay revealed a rapid disappearance of EPTC from soil. However, evolution of CO_2 occurred slowly, indicating detoxification without

appreciable mineralization of the ethyl moiety. The low sorptive capacity of the Bet Dagan soil is an additional factor contributing to the rapid disappearance of EPTC. Correlations between the loss of EPTC by evaporation of the soil water and the amount of organic matter and/or clay content have been observed (Kaufman, 1974).

TABLE 16
Persistence of Chlorpyrifos, Metolachlor and Fenamiphos
(% Recovered ± SD)

Initial concentration (ppm)	Application in:	Chlorpyrifos		Metolachlor		Fenamiphos	
		Incubation time (days)					
		14	35	14	35	14	35
1		17.35 ± 2.04	4.10 ± 0	58.44 ± 3.90	22.73 ± 0.	5.62 ± 0.	<1
10	Water	27.69 ± 0.98	8.10 ± 0.65	77.84 ± 4.55	61.46 ± 2.66	25.74 ± 2.97	5.95 ± 0.80
100		60.28 ± 1.18	47.60 ± 5.66	78.76 ± 7.00	77.90 ± 4.01	95.55 ± 4.76	-
1		21.74 ± 2.17	5.10 ± 1.02	65.79 ± 7.89	50.00 ± 1.97	29.63 ± 7.41	<1
10	(NH ₄) ₂ SO ₄	27.61 ± 0.76	9.70 ± 1.60	89.04 ± 4.61	76.49 ± 2.65	57.76 ± 5.41	33.46 ± 0.62
100		68.84 ± 5.96	47.10 ± 3.42	86.09 ± 2.25	81.36 ± 3.61	98.32 ± 6.34	92.70 ± 7.27

FIGURE 5

Chlorpyrifos disappearance from soil, as
affected by the initial concentration.

3. The effect of pesticides and environmental stress on ammonium oxidation in soil

The impact of pesticides on the biological cycles of the soil has been a matter of concern from the very beginning of the introduction of synthetic organic chemicals for crop protection (e.g. Wilson and Choudri, 1946). Because of the major role of nitrogen in plant nutrition and the interest in the optimization of the efficiency of the extensively used N-fertilizers, the effect of pesticides on soil microbial processes involved in nitrogen transformations in soil has received special attention. In spite of the considerable number of research papers and reviews concerning this issue over the last 40 years (e.g. Simon-Sylvestre and Fournier, 1979; Goring and Laskowski, 1982), the use of data to draw general conclusions, or predict the effect of pesticides is still very difficult.

It is generally accepted that one of the processes that are most affected by pesticides is nitrification. Soil nitrification is primarily mediated by the chemoautotrophic family Nitrobacteriaceae. These nitrifying bacteria derive energy required for growth from the oxidation of NH_4 or NO_2 . The ammonia-oxidizing species have an obligate CO_2 or HCO_3^- requirement for growth while some nitrite-oxidizing Nitrobacter species can utilize organic sources for growth (Schmidt, 1982).

3.A. CO_2 -nitrification relationships

The main environmental factors which limit nitrification in soil are inorganic N source, O_2 , CO_2 , pH and temperature. The effect of these factors on nitrification have been extensively studied (Focht and Verstraete, 1977), with the exception of CO_2 , which in soil has generally

been regarded to exceed the biological demand of the nitrifiers (Alexander, 1965). Buyanovsky and Wagner (1983) reported soil CO_2 concentrations in the field which ranged between <1.0 and 70 ml l^{-1} . Clark (1968) measured soil nitrification over a range of CO_2 concentrations and found that maximal rates occurred between 6 and 29 ml l^{-1} . Thus, under field conditions, CO_2 concentrations in the soil may be below or in excess of the optimum for maximal nitrification rates.

While studying pesticide effects on soil nitrification in closed vessels we observed that nitrification rates were considerably reduced when we simultaneously measured respiration using alkaline traps. Clark (1968) and Singh and Kanehiro (1972) also reported inhibition of nitrification in the presence of alkaline traps. The most reasonable explanation for this observation was that CO_2 absorption by the alkaline traps reduced the availability of CO_2 for nitrifier growth. In order to understand the relationship between CO_2 and nitrification in closed vessels we checked CO_2 concentration, NH_4^+ oxidation and nitrifier growth in the presence of alkaline traps.

The soil used was the Hamra soil described in Chapter 2.B. The incubations were done in hermetically closed 720 ml glass jars which contained 20 ml vials glued to the interior wall. A 40-g soil sample was added to each jar and moistened with either deionized water or an $(\text{NH}_4)_2\text{SO}_4$ solution to a constant water content equivalent to -0.1 MPa water potential. The NH_4^+ -N addition to the soil was 100 ug N g^{-1} . Ten ml of NaOH at different concentrations were added to the vials to absorb CO_2 . The incubations were done for 7 days at 27°C in a dark temperature-controlled room.

Soil samples, three replicates from each jar, were analyzed for NH_4^+ and $\text{NO}_3^- + \text{NO}_2^-$ by steam distillation (Bremner, 1965) and ammonia-oxidizing bacteria were estimated by the MPN method (Schmidt and Belser, 1982). All results are presented on an oven-dry soil basis. Air samples for CO_2 analysis were taken with a syringe through a rubber septum on the jar lid and injected into a CO_2 infra-red gas analyzer unit.

An estimate was made of the effect of the NaOH concentration in the CO_2 traps on nitrification after a 7-day incubation (Fig. 6). The amount of nitrification was similar (80%) for the control and 10 mM NaOH traps, although the CO_2 concentrations were quite different, 12.6 and 5.3 ml l^{-1} , respectively. In contrast, when the NaOH traps were 50 mM or greater, NH_4^+ -oxidation was less than 30% and CO_2 concentrations were 0.1 ml l^{-1} .

The dynamics of CO_2 evolution, NH_4^+ -oxidation and bacterial populations (NH_4^+ -oxidizers and total) were followed during a 7-day incubation. Again NH_4^+ oxidation and CO_2 concentrations were dramatically reduced in the presence of traps containing 50 and 500 mM NaOH (Fig. 7). Total bacterial populations were unaffected by the NaOH traps (7×10^7 CFU g^{-1} soil) while NH_4^+ -oxidizer numbers were considerably reduced for 4 days before reaching a similar level as the control.

Our results confirm the important role of CO_2 in the nitrification process. When CO_2 concentration was maintained below 0.1 ml l^{-1} by the alkaline traps, growth of the ammonia-oxidizer population and nitrification activity were reduced. Despite the low CO_2 concentrations, there was sufficient CO_2 or HCO_3^- in the soil solution to support growth of the NH_4^+ -oxidizer population. It should be noted that even in the control, CO_2 concentrations during exponential growth were lower than what is considered

the optimum for nitrification (Clark, 1968). CO_2 concentrations in soil, however, are likely to be considerably higher than the above-ground concentrations.

A clear understanding of the effects of CO_2 limitation on the NH_4^+ -oxidizer population is complicated by the inherent high statistical uncertainty of the MPN method. Two distinct growth patterns are consistent with the observed population variability: 1) a 4-day lag before the start of exponential growth, or 2) no lag phase, but a considerably reduced growth rate. The first growth pattern could represent selection for a minor NH_4^+ -oxidizing species which has a higher affinity for CO_2 . Five NH_4^+ -oxidizing species have been identified from soils (Schmidt, 1982), although it is unknown whether they have different affinities for CO_2 . The second pattern represents classical bacterial growth kinetics in which a single required nutrient limits growth (Monod, 1949). Bacteria can compensate for nutrient limitations by induction or depression of high-affinity uptake systems, however this is done at a high energy cost to the organism and will affect growth rates (Tempest and Neijssel, 1978).

Since N oxidation is commonly regarded as a growth-linked process, nitrification rates have often been used to determine nitrifier growth rates (Alexander, 1965). In our work we were surprised to find that the rate of NH_4^+ oxidation in the control appeared to increase after the nitrifier population had reached the stationary growth phase. Schmidt (1974) reported that NO_2^- -oxidation appeared to continue at an exponential rate after Nitrobacter winogradskyi had reached stationary growth in soil. In both soil studies, most of the N was oxidized during the stationary growth phase. A greater nitrification rate following the growth phase is

probably due to an increased energy demand for maintenance and waste metabolism (McLaren, 1971). Many of the conclusions regarding the behavior of nitrifying bacteria have been based on studies in nutrient solution or soil perfusion systems. Whether the energy demand for maintenance and waste metabolism by nitrifying bacteria is greater in static soil incubations is unknown and deserves further study.

Figure Legends

Fig. 6: CO_2 , NH_4^+ and $\text{NO}_3^- + \text{NO}_2^-$ concentrations in closed soil incubation vessels containing NaOH traps after 7 days incubation.

Fig. 7: CO_2 , NH_4^+ oxidation and NH_4^+ -oxidizer population dynamics as affected by NaOH traps.

Figure 6

Figure 7

3B. The effect of pesticides on ammonium oxidation in the Hamra soil

In general, following the addition of an ammonium source, the number of ammonium oxidizers gradually increases, up to a steady state, corresponding to the slow rate and the maximum rate phases of ammonium oxidation, respectively. These are followed by a decrease in the oxidation rate, corresponding to the depletion of the substrate (Walker, 1975). Since the rates of the first two phases may be affected by environmental factors (Sabey et al., 1969), the effect of the chemical and CO₂ stresses on these phases will be considered.

The quantitative evaluation of the stress effects was done by using the criteria proposed by K.H. Domsh (Greaves and Malkomes, 1980). These are "the amplitude of the maximal depression" (AMD), which is the maximal decrease in the activity of a biological system produced by the stress conditions, and "the maximal time deficit" which is the time required for the restitution of the normal microbial activity after the end of the stress condition. We considered the maximal time deficit for 90% restoration of the normal activity (TD₉₀).

The effect of the four pesticides investigated (Table 3), at different initial concentrations on the oxidation of the ammonium substrate was checked, both under optimal and under CO₂ stress conditions. Since for a great number of pesticides the recommended rates of application are between 1 and 10 ppm, concentrations in this range were used, as well as fivefold and tenfold higher concentrations.

Optimal incubation conditions The oxidation rate of ammonium as affected by the presence of pesticides at different initial concentrations is shown in Fig. 8. At 5 and 10 ppm, chlorpyrifos did not significantly

inhibit the oxidation process, although some effect on the slow rate phase is evident at 10 ppm initial concentration (Fig. 8A). The oxidation rate in both the slow rate and the maximum rate phases decreased in the presence of 100 ppm chlorpyrifos. However, this effect was temporary; the AMD was 37% and the TD_{90} 2.5 days only.

At all the concentrations tested, metolachlor inhibited the slow rate phase (Fig. 8B); after 4 days of incubation the inhibition was 13% at 5 and 10 ppm, 20% at 50 ppm, and 32% at 100 ppm. The maximum rate phase was not significantly affected at 5 and 10 ppm, but at 100 ppm the AMD and TD_{90} were 42% and 5 days, respectively. A slight inhibitory effect was also observed at 50 ppm; AMD 25%, and TD_{90} , one day.

Fenamiphos, at the initial concentrations of 5 and 50 ppm had no significant effect on the oxidation rate, except for a slight inhibitory effect on the slow rate phase (Fig. 8C). However, the oxidation rate significantly decreased in the presence of 100 ppm fenamiphos; the AMD was 46% and the TD_{90} was 5 days.

At 5 ppm initial dose, EPTC did not affect the oxidation rate, but at 50 ppm a slight inhibition of the slow rate phase occurred (Fig. 8D). At the high application rate the inhibition effect was significant - AMD 40% - but the time required for the restitution of normal biological activity was very short - TD_{90} 1.5 days.

The results presented above are in agreement with the conclusions of almost all the pertinent literature that application of herbicides and insecticides in the range of the recommended doses does not affect the nitrification rate in soil.

For higher application rates the data available are contradictory, even for the same compound, because of the great variability of soils and environmental conditions under which experiments are performed. In the present study all the pesticides tested, at an initial concentration of 100 ppm, inhibited ammonium oxidation. The inhibition was reversible, with AMD between 37 and 46% and TD_{90} no longer than 5 days. With all the pesticides the inhibitory effect was on the slow rate phase, and the nitrifying population reached a similar steady-state in the maximal rate phase (9-10 $mg\ kg^{-1}\ d^{-1}$).

The inhibitory effect of the pesticides tested seems to be related mainly to their persistence in the soil since the order of the magnitude of their inhibitory effect at the high concentration tested was similar to the order of their persistence: fenamiphos > metolachlor > chlorpyrifos > EPTC.

CO₂ stress conditions Fig. 9 shows the combined effect of CO₂ stress and pesticides on the oxidation rate of ammonium. The greater sensitivity of the ammonium oxidizers to pesticides under stress conditions is indicated by the inhibitory effect of even the low application doses. Both the slow and the maximum rate phases were affected at these application rates; the magnitude of the effect was dependent on the nature of the pesticide. At the initial concentration of 10 ppm, the TD_{90} was 12 days for chlorpyrifos and 2.5 days for metolachlor; at 5 ppm these values were 11 and 3 days for fenamiphos and EPTC, respectively.

At the high application rate, all the pesticides had a significant inhibitory effect. The AMD was 53-59% with chlorpyrifos, metolachlor and EPTC, and 70% with fenamiphos. The TD_{90} was 13-14 days for metolachlor and

EPTC. In this case, the effect of the CO₂ stress and pesticides on the oxidation rate of ammonium seems additive, since the time delay caused by the CO₂ stress was about 8 days, and that caused by pesticides under optimal incubation conditions was between 1.5 and 5 days.

The inhibitory effect of chlorpyrifos and fenamiphos at the initial dose of 100 ppm was much stronger. By taking into account the linear oxidation rate in the third and fourth weeks of incubation, the assumed TD₉₀ would be 59 days for chlorpyrifos and 64 days for fenamiphos. Such long time delays suggest that the combined effects of CO₂ stress and pesticides is synergistic; the delays were about fourfold longer than those expected from a mere additive effect.

Unlike the optimal incubation conditions, the magnitude of the combined effect of pesticides and CO₂ stress was not related only to the persistence of pesticides. Fenamiphos, which was the most persistent was also the most toxic, but the effect of chlorpyrifos was rather similar to that of fenamiphos, although it was much less persistent.

In conclusion, the four pesticides investigated affected the oxidation rate of an ammonium source added to the sandy Bet Dagan soil. The magnitude of the effect was dependent on the nature and persistence of pesticides, their application rates, and the existence of an additional stress condition. Since actually, stress conditions due to the fluctuations of environmental factors are very common, the impact of the combined effect of pesticides and environmental stress need to be considered.

In the range of the recommended application rates (1-10 ppm) the pesticides tested did not inhibit the ammonium oxidizing population under optimal incubation conditions, but they had an inhibitory effect under the

CO₂ stress condition. The maximal decrease in the activity of ammonium oxidizers was 25-30%, and the time required for the restitution of the normal activity varied between 3 and 12 days. The fact that, at these application rates, pesticides that did not inhibit ammonium oxidation under no stress situations might do so in a stress condition, must be considered for its agronomic implications. The magnitude of the effect of pesticides will probably be dependent on the magnitude of the stress condition.

At the high application rate (100 ppm)- ammonium oxidation activity was significantly depressed by all the pesticides, both under optimal and CO₂ stress incubation conditions. This high initial concentration is not only hypothetical; pesticide accumulation might occur under some circumstances, as for example in the case of nonhomogeneous or repeated applications, or by accumulation around a point source of applications. Without stress, the maximal depression due to pesticides was 37-46% and the time deficit did not exceed 5 days. Under CO₂ stress the maximal depression was 53-70% and the time deficit was 13-14 days for metolachlor and EPTC, and 59-64 days for chlorpyrifos and fenamiphos. In the latter case, the effect of pesticides and CO₂ stress was synergistic. In all cases, the inhibitory effect decreased with time due to the disappearance of pesticides and probably also to the development of more resistant ammonium oxidizers.

The long delays in the time required for the restitution of a normal microbial activity as those caused by fenamiphos and chlorpyrifos can have significant agronomic impacts on plant nutrition, and nitrogen losses through leaching and denitrification. The possible synergistic effect of chemical and environmental stresses on ammonium oxidation point out to the

need for studies of the combined effect of such stresses, for a more realistic evaluation of the side-effects of pesticides.

FIGURE 8

The effect of pesticides on ammonium oxidation (A-chloropyrifos; B-metaloachlor; C-fenamiphos; D-EPTC).

FIGURE 9

The effect of pesticides and CO_2 stress on ammonium oxidation.
(A-chloropyrifos; B-metaloachlor; C-fenamiphos; D-EPTC).

3.C. Ammonium oxidation in the Tifton loamy sand soil

The Tifton soil which has an acidic pH (4.2 in a 1:2.5 slurry) is usually amended in the field with dolomitic limestone containing 29.3% Ca and 5.1% Mg. In the laboratory a soil sample was amended with a mixture containing 81 and 19% CaCO_3 and MgCO_3 , respectively. Distilled water was added to bring the soil moisture up to 80% field capacity, and the soil was incubated at room temperature for one month. Then, it was air-dried and sieved through a 2-mm sieve. The pH of the amended soil was 7.1. The experimental procedure to check ammonium oxidation and the effect of pesticide and CO_2 stress was previously described (3B).

As compared to the Hamra soil, Tifton soil has a lower nitrification capacity. The time required for the oxidation of 100 ppm added ammonium was about 25 days, with a slow rate phase of 5 days, and a rate of $13 \text{ mg kg}^{-1} \text{ d}^{-1} \text{ NH}_4^+-\text{N}$ in the maximal rate phase (Fig. 10). Under CO_2 stress conditions, the duration of the slow rate phase increased about fivefold, as compared to only a 2.5-fold increase in the Bet Dagan soil. The calculated time required for the oxidation of 100 ppm ammonium under CO_2 stress conditions will be about 100 days. The intensity of the CO_2 stress measured by AMD and TD_{90} was 100% and 77 days, respectively; the inhibitory effect was reversible. According to the interpretation of Greaves and Malkomes (1980), delay periods of 30 days following a 90% depression are normal in natural environments. However, a delay longer than 60 days might indicate critical situations.

The effect of pesticides on ammonium oxidation in the Tifton soil, under optimal and CO_2 stress incubation conditions was checked by using chlorpyrifos and fenamiphos, at initial concentrations of 5 and 50 ppm.

Under optimal incubation conditions the oxidation rate of ammonium was not affected by the presence of chlorpyrifos. Fenamiphos slightly decreased the rate of the slow oxidation phase only. It was no significant difference between the two initial concentrations checked (Fig. 10). Neither chlorpyrifos, nor fenamiphos affected the oxidation rate of ammonium in soil incubated for 45 days under CO₂ stress conditions.

Figure 10

The effect of fenamiphos and CO_2 stress on ammonium oxidation in Tifton loamy sand soil.

4. The combined effect of herbicides and nitrogen source on plants

4.A. Metolachlor

The chloroacetamide herbicides are applied for control of preemergent grasses and some broadleaf weeds. They are general growth inhibitors affecting root and shoot growth following seed germination.

Metolachlor is considered a very effective and rather safe herbicide; nevertheless, there have been reports on crop injury (Deal and Hess, 1980; Pillai, Davis and Truelove, 1979; Braverman, Lavy and Talbert, 1985). α -Chloroacetamides are known to inhibit: a) seed germination and development (Pillai et al., 1982); b) protein synthesis (Deak et al., 1980); c) lipid synthesis (Mellis et al., 1982) and α -amylase synthesis (Devlin and Cunningham, 1970). Cucumber plants were shown to be moderately susceptible to metolachlor (Mellis, Pillai, Davis and Truelove, 1982; Sloan and Camper, 1986) at concentrations of 10^{-5} M or higher. Organic chemicals such as herbicides may affect soil properties, and as a result the availability of nutrients to plants, and consequently their nutritional requirements can also be affected (Hance, 1981). For example, Wilson and Stewart (1973) reported that P uptake has been affected by trifluralin, a herbicide that reduces root growth. Notable restrictions in nutrient uptake were observed in corn shoots at metolachlor levels above 3.5×10^{-6} M (Ellis, Wilson, Mascianica and Janssen, 1983).

Preliminary research in our laboratory (unpublished data) showed growth retardation of cucumber seedlings exposed to 3.65×10^{-6} M metolachlor.

Nitrogen is central to the growth and development of all crop plants and is required in large amounts. Plants take up nitrogen either as nitrate (NO_3^-) or as ammonium (NH_4^+) ions. The ratio $\text{NO}_3^-/\text{NH}_4^+$ supplied to plants is of great importance as it influences crop yield and the levels of carbohydrates, amino acids and proteins (Hiatt, 1978). Usually less than optimum growth was found with NH_4^+ .

The purpose of this study was to further investigate the effect of subtoxic concentrations of metolachlor on cucumber plants grown in nutrient solutions differing in their $\text{NO}_3^-/\text{NH}_4^+$ ratio and to determine the reason for the observed inhibition.

The experimental procedure was as follows:

Cucumber plants (Cucumis sativus L. cv. 'Delilah') were grown in a growth chamber at $25 \pm 1^\circ\text{C}$ and $50 \pm 5\%$ relative humidity in continuously aerated half-strength Hoagland solution (Arnon, 1938). A light intensity of $450 \text{ uE m}^{-2} \text{ s}^{-1}$ at the plant tops was provided by fluorescent lamps for 13 h per day. The $\text{NO}_3^-/\text{NH}_4^+$ ratio in the Hoagland solution was 15:1. In some treatments this ratio was altered to 5:5 by replacing the nitrate source by ammonium nitrate; these solutions will be referred to as ammonium nitrate.

The stock solutions of the nutrient media were:

Hoagland solution

Ammonium nitrate

Sequestrene

Sequestrene

Micro-elements

Micro-elements

As it can be seen, the concentrations of K^+ in ammonium nitrate was reduced, but was still within the limits of plants requirements. Initial N concentration in all the nutrient solutions was 126 ppm. Half of the seedlings were transferred to nutrient solutions containing 0.05 ppm ($1.75 \times 10^{-7} M$) metolachlor and the others served as controls. Solutions were changed weekly, their pH adjusted to 6.5 and deionized water was added regularly to replace loss due to transpiration.

For metolachlor analysis, fresh plant material (3 g) was homogenized in 15 ml of 1% toluene, agitated for 1 h and centrifuged at 15000 rpm for 15 min. The procedure was repeated following the addition of 30% (w/v) ammonium sulfate. All steps were carried out at $4^{\circ}C$. The supernatants were extracted with 5 ml ethyl acetate and dried over sodium sulfate. Metolachlor was determined by gaschromatography, as previously described (2.B.).

The following physiological measurements were carried out:

Plant growth: Once a week, six plants were sampled and weighed to determine plant growth and accumulation of dry matter. The plants were separated into leaves and roots and their fresh or dry weight accumulation was followed individually.

Leaf area: Samples of 50 leaf discs, 1 cm in diameter, were removed and immediately weighed. Total leaf area was calculated knowing the weight of a certain leaf area and the total leaf weight.

Ion content: Ion content was determined on dry material. One hundred milligram samples of dry material were wet ashed with H_2SO_4 and H_2O_2 for analysis of total organic N and with HNO_3 for Ca^{+2} . For potassium and nitrate determination, similar samples were extracted with water. K^+ was determined with an Evans electroselenium flame photometer, Ca^{+2} with a Perkin Elmer 460 atomic absorption spectrophotometer and Cl^- with a Buckler-Cotlove chloridometer. The NO_3^- content was determined by steam distillation (Bremner, 1965).

N content: Total N was determined by a micro-Kjeldahl method (Stubblefield and DeTurk, 1940).

Protein content: Leaf protein was measured in crude extracts by the method of Lowry et al. (1951), based on a standard bovine serum albumin calibration curve.

CO_2 fixation by leaves: Leaf photosynthesis and initial transpiration were measured with a Licor 6000 apparatus.

A response curve of cucumber plants to a range of metolachlor concentration (0-20 ppm) was carried out for a one-week period of growth. Root growth was severely inhibited already at 0.5 ppm metolachlor (Fig.11). The percentage of inhibition was 35 and 80 for leaves and roots, respectively. Following these results, a more detailed response curve was tested, especially at concentrations below 0.5 ppm, with plants grown in two nutrient solutions. Growth was inhibited even at 0.04 ppm metolachlor in both growth media (Fig.12). As expected, root growth was more sensitive to the herbicide than the leaves. A similar effect has been shown in sorghum (Wilkinson, 1981), peas (Deal and Hess, 1980), soybeans (Gerber et

al., 1987), etc., but contradicts that reported by Pillai et al (1979) on cucumber seedlings treated with 0.3 ppm metolachlor. Determination of N and other ions in plant organs did not show nutrient deficiency (data not shown). Following these results we decided to carry out all our experiments with plants exposed to 0.05 ppm metolachlor.

The response of plant growth, expressed as accumulation of fresh weight, was followed for 4 weeks in two nutrient solutions differing in their $\text{NH}_4^+:\text{NO}_3^-$ ratio and in the presence or absence of 1.75×10^{-7} M metolachlor. Leaf growth showed 15% inhibition, 2 weeks after exposure to the herbicide (Fig. 13A), and was further inhibited during the third week of growth (by 28 and 20% in Hoagland solution and ammonium nitrate, respectively).

At the end of 4 weeks of growth, only a slight inhibition (9%) in leaf weight was obtained in plants grown in ammonium nitrate. Accumulation of fresh weight in roots was significantly inhibited by metolachlor starting with the first week of growth (Fig. 13B). This occurred to a greater extent in Hoagland solutions.

The percentage of inhibition was, respectively, 19, 47 and 42 for the first, second and third weeks of growth in Hoagland solution, and 32, 36 and 27 for root growth in ammonium nitrate. Full recovery of root weight was obtained in plants grown in Hoagland solutions after the forth week, while a 10% inhibition could still be observed in all plant organs grown in NH_4NO_3 in the presence of metolachlor. In general, well-developed plants suffered more from the herbicide at the beginning of their growth cycle, but also recovered faster from the stress.

Growth was also affected by the $\text{NO}_3^-/\text{NH}_4^+$ ratio, regardless of the presence of the herbicide (Fig. 13). Leaf growth was reduced by 9 and 20%

after 3 and 4 weeks in ammonium nitrate ($5\text{NO}_3:5\text{NH}_4$) solutions when compared with growth in Hoagland solution. Root growth was severely inhibited in ammonium nitrate; 48.6% after the third week and 32.1% after the fourth one (Fig. 13B). These results are similar to those reported in the literature (Van de Driessche and Dangerfield, 1975; Reisenauer, 1978;; Ganmore-Neumann and Kafkafi, 1983). Plants grown in ammonium nitrate developed necrotic areas on their leaves that might be attributed to a toxic NH_4^+ accumulation. Ammonium tolerance limits are generally low (Givan, 1979) and dependent on the pH of the root medium. The pH of the external medium showed a tendency toward an increase in Hoagland solution and a corresponding decrease in ammonium nitrate (Table 17). The low pH of the Hoagland solutions after the first week, is due to technical problems with the column that supplied the distilled water to prepare these media.

Dry matter accumulation showed a different effect (Fig. 14). As expected, the accumulation of dry matter increased with age and was non-significantly stimulated by the herbicide, reminiscent of the response to an imposed stress. Thus, after 4 weeks, dry matter values exceeded those of the controls, mainly in leaves (Fig. 14A). Roots of plants grown in ammonium nitrate gained more dry weight than those grown in Hoagland solution.

Metolachlor almost did not affect NO_3^- content in leaves. During the first week of growth, leaves of plants exposed to metolachlor or grown in ammonium nitrate accumulated more free NO_3^- (Fig. 15A). Ammonium nitrate plants always accumulated less NO_3^- in their organs, mainly in their roots

(Fig. 15B). There was almost no effect of the herbicide's presence in the nutrient solutions.

Total N content as determined by wet ashing, in the cucumber plants was not significantly affected by metolachlor (Fig. 16). In general, the N content of plants grown in ammonium nitrate was much higher than that of those grown in Hoagland solution. A similar trend was found by Kirkby and Mengel (1967) with tomato plants. This increase might be partly attributed to concentration effects because of lower growth rates in ammonium nitrate.

Since nutrient uptake might be affected by herbicides that reduce plant growth (Wilson and Stewart, 1973), the accumulation of K^+ , Cl^- and Ca^{+2} in plant organs was determined. Potassium content in leaves was increased in the presence of metolachlor in both nutrient solutions (Fig. 17), but was drastically reduced in ammonium nitrate nutrition as compared with Hoagland solution. It has already been reported that increased levels of NH_4^+ are associated with slower growth and intake of K^+ , sometimes leading to K^+ deficiency (Ajayi, Maynard and Barker, 1970). The concentration of K^+ in the leaves decreased as may be expected during leaf expansion and maturation (Mengel and Kirkby, 1982). Cucumber plants grown in Hoagland solution had much higher tissue concentrations of Ca^{+2} than those grown in ammonium nitrate (Fig. 18). This finding is in good agreement with other reports in the literature (Kirkby and Mengel, 1967; Van den Driessche and Dangerfield, 1975). The increase of Ca^{+2} content with age is strange and without explanation. Metolachlor reduced Ca^{+2} content mainly in ammonium nitrate treatments. Besides NO_3^- , the only anion accumulation determined was that of Cl^- . Higher concentrations of Cl^- were obtained in

ammonium nitrate grown plants (data not shown) which might be attributed to the addition of Cl^- to the growth medium since $\text{Ca}(\text{NO}_3)_2$, one of the components of Hoagland solution, was replaced here by $\text{Ca}(\text{Cl}_2)$. For any unexplained reason, metolachlor slightly increased Cl^- content in plant tissue, mainly in leaves, but this effect was not consistent. One explanation for this might be that a process of dechlorination of the herbicide occurs during metolachlor degradation. The mechanism of detoxification is still not understood.

It is known that one of the major processes controlling plant growth is photosynthesis. Chandler et al. (1972) have already reported that photosynthesis is not sensitive to α -chloroacetamides. On the other hand, high concentrations of metolachlor were shown to inhibit photosynthesis in *Chlorella* (Pillai and Davis, 1975). Although we used much lower concentrations of the herbicide, CO_2 fixation was significantly reduced in cucumber seedlings (Table 18). Leaf area was also remarkably affected following plant exposure to metolachlor (Table 18). Since the inhibition of leaf expansion is more serious than the reduction in weight, it is obvious that in treated plants, leaf thickness was increased. This is a well known behavior of stressed plants.

The leaf protein content per unit leaf weight of the cucumber plants was not affected at the first two weeks of growth (data not shown), suggesting that the inhibition of photosynthesis was due to a direct effect on the photosynthetic apparatus.

Biosynthesis of enzymes and storage proteins is the main process in which the N taken up by the plants is involved. Although the N content in the plants was not seriously affected by metolachlor, it was of interest

to determine its possible effect on protein production. In ammonium nitrate grown plants, metolachlor decreased total leaf protein content during the third and fourth weeks of growth by 29 and 36%, respectively (Fig. 19). This effect occurred also in plants grown in Hoagland solution, but at a lower level, 13 and 16%, for the third and fourth week of growth, respectively. Inhibition of protein synthesis by metolachlor in oats was reported by Deal, Reeves, Larkins and Hess (1980). One possible explanation for this is the effect on CO_2 fixation, which was also reduced by 16% by metolachlor (Table 18). It is known that the conversion of NO_3^- to NO_2^- , the first step in N assimilation, may be facilitated by primary products of photosynthetic CO_2 fixation supplying NADH as the reducing power.

Leaf protein content increases with age in all treatments. Enhanced protein synthesis was found between the first and second weeks of growth (five-fold in Hoagland, six to seven-fold in ammonium nitrate). This increase was only two times between the second and third weeks and between 1.3 and 1.4 times during the last week (fourth) of growth. Throughout the entire period of the experiments, ammonium nitrate grown plants contained much more protein in their leaves than did the plants grown in Hoagland solution. The reason for this is probably a greater availability of NH_4^+ and a lesser amount of NO_3^- that had to be taken up and metabolized. The concentration of protein per unit of leaf weight also decreased, by approximately 27%, between the third and fourth weeks of growth in both nutrient solutions. As this was the period when leaf weight (Fig. 13A) in plants grown in Hoagland solution recovered, total protein content in these leaves seemed less affected by the herbicide (total leaf

protein was obtained by multiplying mg protein per unit leaf weight by total leaf weight). The inhibition of protein synthesis lasted for a long period of time and could be found also at the time when metolachlor was no longer detected in the leaves. The disappearance of metolachlor from the leaves started after the second week of growth (data not shown). To sum up, the exact reason for the reduction in protein content is still not clear and requires further investigation.

The most striking response obtained in this study was the accumulation of metolachlor in cucumber leaves following plant exposure to such low concentrations (Table 19). It can be seen that in the first week of growth, the plants were taking up 87% and 66% of the total amount of the herbicide present in the Hoagland solution or NH_4NO_3 growth medium, respectively.

The accumulation of metolachlor in the leaves is an active process and not a passive uptake of the compound followed by xylem transport. If the latter were the case, and taking into consideration a total transpiration per plant of $2.92 \text{ mg H}_2\text{O/m}^2 \times \text{sec}$, the concentration of the herbicide should be 0.15 ppm. A process of degradation of metolachlor took place between the second and third weeks when leaf growth was mostly inhibited. This statement is based on the appearance of three new peaks on the chromatograms, which have not yet been identified. It might be suggested that at the first step of detoxification, the metabolites produced are more toxic than the parent compound and only further on is this process completed, followed by full recovery of growth.

When metolachlor concentration was determined per unit of leaf weight, a gradual weekly reduction could be observed (Fig. 20). Metolachlor uptake

and translocation to the shoot were enhanced during the first week of growth in Hoagland solution. The accumulation of metolachlor in the leaves was further proved by using labelled material. Only traces could be found in the roots and most of the ^{14}C -metolachlor applied was detected in the leaves. Small concentrations of metolachlor such as 0.25 and 0.56 ug/g fresh weight were found in cucumber fruits when plants were grown in Hoagland solution or NH_4NO_3 , respectively.

In conclusion, concentrations below 10^{-6} metolachlor, considered to be subtoxic for cucumber plants, had a remarkable effect on plant growth, especially shortly after exposure to the herbicide. Thus, the concept that these concentrations are harmless to cucumber should be reconsidered. The mechanisms responsible for this growth inhibition is still not well understood and has to be further investigated.

Table 17: The effect of $\text{NO}_3^-/\text{NH}_4^+$ ratio on the pH of the growing media.

Starting pH was 6.5-7.0. The pH was measured at the end of the week before new solutions were prepared.

Treatments	Weeks			
	I	II	III	IV
Hoagland solution	4.4	6.8	6.8	6.8
Hoagland solution + metolachlor	4.6	7.2	7.3	7.2
Ammonium nitrate	4.4	4.7	4.0	4.2
Ammonium nitrate + metolachlor	4.2	4.9	4.2	4.5

Table 18: The effect of metolachlor on leaf area and photosynthesis of cucumber plants.

Treatment	Photosynthesis ¹ (mg CO ₂ xm ⁻² xsec)	Inhibition (% of control)	Leaf area (cm ²)	Inhibition (% of control)
Hoagland	0.43(±0.06)	100	301	100
Hoagland	0.36(±0.05)	84	252	84
+ Metolachlor				
NH ₄ NO ₃	0.37(±0.04)	100	335	100
NH ₄ NO ₃	0.30(±0.01)	81	245	74
+ Metolachlor				

Table 19: Total metolachlor content in cucumber leaves. The results are expressed as ppm metolachlor. Six plants were grown in a 5L container at the concentration of 0.05 ppm metolachlor, the leaves of which were weekly sampled.

Treatment	Weeks			
	1	2	3	4
Hoagland	217	211	30	30
NH ₄ NO ₃	166	160	22	0

List of Figures

Fig. 11: Response curve of cucumber plants to metolachlor. Standard errors of the means are given in numbers about each observation on the curves.

Fig. 12: Plant growth in the presence of different concentrations of metolachlor. A = Hoagland solution; B = Ammonium nitrate.

Fig. 13: The response of fresh weight accumulation in the leaves (A) and roots (B) of cucumber plants to exposure to 0.05 ppm metolachlor. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor; 3) ammonium nitrate; 4) ammonium nitrate + metolachlor. Averages of six replicates.

Fig. 14: Dry matter accumulation in the leaves (A) and roots (B) of cucumber plants exposed to 0.05 ppm metolachlor. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor; 3) ammonium nitrate; 4) ammonium nitrate + metolachlor. Average of six replicates.

Fig. 15: The effect of metolachlor on free NO_3^- content in the leaves (A) and roots (B) of cucumber plants. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor; 3) ammonium nitrate; 4) ammonium nitrate + metolachlor. Average of six replicates.

Fig. 16: Total N content in the leaves (A) and roots (B) of cucumber plants as a function of $\text{NO}_3^-/\text{NH}_4^+$ ratio and the presence of metolachlor in the growth medium. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor; 3) ammonium nitrate; 4) ammonium nitrate + metolachlor. Average of six replicates.

Fig. 17: The effect of metolachlor on K^+ content in the leaves (A) and roots (B) of cucumber plants. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor; 3) ammonium nitrate; 4) ammonium nitrate + metolachlor. Average of six replicates.

Fig. 18: Calcium content in the leaves (A) and roots (B) of cucumber plants as a function of $\text{NO}_3^-/\text{NH}_4^+$ ratio and presence of metolachlor in the nutrient solution. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor; 3) ammonium nitrate; 4) ammonium nitrate + metolachlor. Average of six replicates.

Fig. 19: The effects of metolachlor on protein content in cucumber leaves. The results are averages of four replicates and express total leaf protein obtained by multiplying content per leaf unit by total leaf weight. Treatments: 1) Hoagland solution; 2) Hoagland solution + metolachlor.

Fig. 20: Metolachlor concentration in cucumber leaves as a function of age and the growing media. Leaf samples were removed weekly, extracted and the herbicide content determined by gaschromatography.

Figure 11

FIGURE 12A

FIGURE 12B

FIGURE 13

Figure 14

FIGURE 15

FIGURE 16

FIGURE 17

FIGURE 18

FIGURE 19

Figure 20

4.B.EPTC

EPTC, a thiocarbamate herbicide, is widely used to control preemergence of annual grasses and broadleaf weeds. Its main use is for grass suppression in orchards (Young, 1985), alfalfa (Bell, 1977), potatoes (Vitolo et al., 1982) and other vegetables or ornamentals. Although it is considered a rather safe herbicide, reports on crop injury are available (Holmsen, 1980; Donald et al., 19789; Kvasov and Nikulnikov, 1985), when EPTC concentration was 10^{-5} or higher. EPTC interferes with respiration, increases peroxidase activity, changes starch and lipid contents and leads to chlorophyll accumulation (Jamil and Devi, 1986; Weinberg and Castelfranco, 1975).

The purpose of this study was to investigate the effect of low concentrations of EPTC on cucumber plants grown in nutrient solutions differing in their $\text{NO}_3^-/\text{NH}_4^+$ ratio.

The experimental procedure was as described in 4.A., and the analytical method for EPTC as in 2.B.

A response curve of cucumber seedlings to EPTC concentrations ranging from 0 to 20 ppm was obtained after plant exposure for 6 days. This supplied us preliminary information on cucumber sensitivity to EPTC as no such information is available. Exposure to only 0.1 ppm EPTC resulted in a remarkable inhibition of both shoot and root growth (Fig. 21). Shoot growth was reduced by 36% and root growth by 20%.

Similar results were reported by Holmsen (1980) with corn treated with EPTC at a range of 0.28 to 28 ppm. Following these results we decided to

carry out all the experiments at a concentration of 0.05 ppm ($3 \times 10^{-7} \text{M}$) EPTC.

The effect of exposure to EPTC on plant growth was determined with cucumber plants grown in three different nutrient solutions, Hoagland, ammonium nitrate and urea. The treatment of urea enabled to substitute one main ionic component of the nutrient solution by an undissociable molecule. It was thus possible to compare systems in which the main nutrient taken up by the plants was in the form of an anion, molecule or cation. Accumulation of leaf fresh weight was mainly affected in plant growth in urea and ammonium nitrate (Fig. 22A).

Leaf weight slightly decreased after three weeks in Hoagland solution in the presence of EPTC and growth was even stimulated by the herbicide within four weeks. Similarly, enhancement of stem growth by EPTC was observed in corn (Donald et al., 1979). EPTC significantly reduced leaf growth in urea and ammonium nitrate (23 and 30% respectively) after three weeks. An inhibition of about 15% in both media could still be found after the fourth week of growth. At the same period of time, a remarkable reduction in leaf growth was obtained as a function of $\text{NO}_3^-/\text{NH}_4^+$ ratio, mainly in urea. The reason for this phenomenon might be a difference in the nutrient uptake by the plants. It is known that the rate of urea uptake is less than that of NH_4^+ (Heutschel, 1970) or NO_3^- (Kirkby and Mengel, 1970). Moreover, cucumber is a plant that doesn't have urease in the root (Bollard, 1959), so that the urea taken up by the plant has to be translocated to the leaves where it is metabolized. No difference could be detected within the first two weeks of growth in Hoagland solution or in ammonium nitrate as it is known that young plants absorb NH_4^+ more readily than NO_3^- and as the plant

ages, the converse is true (Michael et al., 1970). Older plants grown in ammonium nitrate developed necrotic areas on their leaves, that might be attributed to a toxic NH_4^+ accumulation. Ammonium tolerance limits are generally low (Givan, 1979) and dependent on the pH of the root media. The pH of the external media showed a tendency toward an increase in Hoagland solution and a corresponding decrease in urea and ammonium nitrate (Table 20). Accumulation of fresh weight in roots was significantly inhibited by EPTC in plants grown in urea and especially in ammonium nitrate (Fig. 22B). This inhibition was more severe than in leaves. After four weeks, the percentage of inhibition was 27 and 19 for urea and ammonium nitrate, respectively. Root growth was affected by the $\text{NO}_3^-/\text{NH}_4^+$ ratio throughout the entire experiment.

Accumulation of dry matter in leaves showed no response to EPTC in all nutrient solutions (Fig. 23A). Root dry matter content was increased by the herbicide and by the $\text{NO}_3^-/\text{NH}_4^+$ ratio, being lowest in roots grown in Hoagland solution (Fig. 23B).

Nitrate content in plants was increased by EPTC, mainly after the fourth week (Fig. 24). Ammonium nitrate treated plants always accumulated less NO_3^- in their organs, and as expected, only traces could be found in urea treated plants. Nevertheless, total N content was not affected by EPTC (Fig. 25). A trend of higher amount of N in the leaves of ammonium nitrate treated plants was observed (Fig. 25A), similar to that obtained by Kirkby and Mengel (1967) with tomato plants and by Jung et al. (1972) with corn.

Since nutrient uptake might be affected by herbicides that reduce plant growth (Wilson and Stewart, 1973) as well as the accumulation of ions by the forms of N supplied (Barker and Manyard, 1972), the content of K^+ ,

Ca^{+2} and Cl^{-} in plant organs was determined. EPTC slightly increased K^{+} content mainly in the roots (Fig. 26B) in all nutrient solutions. The $\text{NO}_3^{-}/\text{NH}_4^{+}$ ratio remarkably affected its content; the content of K^{+} in the leaves was decreased by 34 to 45% in urea and by 56 to 69% in ammonium nitrate as compared with Hoagland solution (Fig. 26A). The same effect was found in cucumber roots. These results are in good agreement with those reported by Barker and Maynard (1972) who also showed a significant effect of N nutrition. An even more dramatic effect was found with Ca^{+2} content (Fig. 27). Ammonium nutrition suppressed Ca^{+2} accumulation in cucumber leaves and roots by 98% as compared with nitrate nutrition. A very non-significant decrease in Ca^{+2} content was observed in leaves from plants grown in Hoagland solution (Fig. 27A). Higher concentration of Cl^{-} were found in plants grown in urea (data not shown), but was not changed by the exposure to EPTC.

One major process that controls growth in plants is photosynthesis. Thus, it was of interest to determine any possible effect of the herbicide on the CO_2 fixation. Moreover, it is known that EPTC interferes with respiration and at certain concentrations it leads to a decrease in the chlorophyll content (Jamil and Devi, 1986). Photosynthesis was inhibited by the herbicide in plants grown in urea or ammonium nitrate by 36 and 27% respectively (Table 21). It is of interest to mention that there was no direct correlation between leaf growth and CO_2 fixation in the first two weeks of growth, as EPTC affected accumulation of leaf fresh weight only in ammonium nitrate treatment (Fig. 22A). A reduction in photosynthesis of about 16% was found in urea and ammonium nitrate grown plants in the absence of EPTC. Higher net photosynthesis in NO_3^{-} fed plants was already

reported for other plants, as for example, beans (Marques et al., 1983). However, the main effect of $\text{NO}_3^-/\text{NH}_4^+$ ratio is a different distribution of the photosynthetically fixed carbon (Kanazawa et al., 1972). In all nutrient solutions, leaf area was significantly reduced in the presence of EPTC (Table 21). Leaf expansion was inhibited only in urea grown plants. The response of the leaf conductance as well as the transpiration rates in the EPTC treated plants is a typical response to an imposed stress, followed by a closure of the stomata.

Biosynthesis of enzymes and storage proteins is the main process in which the N taken up by the plants is involved. Although N content was not affected by EPTC (Fig. 25) the inhibition of CO_2 fixation suggested that there is an effect on the protein metabolism of the plants exposed to the herbicide. Total leaf protein content was reduced during the third week of growth in all nutrient solutions (Fig. 28). Inhibition of protein synthesis by EPTC was already shown in barley segments exposed to 2 ppm (Mann et al., 1965). Plants grown in urea contained much lower levels of protein throughout the entire experiment than those grown in Hoagland solution or ammonium nitrate. Plants grown in ammonium nitrate also contained less protein during the third and fourth weeks of growth, than plants grown in Hoagland. The reason for this is not clear and has to be further investigated.

In conclusion, low concentrations of EPTC, such as 10^{-7}M were found to be toxic to cucumber plants grown in urea or ammonium nitrate, leading to a remarkable reduction in growth and nutrient accumulation. This effect cannot be attributed to the accumulation of the herbicide in plant organs, as only traces of EPTC could be detected in leaves or stems.

Table 20: The pH of the growing media as a function of $\text{NO}_3^-/\text{NH}_4^+$ ratio.

Starting pH was 6,5-7,0.

Treatments	<u>Weeks</u>		
	II	III	IV
Hoagland Solution	6.8	6.8	6.8
Hoagland Solution + EPTC	7.2	7.2	7.3
Urea	4.32	4.25	4.23
Urea + EPTC	4.09	4.33	4.47
Ammonium nitrate	4.66	4.24	4.72
Ammonium nitrate + EPTC	4.32	4.23	4.01

Table 21: The effect of EPTC on the photosynthesis, transpiration, leaf conductance and area of cucumber plants grown in three different nutrient solutions. Plants were two weeks old when sampled. Standard errors of the means are given in parenthesis. Averages of ten replicates.

Treatment	Photosynthesis $\text{mgCO}_2/\text{m}^2 \times \text{sec}$	Leaf area cm^2/plant	Transpiration $\text{mg H}_2\text{O}/\text{m}^2 \times \text{sec}$	Conductance mm/sec
Hoagland solution	0.43 (0.08)	140 (10)	246 (13)	1.56 (0.06)
Hoagland solution + EPTC	0.43 (0.07)	135 (6)	217 (11)	1.37 (0.05)
Urea	0.36 (0.07)	70 (5)	210 (14)	2.49 (0.19)
Urea + EPTC	0.23 (0.04)	60 (3)	192 (7)	1.22 (0.05)
Ammonium nitrate	0.37 (0.08)	158 (10)	305 (26)	2.10 (0.16)
" " + EPTC	0.27 (0.08)	100 (8)	235 (10)	1.42 (0.06)

Figure Legends

Fig. 21: The response of shoot and leaf growth of cucumber plants exposed to different concentrations of EPTC. Standard errors of the means are given above each curve. Average of six replicates.

Fig. 22: Accumulation of fresh weight in plants exposed to 0.05 ppm EPTC in three nutrient solutions. Treatments: 1) Hoagland solution; 2) Hoagland solution + EPTC; 3) Urea; 4) Urea + EPTC; 5) Ammonium nitrate; 6) Ammonium nitrate + EPTC. A = leaves; B = roots. Average of six replicates. Standard errors of the means are presented above each bar.

Fig. 23: Dry matter accumulation in the leaves (A) and roots (B) of cucumber plants exposed to 0.05 ppm EPTC. Treatments: as in Fig. 22. Average of six replicates.

Fig. 24: The effect of EPTC on NO_3^- content in the leaves (A) and roots (B) of cucumber plants. Treatments: as in Fig. 22. Average of six replicates.

Fig. 25: Total N content in the leaves (A) and roots (B) of cucumber plants as a function of $\text{NO}_3^-/\text{NH}_4^+$ ratio and the presence of EPTC in the growth media. Treatments: as in Fig. 22. Standard errors of the means are presented above each bar. Average of six replicates.

Fig. 26: The effect of EPTC on K^+ content in the leaves (A) and roots (B) of cucumber plants. Treatments: as in Fig. 22. Standard errors of the means are presented above each bar. Average of six replicates.

Fig. 27: Calcium content in the leaves (A) and roots (B) of cucumber plants exposed to 0.05 ppm EPTC. Treatments: as in Fig. 22. Standard errors of the means are presented above each bar. Average of six replicates.

Fig. 28: The effect of EPTC on total leaf protein content. The results are averages of four replicates and express total leaf protein obtained by multiplying protein content per leaf unit by total leaf weight. Treatments: as in Fig. 22. Standard errors of the means are presented above each bar.

FIGURE 21

FIGURE 22

FIGURE 23

FIGURE 24

FIGURE 25

FIGURE 26

FIGURE 27

FIGURE 28

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5. Fertigation and chemigation - Field and greenhouse experiments

The field and greenhouse experiments were carried out at the Coastal Plain Experiment Station, Tifton, Georgia. The general research objective was to develop the required technology for the combined application of fertilizers and pesticides along with irrigation by both sprinkler and drip irrigation systems. This included the development or modification of equipment, comparing irrigation water rates and varying methods of injection to determine agrichemical distribution in the soil.

5.A. Drip Irrigation

The first several months of 1986 were spent planning, designing and fabricating equipment that would allow small plot research chemigation through drip irrigation. The final equipment design to supply water for drip irrigation research was a small pressurized tank and a nurse supply tank containing water, mounted on a 2-wheel trailer for mobility. The small water tank was pressurized with an air compressor powered by a portable generator that delivered water to the drip irrigation parts at a controlled pressure of 15 psi. This design allowed us to select an experimental site without restrictions to water supply or power.

Commercially available water supply filters with a 1200 ml capacity were adapted as injection containers. An outlet with a disc orifice was constructed in the bottom of each container, so that the amount of chemical mixture could be regulated by orifice size and air pressure applied through an air compressor. The injection containers were capable of delivering 1200 ml to the drip irrigation system from a matter of minutes (approximately

10) to about one hour. The actual rate of injection was determined by the specific research objective.

Small plot cochemigation drip irrigation research was conducted on a Tifton loamy sand (fine, loamy, siliceous, Plinthic, Paleudult) and Lakeland sand (thermic, coated, Typic Quartzitsamment). Drip irrigation application rates were 4.0 and 8.0 l/h with durations of 2, 4, or 6 hours. Preliminary studies indicated a wetted area of approximately 90 cm in diameter could be obtained from a single emitter. All pesticide calculations were based on this wetted area. Each treatment was replicated three times with emitters spaced 91 cm apart. Unless specified differently, all irrigation was initiated at a soil tension of 30 cb.

Several experimental variables were measured in separate experiments. They include freshly prepared and stale seedbed; dry, field capacity, and wet soil; pesticide or fertilizer applications, early or late in the irrigation cycle, and length of injection time.

In drip irrigation experiments, the movement of fertilizer and nematicide in the soil profile during irrigation was measured by analytical methods. The movement of herbicides in the soil profile was measured by field and greenhouse bioassay techniques using barnyard grass as a bioassay indicator.

Movement of fertilizers injected through drip emitters. To determine the movement of N, P, and K applied at a point by drip irrigation emitters, three liquid fertilizers were injected on a Tifton loamy soil and a Lakeland sand. The experiment was accomplished at three soil moisture levels and with drip emitters of two sizes. Two days following application,

the spacial distribution of the applied nutrients were determined by sampling.

The experimental parameters were as follows:

1. Plots were 2.74 x .91 m which conformed to a drip line with three emitters at .91 m intervals. A total of 108 plots were included in the experiment (2 soils, 3 fertilizers x 3 moisture levels x 2 volumes of emitters x 3 replications).

2. Fertilizers were: 32-0-0, pH 6.6, Urea ammonium nitrate (UAN)

8-0-4, pH 6.9, UAN + KCL

8-2-4, pH 6.1, UAN + 10-34-0 + KCL

Applications were adjusted so that an equal rate of N was applied for each fertilizer.

3. Soil moisture levels were approximate to conform to: 1. Very dry soil accomplished by covering the plots for several weeks prior to application (>30cb at 6 in. depth); 2. Moderately moist (25 cb), and 3. Very wet (saturated by heavy watering several days prior to application). Soil moisture probes and soil thermometers were used to record moisture and temperature. The spacial distribution of soil moisture was determined by moisture measurements for each sample.

4. Emitters: 4 and 8 L/h. The total application was 6 hours in every treatment, therefore, the applications were 24 and 48 L.

5. Injection: The liquid fertilizer (diluted to a total of 1200 ml) was injected into the irrigation line by air pressure slightly higher than the water pressure. The injection was accomplished in the first 50 minutes of the 6-h irrigation.

6. Soil sampling: Two days following injection, soil samples were collected. A template was designed to obtain samples at distances of 0, 7.6, 15, 22.9, 30, 38, and 45.7 cm from the drip point. At each distance the samples were collected at depths of 0-5, 5-10, 10-15, 15-30, and 30-45 cm. Samples from the three emitters were combined because of the need to limit the number of samples for analyses. Samples were stored in the refrigerator in sealed plastic bags.

7. Laboratory analyses: Samples were analyzed for soil moisture, mineral N (NH_4 and $\text{NO}_3\text{-N}$), soil test P and soil test K. The procedures are gravimetric for moisture, semi micro Kjeldahl using 2 N KCl as an extractant for mineral N, and Mehlich I extractable P and K.

Movements of N, P, K and water applied were evaluated 2 days following injection and were summarized by contour graphs of the form $Z = a + bx + cx^2 + dy + ey^2 + fxy$. Nitrogen movement was similar regardless of the fertilizer used and therefore reported results are from the complete N, P, K fertilizer (8-2-4).

Four cylinders of different dimensions were visualized beneath the drip point. Elemental concentration, mass, change from check and the percentage of applied that was retained in the 4 sizes of cylinders, are presented in Tables 22, 23, 24 and 25, respectively. The percentage of N, P, and K retained for the 4 cylinders is further summarized in Table 26.

Several generalizations can be made from the data:

1. Soil retention of $P > K > N$.
2. Retention of N and K decreased with an increase in drip rate from 4 to 8 L/h.

3. Differences in N and K retention due to drip rate were most pronounced for the small cylinder size(s).

4. Both drip rates and/or total irrigation amounts were too high for small plants with limited root systems. Less than 1, 16 and 55% of the applied N, P, and K, respectively were retained in the smallest cylinder ($r=11.5$, $h=10$ cm) when soils, drip rates and initial soil moistures were averaged.

5. Over 60% of the applied N appeared to be lost from even the largest cylinder ($r=50$, $h=46$ cm). It is likely that some of the loss was from volatilization of ammonia and/or denitrification and was not all due to leaching beyond the cylinder boundaries.

6. Most of the K and all of the P appeared retained within the largest cylinder 2 days after application. However, the data for K but especially for P are not easily interpreted with significantly more than 100% of the applied accounted for in the soil test. Very likely the methodology needs reconsideration. It is likely that Mehlich 1 extractable P and K are not appropriate tests to evaluate P and K applied only 2 days or some concentrations of P and K were encountered in the 2d soil samples.

7. Soil retention of N and K was very significantly affected by soil moisture prior to making the drip application. Apparently high initial soil moisture allowed applied N and K to rapidly move out of a small plant rooting zone.

8. Retention of N was greater on Lakeland sand than on Tifton loamy sand, a result not expected from soil texture. A close analysis of the data indicates that the result is mostly due to a high retention for Lakeland in the low initial soil moisture regime. The soil in that regime appeared

hydrophobic causing some of the drip applied N to run on the surface and possibly cause some abnormalities in the data.

Movement of pesticides applied through drip emitters

Fenamiphos

In 1987, a nematicide, fenamiphos, was applied to soil (6.7 kg/ha) via injection in drip irrigation system. Soil samples were collected 0-5 cm (H1), 12.1-17.8 cm (H2), and 23.4-30.5 cm (H3) from the emitter in increments 0-10 cm (V1), 10-20 cm (V2), and 20-30 cm (V3) deep. Samples were collected 2, 7, and 14 days after the two methods of application (early and late) and analyzed for the parent nematicide, fenamiphos, and its metabolites, f. sulfoxide and f. sulfone. Soil samples (ca. 300 g) were air dried, thoroughly mixed and stored under refrigeration pending analysis. Samples were extracted by shaking for two hours with 50% chloroform-methanol. After extraction, fenamiphos was converted to fenamiphos sulfone by oxidation with magnesium sulfate and potassium permanganate, partitioned into methylenechloride, and determined by gas chromatography, using a thermionic detector operated in the nitrogen mode. Recoveries by this method were greater than 95%, with detection limits of 0.005 ug/g soil.

Concentrations of fenamiphos, f. sulfoxide, and sulfone found in soil with time and depth are shown in Figs. 29-31. Concentrations are averages of three replications. Concentrations of fenamiphos, f. sulfoxide, and f. sulfone in the soil were consistently greater following late application than early application in the irrigation activity. Apparently the

additional water in the early application following injection of fenamiphos moved the nematicide deeper into the soil profile. Two days after the late application, concentrations of fenamiphos ranged from 4 to 6 ppm near the emitter (H1) at all vertical depths (Fig. 29 A) and decreased with distance from the emitter both horizontally and vertically over time (Figs. 29 B, 29 C).

Concentrations of f. sulfoxide near the emitter (H1) two days after application were about 2 ppm at all vertical depths (Fig. 30 A), increased on days 7 (Fig. 30 B) and day 14 (Fig. 30 C) and decreased with distance from the emitter both horizontally and vertically over time. The concentrations of f. sulfone in the soil were less than 1 ppm on all sampling dates (Figs. 31 A-31 C).

The outflow water from two drip irrigation emitters was monitored in order to determine if the injection of fenamiphos formulation into the irrigation lines results in a smooth pulse of fenamiphos emerging from the emitters.

On the irrigation tests of May 27 and June 2, 1987, irrigation began at 8:00 a.m. and the fenamiphos injections (approximately 1 hour in duration) were made at either 830 or 1300 hours. At the end of these tests, irrigation systems operating at 4 L/h (5/27) and at 8 L/h (6/2) irrigation rates were set aside from the test and allowed to continue flowing.

We injected 1200 ml of water mixed with 1.1 ml of fenamiphos (0.36 kg/l) using pressurized reservoirs. Total flow during the sampling period was measured by placing the near and far emitter over jars; the middle emitter

was sampled by collecting outflow in a glass vial every two minutes. The following results were obtained:

Test date	Total water flow (ml) during sampling period		Sampling period (min)	Fenamiphos Av. conc. (ppm)	Total Amt. Inj. (mg)
	near emitter	far emitter			
5/27	5640	5830	75	15.2 $\pm$ 9	87
6/2	8600	10000	76	15.5 $\pm$ 10	144

The actual concentration while fenamiphos was emerging was fairly uniform and consistent between the two tests (Fig. 9f). Apparently, the second test shows the effect of a temporary plug-up of the injection system.

Note that all the samples containing fenamiphos also contained 2 to 3 ppm fenamiphos sulfoxide, but this amount was not correlated with the amount of fenamiphos, suggesting this product formed a breakdown of the parent fenamiphos compound during sample storage.

These results indicate the drip irrigation system was doing a good job of supplying a "plug" of fenamiphos to the soil.

Herbicides

Two field experiments with drip irrigation were conducted in 1986 under field conditions. The research objectives were to determine the potential vertical and lateral movement of the herbicides EPTC, bensulide, and metolachlor applied through drip irrigation and to develop suitable sampling and bioassay techniques for determining herbicide movement applied through drip irrigation. One experiment was conducted on a stale (prepared more than 30 days before treatment) seedbed, and the other experiment was conducted on a freshly prepared seedbed.

The experimental variable was the rate of irrigation application of 4 and 8 L/h. Preliminary experiments indicated a wetted zone around the irrigation emitter would be approximately 90 cm in diameter. The recommended rate of herbicide application was calculated on this basis. The herbicide rates were: EPTC 4.5 kg/ha, bensulide 5.6 kg/ha, and metolachlor 2.2 kg/ha. The soil type was a Tifton loamy sand. Each treatment was replicated three times with emitters spaced 91-cm apart.

The calculated amount of herbicide was diluted to 1,200 ml in the injection container. The herbicides were applied during the first hour of irrigation application, and irrigation was continued for an additional 3 hours.

The stale seedbed experiment was allowed to equilibrate for 48 hours. On one-half of each wetted area, barnyard grass was planted on a radial line beginning at the emitter point to approximately 90 cm from the emitter point. On the other half of the wetted area, for each treatment, soil samples to a depth of 28-30 cm were collected at 0-5, 10-15, and 20-25 cm from the emitter point. These undisturbed samples were placed directly into planting trays, transferred to the greenhouse and planted with barnyard grass to determine depth of herbicide movement at specified distances from the emitter. Bioassay data response were collected approximately 14 days after planting.

A field bioassay indicated irrigation application rate did not affect lateral movement of the three herbicides on a stale seedbed (Table 27). But, on a freshly prepared seedbed, bensulide applied in 8 L/h of water moved nearly twice as far from the emitter as when applied in 4 L/h of

water (29.3 vs. 15.3 cm). The herbicides were detected at greater distances from the emitter point on the stale seedbed than on the fresh seedbed.

The depth movement was checked in the greenhouse. At 0-5 cm from the irrigation emitter on the stale seedbed, EPTC and metolachlor moved downward in the soil profile to the extent of our sampling depth (28-30 cm). Bensulide moved downward in the soil profile 18 cm in 4 L/h of water and to 23 cm in 8 L/h of water. On the freshly prepared seedbed, all herbicides were detected to a depth of 28-30 cm except bensulide applied in 4 L/h of water which moved to 21.6 cm.

At 10-15 cm from the emitter, in 4 L/h of water, EPTC moved down in the soil profile to 19 cm, bensulide to 9 cm, and metolachlor down to 28 cm in the stale seedbed. In 8 L/h of water, all herbicides moved downward in the soil profile to 28 cm. On the freshly prepared seedbed, EPTC and metolachlor moved 28-30 cm at both irrigation water rates. Bensulide was not detected in the greenhouse samples at 10-15 cm from the emitter point.

At 20-25 cm from the emitter bensulide was not detected in the soil profile by bioassay on the stale or freshly prepared seedbed (Table 28). EPTC was detected to 11-cm depth when applied in 8 L/h of water on the stale seedbed, but not on the freshly prepared seedbed. Metolachlor was detected to 5 cm in 4 L/h of water and 9 cm in 8 L/h of water on the stale seedbed and 10 cm on the freshly prepared seedbed in 8 L/h of water.

The greenhouse bioassay also indicated little difference in herbicide concentration with bensulide on the stale or freshly prepared seedbed in the 0-5-cm zone from the emitter. The highest concentration of EPTC and metolachlor appeared to be in the 15-20-cm zone from the emitter.

The above results indicate the physical condition of the soil at treatment time can affect herbicide movement when applied through drip irrigation. Herbicide solutibility appears to be a major factor in herbicide movement through drip irrigation. Under the conditions of these experiments, downward movement of the herbicide in the soil profile near the emitter point may be a limiting factor in applying herbicide through drip irrigation on Tifton loamy sand soil.

Based on the previous results, an experimental variable of application time and irrigation application rate for the herbicides was initiated. The application time was 30 and 270 min after start of irrigation. The total irrigation time was 360 min and irrigation application rate was 4 and 8 L/h.

Lateral surface movement of EPTC from the emitter was slightly greater when applied early in the cycle than when applied late (Table 29). On the other hand, lateral movement of bensulide and metolachlor was slightly greater when applied late in the irrigation cycle. This indicates that the soil moisture status at time of application may increase lateral movement of selected herbicides. In general, EPTC and metolachlor moved to a depth of 28 cm near the emitter point except for EPTC applied early in the irrigation cycle (Table 30). In general, the irrigation application rate had little effect on herbicide movement. There did appear to be less herbicide movement 20-25 cm from the emitter when applied late in the irrigation cycle. Bensulide moved less than EPTC or metolachlor. The detection of bensulide and metolachlor at 20-25 cm from the injection point applied early in the irrigation cycle would indicate that both volatility and solubility may influence herbicide movement through drip irrigation.

There was always less movement of bensulide, a relatively soluble herbicide than EPTC or metolachlor.

Based on the movement of fertilizers and herbicides in previous experiments, it was decided to inject the herbicides rapidly into the irrigation system late in the irrigation schedule. It was felt that lateral movement may be increased and vertical movement decreased if the herbicides would move with the free surface water. The results in Tables 31 and 32 show that rapid injection of the herbicides did not improve lateral movement and did not decrease vertical movement. Irrigation rate did not greatly influence lateral surface movement of the herbicides (Table 31). At the emitter point and at 10-15 cm from the emitter point, EPTC and metolachlor were detected at about 24-28 cm in the soil profile. These results were basically no different from previous experiments. Bensulide was detected to a depth of 16.7-18.3 cm at the emitter point. These results indicate that rate of chemical injection or irrigation water rate may not influence movement of pesticides in the soil.

In addition to the movement of pesticides, the moisture distribution through drip irrigation was studied. Tests were conducted to determine the effects of antecedent soil moisture levels on vertical and horizontal movement of irrigation water. A network of soil moisture sensors was installed in plots of Tifton loamy sand soil at two levels of antecedent soil moisture: (1) Field capacity and (2) 15-centibar available soil water. A single 8 L/h emitter was operated for one hour and changes in soil moisture content were monitored for several days thereafter. Analyses of the data showed that the drip-irrigated water penetrated to greater depths (greater than 50 cm) and lesser horizontal distances (20 cm) when the

depths (45 cm) and greater horizontal distances (40 cm) for antecedent soil water tension at 15 centibar. Also, the vertical percolation of the water proceeded at a much greater rate under field capacity conditions as compared to 15-centibar soil water tension. These results indicate that antecedent soil moisture can have a very significant effect upon the vertical and horizontal dispersion of chemicals being distributed with the irrigation water.

Based on previous experiments involving individual agricultural chemicals, a cochemigation experiment was initiated in September, 1987, involving fertilizer (N - P_2O_5 - S - B), metolachlor and fenamiphos applied to snapbean. Data collected in this experiment include nutrient uptake as measured by tissue analysis, herbicide movement, and fenamiphos movement and efficacy as measured by bioassay and root-knot indices. A direct comparison of cochemigation was made with conventional application. Field bioassay data indicate that metolachlor moved about 20 cm from the emitter point. There was some snapbean injury as a result of herbicide which indicates the amount of herbicide applied was not uniformly distributed in the calculated wetted area. Fertilizer and fenamiphos movement was similar to that reported earlier.

Table 22: Nitrogen, phosphorus and potassium determinations in a cylinder of $r = 11.5$ and $h = 10$ cm beneath a drip point as affected by soil, drip rate and initial soil moisture.

Soil	Drip rate L/Hr.	Initial soil moisture	N				P				K			
			Conc. ug/g	Mass g	Change Δg	Applied retained %	Conc. ug/g	Mass g	Change Δg	Applied retained %	Conc. ug/g	Mass g	Change Δg	Applied retained %
Lakeland sand	4	L	118.7	0.74	0.65	17.4	33.7	0.21	0.05	13.4	117.1	0.73	0.59	38.0
		M	14.4	0.09	0.01	0.3	40.1	0.25	0.09	21.8	25.7	0.16	0.01	1.3
		H	11.2	0.07	0.00	0.0	40.1	0.25	0.09	22.1	19.3	0.12	0.00	0.1
		X	48.1	0.30	0.22	5.9	38.0	0.24	0.08	19.1	54.0	0.34	0.20	13.1
	8	L	12.8	0.08	0.00	0.0	36.9	0.23	0.06	15.7	20.9	0.13	0.01	0.4
		M	8.0	0.05	0.00	0.0	36.9	0.23	0.07	17.7	19.3	0.12	0.00	0.2
		H	8.0	0.05	0.00	0.0	38.5	0.24	0.08	19.9	11.2	0.07	0.01	0.0
		X	9.6	0.06	0.00	0.0	37.4	0.23	0.07	17.8	17.2	0.11	0.01	0.2
Tifton loamy sand	4	L	14.4	0.09	0.04	1.0	30.5	0.19	0.10	23.4	57.8	0.36	0.11	7.2
		M	11.2	0.07	0.02	0.5	N.D.	N.D.	N.D.	N.D.	65.8	0.41	0.16	10.4
		H	11.2	0.07	0.03	0.7	25.7	0.16	0.06	15.4	43.3	0.27	0.03	2.1
		X	12.3	0.08	0.03	0.7	18.7	0.12	0.05	12.9	55.6	0.35	0.10	6.6
	8	L	9.6	0.06	0.01	0.2	27.3	0.17	0.07	17.0	41.7	0.26	0.04	2.3
		M	8.0	0.05	0.01	0.1	27.3	0.17	0.07	17.0	40.1	0.25	0.04	2.6
		H	6.4	0.04	0.01	0.0	20.9	0.13	0.03	7.6	40.1	0.25	0.01	0.9
		X	8.0	0.05	0.01	0.1	25.2	0.16	0.06	13.9	40.6	0.25	0.03	1.9

Table 23: Nitrogen, phosphorus and potassium determination in a cylinder of r = 19.5 and h = 15 cm beneath a drip point as affected by soil, drip rate and initial soil moisture.

Soil		Drip rate L/Hr.	N				P				K			
			Initial soil moisture		Applied		Mass		Change		Applied		Mass	
			Conc. ug/g	Change Δg	% retained	Conc. ug/g	Conc. ug/g	g	Δg	%	Conc. ug/g	Change Δg	g	% retained
Lakeland sand	4		L	60.3	1.31	34.9	21.6	0.58	0.06	14.9	53.9	0.95	1.45	60.8
			M	16.7	0.14	3.8	27.5	0.74	0.14	33.5	22.3	0.11	0.60	7.0
			H	13.4	0.36	1.8	29.4	0.79	0.16	39.6	21.2	0.09	0.57	5.9
			X	30.1	0.50	13.5	26.0	0.70	0.12	29.3	35.5	0.38	0.87	24.6
	8		L	13.8	0.37	1.7	28.6	0.77	0.15	36.4	22.7	0.12	0.61	7.9
			M	7.1	0.19	0.0	27.2	0.73	0.11	26.8	17.1	0.02	0.46	1.3
			H	8.6	0.23	0.0	27.9	0.75	0.14	35.0	14.5	0.00	0.39	0.0
			X	9.7	0.26	0.6	27.9	0.75	0.13	32.7	18.1	0.05	0.49	3.1
Tifton loamy sand	4		L	13.4	0.36	4.5	19.3	0.52	0.13	32.2	50.2	0.35	1.35	22.5
			M	11.5	0.31	3.1	11.9	0.32	0.07	17.4	52.5	0.46	1.41	29.7
			H	10.8	0.29	2.4	26.4	0.71	0.29	71.7	48.4	0.28	1.30	18.1
			X	11.9	0.32	3.3	19.2	0.52	0.16	40.4	50.4	0.36	1.35	23.4
	8		L	13.8	0.37	4.6	21.2	0.57	0.16	39.5	57.7	0.54	1.55	34.6
			M	8.9	0.24	1.1	20.8	0.56	0.15	35.5	43.5	0.17	1.17	10.9
			H	7.1	0.19	0.2	19.7	0.53	0.12	30.2	40.2	0.07	1.08	4.4
			X	9.9	0.27	2.0	20.5	0.55	0.14	35.0	47.1	0.26	1.27	16.6

Table 24: Nitrogen phosphorus and potassium determination in a cylinder of $r = 34$ and $h = 30$ cm beneath a drip point as affected by soil, drip rate and initial soil moisture.

Soil	Drip rate L/Hr.	Initial soil moisture	N				P				K			
			Conc. ug/g	Mass g	Change g	Applied retained %	Conc. ug/g	Mass g	Change g	Applied retained %	Conc. ug/g	Mass g	Change g	Applied retained %
Lakeland sand	4	L	25.1	41.0	2.51	66.7	14.5	2.37	0.06	14.9	20.5	3.35	1.22	78.4
		M	13.6	2.22	0.61	16.3	20.4	3.34	0.14	33.8	12.9	2.11	0.18	11.3
		H	12.4	2.02	0.45	11.9	21.2	3.47	0.20	50.0	12.3	2.01	0.13	8.1
		X	17.0	2.78	1.19	31.6	18.7	3.06	0.13	32.9	15.2	2.49	0.51	32.6
	8	L	18.7	3.05	1.46	38.9	22.1	3.61	0.35	85.7	24.7	4.03	1.77	113.5
Tifton loamy sand	4	M	6.8	1.11	0.00	0.0	21.9	3.58	0.27	64.8	15.1	2.46	0.28	18.1
		H	7.2	1.18	0.00	0.0	20.1	3.29	0.18	43.9	12.9	2.11	0.10	6.6
		X	10.9	1.78	0.49	13.0	21.4	3.49	0.27	64.8	17.6	2.87	0.72	46.1
		L	13.1	2.14	1.01	26.9	17.0	2.78	0.41	99.8	48.5	7.92	1.50	96.1
	8	M	11.6	1.89	0.78	20.9	12.8	2.10	0.23	55.3	33.6	5.49	0.62	39.5
	4	H	9.4	1.54	0.42	11.1	23.3	3.80	1.37	333.7	43.2	7.06	0.62	39.5
		X	11.4	1.86	0.74	19.6	17.7	2.89	0.67	162.9	41.8	6.82	0.91	58.4
		L	13.5	2.21	1.08	28.9	17.4	2.84	0.45	110.1	47.7	7.80	1.53	98.2
		M	9.6	1.57	0.45	12.0	18.1	2.95	0.54	130.6	45.1	7.37	0.96	61.5
	8	H	5.9	0.96	0.01	0.4	16.9	2.77	0.36	88.9	35.9	5.87	0.14	9.2
	4	X	9.7	1.58	0.51	13.8	17.4	2.85	0.45	109.9	42.9	7.01	0.88	56.3
		L	13.5	2.21	1.08	28.9	17.4	2.84	0.45	110.1	47.7	7.80	1.53	98.2
		M	9.6	1.57	0.45	12.0	18.1	2.95	0.54	130.6	45.1	7.37	0.96	61.5
		H	5.9	0.96	0.01	0.4	16.9	2.77	0.36	88.9	35.9	5.87	0.14	9.2
	8	X	9.7	1.58	0.51	13.8	17.4	2.85	0.45	109.9	42.9	7.01	0.88	56.3

Table 25: Nitrogen phosphorus and potassium determination in a cylinder of r = 50 and h = 46 beneath a drip point as affected by soil, drip rate and initial soil moisture.

Soil	Drip rate L/Hr.	Initial soil moisture	N				P				K			
			Conc. ug/g	Mass g	Change Δg	Applied retained %	Conc./Mass ug/g g	Change Δg	Applied retained %	Conc. ug/g	Mass g	Change Δg	Applied retained %	
Lakeland sand	4	L	13.7	7.42	3.93	104.6	9.1	4.93	0.06	14.9	11.7	6.35	1.50	96.2
		M	10.0	5.43	1.87	49.7	13.8	7.46	0.14	34.5	8.5	4.61	0.18	11.8
		H	9.2	5.01	1.50	40.0	15.8	8.55	0.68	165.3	8.8	4.75	0.15	9.5
		X	11.0	5.95	2.43	64.8	12.9	6.98	0.29	71.6	9.7	5.24	0.61	39.2
Tifton loamy sand	8	L	14.9	8.07	4.48	119.0	16.2	8.79	1.06	259.2	16.9	9.16	3.48	223.5
		M	5.8	3.16	0.56	14.9	16.5	8.92	1.04	254.2	12.5	6.79	1.18	75.9
		H	6.1	3.28	0.58	15.4	14.6	7.90	0.44	107.6	10.1	5.50	0.29	18.8
		X	8.9	4.84	1.87	49.8	15.8	8.54	0.85	207.0	13.2	7.15	1.65	106.1
Tifton loamy sand	4	L	8.4	4.56	1.49	39.6	14.2	7.69	1.15	281.1	37.5	20.3	2.20	141.0
		M	7.2	3.90	1.00	25.8	11.1	6.03	0.61	148.2	28.6	15.5	0.69	44.2
		H	6.5	3.54	0.55	14.7	17.1	9.26	2.60	634.9	35.4	19.2	0.99	63.4
		X	7.4	4.00	1.01	26.7	14.1	7.66	1.45	354.7	33.8	18.3	1.29	82.9
Tifton loamy sand	8	L	9.1	4.95	2.00	52.6	12.9	7.00	0.61	148.8	37.3	20.2	2.07	132.9
		M	7.2	3.90	0.79	20.9	14.3	7.77	1.78	435.0	42.4	23.0	4.10	262.5
		H	5.2	2.84	0.05	1.2	13.7	7.45	1.08	263.2	31.2	16.9	0.45	28.9
		X	7.2	3.90	0.95	24.9	13.6	7.41	1.16	282.3	36.9	20.0	2.21	141.4

Table 27 Lateral movement of EPTC, bensulide, and metolachlor applied early in drip irrigation cycle¹ on stale and fresh seedbed.

Herbicide	Seedbed	Irrigation Rate	
		4 L/h	8 L/h
<u>movement from emitter (cm)</u>			
EPTC	Stale	28.3	33.3
	Fresh	23.0	23.7
bensulide	Stale	34.7	33.0
	Fresh	15.3	29.3
metolachlor	Stale	49.7	49.7
	Fresh	20.0	22.7

¹4 hours.

Table 28 Vertical movement of EPTC, bensulide, and metolachlor applied early in drip irrigation cycle¹ on stale and fresh seedbed.

Herbicide	Seedbed	Irrigation Rate					
		4 L/h			8 L/h		
		Distance from Emitter (cm)					
		0-5	10-15	20-25	0-5	10-15	20-25
EPTC	Stale	28.0	19.0	0	28.0	28.0	20.0
	Fresh	28.0	28.0	0	27.5	28.0	0
bensulide	Stale	18.0	0	0	23.0	15.3	0
	Fresh	21.7	0	0	28.0	0	0
metolachlor	Stale	28.0	9.6	5.0	28.0	9.6	9.0
	Fresh	28.0	28.0	0	28.0	28.0	10.0

¹4 hours.

Table 29 Lateral movement of EPTC, bensulide, and metolachlor applied early and late in a drip irrigation cycle.

Herbicide	Time	Irrigation Rate	
		4 L/h	8 L/h
<u>movement from emitter (cm)</u>			
EPTC	Early ¹	27.0	23.3
	Late ²	25.3	18.3
bensulide	Early	12.7	10.0
	Late	17.6	14.7
metolachlor	Early	24.3	21.7
	Late	30.0	23.7

¹30 minutes after start of irrigation.

²270 minutes after start of irrigation.

Table 10. Vertical movement of EPTC, bensulide, and metolachlor applied early and late in a drip irrigation cycle.

Herbicide	Time	Irrigation Rate					
		4 L/h			8 L/h		
		Distance from Emitter (cm)					
		0-5	10-15	20-25	0-5	10-15	20-25
EPTC	Early ¹	24.0	26.7	14.7	23.3	21.7	16.0
	Late ²	28.0	15.0	0	28.0	24.0	0
bensulide	Early	18.0	5.3	0	23.3	17.3	11.0
	Late	21.0	4.0	1.3	20.5	0	0
metolachlor	Early	28.0	28.0	3.0	28.0	28.0	22.3
	Late	28.0	24.6	0	28.0	28.0	0.0

¹30 minutes of start of irrigation.

²270 minutes of start of irrigation.

Table 31 Lateral surface movement of EPTC, bensulide, and metolachlor injected in 10 minutes late in irrigation schedule.

Herbicide	Irrigation Rate	
	4 L/h	8 L/h
	distance from emitter (cm)	
EPTC	16.0	16.1
bensulide	15.7	14.1
metolachlor	18.4	15.1

Table 32 Vertical movement of EPTC, bensulide, and metolachlor injected in 10 minutes late in irrigation schedule.

Herbicide	Irrigation Rate					
	4 L/h			8 L/h		
	Distance of Emitter (cm)					
	0-5	10-15	20-25	0-5	10-15	20-25
	Depth (cm)					
EPTC	26.0	23.7	0	27.3	25.0	0
bensulide	18.3	2.0	0	16.7	4.0	0
metolachlor	28.0	20.3	0	28.0	26.7	0

Figure Legends

Figure 29: Concentration of fenamiphos in soil at various distances from the emitter 2 (1a), 7 (1b), and 14 days (1c) after application via drip irrigation. Late = irrigate 4 hours, inject fenamiphos between 4th and 5th hour, and irrigate one additional hour. Early = inject fenamiphos from 0 to 1 hour and irrigate for an additional 5 hours. H1 = 0-5, H2 = 12.5-18, and H3 = 25.5-30.5 cm horizontally from emitter. V1 = 0-10, V2 = 10-20, and V3 = 20-30-cm deep.

Figure 30: Concentration of fenamiphos sulfoxide in soil at various distances from the emitter 2 (2a), 7 (2b), and 14 days (2c) after application via drip irrigation. Late = irrigate 4 hours, inject fenamiphos between 4th and 5th hour, and irrigate for an additional 5 hours. H1 = 0-2, H2 = 5-7, and H3 = 25.5-30.5 cm horizontally from emitter. V1 = 0-10, V2 = 10-20, and V3 = 20-30 cm deep.

Figure 31: Concentration of fenamiphos sulfone in soil at various distances from the emitter 2 (3a), 7 (3b), and 14 days (3c) after application via drip irrigation, Late = irrigate 4 hours, inject fenamiphos between 4th and 5th hour, and irrigate one additional hour. Early = inject fenamiphos from 0 to 1 hour and irrigate for an additional 5 hours. H1 = 0-5, H2 = 12.5-18, and H3 = 25.5-30.5 cm horizontally from emitter. V1 = 0-10, V2 = 10-20 and V3 = 20-30 cm deep.

Figure 32: Fenamiphos (nemacur) concentrations in irrigation emitter outflow as affected by the flow rate.

SAMPLED DAY 2

12

FIGURE 29B

SAMPLED DAY 7

FIGURE 29C

SAMPLED DAY 14

FIGURE 30A

SAMPLED DAY 2

FIGURE 30B

SAMPLED DAY 7

FIGURE 30C

SAMPLED DAY 14

FIGURE 31A

SAMPLED DAY 2

FIGURE 31B

SAMPLED DAY 7

FIGURE 31C

SAMPLED DAY 14

FIGURE 32

FIGURE 9F NEMACUR CONCENTRATIONS IN IRRIGATION EMMITTER OUTFLOW

5.B. Sprinkler Irrigation

Several cochemigation experiments were conducted utilizing small one-tower (0.8 ha) center pivot systems or solid set irrigation systems designed to cover a uniform area. Cochemigation variables included a herbicide plus a nematicide or fertilizers plus herbicide. Irrigation rates for sprinkler cochemigation experiments ranged between 2.5 to 7.5 mm/ha.

All herbicides and nematicides were applied at the label rates. Fertilizer rates were determined by soil tests or experimental variables. All seedbed preparations included deep-turning and smoothing the surface with a power-driven rototiller or bed shaper. The agrichemicals applied in the irrigation experiments are listed in Table 33. Additional materials and methods are included with the individual experiments.

A micro-irrigation system was designed to make water and chemigation applications to plants up to 1 meter in height. The system consisted of a rectangular system 3 by 2 meters with positions for sprinklers at approximately 0.5 meter intervals parallel with the row. Spraying systems D-1-46 hollow cone nozzles were positioned to spray upwards.

Evaluations indicated that sprays from this arrangement traveled upwards sufficiently to wet plants up to 1 meter in height but water distribution was very subject to wind effects. Control of the fall army worm infesting seedling corn was obtained but more data is needed before it can be determined that control of insects infesting the foliage is feasible.

In 1986, 1987 and 1988, numerous multiple-cropping sequences were grown under small one-tower center pivots that covered 0.8 ha. The center pivots were divided into 0.2 ha quadrants and planted to the various crops.

Chemigation vs. conventional application of selected herbicides and the nematicide fenamiphos were compared. Preplant soil-incorporated treatments were applied before crop planting and incorporated into the soil to a depth of approximately 7.5 cm with a tractor-mounted, power-driven rototiller. Chemigation applications were made after crop planting in a water rate of 6.3 mm. All treatments were compared to an untreated check plot which was covered with plastic during the chemigation application.

Typical results of the cochemigation herbicide-nematicide tests are shown in Tables 34-39. In general, conventional and chemigation treatments were equivalent unless the dominant weed species were tolerant to the herbicide. Fenamiphos was equally effective when applied both conventionally and with cochemigation. Method of application did not appear to affect crop growth or yield.

Cochemigation of K_2O (0-0-60) and selected herbicides was conducted in 1986, 1987, and 1988. All treatments were applied postemergence to soybean and weeds in 6.3 mm of water.

The results of herbicide activity are shown in Tables 40-42. Fertilizer rate did not appear to affect herbicide activity. Fluazifop was equally effective when applied both conventionally and through irrigation. Imazaquin was also equally effective when applied by conventional and irrigation application methods. There did not appear to be an interaction between method of application and the activity of fomesafen. In general, fomesafen was less active when applied with fluazifop in irrigation than when applied by conventional methods. Weed species that were susceptible to the herbicides used in this test were controlled by both conventional and cochemigation techniques. However, weeds that had some resistance or

tolerance to the herbicides were always controlled better by conventional methods than by cochemigation. Individual plots received the same treatment over the 3-year period. Ground cover did increase over the three years. It was quite evident that the control of sicklepod and Florida beggar weed was not acceptable in 1988 which reflects both herbicide selection and rotation effects. These weeds tolerate both imazaquin and fomesafen. The herbicide treatment or method of application did not affect soybean yield. There was no compatibility problem of applying postemergence herbicides with fertilizer in this experiment.

The data obtained in the field and greenhouse experiments carried out at the Coastal Plain Experiment Station, Tifton, Georgia, allow the following conclusive remarks.

1. Selected water soluble or emulsifiable herbicides, nematicides, and fertilizers can be applied by cochemigation through drip irrigation without adversely affecting compatibility or soil distribution.
2. Antecedent soil moisture at time of irrigation may influence both lateral and vertical movement of water and agrichemicals. Greater vertical distribution may occur at or above field capacity and greater lateral distribution may occur at levels below field capacity.
3. In sandy Coastal Plain soils, the rate of drip irrigation during and following fertilizer injection must be carefully controlled in order to retain applied nutrients within the rooting zone of small plants. Soil retention was in the order of $P > K > N$. Movement out from the rooting zone was increased when soil moisture was high prior to injection. Differences in the movement of individual elements were not affected by the fertilizer applied (32-0-0, 8-0-4 or 8-2-4).
4. Application of fenamiphos late in drip irrigation application resulted in concentrations adequate to control nematodes near the emitter but not greater than 5 cm from the emitter.
5. Movement of herbicides in the soil depended on herbicide solubility, soil moisture, and irrigation rate. Under all conditions in this study, vertical movement of the herbicide in the soil profile exceeded acceptable limitations. Vertical movement of herbicides near the emitter exceeded an acceptable depth of 7.5 cm. Lateral movement of herbicides near the soil surface was greater in the stale seedbed than in the freshly prepared

seedbed. Lateral movement near the soil surface was dependent on solubility and volatility properties. Under the conditions of these experiments, emitter spacing would have to be less than 30 cm apart to provide acceptable surface distribution of the herbicides.

6. Applications of selected insecticides through micro-sprinkler systems did not provide adequate distribution for good insect control.

7. Cochemigation of herbicides with fenamiphos or selected fertilizers through sprinkler irrigation did not present compatibility problems. Results of cochemigation with herbicides and nematicides were equal to or better than those by conventional application. Efficacy of selected herbicides was reduced when applied with fertilizer through sprinkler irrigation. This occurred with specific herbicides on specific weed species.

8. Under the conditions of this study, it does not appear that drip irrigation will provide the uniform distribution necessary to apply agrichemicals for crop production on sandy Coastal Plain soils.

Table 33: Pesticides applied through sprinkler irrigation

Herbicides

<u>Common Name</u>	<u>Chemical Name</u>
benefin	N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)benzenamine
chloramben	3-amino-2,5-dichlorobenzoic acid
DCPA	dimethyl tetrachloroterephthalate
fomesafen	5-(2-chloro-4-(trifluoromethyl)phenoxy)-N(methylsulfonyl)- 2-nitrobenzamide
fluazifop	(+)-2-(4-(5-(trifluoromethyl)-2-pyridinyl)oxyphenoxy) propanoic acid
imazaquin	2-(4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H- imidazol-2-yl)-3-quinolinecarboxylic acid
metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1- methylethyl)acetamide
trifluralin	2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine
Nematicide fenamiphos	ethyl 3-methyl-4-(methylthio)phenyl (1-methylethyl) phosphoramidate

Table 34: Cochemigation of trifluralin and fenamiphos on cowpea, Autumn 1987.

	Rate kg/ha	Method of application	Percent					Carpet- weed
			Weed control	Crop injury	Yellow nutsedge	Annual sedge	Wild radish	
trifluralin	0.56	PPI	79	0	59	38	3	0
paraquat	0.56	AC						
trifluralin	0.56	PPI	30	0	66	31	3	0
fenamiphos	3.36	PPI						
paraquat	0.56	AC						
trifluralin	0.56	Chem	63	0	87	10	3	0
fenamiphos	3.36	Chem						
paraquat	0.56	AC						
check			70	0	23	74	0	3

35
Table Cochemigation of metolachlor and fenamiphos on snapbean, Autumn 1987.

	Rate kg/ha	Method of application	Weed control	Crop injury	Percent			Yield kg/plot
					Annual grasses	Wild radish	Carpet- weed	
metolachlor	2.24	PRE-N	100	3	0	0	0	6.8
fenamiphos	3.36	PPI						
- nitrogen								
metolachlor	2.24	PRE-N	99	4	0	100	0	6.9
fenamiphos	3.36	PPI						
metolachlor	2.24	Chem+N	99	0	0	67	33	8.7
fenamiphos	3.36	Chem						
check + N			82	1	18	15	67	8.4

Table 36: Cochemigation of chloramben and fenamiphos on direct-seeded squash, 1987.

	Rate kg/ha	Method of application	Weed control	Percent					Total Yield	
				Crop injury	Yellow nutsedge	Annual sedge	Carpet- weed	Corn spurry weeds	Dixie no/ kg/ plot	Senator no/ kg/ plot
chloramben	3.36	PRE	95	14	44	0	56	0	49	15
chloramben	3.36	PRE	98	11	90	0	10	0	56	23
fenamiphos	3.36	PPI								
chloramben	3.36	Chem	99	5	50	0	0	50	56	26
fenamiphos	3.36	Chem								
check			78	20	13	33	29	25	40	18

Table 37: Cochemigation of DCPA and fenamiphos on direct-seeded cabbage, Autumn 1987.

Rate Method of kg/ha application		Percent										Total Yield			
												Cabaret	Market Prize		
		Weed control	Crop injury	Yellow nutsedge	Annual sedge	Annual grasses	Florida pusley	Evening primrose	Corn spurry	Other weeds	no/ plot	kg/ plot			
DCPA	8.96	PRE	66	19	11	24	3	0	26	26	10	15	8.5	19	14.2
DCPA	8.96	PRE	80	15	20	24	0	0	26	10	20	6	3.7	13	12.7
fenamiphos	3.36	PPI													
DCPA	8.96	Chem	69	24	1	6	3	1	53	3	33	15	10.7	19	15.4
fenamiphos	3.36														
check			77	16	5	13	1	0	45	13	23	13	8.1	19	13.6

Table 38. Cochemigation of trifluralin and fenamiphos on carrots in Autumn 1987 and Winter 1988.

	Rate kg/ha	Method of application	1987 Percent									
			Weed control	Crop injury	Yellow nutsedge	Annual sedge	Bermuda- grass	Annual grasses	Evening primrose	Volunteer mustard	Volunteer corn	Other weeds
trifluralin	0.56	PPI	16	53	9	18	0	1	57	8	4	3
linuron	1.12	POST										
trifluralin	0.56	PPI	28	53	9	26	0	1	47	8	4	5
fenamiphos	3.36	PPI										
linuron	1.12	POST										
trifluralin	0.56	Chem	34	48	11	16	3	0	56	4	6	4
fenamiphos	3.36	Chem										
linuron	1.12	Post										
check			0	75	8	33	0	20	22	5	4	8

	Rate kg/ha	Method of application	1988 Percent				Total Yield	
			Weed control	Crop injury	Evening primrose	Danvers no/plot	kg/plot	Nantes no/plot
trifluralin	0.56	PPI	79	31	100	51	1.4	64
linuron	1.12	POST						2.5
trifluralin	0.56	PPI	80	24	100	45	1.4	65
fenamiphos	3.36	PPI						2.3
linuron	1.12	POST						
trifluralin	0.56	Chem	90	36	100	24	1.3	46
fenamiphos	3.36	Chem						1.7
linuron	1.12	Post						
check			86	75	100	34	0.9	32
								1.4

Table 39: Cochemigation of benefin and fenamiphos on lettuce in Autumn, 1987.

Rate kg/ha	Method of application	Percent									
		Weed control	Crop injury	Yellow nutsedge	Annual sedge	Bermuda- grass	Evening primrose	Wild radish	Corn spurry	Other weeds	
benefin	1.25	PPI	70	20	3	21	38	8	3	21	6
benefin	1.25	PPI	71	35	5	26	31	11	8	14	5
fenamiphos	3.36	PPI									
benefin	1.25	Chem	48	43	5	5	61	16	10	3	0
fenamiphos	3.36	Chem									
check			25	30	3	14	38	9	3	24	9

Table 40: Ground cover, weed control, and weed species composition following conventional and herbicide treatments applied with irrigation to soybean on Bonifay sand. Tifton, Georgia - 1986.

Treatment			K ₂ O kg/ha	Ground cover %	% Weed Species Composition ¹				
No.	Herbicide	Rate kg/ha			Texas panicum	Sickle- pod	Tall morning- glory	Crabgrass	Pigweed
Conventional Method									
1)	fluazifop + imazaquin	0.28 + 0.28	56	5	0	1	61	38	0
2)	fluazifop + imazaquin	0.28 + 0.28	112	6	0	27	73	0	0
3)	fluazifop + imazaquin	0.28 + 0.28	168	5	0	55	40	5	0
4)	fluazifop + fomesafen	0.28 + 0.6	56	6	0	92	3	5	0
5)	fluazifop + fomesafen	0.28 + 0.6	112	3	0	100	0	0	0
6)	fluazifop + fomesafen	0.28 + 0.6	168	4	0	95	5	0	0
Cochemigation Method									
7)	fluazifop + imazaquin	0.28 + 0.28	56	9	7	70	20	0	3
8)	fluazifop + imazaquin	0.28 + 0.28	112	2	0	63	37	0	0
9)	fluazifop + imazaquin	0.28 + 0.28	168	2	0	13	87	0	0
10)	fluazifop + fomesafen	0.28 + 0.6	56	13	0	57	43	0	0
11)	fluazifop + fomesafen	0.28 + 0.6	112	14	0	87	13	0	0
12)	fluazifop + fomesafen	0.28 + 0.6	168	10	0	83	17	0	0

¹Data collected August 4, 1986.

Table 41: Ground cover, weed control, and weed species composition following conventional and herbicide treatments applied with irrigation to soybean on Bonifay sand. Tifton, Georgia - 1987.

- 150 -

Treatment		Rate kg/ha	K ₂ O kg/ha	Ground cover %	Weed control %	% Weed Species Composition ¹			
						sickle- pod	Tall morning- glory	Crabgrass	Florida beggar- weed
No.	Herbicide								
Conventional Method									
1)	fluazifop + imazaquin	0.28 + 0.28	56	9	91	89	96	100	75
2)	fluazifop + imazaquin	0.28 + 0.28	112	4	96	99	90	100	95
3)	fluazifop + imazaquin	0.28 + 0.28	168	4	95	95	93	100	96
4)	fluazifop + fomesafen	0.28 + 0.6	56	11	91	74	97	100	94
5)	fluazifop + fomesafen	0.28 + 0.6	112	8	91	85	99	100	87
6)	fluazifop + fomesafen	0.28 + 0.6	168	9	89	80	99	100	83
Cochemigation Method									
7)	fluazifop + imazaquin	0.28 + 0.28	56	8	93	91	90	97	95
8)	fluazifop + imazaquin	0.28 + 0.28	112	7	92	95	90	100	93
9)	fluazifop + imazaquin	0.28 + 0.28	168	6	94	94	88	100	93
10)	fluazifop + fomesafen	0.28 + 0.6	56	39	59	35	64	100	57
11)	fluazifop + fomesafen	0.28 + 0.6	112	47	51	30	69	100	46
12)	fluazifop + fomesafen	0.28 + 0.6	168	47	50	31	77	100	70

¹data collected July 11, 1987.

Table 42: Ground cover, weed control, and weed species composition following conventional and herbicide treatments applied with irrigation to soybean on Bonifay sand. Tifton, Georgia - 1988.

Treatment		Rate kg/ha	K ₂ O kg/ha	Ground cover %	% Weed Species Composition ¹				
No.	Herbicide				Sickle- pod	Crabgrass	Carpet- weed	Tall morning- glory	Florida beggar- weed
Conventional Method									
1)	fluazifop + imazaquin	0.28 + 0.28	56	24	44	1	7	1	46
2)	fluazifop + imazaquin	0.28 + 0.28	112	19	19	3	1	7	70
3)	fluazifop + imazaquin	0.28 + 0.28	168	19	20	0	20	23	43
4)	fluazifop + fomesafen	0.28 + 0.6	56	11	56	0	0	0	44
5)	fluazifop + fomesafen	0.28 + 0.6	112	15	60	3	0	0	37
6)	fluazifop + fomesafen	0.28 + 0.6	168	9	54	0	0	0	46
Oochemigation Method									
7)	fluazifop + imazaquin	0.28 + 0.28	56	29	30	0	7	0	63
8)	fluazifop + imazaquin	0.28 + 0.28	112	21	33	0	1	0	66
9)	fluazifop + imazaquin	0.28 + 0.28	168	17	27	0	4	23	46
10)	fluazifop + fomesafen	0.28 + 0.6	56	19	60	0	3	1	36
11)	fluazifop + fomesafen	0.28 + 0.6	112	35	38	0	0	5	30
12)	fluazifop + fomesafen	0.28 + 0.6	168	36	75	0	0	0	25

¹Data collected July 2, 1988.

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III. Description of cooperation

Three research groups (from Israel, Beltsville and Georgia (U.S.A.) collaborated in the framework of the project. The collaboration was by exchanging soil samples, weed seeds and computed literature search. However, the major cooperation has been the sharing of ideas and research results. The exchange of information and technical consultations were achieved during the visits of Dr. C.S. Helling and Dr. C.C. Dowler in Israel, and of Dr. Bruria Heuer in the U.S.A.

IV. Evaluation of the major research achievements

The main expected advantage of the combined application of fertilizers and pesticides through irrigation is primarily economic: time- and labor-saving, and reduction in energy consumption, as compared to conventional practices. In order to develop a management program including the supply of the agricultural chemicals through irrigation systems, whenever necessary, some major questions have to be answered.

One of the questions is about the physical compatibility between the large variety of fertilizers and pesticide formulations, when applied in combination through irrigation systems. In the framework of this project, the Israeli group developed a rapid, qualitative test to estimate the compatibility between emulsifiable concentrate formulations and liquid fertilizers. This test is based on the fact that, for each formulation, the relationships between the emulsion stability and the electrical conductivity of different fertilizer solutions, are fairly similar.

Another problem is the behavior of soil applied pesticides in the presence of nutrient solutions. Studies carried out at the Pesticide Degradation Laboratory, U.S.D.A., Beltsville, showed that it was not definite effect of the fertilizers, neither on pesticide adsorption nor on their soil mobility. The order of adsorption and mobility among selected pesticides and soils has been established.

The persistence of pesticides in soil was also unaffected by the presence of fertilizers.

The effect of pesticides on soil biological processes, and hence on the nutrient status in soils is especially relevant in the combined fertilizer

pesticide application. The Israel group concentrated its studies on the effect of pesticides on the nitrification process. It has been found that the pesticides investigated inhibited the oxidation rate of an ammonium source added to the sandy Bet Dagan soil. The magnitude of the effect was dependent on the nature and persistence of pesticides, their application rates, and the existence of additional stress conditions. In some cases, the chemical and environmental stresses had a synergistic effect. Although the inhibitory effect was, in all cases temporary, the long delays in the time required for the restitution of a normal microbial activity, as those caused by feramiphos and chlorpyrifos under stress conditions, might have significant agronomic impacts.

The combined effect of the nitrogen nutrition and herbicides on plants grown in nutrient solutions was investigated by the Israeli scientists. The data obtained demonstrated that low concentrations of the herbicides metolachlor and EPTC (below 10^{-6} M) had a remarkable inhibitory effect on the growth of cucumber plants. Accumulation of metolachlor in the leaves of young plants have been observed. An important idea arising from these studies is that, in some cases, the concept of the effect of subtoxic concentrations of herbicides on cultivated plants, should be reconsidered.

Another category of problems is related to the application technology of fertilizer-pesticide combinations through irrigation systems. The field and greenhouse experiments carried out at the Coastal Plain Experiment Station, Tifton, Georgia, were aimed to develop the required technology for the combined application of fertilizers and pesticides by both sprinkler and drip irrigation systems. The data obtained indicated that selected

pesticides and fertilizers can be applied by cochemigation through drip irrigation without adversely affecting compatibility or soil distribution. The lateral and vertical distribution of the agrichemicals and water was dependent on the solubility and/or volatility of pesticides, on the soil moisture content at time of irrigation and on the irrigation rate. One of the problems related to cochemigation by drip irrigation in sandy soils might be the undesirable movement of agrichemicals out from the rooting zone of small plants. At this stage of the research, it does not appear that drip irrigation provides the proper distribution of agrichemicals in this sandy Coastal Plain soil. However, retention of agrichemicals in the root zone could be controlled by proper soil moisture at irrigation time, by the cultivation system and by the proper spacing of the emitters.

Cochemigation through micro-sprinkler systems did not represent compatibility problems and the efficiency of herbicides and nematicides combinations was equal or better than that obtained by conventional application. Yet, the efficacy of some specific herbicides on specific weed species was reduced when applied with fertilizers through sprinkler irrigation.

Generally, the main achievements of this research are its contribution to a better understanding of the mutual effect of fertilizers and pesticides in soils and plants, to the development of the required technology and to the understanding of the factors affecting the distribution of agrichemicals applied through irrigation systems.

V. List of Publications

1. Saltzman, S., and Brates, N. Stability of emulsifiable concentrate pesticide formulations in liquid fertilizers. Pestic. Sci. 1990, (in press).
2. Saltzman, S., and Brates, N. Effects of pesticides and CO₂ stress on ammonium oxidation in soil. J. Env. Sci. Health, Part B (submitted).
3. Saltzman, S. Urea transformations in a sandy soil as affected by pesticides on CO₂ stress (in preparation).
4. Kinsbursky, R.S., and Saltzman, S. CO₂-nitrification relationships in closed soil incubation vessels. Soil Biol. Biochem. 1990 (in press).
5. Heuer, B. and Brates, N. Growth, photosynthesis and translocation in cucumber plants exposed to low concentrations of metolachlor. Pestic. Sci. (submitted).
6. Heuer, B. Effects of subtoxic concentrations of metolachlor and the NO₃⁻/NH₄⁺ rates on cucumber plants (in preparation).
7. Heuer, B. Response of cucumber plants to low concentrations of EPTC and NO₃⁻/NH₄⁺ ratio (in preparation).