

Movement of Pesticides to Ground Water in an Irrigated Soil

by

Bert Paul Krawchuk

A thesis
presented to the University of Manitoba
in partial fulfillment of the
requirements for the degree of

Master of Science

in the

Department of Soil Science

Winnipeg, Manitoba

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**MOVEMENT OF PESTICIDES TO GROUND WATER IN
AN IRRIGATED SOIL**

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BERT PAUL KRAWCHUK

**A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
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MASTER OF SCIENCE

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ABSTRACT

The movement of pesticide residues to ground water was studied on a commercial farm southwest of Portage la Prairie, Manitoba and in the laboratory using soil columns from the farm site. The farm site had sandy soil with low organic matter content, a high water table, a tile drain system and an irrigation system which applied river water. Records describing pesticide usage on a field by field basis were available from the beginning of commercial operation in 1979, a total of 21 different pesticide formulations had been used in the 5 years of operation.

An initial random sampling of the tile outflow water did not detect any pesticide residues at the 0.02 ppb level in 1981. In 1982, chlorothalonil was detected in the outflow water on a total of 9 occasions from the three outfalls, with a maximum observed concentration of 3.66 ug/L. Chlorothalonil and carbofuran were detected in ground water sampled from one of two stand-pipe wells in the NW quarter of 10-11-7 in 1982 and 1983. The levels observed in 1983 were two orders of magnitude lower than those observed in 1982. In addition, 2,4-D was detected in the ground water in 1983 from the two stand-pipe wells.

The laboratory soil column work found that trifluralin, chlorpyrifos, EPTC, chlorothalonil, diclofop-methyl, carbofuran, metribuzin and bromoxynil as the octanoate, leached through the columns in varying degrees. The leaching rate was directly related to the partition coefficients K_{ow} and K_{oc} and the amount leached to the pesticide's water solubility and the microbial activity of the soil. Precipitation, rain water, leached more of the parent pesticide than did the river water used in irrigation.

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INTRODUCTION

In agricultural uses, pesticides increase net return to the farmer, improve the yield per hectare in many instances, and often contribute to the quality of the agricultural product. At this time, the benefits from the proper use of pesticides far outweigh the hazards that they present. It is the intention of this work to outline one of the potential hazards of pesticide use in the environment. A study was carried out in the Rural Municipality of Portage la Prairie to evaluate the possibility that ground water, and possibly drinking water, had been contaminated by pesticides leached from a local irrigated farm.

The agricultural soils of a large area of southwestern Manitoba, i.e., the area of the old Assiniboine Delta from glacial lake Agassiz, are largely coarse textured (sandy and relatively low organic matter content) and are poor producers under conventional farm practices. However, with the use of irrigation, intensive cultivation and pesticide use, these soils can be made quite productive. Water required for irrigation comes from natural water supplies such as rivers or lakes located within the region. With a lacustrine clay layer 2 to 4 metres below the surface, the water table in the area is quite high (within 1 metre of the surface in areas). Due to this short transport distance, applied pesticides can move more readily from point of application to underlying ground water with the input irrigation water. The problem, however is that once ground water is contaminated, it is difficult and costly to restore it to its former high quality state.

The residents of an area of the Rural Municipality of Portage la Prairie were concerned about the possible contamination of their drink-

ing water supply by agricultural chemicals in the ground water. With this concern in mind the Kroeker Farms' Verway Farm site (10-11-7W) southwest of Portage la Prairie was chosen as the working site (to represent the "worst case situation"). Three features of this farm made it most suitable for study were: (1) the type of soil - sandy soil of low organic matter content, (2) a tile drain system, and (3) an irrigation system. All of these factors enhance the possibility of the ground water being contaminated by leached pesticides.

This study was set up with the following objectives in mind: (1) to determine whether or not applied pesticides leached to ground water under field conditions, and if so, to quantify the degree of movement and identify the parameters affecting movement, (2) to study the leaching of selected pesticides in the laboratory using several soil types under two irrigation regimes (natural river water and triple-distilled water), and (3) to determine the experimental $\log K_{ow}$ (partition coefficient) of the pesticides applied to the fields and the soil columns and compare their extrapolated theoretical behaviour with their actual observed behaviour both in the field and in the laboratory.

The literature review will focus on the last ten years literature covering pesticides leaching to and being found in ground water for all twenty or so active ingredients which were applied to the Verway operation from 1979 to 1983, inclusive. In addition, the degradation and fate of these compounds will be reviewed to provide some insight into the environmental fate of these compounds. The partition coefficient, K_{ow} , will be reviewed and discussed in connection with environmental modelling based on this parameter.

LITERATURE REVIEW

2.1.0 LEACHING

2.1.1 Introduction

Pesticide mobility within a soil or leaching is greatly influenced by four groups of complex interactions between the pesticide, the soil, the plant covering and local environmental/climatic factors (Nose, 1984a & 1984b).

The pesticide group of factors is made up of chemical properties (structure, solubility and volatility), application methods (formulation, rate and mode) and degradation patterns (pathways and metabolite formation). The chemical properties will affect the amount which is mobile both through solubility and volatility. In addition, the chemical characteristics of the pesticide may change as it percolates through the soil zone before it reaches ground water. Volatilization of the pesticide enables transport into the atmosphere. The method of application will also affect the amount available for leaching both directly through rate applied as well as indirectly through where it is applied, i.e., foliar versus directly to the soil. Degradation pathways which are also dependent upon soil conditions will determine in what form the pesticide will be leached and whether or not it will be a hazard.

The major factors which shape the complex interactions within the soil group are: (1) soil properties (nature and amount of soil organic matter, clay and amorphous materials, pH of the soil solution, structure and permeability), (2) soil conditions (moisture, aeration, nutrient status, microbial activity, heterogeneity, and depth to water table),

and (3) land forms (topography, slope length and steepness, and drainage). The soil properties influence the rate at which pesticides leach through the soil as well as how much of the pesticide is held within the soil and in what form. The sorption process can retard or retain the chemicals from moving with leaching water. Soil organic matter can slow down the movement by up to a factor of ten by absorbing the residues. Clay soils have a greater capacity for physicochemical attenuation of contaminants than coarse sands or fissured rocks. Soil conditions primarily influence the microbial activity which in turn affects both the amount of pesticide leached and the form leached. At present the biological and physicochemical changes that occur in contaminants in the unsaturated soil zone are not well understood. The land form will determine to some degree the relative amount of the total input water available for leaching. Soil field capacity and water infiltration have an effect on leaching. Soils with a low water holding capacity and high water infiltration from heavy rainfall, excessively rainy seasons, or over-irrigation are major contributors to leaching. Under "normal" precipitation conditions evapotranspiration and plant absorption normally are enough to retain residues in the root zone.

Species characteristics, stage of growth and root system and rhizosphere are the three factors which make up the plant group of factors. Uptake by plants will remove pesticides from the soil thus reducing the amount available for leaching. Stage of growth will have an effect upon the amount of pesticide reaching the soil surface. All three factors will have an effect on water movement within the root zone and thus will influence leaching through this volume of the soil.

The environmental group of factors are made up of the following five

factors: (1) temperature, (2) precipitation, (3) humidity, (4) air movement and (5) radiation. Temperature can affect leaching in a number of ways, directly on both the solubility and the volatility of the pesticide and indirectly on water movement in the soil. The quantity and quality of precipitation can affect the amount of pesticide leached as well as affect the amount available for leaching through erosion. Volatility and air movement together can effect the amount available for leaching, and air movement resulting in erosion can remove pesticide residues from an area thus reducing the amount available. Solar radiation can affect residue availability either directly through photolysis of the residue on surfaces or in aqueous solution, or indirectly by raising temperature and creating air movement.

These factors will be further pursued and expanded with examples in the following pages. In addition, a number of other topics will be introduced and discussed which pertain to theoretical determinations of certain physicochemical properties and behaviours of pesticides in the environment and their usefulness in assessing their environmental hazard. The behaviour and fate, in the soil and water, of the active ingredients applied to 10-11-7W from 1979 to 1983, inclusive, will be reviewed to give an overview of what is happening to these chemicals in the field.

2.1.2 Field and Laboratory Studies

Retention processes are usually labelled adsorption or simply sorption. Strictly speaking adsorption is an reversible process involving nonspecific attraction of a chemical to the soil particle surface and retention of the chemical on the surface for a longer or shorter period

of time depending on the affinity of the chemical for the surface. Whether a chemical is actually sorbed to a particular surface can not be confirmed as the mechanisms involved in attracting a chemical to the soil surface can not be differentiated by the techniques generally used for retention characterization (Cheng and Koskinen, 1985). The adsorption process has been described, the factors involved outlined, the general characteristics of pesticide adsorption given, some of the consequences of pesticide adsorption detailed, and adsorption study methods reviewed in a series of papers (Calvet et al., 1980 a,b,c,d,e).

Soil bound pesticide residue are defined as "that unextractable and chemically unidentifiable pesticide residue remaining in the fulvic acid, humic acid, and humin fractions after exhaustive sequential extraction with nonpolar organic and polar solvents" (Khan, 1982). With the improvement in identification techniques, this definition has been simplified to "chemical species, originating from pesticide usage, that cannot be extracted by methods commonly used in residue analyses." The main area of concern with bound residues is chiefly addressed in terms of their bioavailability, both in amounts and forms of uptake. Bioavailable bound residues are those bound residues in soil which are not taken up by plants and/or soil-inhabiting animals. The pesticide residue may either be chemically bonded into the soil organic matter or be physically bonded into the soil particle (molecular sieve).

A number of quick-test techniques are widely used to express the degree of sorption of a chemical to soil, one common method expresses the degree of sorption as a ratio of the chemical in solution to the amount of chemical absorbed on the soil (K_d) or alternately a ratio of the chemical partitioned between an organic phase (octanol) and an aqueous

phase (K_{ow}). These distribution ratios are used as an indicator for the potential mobility of a chemical in a soil. A caution is raised (Cheng and Koskinen, 1985) about the use of these parameters for this purpose. Depending on the experimental parameters used, the mobility of a chemical in a particular soil could be classified as either high or low.

Correlations between soil sorption of a chemical and its K_{oc} (organic carbon partition factor), R_t (retention time) and S (water solubility) does not automatically impart any theoretical meaning to the empirical measurement. Such factors as soil solution composition and temperature can affect the amount of pesticide absorbed but cannot be accounted for by these indirect methods. As a result, any measurement which does not take into consideration the role of soil or the environmental variables in the adsorption process can at best be simply an estimate.

The meaning of these correlations should not be extended beyond what the data warrants, i.e., if a significant correlation between sorption and soil organic carbon contents exists, that does not imply that only one mechanism of sorption is involved or that all pesticides interact with all components of soil organic matter by the same mechanism. On the other hand, a lack of correlation between pesticide sorption and soil mineral or clay contents should not be taken to mean that the adsorption to soil minerals is not important. This lack of correlation may only imply that the soil mineral content by weight is not a good index for the extent of mineral surface available for adsorption.

The adsorption process is very complex and should be thoroughly understood by those interested in assessing the impact of sorption on the transport of chemicals to ground water. Mechanisms or forces which are involved can range from Van der Waals-London forces, hydrogen bonding,

ligand and ion exchange, charge transfer, ion-dipole and dipole-dipole forces, hydrophobic bonding, to chemisorption. A simple representation of adsorption such as depicting the process as partitioning into an organic phase ignores the true nature of the processes involved. Even characterization of sorption based solely on solute solvent factors may not be adequate. The pesticide-soil-solution equilibrium may be affected by the composition of the aqueous phase for some pesticides. As an example, the soluble organic matter and metal ions in solution can complex or bind small organic molecules and stabilize them in aqueous solution.

The unsaturated zone properties, such as sand, silt, and clay content vary both laterally and vertically in an agricultural field. These variations can vary leaching by as much as 23% in one field site (Carsel et al., 1986).

The effect concentration (El Beit et al., 1981a), temperature and period of contact (El Beit et al., 1981b) had on the leachability and adsorption of dieldrin, endosulfan, pyrolan, and gamma-HCH in a sandy clay loam soil was determined. Only pyrolan and gamma-HCH showed a direct positive concentration and temperature affect. Elevated temperatures were found to decrease the adsorption of three of the four compounds. This decrease in adsorption was attributed to an increased rate of water movement in the soil and an increase of evaporation and degradation of the pesticide.

The factors affecting adsorption of a systemic insecticide were evaluated on a wide variety of soils using a wet slurry technique (Graham-Bryce, 1967). Air-dried soils adsorbed similarly to the moist field soils from which they were derived. Adsorption was fully reversible if

desorption took place immediately after uptake when the soils were still wet; when the soils were allowed to dry thoroughly between adsorption and desorption, release was modified. Comparison of the slopes of the best-fitting linear relationships showed that adsorption was closely related to the amount of organic matter in the soil.

The movement in soil columns of permethrin, fenvalerate, toxaphene, trifluralin, and metribuzin in a silt loam soil as affected by fertilizer was characterized under saturated conditions (Smith and Willis, 1985). The insecticides were essentially immobile on the columns receiving no ammonia, and slightly mobile on the soil columns receiving the ammonia. Trifluralin showed very little movement in the column which probably reflects a very strong sorption to the mineral components of soil. Further extensive disappearance of trifluralin occurred and was attributed to biodegradation, photodecomposition and volatilization. Metribuzin on the other hand, leached rapidly through the soil with 53 to 74% of the total applied leaching out of the column, the amount leached decreased with the amount of ammonia applied. Application of an alkaline fertilizer, anhydrous ammonia, thus may enhance the downward movement or leaching of some normally immobile pesticides in soil.

Pesticide leaching is not solely confined to the direct movement of the residue, dissolved in the soil water, but can also include indirect movement. The general assumption is that pesticides with very high K_d values are virtually immobile in the soil, though by erosion they may be transported laterally. Vertical movement of "bound" residues has been reported (Vinten et al., 1983) in which DDT and paraquat were found to move under certain conditions. The pesticide was adsorbed onto clay or suspended solids in sewage effluent. The clay suspension or sewage ef-

fluent were then applied to soil columns and the progress of the leaching monitored. Distilled water leached 50% of the applied clay suspension pesticide below the 12 cm level; whereas, a CaCl_2 solution only moved 5% of the pesticide past the 1 cm level. The sewage effluent was also found to transport the pesticide below the surface but not to such extents as the clay suspension. The extent to which this type of transport can occur depends on the amount of clay or organic matter released by the surface soil on dispersion, the mobility of these colloids in the soil profile, the rate at which soil clogging occurs, the K_d value, and the kinetics of desorption of the pesticide from the mobile colloid.

2.2.0 PARTITION COEFFICIENTS - K_{ow}

2.2.1 Theory

The partition coefficient P or K_{ow} is a parameter which recently has received a great deal of attention (Lyman, 1981). Relationships have been developed between the octanol-water partition coefficient and the uptake rate constant (Hawker and Connell, 1985); clearance rate constant from fish (Hawker and Connell, 1985); time to equilibrium (Hawker and Connell, 1985); bioaccumulation (Geyers et al., 1984; Hawker and Connell, 1985); soil sorption isotherms (Karickhoff et al., 1979; Kenaga and Goring, 1980; Chiou, 1981); water solubility (Kenaga and Goring, 1980; Mackay et al., 1980; Chiou, 1981); bioconcentration factor (Kenaga and Goring, 1980; Chiou, 1981); the chromatographic retention parameter, k_w , (Braumann et al., 1983); and environmental fate modelling (McCall et al., 1983). As well, the decomposition (Dekkers, 1978) and the concentration (O'Connor and Connolly, 1980) of a compound has been evaluated in relation to the effect on the partition coefficient.

A review of the concept of partition coefficients and its uses has appeared (Leo et al., 1971). A chemical has a tendency to distribute itself between two separable phases which is measurable in terms of the equilibrium constant of the chemical in the two phases. The term "partition coefficient" is simply this tendency of a chemical to solubilize in two separable phases. The magnitude of K only serves to indicate the preference of a solute for the organic phase relative to water. A high K value does not indicate that a compound has a higher solubility (or lipophilicity) in the organic phase than a compound with a low K . In other words, the octanol/water partition coefficient is not the ratio of a chemical's solubility in octanol to its solubility in water, because the organic and aqueous phases of the binary octanol/water system are not pure octanol and pure water. At equilibrium, the organic phase contains 2.3 mol/L of water, and the aqueous phase contains 4.5×10^{-3} mol/L of octanol. However, K_{ow} is often found to be a function of concentration for concentrations $\gg 0.01$ mol/L.

The presence of small amounts of octanol in the water may have an effect on the solubility of some hydrophobic compounds thus giving a unreliable partition coefficient; based on calculations of the activity coefficients, the solubility of DDT in octanol saturated water is 160% greater and HCB is 80% greater than in pure water (Chiou, 1981). From this, a question arises as to the accuracy of tabulated K_{ow} values for very hydrophobic compounds which have been determined by the Shake-Flask method in light of the possible effect that the dissolve octanol may have on the activity coefficient of the compound in water, a_w .

The individual factors that determine the prediction of octanol-water partition coefficients for liquids are, in descending order, water solu-

bility, compatibility with water-saturated octanol, and the effect of dissolved octanol on water solubility (Chiou et al., 1982). For solids, the effect of melting point on water solubility has to be considered, and at this time it is not sure whether the corresponding supercooled liquids are miscible with octanol; thus the prediction of partition coefficients from solubilities may be less accurate for high-melting solids than for liquids. Conversely for liquids, good predictability should be expected for partition coefficients.

2.2.2 Laboratory Studies

Partition coefficients are directly related to sorption for a chemical in a water-sediment system, with the linear portion of the relationship independent of the sediment concentration in dilute solutions (Karickhoff et al., 1979). The partition coefficient increased linearly with organic matter content according to the following relationship:

$$K_{oc} = K_{ow}/oc$$

where *oc* is the fractional mass of organic carbon in the sediment.

An inverse relationship between concentration of the adsorbing solids and the partition coefficient exists, as the organic content of the soil decreased, the partition coefficient decreased, with the lowest values being associated with material that is primarily sand (O'Connor and Connolly, 1980).

Decomposition of the compound affects both the sorption to a surface and the partition coefficient, even at low degradation levels (Dekkers, 1978).

Aqueous solubilities have been correlated to octanol-water partition coefficient for various types of low-molecular-weight organic liquids.

Aqueous solubility of a compound can be considered as a special form of partition coefficient in which the compound distributes between an "ideal solvent" (itself) and water. The regression equation between $\log K_{ow}$ and $\log S$ for a total of 156 compounds from various classes has been done and was found to cover about 5 orders of magnitude in S and 4 orders of magnitude in K_{ow} (Chiou, 1981). A correlation of 34 compounds, mostly organochlorine and organophosphate pesticides and PCBs was done and was found to extend over 8 orders of magnitude in S and 6 orders of magnitude in K_{ow} .

The capacity factor, $\log k'$ (a relationship of retention times), once corrected for selective factors due to solute-solvent and solute stationary phase interactions, is suitable for quantitatively describing the hydrophobic nature of solutes in a way which is strongly related to the partition coefficient $\log K_{ow}$ (Braumann et al., 1983). The theoretical capacity factor, $\log k_w$, may be a better model for the assessment of the hydrophobicity of a compound in biological systems than $\log K_{ow}$ because of the different effects functional groups have in RPLC and a true liquid-liquid partitioning system.

The Shake-Flask method for K_{ow} determination has been the standard for a number of years. The partition coefficient of terbufos and its two degradation products determined with this method was noted to differ from the previous two report values which themselves varied greatly from each other. The observed differences were attributed to water soluble impurities and experimental techniques (Ruepert et al., 1985).

A number of alternative, indirect methods based on relationships between K_{ow} and chromatographic retention properties (HPLC and TLC) and a derivation from structural data, have become available for K_{ow} determin-

ation since the Shake-Flask method became the recognized method (Eadsforth and Moser, 1983).

In a reversed-phase system, the mobile phase which is partially aqueous and a stationary phase which is lipoidal in nature, mimic, at least in part, the partition between n-octanol and water. This method offers a rapid and inexpensive way of determining partition coefficients provided that their limit of applicability is taken into account.

A calibration curve must be established between the chromatographic data and $\log K_{ow}$ values of reference compounds (same class of compounds) (Toon and Rowland, 1980; Eadsforth and Moser, 1983), which is difficult to do sometimes as the K_{ow} data is sometimes difficult to find or it varies substantially in the literature.

The precision of the HPLC method is equivalent to that of the Shake-Flask method, and the HPLC method gives an adequate estimate of $\log K_{ow}$, comparable to that obtained by the Shake-Flask method (Eadsforth and Moser, 1983). The accuracy can be improved if structurally-related reference compounds are used.

In TLC, a R_M value was derived from the R_F (retention factor) value which was then correlated to the n-octanol/water partition coefficient for reference compounds, then the partition coefficient of an unknown chemical was calculated (Renberg et al., 1980). One of the difficulties encountered with the TLC method was that some compounds do not resolve sharply but give broad bands which resulted in a greater uncertainty in the calculated $\log K_{ow}$ value.

Chemical mobility in soil and K_{ow} can be estimated for organic pollutants from reverse-phase HPLC data (McCall et al., 1980; McDuffie, 1981). Data from column leaching and HPLC experiments developed into a

mobility classification system based on HPLC retention times showed a clear correlation between $\ln K_{oc}$ and $\ln R_t$ (McCall et al., 1980). Thus, laboratory measurements can classify the tendency of a chemical to leach with respect to other chemicals so that comparisons with the known behaviour of certain chemicals in the field can be made. HPLC has been used to determine the K_{ow} 's of a number of compounds from a plot of $\log K_{ow}$ versus a corrected retention time (McDuffie, 1981), give a rapid estimate of soil sorption constants (Swann et al., 1981), to demonstrate a relationship between melting point, solubility and K_{ow} based on physical chemical equations governing solubility and partitioning for a wide range of hydrophobic organic compounds (Mackay et al., 1980). If the soil adsorption coefficient is known along with the organic carbon content of the soil, then predictions regarding movement by leaching can be made, however, other factors in the soil can influence sorption by 20-30% McCall et al. (1981). This data can be used to give a first approximation for fate and hazard assessment of chemicals.

2.3.0 MODELS

2.3.1 Soil Columns

A method has been described for preparing soil columns (Sieczka et al., 1982) in which a 76.2 cm long x 3.8 cm i.d. PVC pipe is driven 61 cm vertically into the soil with a sledge hammer, then withdrawn; the ends are covered with cheesecloth and the entire pipe is frozen and sectioned into 15.2 cm segments beginning at the bottom. The sections are thawed and analyzed for their residue content.

Leaching studies carried out in the field or in the laboratory use soil columns to follow the leaching and in determining the fate of an

applied chemical. Columns filled with about 80 cm of undisturbed soil have been used to examine the fate of long-lived fission products (Poelstra et al., 1973). An automatic control unit was used to control the amount of influent solution delivered to the rain head.

Soil column studies (fine sand soil) have indicated that ground water contamination occurs quickly where there is rapid infiltration of water into the soil (Hutchins et al., 1983). Some of the organics passing through the soil did so without any transformation taking place while others were degraded.

Soil column studies have also correlated the soil adsorption coefficient with movement. In one study, soil columns were eluted under controlled conditions using nine chemicals and three soil types (McCall et al., 1981). The following simple relationship was developed:

$$\text{cms moved by chemical} = (K_d)^{-1} (\text{cm H}_2\text{O entering soil} / (1 - \phi^{2/3}) d_s$$

where K_d is the soil sorption constant, ϕ is the pore fraction of the soil, d_s is the bulk density of the soil solids. This expression makes use of the organic carbon content of the soil in the expression,

$$K_{oc}(\%OC/100) = K_d$$

Thus, knowing the soil adsorption coefficient and the soils organic matter content, predictions regarding movement by means of leaching can be made. The sorptive behaviour of a number of nonpolar organic compounds was elucidated from batch and column experiments (Schwarzenbach and Westall, 1981).

An acidic herbicide leached readily through a number of Canadian Prairie soils, with the greatest movement being in soils with low organic matter and clay contents (Grover, 1973). Black soils with a high organic matter content showed the least movement of the herbicide

through the soil column. Leaching ability was related to the adsorptive and water-holding capacities of the soils. In addition, the amount of water applied to the soil influenced the movement of the herbicide. Sub-irrigation of the soil caused the herbicide to move upward.

Field mini-lysometers, containing soils from three U.S. states, were treated with a 1:1 mixture of 2,4-D and 2,4,5-T, the *n*-butyl esters, and the leachate from the columns was collected and analyzed (Majka et al., 1982b). Little 2,4-D leached through the soils in the first two years, in the third year 30 ppm of 2,4-D was detected in the leachate from two of the soils. The majority of the undegraded herbicides were found in the top 10 cm of soil after two to three winters. Soil TLC showed that the ester form of the herbicides are relatively immobile, and that the acid form was less mobile in the one soil (sandy loam) than in the other two (silt loam and clay loam).

Columns of grassed and fallow soil were treated with aldicarb then dug into the soil at a test site in the spring (Smelt et al., 1983b). Precipitation and soil temperature data was collected. All residues were either the sulfoxide or the sulphone, no parent compound was observed. In loam soils, the majority of residues were in the 10 to 20 cm level for the fall sampling. By spring the majority of residues had leached out of the root zone. In humic sand soils, the residues were more evenly spread out down to the 60 cm depth in the fall sampling. By the spring sampling virtually all the residues had leached right out of the column. The column study showed that ground cover (i.e., crop) versus fallow soil affected the movement and conversion of aldicarb in the soil profile.

2.3.2 Field/Laboratory Studies

Ground water is subsurface water which occurs in fully saturated soils and geological formations and constitutes approximately 4 percent of the water in the hydrological cycle, second only to the oceans and sea, which account for 94 percent (Pye and Patrick, 1983). The volume of ground water in storage exceeds the volume of fresh water in lakes, streams, and rivers. During dry periods, ground water supplies most, if not all, of the low water flow in streams.

Aquifers may be composed of permeable or porous geological material, either unconsolidated sand and gravel or consolidated material such as carbonate rocks, volcanic rocks, or fractured igneous, metamorphic, or sedimentary rocks. Unconfined aquifers are the most susceptible to contamination as they are not overlain by impermeable material and are recharged by water seeping through the soil, and they may be close to the surface of the land. Water in unconfined aquifers at the saturated-unsaturated interface is at atmospheric pressure and the volume in storage may fluctuate according to seasonal cycles of natural recharge due to precipitation and man's use of the aquifer.

The fate and movement of organic chemicals which enter the subsurface environment are largely governed by sorption and chemical and biological degradation. Sorption affects the rate of movement of organics relative to that of water through subsurface systems. Sorption also allows for the accumulation of organic compounds on subsurface soil (McCarty et al., 1981). The extent of sorption to particles appears to be a function of organic carbon within the subsurface matrix. The partitioning of hydrophobic organics between the water phase and the subsurface organic particulates can be estimated from the octanol-water partition coefficient.

ent for each organic compound. The significance of the organic matter for hydrophobic solute retention depends upon the sorptive characteristics of the solutes. Interactions of hydrophobic solutes with organic matter have been shown to be reasonably predictable over a wide range, interactions with inorganic surfaces do not generally follow a simple pattern. The role of the inorganic matrix is likely to dominate not only the solute transport of polar and ionized species, but also of non-ionized, hydrophobic solutes if the organic content is below the critical level (f_{oc}^* , which is a ratio between the inorganic and organic partition functions). The ultimate fate of organic chemicals in the subsurface system strongly depends upon their biodegradability. Some of the available evidence indicates there is a minimum concentration to which a single organic material can be decomposed under steady-state conditions (McCarty et al., 1981). This concentration is a function of the growth and decay coefficients of the bacteria, which in turn are functions of environmental variables such as temperature, pH, bacterial species and available electron acceptors. Trace organics may be biodegradable, but are often below the minimum concentration required for a primary substrate. Biodegradation of such materials will generally occur only if they are used as secondary substrates.

Ground water contamination by pesticides has occurred in a number of areas in the United States (Spalding et al., 1980; Page, 1981; Pionke and Urban, 1985; Wyman et al., 1985; Cohen et al., 1986) with a positive correlation to land usage, agricultural, in the area (Page, 1981; Greenberg et al., 1982; Pionke and Urban, 1985). The presence of pesticide residues in the ground water was attributed to leaching of the pesticides through the soil column (Spalding et al., 1980). Page (1981)

using data on the concentration of 56 toxic substances in samples of both ground water and surface water from New Jersey, found the same pattern of contamination in the ground water as in the surface water and in some cases the ground water was contaminated at the same levels as the surface water. Atrazine, alachlor and dieldrin follow definite areal, vertical, and temporal trends in concentration based on samples collected from monitoring wells and surface water (Junk et al., 1980). Peak atrazine concentrations were observed in shallow well water down gradient from irrigated fields at the end of the irrigation season.

A summary update, for 17 pesticides in ground water throughout the United States, outlines what areas of the country are being actively monitored for specific pesticides (Cohen et al., 1986). Atrazine was found in ground water of 5 states at levels ranging from 0.3 to 3.0 ug/L; carbofuran in the ground water from 3 states at levels from 1 to 50 ug/L; metribuzin, a recent addition, in one state at levels ranging from 0.09 to 4.35 ug/L.

Pesticide concentrations and total amounts in surface runoff and tile drain water from irrigated fields in the Imperial Valley area of California were found to be dependent upon the characteristics of the pesticides, their method and rate of application, the time elapsed between application and the first irrigation, the number of irrigations since the pesticide application, irrigation efficiency, and other soil management practices (Spencer et al., 1985). The highest runoff rates were observed when herbicides were applied in the irrigation water. None of the monitored pesticides were found in the tile drain water at concentrations above the minimum detectable levels of 1 to 2 parts per trillion.

A 10 year study of the ground water quality of a small Pennsylvania watershed correlated the ground water contamination pattern with land usage in the area (Pionke and Urban, 1985). Down gradient from the agricultural use area the ground water passed through a geological zone in which the chemical load concentration was greatly decreased due to mixing and dilution.

In the Ionic coastal arch north of Taranto, Italy, where the agricultural area is intensively cropped with vegetable crops, grapevines and citrus, irrigation water contained residues of DDT and its degradation product DDE even though their use has been banned for several years (Polemio et al., 1983). The concentrations of residues increased with time, with a positive correlation to the precipitation pattern in the region.

Muir and Baker (1978) detected residues of triazine herbicides in tile drainage water, in Quebec, indicating vertical movement through the soil column. In Nebraska, the leaching of atrazine from the soil surface to below the root zone was measured in an alluvial soil under irrigated conditions (Wehtje et al., 1984). Samples of soil water (1.5 m depth) indicated that about 0.072% of the atrazine applied over a two year period had leached to that depth. Hoque et al. (1981) in comparing the mobility of four residual orchard herbicides, in two soils from the Okanagan valley in British Columbia, found a greater mobility of all four herbicides in the sandy loam than in the loam soil. Grover (1973, 1977) using soil columns, for eight Saskatchewan soils, found that picloram, dicamba, and 2,4-D were readily leached in all the soils studied, the greatest movement being observed in the sandy loam. The concentrations of the pesticides in the column effluents were found to be

well below the pesticide aqueous solubility. The pesticide levels in the column effluent were inversely related to the distribution coefficients thus indicating an inverse relationship between adsorption and mobility.

Soil column studies with buthidazole and its metabolites under unsaturated-flow conditions in four soils determined that similar amounts of the herbicide leached through each of the four soils, but the distribution of the compound in the soils varied greatly (Weber and Peeper, 1982). Under unsaturated-flow conditions, bromacil was more mobile than buthidazole, and both of these herbicides were more mobile than atrazine, prometon, or diuron primarily due to their water solubility (Weber and Whitacre, 1982). Saturated-flow studies found substantial amounts, 77.1 to 84.5% of total applied buthidazole, tebuthiuron and CN-10-3510 in the leachate. The distribution of the portion remaining on the soil column was similar for each of the three herbicides. These three herbicides have weakly basic properties, have relatively similar water solubilities, and they adsorbed to the soil in similar amounts at pH levels ranging from 4.7 to 6.0.

Wilson et al. (1981) assessed the minimal protection that soil can be expected to provide ground water. The transport and fate of 13 organic pollutants was evaluated in a sandy soil of low organic matter content (0.087% org. C). A simple mathematical model based on water solubility of the compound and the organic carbon content of the soil was developed to predict the retardation factor.

Surface water quality is of great concern due to the uses it is put to; e.g., domestic consumption, industrial uses, and agricultural purposes such as irrigation and livestock watering. Consequently, ground water quality is of interest, especially where it is brought to the sur-

face by tile drainage or it collects in surface depressions. Contaminated ground water thus has a potential to contaminate surface waters whenever it is brought to the surface. Guidelines have been set which set an upper limit on the concentration of pesticides which can be found in the water and the water still be used for human and/or animal consumption (Health and Welfare, Canada 1978; Manitoba Department of Environment and Workplace Safety and Health, 1983). These Federal and Provincial guidelines both limit total pesticide content to 100 ug/L for those pesticides listed as well as place upper limits on certain pesticides especially certain of the organochlorines. Both 2,4-D (acid) and methoxychlor have an individual upper limit of 100 ug/L whereas, aldrin and dieldrin have upper limits of 0.7 ug/L.

In addition to human use, environmental concerns should be taken into account, i.e., what direct effect is there on the fauna and flora from contaminated ground water entering surface waters? Webster (1974) reviewed the environmental concerns of pesticide use from a water quality viewpoint, taking into account the various uses of water. The detrimental effects of pesticide usage are covered where non-target species are affected, where the pesticide is transported to a body of water in a watershed either through direct dissolution in runoff water or physical transport of adsorbed residues on soil particulates.

Much concern has been raised about the pesticide content of agricultural runoff waters and its affects on aquatic species in surface waters. Phenoxy acid herbicides are used to control broad-leaf weeds and woody plants in a number of crops and aquatic vegetation in waterways. Aquatic toxicities for 2,4-D acid will vary depending upon the buffering capacity of the water, i.e. water quality (Alexander et al., 1985).

Persistent pesticides produce greater long term losses to runoff; the longer the persistence the longer the pesticide is available to runoff forces and the greater the potential loss by runoff (Willis and McDowell, 1982). Rate and mode of application also have an effect on runoff losses, surface-applied pesticides have a greater runoff loss than soil-incorporated pesticides (Wyman et al., 1985). In addition, the following factors contribute to losses to runoff: rainfall characteristics, time interval between application and first rainfall, pesticide properties, soil texture and topography, antecedent moisture, type and amount of ground cover, and distance of transport. Of the listed factors, rainfall characteristics, time between application and first rainfall and pesticide properties are the most important in determining pesticide losses from unit source areas. After a "catastrophic" rainfall 12 to 17% of the applied triazine herbicide, atrazine, was found in the runoff water and phenoxyacetic acid herbicides ranged from 2 to 10% of total applied (Weber et al., 1981).

The greatest potential environmental hazard of pesticides is to aquatic organisms, as they are more susceptible to pesticides due to continuous exposure. Once a pesticide enters the aquatic ecosystem, local environmental conditions begin to influence the impact the pesticide has on that ecosystem. The pesticide is transported and dispersed rapidly throughout the system as a function of the hydrological and limnological factors. The limnological characteristics of the system affect (a) the spatial distribution of the pesticide, (b) the nature of the chemical regime to which the pesticide is exposed, (c) the partitioning of the pesticide among the various system components and (d) the persistence of the pesticide within the system. Contact with a pesticide is rapid and

complete for aquatic biota because they are surrounded by water containing the chemical.

2.4.0 FATE OF PESTICIDES IN SOIL AND WATER

2.4.1 General

A review of herbicides and the soil environment in Canada recently appeared (Smith, 1982b) in which the fate of herbicides in Canadian field soils and their effect on soil fertility were discussed. The persistence of a number of herbicides is documented as well as if any leaching had been observed for the soil type. In addition, the effect if any of the herbicide on the soil microorganism population was discussed and how fertility may be affected. In a persistence study of three herbicides (Smith & Hayden, 1982b) applied in the fall and sampled in the spring applied on two soil, a heavy clay and a sandy loam, from 19 to 76% of the applied herbicide was recovered in the spring. At sampling time virtually all the chemical residues were in the top 5 cm soil level and less than 2% of the applied herbicides were detected in the 5 to 10 cm depths at any site indicating little to no leaching of the three herbicides which agrees with the previous work.

What happens to pesticides in the environment? There are a variety of processes acting on herbicides in the environment which add to the complexity of the problem (Weber et al., 1973). Once a chemical, herbicide, has been introduced into the environment, outside forces begin acting on it immediately. The ultimate fate of the chemical is determined by a combination of two major processes, degradation and transfer. There are three specific degradation processes which serve to breakdown

herbicides and change their chemical composition:

- 1) biological decomposition - degradation by a living organism;
- 2) chemical degradation - breakdown by a chemical process in the absence of a living organism;
- 3) photodecomposition - breakdown by purely chemical processes involving radiant energy (sunlight).

Under transfer processes there are a number of processes which determine what happens to herbicides in the environment:

- 1) adsorption and exudation by plants and animals - herbicides can either penetrate through tissues into an organism (absorption) or be discharged from inside an organism to the surrounding environment (exudation);
- 2) uptake by plants and retention in vegetation and then transference in the harvested product;
- 3) adsorption by soil particles, a process by which herbicides transfer from solution or vapour to a solid surface (soil particle);
- 4) movement through the air and into the atmosphere - this is a result of volatilization;
- 5) surface runoff of herbicides into ponds, rivers, and oceans - the herbicide may be either dissolved or suspended in water or be adsorbed to eroding soil particles from treated areas;
- 6) movement through the soil either laterally as liquid or gas or vertically (downward by capillary flow);
- 7) drift - movement of soil particles by air;
- 8) sedimentation - washout from precipitation.

All of these processes are involved in herbicide degradation intimately. Adsorption, which directly influences all the others, is probably the

key process.

The term "transformation" can be used as a general term to describe any and all changes in the chemical structure or composition of the pesticide compound. The term degradation should only be associated with the breakdown processes, even though it is used to describe other transformation processes. For most pesticides, transformation processes take the original toxic material and render it non-toxic, but for some pesticides, transformation processes can yield equally or more toxic products. Only by degradation is a pesticide totally eliminated from the environment.

Pesticides can be transformed by chemical, photochemical, and biochemical means. The soil can provide the conditions or serve as the catalyst or component for chemical reactions. Chemical reactions can be mediated by such soil properties as pH or catalyzed by soil minerals. Photolysis can occur either directly from absorbing radiation or indirectly by reaction with another chemical which is activated by absorbed radiation. The predominant means of transformation is microbial or enzymatic.

The kinetics of pesticide degradation are affected by (a) the quantity and the availability of the pesticides, (b) the presence of microorganisms or enzyme systems capable of degrading the pesticide, and (c) the activity level of the microorganisms as affected by the nutrients available to sustain the microbial population; by environmental conditions such as temperature moisture, oxygen supply, aeration; and by various soil parameters.

Foreign chemicals are metabolized, by plants and soils, by way of oxidation, reduction, hydrolysis, or conjugation with one or more of

these pathways operating in tandem (Freed and Montgomery, 1963). Soil microorganisms metabolize aromatic compounds by oxidative ring opening while plants may be less able to bring about this fission despite the fact that early stages of metabolism are similar.

Microbial degradation of pesticides is one route by which toxicants are lost from the soil. As a result, knowledge of degradation rates is required so that application methods and rates are such that the pesticide is effective against the targeted pest and that the soil ecosystem can cope with the application. Thus, the accumulation of pesticides and their residues in food chains, or risks resulting from the impact of pesticides upon beneficial soil microorganisms must be avoided. In the soil there are four significant interactions for which there is substantial evidence (El Beit, 1981c), they are as follows:

- (1) the pesticide is not degraded by microorganisms and the microorganisms are not affected by the pesticide;
- (2) the pesticide is not degraded or may be degraded to a limited extent, but it does not inhibit growth of the microorganisms;
- (3) the pesticide is degraded, but it does not inhibit the growth of the microorganisms and possibly even stimulates the growth; and
- (4) the pesticide is degraded and the growth of microorganisms is inhibited by the pesticide.

The first category includes those pesticides which do not interact with soil microorganisms where the pesticide is applied at low concentrations to a soil with a high organic or clay content, or with a high pH and temperature. Under these conditions the compound is adsorbed, chemically degraded or rapidly evaporated, and therefore rendered unavailable for interaction with microorganisms.

Field degradation rates or real world rates differ from laboratory rates because they occur at anything but standard conditions (Laskowski et al., 1983). Laboratory degradation rates are useful in getting a handle on what is occurring in the environment and a tentative ranking of the chemical can be made until more definitive studies can be done. In addition, by varying some the standard conditions, some of the climatic factors can be simulated and thence their influence on degradation can be evaluated.

Laboratory studies for determining soil degradation rates are often done using soils which have been air-dried and stored for some length of time. Drying and storage affects the soil aggregate and thus the behaviour of soil microorganisms. Prolonged storage of the soil under air-dried conditions significantly lowers the ability of metabolizing microflora to develop further (Soulas and Fournier, 1981). Rewetting and incubation for a number of days partially restores this ability.

The movement and degradation of a pesticide, in the unsaturated and saturated zones is a complex process which is affected by soil and hydrological properties, climatic conditions, and agricultural practices (Jones, 1985). Soil pH, temperature, moisture content and microbial populations all have an effect on the degradation of a pesticide. In acidic soils, microbial degradation is believed to be the most important mechanism in the root zone or the upper strata of the unsaturated zone. In cases where there was rapid transport of the pesticide into the saturated zone, degradation of the pesticide continued, mainly by chemical hydrolysis. Even in deep ground water catalytic factors are present (microbes, metals, surface effects, dissolved organic matter, etc.) which speed up the degradation of these compounds.

The effect of soil pH on the disappearance rate profile has been evaluated at 25°C for 24 insecticides at 4 to 5 pH values over the range 4.5 to 8.0 in a sterile buffer medium (Chapman and Cole, 1982). At pH 8 the half lives were found to be generally smaller than at lower pH values. When persistence on alumina (acidic, basic & neutral), mineral soils amended with aluminum sulfate or calcium hydroxide to different pH values and four natural soils of different pH values was examined no correlation was found between the measured pH of these solids and the rate of disappearance of the selected insecticides applied to them. Carbofuran had a half-life of 1 week at a pH of 8.0 in buffer solution, while at a pH of 5.0-6.0 the half life was 690 weeks. Chlorpyrifos at a pH of 8.0 had a half life of 2.7 weeks, while at a pH of 4.5-5.0 the half life increased to 11 weeks. Aldicarb, on the other hand, had a fairly constant half life of 35-38 weeks through the pH range 6.0-8.0, with a slight decrease in half life to 25 weeks at a pH of 4.5.

The rate of transformation of a pesticide may be a function of the area of the field from which the soil sample is taken. The first-order half-life for metribuzin degradation gave a coefficient of variation of 21.1% while for simazine it was less than 7% (Walker and Brown, 1983). The variation in this case was attributed to the unevenness of the initial application, done by boom sprayer as opposed to knapsack sprayer. In the field other factors which would cause an unevenness in degradation rates would include different levels of organic matter, differing bacterial populations, etc.

The effects of organic matter and chemical fertilizers on the degradation of two herbicides were influenced by the incubation conditions, reductive and oxidative-flooded, of the soil (Duah-Yentumi and

Kuwatsuka, 1980). Under reductive-flooded conditions degradation was slow and the various soil amendments did not have any effect. The greatest degree of degradation of the herbicides was observed under the compost plus NPK treatments, rice straw gave the next highest degradation with compost alone third for the upland conditions. Under the oxidative-flooded conditions, the compost plus NPK treatment was only slightly more degradative than the control conditions.

Part of the observed transformation of pesticides in soils may be carried out by extracellular enzymes, indigenous catalytic component or "accumulated" enzyme, which are closely associated with the humic colloids (Burns and Edwards, 1980). In being intimately associated with the soil humic colloids the extracellular enzyme is provided protection against destructive abiotic factors such as, inactivation by anionic clays and pH-induced denaturation, and biotic factors such as the indigenous microflora. These immobilized enzymes could be used as agents for alleviating environmental pollution problems.

Humic material in the soil influences the behaviour and fate of pesticides, as both humic acid and fulvic acid can solubilize in water certain organic compounds and are important carriers of pesticides in soil. In addition to enzyme associated degradation of pesticides, soil humic material has the potential for promoting the nonbiological degradation of many pesticides. Soil organic matter may be classified into two main groups: non-humic substances which include carbohydrates, proteins, peptides, amino acids, fats, waxes, and low molecular weight organic acids; and humic materials which are more stable and constitute the bulk of organic matter in soil. They are acidic, dark coloured, predominantly aromatic, chemically complex materials of molecular weights ranging from

a few hundred to several thousand. In grassland soils the humic fraction is predominated by humic acid, while forest soils are rich in fulvic acid. Humic acid is the portion which precipitates when the alkaline extract is acidified, the fulvic acid is the humic fraction which remains in solution, that is, it is soluble in both dilute acid and base, the third fraction, humin is that portion of humic matters which is not extracted from soils or sediments. The major difference between the humic and fulvic acids are molecular weight and functional group content, with fulvic acids being lighter and containing more oxygen-containing functional groups per unit weight. The humic fractions are resistant to microbial degradation, they have the ability to form water soluble and water-insoluble complexes with metal ions and hydrous oxide, they interact with clay minerals, hydrophobic organic compounds such as alkanes, fatty acids, dialkyl phthalates, pesticides and other organic pollutants. Fulvic acids are twice as acidic as the humic acids containing 9.1 meq./g COOH functional groups to 4.5 meq./g for humic acids (Khan, 1980).

Sodium humate increases the water solubility of DDT by a factor of twenty by substantially lowering the surface tension, thereby suggesting that sodium humate may be capable of solubilizing other "insoluble" pesticides. Urea applied to a column of well mixed forest soil caused a 30 fold increase in the amount of DDT to leach through the soil by raising the pH of the naturally acidic humus layer, thereby promoting leaching of those carrier substances having humic acid properties.

Present in many surface waters and imparting a yellow to brown colour to natural waters because of the acidic functional groups, fulvic acids may chemically degrade a wide variety of pesticides. Where natural sur-

face waters are used for irrigation in agricultural, the fulvic acid content of these waters may affect the persistence of pesticides applied to the field as well as solubilize some of the "insoluble" ones thereby increasing their leaching potential. In addition, the presence of fulvic acids in natural waters may enhance the photodecomposition of pesticides in these waters as the humic material may act as photosensitizers for nonabsorbing pesticides.

Aquatic humus acts as a chelating agent for inorganic and organic compounds, solubilizing compounds which are practically water insoluble and thereby acting as vehicle for the mobilization and transport of these substances in the aquatic environment. Conversely, aquatic humus may decrease the amount of a compound available for uptake by binding to it (Carlberg and Martinsen, 1982). Both liquid-liquid extraction and resin adsorption gave poor recoveries of compounds from humic water as compared to distilled water. Humic material interferes in the adsorption process on resin columns allowing material to pass straight through the column.

2.4.2 Specific Pesticides (applied to 10-11-7W)

The following section reviews the fate of specific pesticides which were applied to 10-11-7W during the period 1979 to 1983. The review will be limited to transformation losses and movement into ground water and will cover the literature for the last ten years.

Aldicarb: The major metabolic pathway of aldicarb in soils is rapid oxidation of the parent compound to aldicarb sulfoxide followed by slower oxidation to aldicarb sulphone or hydrolysis to aldicarb sulfoxide oxime (Ou et al., 1985a, 1985b). The oxime undergoes further degra-

dation to the corresponding nitrile. Aldicarb in ground water under slightly alkaline conditions (pH 7-7.4) degrades rapidly to the nitrile compound under anaerobic conditions.

Studies of the kinetics of aldicarb degradation via its sulphoxide and sulphone in soils, under different moisture and temperature conditions, found that all reactions followed first-order kinetics (Bromilow et al., 1980; Smelt et al., 1978a, b, c) It was noted that the higher the organic matter content of the soil the lower the rate constant. This data indicates that the rate constant does not follow an Arrhenius relationship with temperature. It was stated that the low pH values of some of the soils may have retarded degradation to some degree.

Aldicarb detected in Florida ground water related to its use in citrus agriculture has renewed interest in the fate of aldicarb in ground water. Under aerobic and anaerobic conditions (Delfino and Miles, 1985) and in the presence of limestone (Miles and Delfino, 1985) aldicarb degraded very slowly in ground water at a pH of 7.7 via a hydrolysis pathway. At a higher pH and in microcosms without limestone degradation was slightly faster. Studies conducted by Union Carbide in 14 states over a period of six years have shown that in areas where aldicarb has reached ground water that lateral movement of ground water and continuing degradation limit the presence of aldicarb residues to shallow ground water near the treated fields (Jones, 1985). Where movement to ground water did occur, low field capacity and high water infiltrations from heavy rainfall, excessively rainy seasons, or over-irrigation were the major factors contributing to leaching.

Atrazine: Long-term persistence of atrazine and its metabolites under field conditions, found that 50% of the initially applied herbicide (ra-

radioactively labeled) was still present nine years after application with a substantial portion as the parent compound (Capriel et al., 1985). All of the residues were in the form of bound residues (nonextractable) which raises the question whether analysis of the extractable residues alone is a valid criteria in determining the persistence of a herbicide under outdoor conditions. Rohde et al. (1981) found that atrazine persisted for 115 days in the surface 10 cm of soil (loamy sand) with none detected at greater depths after 58 days. A half life of 37 and 46 years for the two soils, respectively, was determined at 20° in another study (Hance, 1967). The velocity constant at 20° was extrapolated and it was found that decomposition by purely chemical means was not an important pathway of degradation.

Atrazine degradation occurs by either microbial or chemical means. Microbial degradation results in *N*-dealkylation to produce deethylated atrazine and/or deisopropylated atrazine. Chemical degradation is characterized by a hydrolysis reaction at the number two carbon producing hydroxyatrazine. Microbial degradation is temperature dependent and requires additional C and energy sources in the soil. The pathway is minor when compared with chemical hydrolysis especially at pH levels <6, contrary to what was indicated previously. Adsorption onto soil colloids is the only prerequisite for hydrolysis (Wehtje et al., 1984). Biocidal treatment of the soil was found to retard atrazine degradation thus prolonging the effective period of the herbicide (Avidov et al., 1985) .

The movement and degradation of atrazine in a sandy loam soil has been measured and simulated (Nicholls et al., 1982). Atrazine was found to be less mobile than metribuzin, however for both compounds the great-

est concentration after 83 days was in the surface 2-3 cm of soil.

Over a 1-year study period the concentration of atrazine ranged from 0.01 to 8.29 ppb in ground water recovered from 41 monitoring wells in the state of Nebraska, fluctuating sufficiently with the seasonal pattern to indicate that dissipation of the herbicide was occurring in the ground water (Wehtje et al., 1983). The reduction in concentration was attributed to adsorption, dispersion and degradation. The level observed is said to be the steady state situation for the levels of atrazine usage in the area. A decline in atrazine usage would be reflected in the future as ground water concentrations would decrease. The current levels are not high enough to affect atrazine-sensitive crops.

Muir and Baker (1978) reported atrazine residues in tile-drain water from plots where atrazine had been applied for three consecutive years. The residue levels of *N*-deethylated atrazine in the tile drain water were usually greater than those of the parent compound.

Azinphos-methyl: The kinetics of azinphos-methyl losses in sterile and nonsterile soil, as affected by temperature and moisture content, is a two-stage process (Yaron et al., 1974). Azinphos-methyl loss in the soil environment is affected by both chemical and biological processes; and that temperature affects the lag period and the rate of degradation.

The main degradation products of azinphos-methyl in soil and by selected soil microorganisms are benzazimide, thiomethylbenzazimide, bis-(benzazimidyl-methyl)disulphide, and anthranilic acid. The sole transformation product formed by action of *Pseudomonas* sp. DSM 5030 on benzazimide was 5-hydroxybenzazimide which is incorporated into soil organic matter to a greater extent than benzazimide due to its higher polarity (Engelhardt and Wallnofer, 1983). A total of 16 metabolic degradation

products of azinphos-methyl have been isolated and identified in soil (Engelhardt et al., 1984). Of the 16 metabolites identified, 3 are cleaved by *Pseudomonas fluorescens* DSM 1976, forming anthranilic acid as the main metabolite.

Azinphos-methyl was found to be least persistent after field application as an emulsion and left on the soil surface, 50% loss within 12 days of soil application (Schulz et al., 1970). The granular form was more persistent, 50% loss within 28 days, after incorporation into the upper 10 - 12 cm of the soil. Virtually all the applied insecticide was degraded within a year of application. The persistence of organophosphorus insecticides in nature is affected by their susceptibility to phosphatases; enzymes do not act on adsorbed insecticides on soil surfaces; interaction between azinphos-methyl and soil phosphatases occurs only when both components are not adsorbed, i.e. are in soil solution (Heuer et al., 1976).

Primary UV light (253.7 nm) and to a lesser extent sunlight, degrades azinphos-methyl in water to benzazimide, anthranilic acid, methyl benzazimide sulphide, N-methyl benzazimide and a number of unidentified water-soluble compounds (Liang and Lichtenstein, 1972). In addition to the above mentioned degradation products, trace amounts of mercaptomethyl benzazimide and the oxygen analogue of azinphos-methyl were detected. Azinphos-methyl was found to be relatively stable in aqueous solution below pH 10.

Bromoxynil: Temperature and moisture conditions affect the degradation of bromoxynil in soil (Smith, 1971). The half-life of bromoxynil at 25°C and at moisture levels in excess of the wilting point was about 14 days, at 18°C it was longer. At 20% moisture content, the half-life

decreased to just over 7 days. Raising the moisture content decreased the amount the bromoxynil remaining in the soil. Very little degradation occurred in sterilized soil, less than 10% after 3 weeks, indicating that microbial degradation may be an important factor contributing to bromoxynil breakdown under field conditions. 3,5-dibromo-4-hydroxybenzamide and 3,5-dibromo-4-hydroxybenzoic acid were identified as degradation products.

The presence of other chemicals co-applied with bromoxynil had no effect on the degradation of this herbicide (Smith, 1984).

Bromoxynil Octanoate: The initial step in the metabolism of bromoxynil octanoate is the hydrolysis of the octanoate to the phenol or free bromoxynil (Buckland *et al.*, 1973). Following the initial hydrolysis there are three consecutive or concurrent steps (a) hydrolysis of the cyano group to the amide and carboxylic acid, followed by decarboxylation, (b) replacement of one or both bromine atoms by hydroxy groups, and (c) replacement of one or both bromine atoms by hydrogen. Some of the phenolic acids or phenols formed are natural plant constituents.

The herbicide, bromoxynil octanoate, was fairly rapidly and extensively degraded at 15°C in five different soil types, at application rates 5 to 25 times the recommended rate (Collins, 1973). Soils with a high organic matter content produced $^{14}\text{CO}_2$ most rapidly from the labeled herbicide. The rate of decline in bromoxynil octanoate residue levels is inversely related to the sum of the organic matter and clay components of the soils (Ingram and Pullin, 1974). A 7 day lag period before degradation begins was explained by two factors: (a) the time taken for bromoxynil octanoate to hydrolyze chemically to bromoxynil, and (b) the time required for the soil microflora to adapt their metabolism pro-

cesses to the degradation of bromoxynil and/or the octanoate.

When applied as a mixture with either asulam or MCPA or difenzoquat there is no inhibition of the degradation by any of these herbicides (Smith, 1980a).

Carbofuran: A study conducted to determine the effect of soil temperature and soil moisture on degradation and metabolism of carbofuran in soils found that both mineralization rate and solvent-extractable ^{14}C -activity disappearance rate approximated first-order kinetics (Ou et al., 1982).

In buffer solution the half-life increased in length as the pH decreased from 8 to 4.5 (Chapman and Cole, 1982). In a soil system, pH appeared to have very little effect of the persistence of carbofuran, as two mineral soils, pH 8.0 and 6.8, showed little to none degradation of carbofuran over three weeks at two application rates (1 & 20 ppm). Two organic soils on the other hand showed 40 - 50% degradation after 3 weeks at the lower application rate and 27% degradation at the higher rate at 3 weeks.

Persistence and degradation of carbofuran and 3-hydroxycarbofuran in soils as influenced by soil sterilization and soil pH was determined in a number of soil (Getzin, 1973). Sterilization had no effect on the degradation of carbofuran in one soil and only a slight effect in two other soils. In a fourth soil a large difference in degradation rates was observed between the sterilized and non-sterilized soil where the half-life for carbofuran in the sterilized soil was 6X that in the non-sterile soil. Degradation of carbofuran occurred 7-10 times faster in alkaline soil (pH 7.9) than in acid or neutral soils (pH 4.3-6.8). Carbofuran phenol the expected hydrolysis product of carbofuran was only

detected in minute quantities. Addition of ^{14}C -labelled carbofuran phenol to the soil found that the phenol was rapidly adsorbed into a non-extractable bound state from which it is slowly degraded. The indirect evidenced obtained in this study indicated that carbofuran is hydrolyzed to its phenol which is immediately bound to soil constituents and then slowly metabolized by soil microorganisms.

Two bacteria species, *Achromobacter* sp. and *Pseudomonas* sp. have been isolated from a soil with a history of continuous carbofuran use which degraded the insecticide quickly (Felsot et al., 1981). A number of actinomycetes have been found which were particularly active in carbofuran degradation as well (Williams et al., 1976).

Carbofuran, applied as the granule in the subsurface soil, moves upward to the surface when there was soil moisture movement upward from the subsoil (Read and Gaul, 1983).

Water percolating through carbofuran treated soils had removed 49% of the soil applied carbofuran, while only 37% was still associated with the soil and crop (Koeppel and Lichtenstein, 1982). In a non-percolated experiment 80% of the soil applied carbofuran was still associated with the soil and crop. This mobility of carbofuran in the percolated soil was related to the relative high water solubility of carbofuran (320 ppm). The addition of captofol resulted in a more rapid disappearance of carbofuran from the soil and a reduced uptake by the crop. EPTC had no effect on carbofuran metabolism or uptake.

Chlorothalonil: Chlorothalonil's fungicidal ability and mode of action have been described in detail (Turner et al., 1964; Turner and Lamont, 1965; Vincent and Sisler, 1968; Turner and Battershell, 1969) as well as the factors which influence the fungicidal activity and the

chemical reactivity (Turner and Battershell, 1969 & 1970).

There have been a number of reports (Binkley *et al.*, 1977; Loeffler, 1978; Satoh, 1979; Khan and Akhtar, 1983) describing the photodecomposition of chlorothalonil.

A study of the fate of chlorothalonil on foliage (Gilbert, 1976), under field and laboratory conditions, found no apparent evidence of the expected chemical breakdown product, 4-hydroxy-2,5,6-trichloroisothalonitrile, of chlorothalonil.

The breakdown of chlorothalonil in soil is dependent on the moisture content, temperature and pH of the soil. In aqueous solutions below pH 9 chlorothalonil is stable towards hydrolysis, while at pH's above 9, chlorothalonil hydrolyzes to give 3-cyano-2,4,5,6-tetrachlorobenzamide and 4-hydroxy-2,5,6-trichloroisophthalonitrile (Ballee *et al.*, 1976). Chlorothalonil has a half-life of 6 to 12 weeks, depending on soil type, in temperate regions with moderate levels of moisture.

Hydrolysis of chlorothalonil, as a function of pH (Szalkowski and Stallard, 1977) did not occur at either acidic (5) or neutral (7) pH's. In basic solution (pH 9), there was, however, a significant decrease in concentration (80% after 89 days), yielding two products which were identified as: 3-cyano-2,4,5,6-tetrachlorobenzamide and 4-hydroxy-2,5,6-trichloroisophthalonitrile. Thus, under basic conditions (pH 9) there are two different routes of hydrolysis of chlorothalonil, one giving the hydroxy substitution product the other an amide water addition product.

In the published literature on chlorothalonil there is none that deals with the movement of chlorothalonil in the soil environment.

Chlorpyrifos: In aqueous solution the half-life of chlorpyrifos was found to increase (from 2.7 to 11 weeks) as pH decreased from 8.0 to 4.5

(Chapman and Cole, 1982). Pseudo-first-order kinetics were observed over the pH range of 1 - 13 for the disappearance of chlorpyrifos in water. There was little or no influence by microorganisms on the rate of degradation of chlorpyrifos in natural water samples. In the environmentally relevant pH range of 4 - 7.5 chlorpyrifos undergoes a pH-independent hydrolysis reaction which observes first-order kinetics, with a half-life of 11 weeks. Above pH 8, alkaline hydrolysis predominates, but the reaction is not second-order.

Losses of chlorpyrifos were greatest during the first 8 days post spraying, and there after declined gradually (MacDonald et al., 1983). The rate of loss of chlorpyrifos appeared to be less related to the concentration of the active ingredient than to the subsequent conditions the pesticide was exposed to.

Soil moisture appears to have no effect on the degradation rate of chlorpyrifos, while formulation does (Tashiro and Kuhr, 1978).

2,4-D: Surface litter and soil accounted for 70% of the recovered 2,4-D residues, the remaining residues were in the vegetation (Radosevich and Winterlin, 1977). At the end of 360 days, only 0.05% of the applied 2,4-D was still present.

The kinetics of microbial decomposition of 2,4-D has been studied with respects to the effects of herbicide concentration (Parker and Doxtader, 1982) and the effects of temperature and moisture (Parker and Doxtader, 1983). The rate of decomposition decreased as moisture tension increased due to decreased activity of 2,4-D degrading microorganisms arising from reduced water availability.

2,4-D rapidly degrades in soil (Stott et al., 1983), with 86 to 94% of the side-chain and 73 to 85% of the ring-carbons evolved as CO₂, none

of the 2,4-D linked with any of the soil humic material.

In soils previously treated with herbicides and other pesticides (Smith, 1980b), the half-life of 2,4-D was similar regardless of whether the soil had, or had not, received any pretreatment thus indicating that the presence of other chemicals did not affect the degradation rate of 2,4-D in any way.

The mobility of 2,4-D in five Canadian prairie soils (Grover, 1977) followed an inverse relationship which related adsorption to mobility. The distribution coefficients (k_d) were significantly related to the soil organic matter content and to a lesser degree the soil pH, and not at all to the clay content.

The dissipation and mobility of 2,4-D in agricultural soils and in forest soils was affected by environmental factors such as: soil temperature, precipitation, pH and organic matter content (Thompson et al., 1983; Majka et al., 1982a, 1982b). Low temperatures and soil pH values reduced dissipation while soil organic matter and pH promoted greater adsorption.

In the aquatic environment the degradation rate of 2,4-D in sediment under anaerobic conditions was six times slower than under aerobic conditions for the same sediment (DeLaune and Salinas, 1985).

A behaviour assessment model based on the organic carbon partition coefficient (K_{oc}), Henry's constant (K_H), and the net first-order degradation rate or chemical half-life judged (Jury et al., 1983) 2,4-D to be mobile, with rapid degradation, and only slightly susceptible to losses due to volatilization.

Deltamethrin: Extractable residues of deltamethrin decreased over time in an organic soil with a corresponding increase in bound residues

with anaerobic conditions slowing degradation (Zhang et al., 1984).

Soil persistence of deltamethrin was about 6.9 weeks for field and 4.9 weeks for indoor experiments with no evidence of residue movement in the soil (Hill, 1983). Dissipation of deltamethrin from soil is first-order when plotted against degree-days₀ (Hill and Schaalje, 1985).

Deltamethrin degraded more slowly in sterilized and organic soils than in natural and mineral soils, respectively, thus indicating that soil microorganisms are much more important in the degradation process than purely physical or chemical processes (Chapman et al., 1981).

Deltamethrin was found to be immobile in soil with > 92% of the applied insecticide remaining in the top 1 cm of soil (Kaufman et al., 1981).

In the environment, deltamethrin partitions rapidly upon addition to water into; suspended solids, plants, sediment, and air, with a half-life of 2-4 hours in water (Muir et al., 1985).

Dicamba: Dicamba was found to degrade completely in three weeks in three Canadian Prairie soils (Smith, 1974; Smith and Hayden, 1976). In steam sterilized soil the breakdown of dicamba was negligible indicating that the primary transformation pathway is microbial degradation. The degradation of dicamba is unaffected by the presence of other herbicides co-applied to the soil (Smith, 1984). Literature dealing with either transformation or leaching for the period 1976 - 1986 was either nonexistent or in foreign language journals.

Diclofop-methyl: Under aerobic conditions the half-life of diclofop was 6 to 9 days in a sandy soil and within 23 or 38 days in sandy loam. Under anaerobic conditions the loss is much slower. The fourfold slower degradation of diclofop-methyl in the sandy loam indicates that soil

properties are a deciding factor in the decomposition rate of the herbicide.

The degradation of diclofop-methyl under moist nonsterile conditions in soil proceeds via an initial and very rapid hydrolysis of the ester to the corresponding acid which was then followed by a much slower hydrolytic process (Smith, 1977; Martens, 1978). On air-dried soils less than 5% of the ester converted to the acid after 24 hours. Diclofop-methyl exhibited a reduced degradation rate in the more acidic soils (Smith, 1977; Martens, 1978). Soil pH may be the primary factor in the hydrolysis step in the conversion of the ester bond to a free acid. It appears that the more alkaline the soil, the greater the conversion of the ester to the acid.

Less than 2% of the applied amount (1.5 kg/ha) of diclofop-methyl remained at the end of the growing season as the free acid, bound acid residues totalled to less than 10% (Smith, 1979a & 1979b).

Disulfoton: The primary breakdown of disulfoton and other organophosphorus insecticides is due to soil microflora and is thus influenced by soil temperature. At lower temperatures the breakdown of these compounds is slowed down. With disulfoton, significant amounts were found to have leached beyond the 20 cm level (Suett, 1975). With soil moisture at or near field capacity, winter soil conditions (6 to 7°C) tend to favour desorption and leaching, particularly of the polar oxidation products of thioester insecticides such as disulfoton.

In sandy loam soil detectable residues of disulfoton were observed for 42 days (Szeto et al., 1983). Degradation on vegetation also, proceeds via oxidation to the corresponding sulfoxide and sulphone (Szeto et al., 1985).

EPTC: A photodegradation rate for EPTC in hexane solution was determined 0.02 and four photolysis products were isolated and identified (DeMarco and Hayes, 1979). For some of the thiolcarbamate herbicides the photolysis products are more toxic than the parent herbicide.

Volatilization of EPTC from water and wet soil caused losses of up to 74% of the applied herbicide where it was added as the EC formulation to irrigation water (ditch irrigation) (Cliath et al., 1980).

Field studies on the persistence of EPTC incorporated to the 10 cm depth, found that < 2% of the applied amount remained after 22 weeks (Smith and Hayden, 1982a). It was concluded EPTC is not particularly persistent in Saskatchewan soils when applied under field conditions.

The degradation of EPTC is dependent upon soil moisture from below 3% and independent of soil moisture above 3%, where up to 68% of the applied EPTC was evolved as CO₂ after 50 days (Obrigawitch et al., 1982 & 1983). Soils with a prior history of EPTC use also degraded the compound more rapidly than those without any prior use history. Storage (12 months) of soil affected degradation rates of EPTC in treated and non-treated soils, by lengthening the half-life particularly in those soils with a previous history of EPTC use (Lee et al., 1984). Sterilized soils showed a very small degradation ability.

Raising soil pH from 5 to 7 increased the level of the microflora in the soil and decreased the phytotoxic period by 14 to 21 days in greenhouse experiments (Lode and Skuterud, 1983). Thus, EPTC could be ineffective in soils with a high microbiological activity, and conversely could be damaging to crops in an acidic soil due to delayed breakdown.

Mancozeb: Mancozeb reduced the populations of bacteria, fungi, and actinomycetes, altered nitrogen mineralization and reduced nitrification

for a 3 month period (Doneche et al., 1983). Degradation in soil occurred both via a chemical pathway as well as via a biological pathway. Bacteria from the genus *Bacillus* were isolated which were found to be able to degrade mancozeb.

MCPA: MCPA, in three Saskatchewan soils had a half-life in the order of 5-7 days (Smith and Hayden, 1981). The half-life of MCPA (ca. 13 days) in soil is not affected by the presence of other herbicides (Smith, 1982a). In both studies (Smith and Hayden, 1981; Smith, 1982a) the same soils were used, i.e., they were subsamples of the same sample, the samples were spiked with MCPA at the same level and incubated under the same conditions and yet in the second study the half-life determined is double that determined in the first study. The difference between these two studies may be due to a difference in microbial population levels. Storage of air-dried soils has an effect on soil microbe population levels. Here is a case where the soil was collected in October, 1980 dried and stored. The first study was conducted 4 weeks after the soil was collected and the second study, 20 weeks after of storage. Soulas and Fournier (1981) have shown that prolonged storage of soil in the air-dried state has an effect of lowering the ability of metabolizing soil microflora to develop further and, that, rewetting and incubation only partially restores this ability. Lee et al. (1984) have also reported the effect of soil storage on the degradation of a herbicide.

Under sunlight irradiation, 80% of applied MCPA was lost from a glass surface after 6 days, and that after 31 days only 10% remained (Crosby and Bowers, 1985). MCPA would be expected to undergo photolytic chemical degradation as long as it remained airborne as spray drift.

MCPA, as its dimethylamine (DMA) salt dissipated with a half-life of 4.6 days in sunlight and moving air as opposed to 3.9 days for MCPA/DMA deposits on glass surfaces (Freiberg and Crosby, 1986). The main dissipative force was established as photolysis, with volatilization making a very minor contribution.

Mecoprop: Mecoprop breaks down rapidly in the moist soil with a half-life of 8 days (Smith and Hayden, 1981). In air-dry soil there was very little degradation with 87-90% of the applied mecoprop still present 21 days post application. Degradation of mecoprop based on microbial action was thought to occur either through the formation of MCPA as an intermediate through decarboxylation and oxidation or via direct side-chain cleavage to give the phenol (Lindholm et al., 1982).

Metribuzin: Metribuzin is non-persistent, weakly adsorbed, microbially degraded, and highly mobile in a number of soils (Bouchard et al., 1982).

Simulation of the movement of metribuzin in a sandy loam soil after a spring application indicated that metribuzin was less persistent than atrazine (Nicholls et al., 1982). Large discrepancies noted between laboratory and field data were due to differences in soil conditions between the field and the laboratory.

Field persistence of metribuzin in three Saskatchewan soils over a three year period was variable (Smith and Hayden, 1982a). One year, no residues (<2%) were detected in the top 10 cm of soil 22 weeks post application while in the other two years residues were recoverable from the top 5 cm at the 22 week post application sampling time. In addition, residues were recovered from the 5 to 10 cm level in the soil. The increased depth of leaching observed one year was attributed to the

increased rainfall during that particular year. In a sandy Manitoba soil the rate of degradation for metribuzin was found to be related to temperature (Webster and Reimer, 1976). Less than 10% of the applied herbicide was carried over to the following year.

Paraquat: Long-term persistence of paraquat has been noted in a sandy loam soil where analysis of soil samples taken to a depth of 36 cm indicated that essentially all the applied paraquat was still present (seven years cumulative application) (Fryer et al., 1975). The majority of the paraquat was found in the upper 5 cm layer but significant amounts had reached the 25-36 cm layer. The soil microflora was capable of degrading paraquat slowly if at all under field conditions. Neither photochemical nor microbiological processes play a significant role in degrading paraquat in the field. The only significant amount of microbiological degradation was observed when the paraquat added to the soil exceeded the "strong adsorption capacity". A follow-up study (Hance et al., 1980) showed that some paraquat had disappeared from the plots whereas the pre-1973 results (Fryer et al., 1975) suggested that there was no loss. The basic process of decay followed a reaction rate which approached first order, approximating an annual loss of 10% produced a half-life of 6.6 years for paraquat.

Adsorbed paraquat (75%) could be recovered from the soil by displacement with ammonia ions, the remaining 25% could only be recovered by destroying the soils structure (Smith and Mayfield, 1978). Paraquat was adsorbed by a number of soil components, including organic matter, non-expanding and expanding-lattice clays. Desorption of paraquat from the soil depends on the adsorption capacity of the soil and the kind and concentration of the desorbing cation.

In solution, paraquat is subject to photochemical decomposition giving methylamine and 4-carboxy-1-methylpyridinium ion as well as a number of other products (Kearney et al., 1985).

Propanil: A proportion of natural substrate decomposition in soil is effected by extracellular enzymes tenaciously associated with the humic colloids. Propanil and its major metabolite, 3,4-dichloroaniline, are just two compounds which are degraded by accumulated soil enzymes (Burns and Edwards, 1980). The soil microbe *Pseudomonas* sp. was able to degrade propanil's major metabolite 3,4-dichloroaniline but was unable to work with propanil itself (Zeyer and Kearney, 1982).

Degradation of propanil was rapid in three Saskatchewan soils with only 5% of the applied amount remaining after 7 days (Smith, 1984). Other herbicides co-applied with propanil had no effect on the degradation rate for propanil. Earlier work (Smith and Hayden, 1982a) found < 2% of the applied propanil remained in the three soils 22 weeks post-application, in each of the three study years.

Trifluralin: The rate (first order) of trifluralin degradation can be directly correlated with temperature and moisture content of the soil (Zimdahl and Gwynn, 1977).

Trifluralin applied at low rates did not persist in most soils at toxic amounts, while higher rates of application persisted at toxic levels to sensitive species (Rahman, 1977). Trifluralin residues are influenced only by soil organic matter, the amount of rainfall had no effect on the persistence. Under field conditions in Nova Scotia, persistence of phytotoxic levels of dinitroaniline herbicides, particularly, trifluralin, may extend beyond the 4 month growing season (Jensen and Kimball, 1980). Under Canadian prairie conditions, sufficient amounts

of trifluralin carried over from a fall application to the following spring to give early weed control (Smith and Hayden, 1976 & 1982b).

Direct sunlight has an effect on the amount of trifluralin remaining in the soil (Savage and Jordan, 1980). The difference in amounts remaining may be due to thermal differences between the shaded and unshaded plots rather than photodecomposition of the trifluralin. Field measured losses of trifluralin were 5-6 times greater than what was predicted from laboratory measurements based on saturation vapour density (Glotsfelty et al., 1984). There was very little volatilization of trifluralin from a soil after trifluralin incorporation and, while the soil was relatively dry (Hollingsworth, 1980).

Trifluralin, absorbs sunlight strongly in the visible region, has a photolysis rate that is over two orders of magnitude greater than that of carbaryl (Zepp and Cline, 1977). Photolysis half-lives were calculated as a function of season, latitude, time-of-day, depth of water bodies, and ozone layer thickness. Photodecomposition (unfiltered solar radiation) of trifluralin was higher for sunlight exposed samples than for dark samples (Parochetti and Dec, 1978). As well, thermal decomposition was noted for trifluralin and a number of other dinitroaniline herbicides. Three azoxybenzene derivatives and two azobenzene derivatives and *N*-propyl-2,2'-azobis(*a,a,a*-trifluoro-6-nitro-*p*-toluidine)) are formed when trifluralin is photolyzed in benzene (Sullivan et al., 1980).

Trifluralin undergoes a rather complex degradation pathway, with no buildup of any product. Twenty-eight transformation products have been isolated from soil and identified (Golab et al., 1979). No significant leaching of trifluralin or any of its degradation products was found

below the 15 cm depth. Smith (1972) has also reported that trifluralin was not easily leached under field conditions for two Saskatchewan soils.

Soil microorganisms actively participate in the degradation and binding of trifluralin in the soil, as soil sterilization, reduced the amount of trifluralin in the organic fraction of soil by 50%, reduced degradation by 31%, and resulted in a 59% decrease in extractable degradation products (Nelson et al., 1983). In general, degradation is more extensive under aerobic conditions and the number of degradation products is not soil dependent (Camper et al., 1980). In acidic soils, fungi are the dominant active microorganisms at low pH and are generally involved in degrading more complex substrates under aerobic conditions.

Movement of trifluralin below the 20 cm depth was virtually nil, but considerable movement occurred to the 20 cm depth (Duseja and Holmes, 1978). Movement of trifluralin below the zone of incorporation depends on factors other than rainfall or irrigation, some of these factors are rainstorm intensity, soil-moisture condition at the time of rainfall, temperature, humidity, and wind velocity. In a terrestrial microcosm chamber there was little movement of trifluralin in the soil and no detectable residues in ground water (Gile et al., 1980).

2.5.0 EXTRACTION OF PESTICIDE RESIDUES FROM WATER

2.5.1 Extraction Cartridges

Previously, trace enrichment was done directly on a HPLC column and then by changing the solvent composition selectively eluting the adsorbed compounds. The extraction cartridge or short column came about from a need to do sample enrichments in the field rather than handling and

transporting large volumes of water to the laboratory.

The use of a cartridge allows for recovery of all chemical forms of the pesticide as they exist in a water sample, concentration of the sufficient material for detection regardless of original sample concentrations. A method has been outlined (Waters Scientific, 1982) in which phenoxyacetic acid herbicides and their esters can be isolated, concentrated and analyzed in one-half hour. Trace organic and PCBs analysis can be greatly enhanced by on-site enrichment using Sep-Paks (Waters Scientific, 1978 & 1979), where 1000:1 or greater concentrations can be done directly on-site, the Sep-Pak cartridge is then taken back to the laboratory where the concentrated organic compounds can be selectively eluted with a minimum amount of solvent and analyzed. Cleanup and concentration are accomplished in one step, in addition, time consuming liquid-liquid extractions, large quantities of hazardous and expensive solvents, preservation and transport of multiple-litre samples to the laboratory, and emulsion problems are eliminated. As well, losses to container walls, especially to glass bottles, is greatly reduced thus reducing the possibility of erroneous low results for the amount of trace organics in environmental water samples.

Sep-Paks can concentrate environmental samples to a level where UV or fluorescence detection can determine trace quantities in the ppb range (Wolkoff and Creed, 1980). Loading capacity or breakthrough on the cartridges was determined using carbamate pesticides and polynuclear aromatic hydrocarbons (PNA's). Fairly high concentrations were used so as to check the loading capacity of the cartridges and to make small percentages of breakthrough easily detectable. The carbamate pesticides used were: carbofuran (7065 ng), carbaryl (1755 ng), IPC (9270 ng), and CIPC

(3150 ng). With a minimum detectable amount of approximately 0.05 - 0.3 ng, no breakthrough of the carbamate pesticides was observed. A small amount of breakthrough was observed with the PNAs, benzanthrone and benzo(ghi)perylene less than 2%, fluoranthrene 0.7 - 9%, and benzo(a)pyrene 3 - 15%.

The extraction cartridge method was used to compare liquid-liquid extraction and adsorption onto a XAD resin (Monarca et al., 1985a & b) for concentrating mutagens present in surface waters. The technique was rapid, efficient, and practical for concentrating in situ and its sensitivity was such that it permitted concentration of smaller water volumes (0.5 L/cartridge as compared to 25 L/XAD column or 40 L/liquid-liquid extraction) (Monarca et al., 1985a). The extraction cartridge technique adsorbs 5 times higher quantities of organics than the XAD resin technique using 100 times less sample volume (0.5 litres compared to 50 litres) (Monarca et al., 1985b). As the sample volume passed through the extraction cartridge increased, extraction efficiencies decreased, and rinse water decreased the extraction efficiency (Saner et al., 1979).

A C₁₈ extraction cartridge was used to remove soil organic matter in the analysis of fluometuron in soil at trace levels (Mattice, 1983). Paraquat has been extracted and concentrated from water samples (Ahmad, 1983) with an average recovery rate of 99.5% (minimum 93%). The use of an ion-pairing reagent caused the recoveries to drop to 60%.

2.6.0 EXTRACTION OF PESTICIDE RESIDUES FROM SOIL

Pesticide residue extraction and analysis has been reviewed biannually with a special emphasis on current areas of research in pesticide chemistry (Thornburg, 1977 & 1979; Sherma and Zweig, 1981, 1983, & 1985;

Fishman et al., 1981 & 1983; Garbarino et al., 1985).

A general method for the extraction and cleanup of pesticide residues in a number of matrices, using acetone to extract the residues from plant material, soil, or water then dichloromethane to partition the residues, can be used to determine organophosphates, organochlorines, carbamates, thiocarbamates, ureas, triazines and other types of pesticides (Ambrus et al., 1981a). Extractable residues of carbamate, organochlorine, organophosphate, and triazine-type compounds are completely recovered, phthalimides require repeated extraction. The clean up procedure for the major classes of pesticides has been described as well as the TLC and GC determination and confirmation (Ambrus et al., 1981b & c)

Smith (1981) compared a number of solvent systems for the extraction of atrazine, benzoyleprop, flamprop, and trifluralin from weathered soil. Aqueous acetonitrile (10%) was found to be a suitable extractant for both atrazine and trifluralin, with aqueous methanol as an alternative choice.

Extraction procedures for individual pesticides are given in the Manual of Chemical Methods for Pesticides and Devices (U.S. Environmental Protection Agency, 1982). The manual also details analytical procedures for identification and confirmation. A review article covered the analytical methods and chemistry of bound pesticide residues in the soil (Khan, 1982). A 1979 symposium on pesticide analytical methodology has been published (Harvey and Zweig, 1980). A number of the volumes in the "Analytical Methods for Pesticides and Plant Growth Regulators" contain information on analytical methodology for recently released pesticides (Zweig and Sherma, 1976, 1977, 1978, 1980, & 1984).

MATERIALS AND METHODS

3.1.0 SITE LOCATION & HISTORICAL DESCRIPTION

This study addressed a "worst case situation" by working in a region of sandy soils of low organic matter content. The site used was situated on a commercial farm located 5 km southwest of Portage la Prairie, Manitoba (Fig. 1) (Almasippi Association, sand and loamy sand). A brief history of this farm is as follows: Section 10-11-7W was purchased by A. A. Kroeker and Sons Ltd. of Winkler from John Verway of Portage la Prairie in October 1977. At this time, most of the natural vegetation cover of aspen, oak, ash and willow had been cleared from the land by Mr. Verway. The small amount of remaining bush was cleared between October 1977 and October 1979; four quarter section irrigation pivots were installed and a subsurface tile drainage system was established. A Water Rights License to withdraw $6.907 \times 10^5 \text{ m}^3/\text{year}$ of water from the Assiniboine River for irrigation purposes was issued to A. A. Kroeker and Sons Ltd. in July 1978.

The subsurface tile drainage system (Fig. 2) was installed in conjunction with the surface irrigation due to the depressional topography of the land in which the higher areas were dry and wind blown and the depressions extremely wet. These wet areas were caused by to the high water table in the surface sand and the tile drainage was installed to eliminate these wet areas. Irrigation was required due to the sandy nature of the soils which would dry out quickly with infrequent precipitation.

The subsurface drainage tile was installed from June to September 1979 by Western Drainage Development. The tile drainage system consists

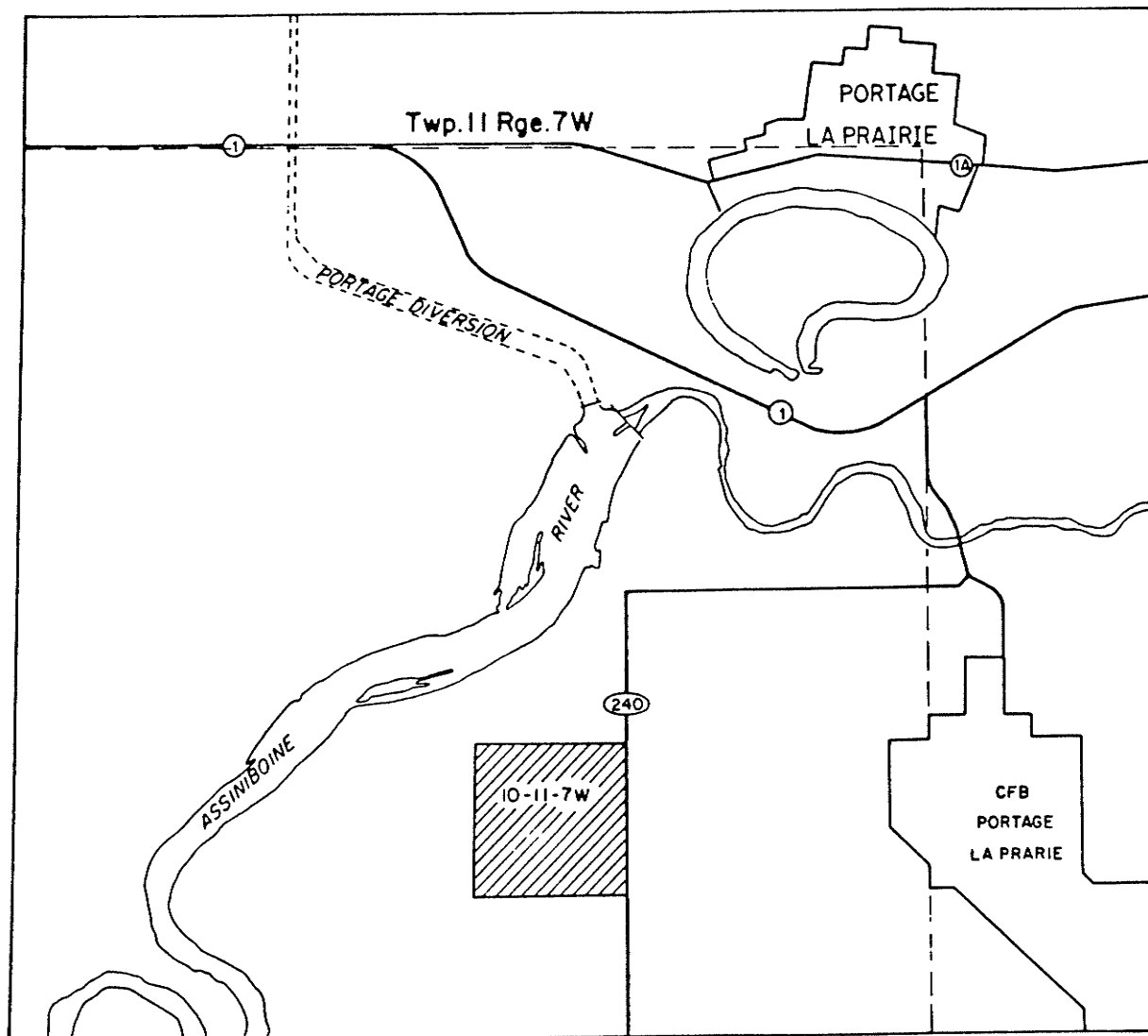


Figure 1. Map of the Portage la Prairie region showing the location of the field site (shaded area) with respect to the Assiniboine River and the City of Portage la Prairie. The irrigation pump inlet site is due north of the west side of the farm on the river.

of the following:

609.6 metres of 30.5 centimetre diameter perforated filter tubing
2999.2 metres of 25.4 centimetre diameter perforated filter tubing
3054.1 metres of 20.3 centimetre diameter perforated filter tubing
4633.0 metres of 15.2 centimetre diameter perforated filter tubing
8153.4 metres of 10.2 centimetre diameter perforated filter tubing
19449.3 metres total perforated filter tubing installed.

Figure 2 which shows the placement of the buried tile was prepared from an aerial photograph taken of Section 10-11-7W on April 23, 1980 by Prairie Agriphoto of Carmen, Manitoba for the Department of Mines and Natural Resources. The depth of burial was reported to be 0.8 to 2.0 m below the land surface.

The surface deposits in the area of the subsurface tile drainage project are fine to medium grained sand. The thickness of the sand deposit is 7.6 m at the southwest corner of the section and thins to 3.0 m at the northeast corner (Fig. 3). The sand is underlain by clay which has a thickness of 30.5 to 45.7 m. Figure 4 illustrates the sand and clay thickness along the west side of the section in a south to north line (Water Resources Branch, 1983).

The soil ranges from sand (0.4% org C) to loamy sand (1.7% org C) to a fine sandy loam (10.9% org C) with the predominant type being loamy sand. The following descriptions of these soil types is condensed from the 1972 Manitoba Soils Survey Report No. 17.

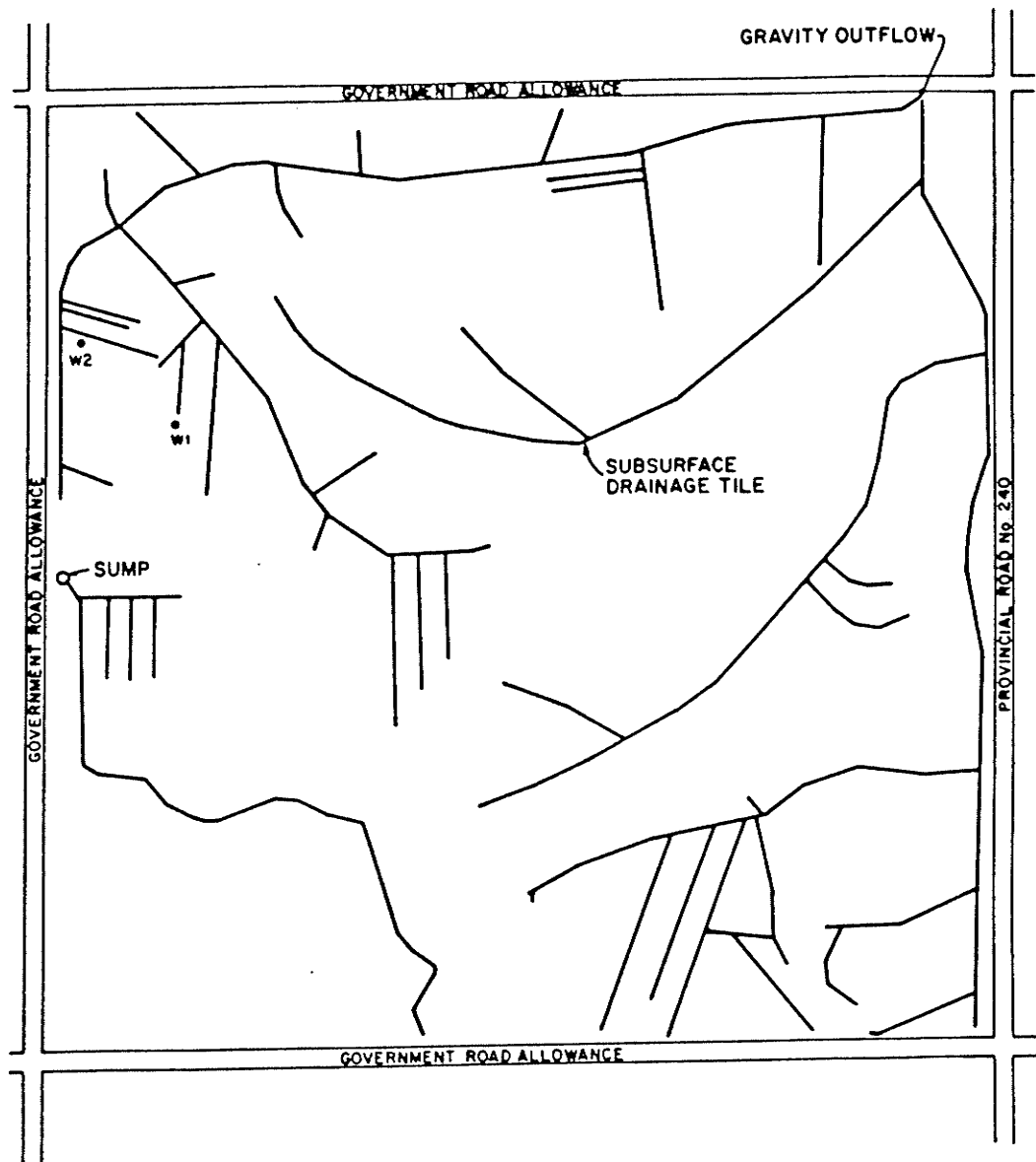


Figure 2. Schematic of the tile drain system on section 10-11-7W based on aerial photographs taken of the section on 8-9-79 (infra-red) and 23-4-80 (black & white). The two sampling wells, W1 and W2 are shown in the northwest quarter.

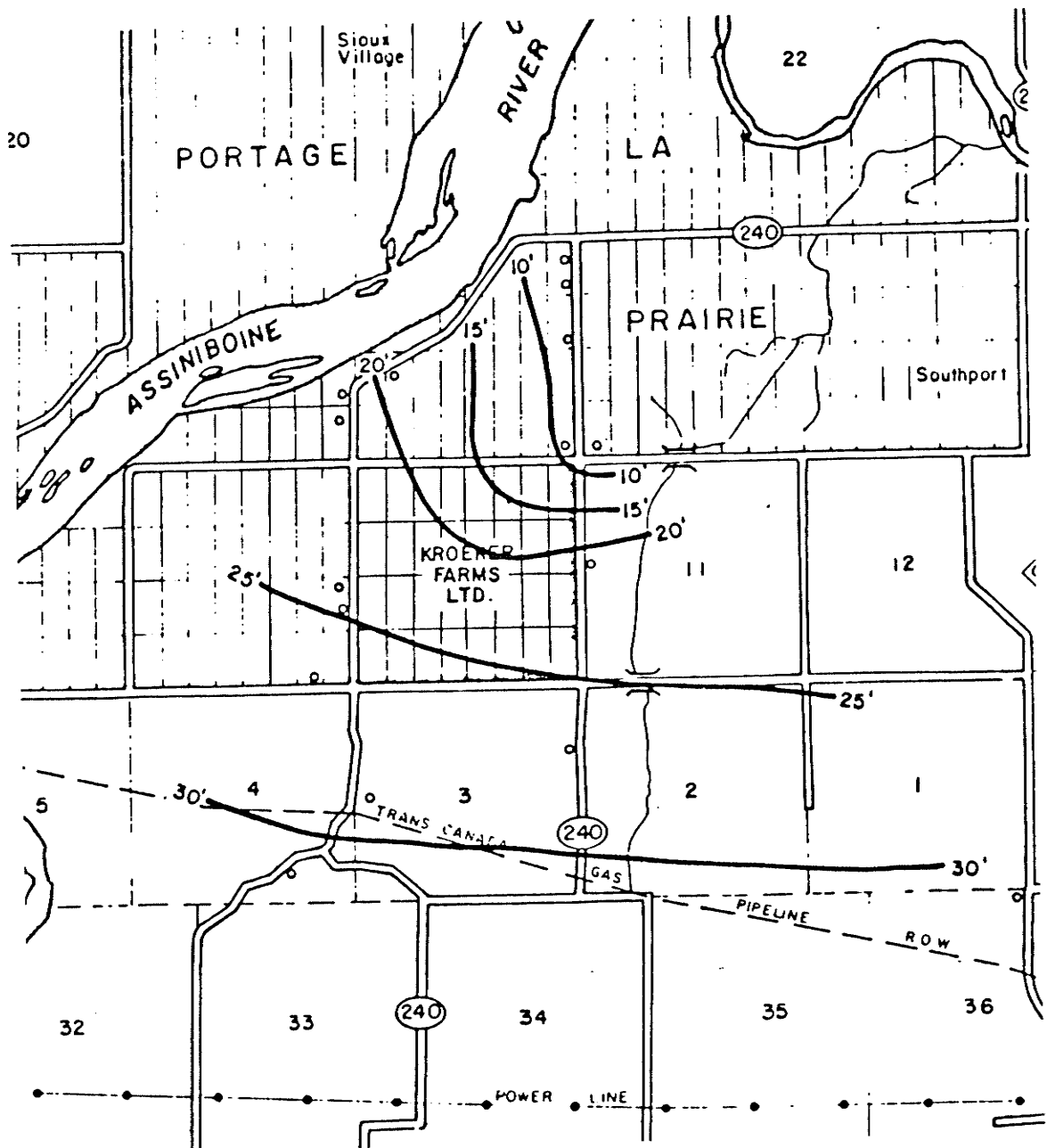


Figure 3. Thickness of surface sand in the area of 10-11-7W southwest of Portage la Prairie (Water Resources Branch, 1983).

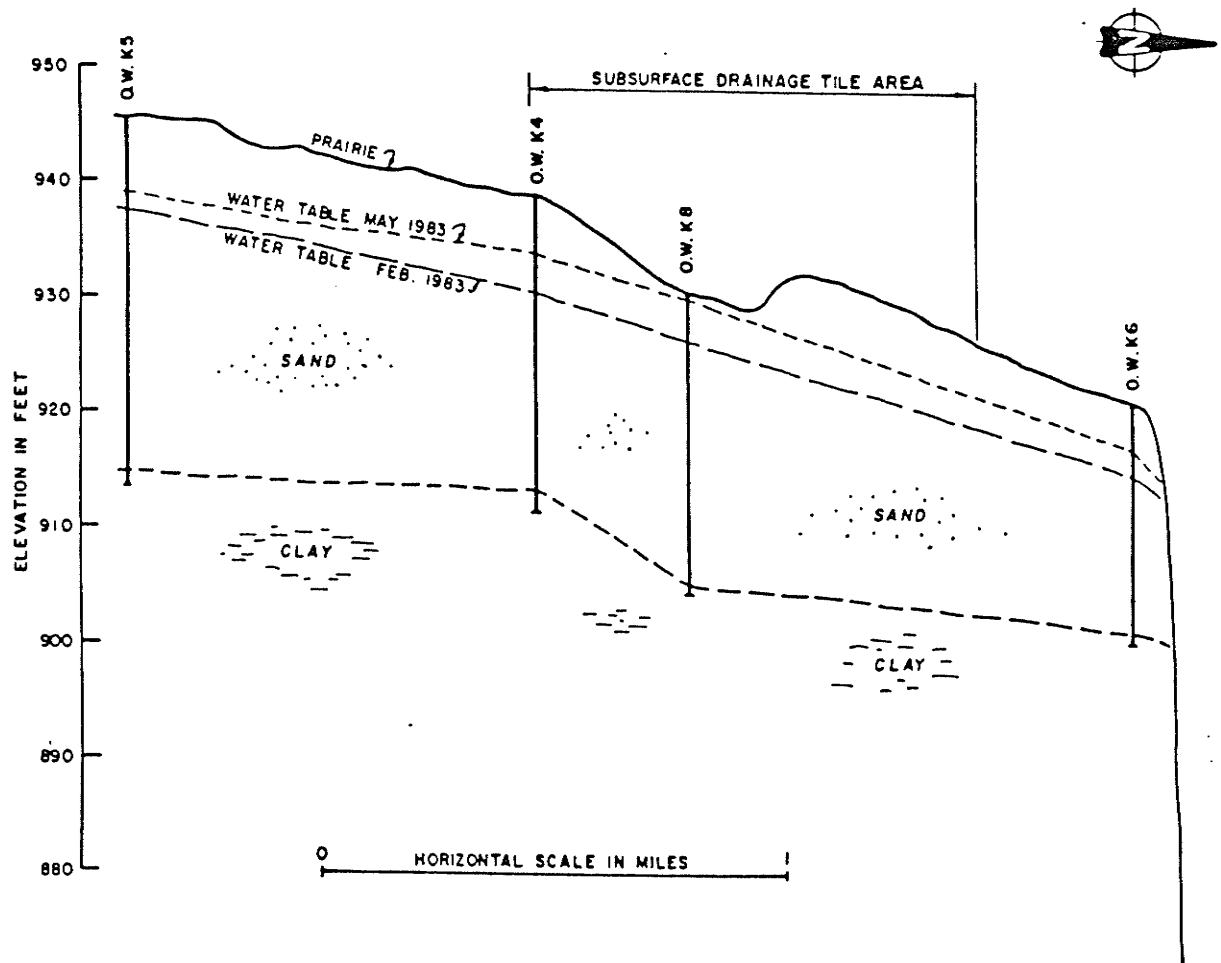


Figure 4. A cross-section view of the sand thickness in a south-north line along the west edge of section 10-11-7W (Water Resources Branch, 1983).

3.1.1 Almasippi Loamy Fine Sand

An imperfectly drained Gleyed Carbonated Rego Black soil developed on moderately calcareous, moderately coarse to very coarse textured deltaic deposits. These soil occur on level to very gently rolling terrain above the Gladstone Beach (269 metres above sea level) south and west of Portage la Prairie. The surface texture ranges from fine sandy loam to loamy fine sand and gradually grades into fine sand. Lacustrine clay occurs at approximately 1.3 metres below the surface in the area of Gladstone Beach (269 metres above sea level) and gradually increases in depth in a southwesterly direction until it is 3 or more metres below the surface. The mean depth of the lacustrine clay is approximately 2 metres. These soils have a high water table due in part to this fine textured substrate. The native vegetation on undisturbed sites is dominantly aspen.

The soil is characterized by a very dark gray Ah Horizon 18 to 54 cm thick, a very dark gray AC horizon 10 to 20 cm thick and a light brown C horizon with prominent iron mottles. Analytical data is presented in Table 1 below (Manitoba Soils Survey, 1972)

Table 1. Analysis of Almasippi Loamy Fine Sand

Horizon	Depth	%	%	%	%	%	pH
	(cm)	sand	silt	clay	moisture	org. C	
					1/3 atm		
Apk	0 - 17	85	9	6	10.6	1.7	8.0
Ahk	17 - 30	83	8	9	11.7	1.5	8.2
ACkgj	30 - 40	83	8	9	8.4	0.3	8.0
Ckg	40 - 75	93	5	2	5.4	0.06	7.9

3.1.2 Long Plain Fine Sand

An imperfectly drained Gleyed Orthic Regosol soil developed on weakly to moderately calcareous sandy deltaic deposits. These sandy deposits are underlain by fine textured lacustrine sediments at depths from 2 to 4 metres below the surface. These soils have a high water table because of the position and the occurrence of the clay substrate. Topography is level to gently sloping, runoff is moderately slow, and permeability is rapid in the surface but impeded at lower depths due to the high water table. The soil is characterized by a weakly developed profile with a gray to dark gray Ap horizon, a somewhat leached C horizon (45 to 65 cm thick) with numerous iron mottles (Figure 5). A moderately to strongly calcareous calcium carbonate layer may occur in the strongly iron mottled subsoil. The texture through this profile ranges from a fine sand to a medium sand. The pH ranges from neutral to moderately alkaline.

Table 2. *Analysis of Long Plain Fine Sand*

Horizon	Depth (cm)	% sand	% silt	% clay	% moisture 1/3 atm	% org. C	pH
Ap	0 - 17	84	11	5	5	0.9	7.6
C	17 - 22	94	3	3	3	0.1	8.0
Cg1	22 - 55	93	3	4	4	0.1	8.0
Cg2	55 - 75	95	2	3	3	-	8.1
Ckg1	75 - 90	90	6	4	4	-	8.2
Ccag	90 - 98	79	10	11	-	-	8.0
Ckg2	98 - 120	94	2	4	-	-	8.3



Figure 5. *Long Plain loamy fine sandy profile, 10-11-7W, from the center of the section in an uncropped area.*

3.1.3 St. Claude Silt Loam

An imperfectly to somewhat poorly drained Gleyed Carbonated Rego Black soil developed on thin, level to gently sloping, medium grading to coarse textured deltaic deposits. Lacustrine clay underlies these sandy deposits at a depth of more than 2 metres. The natural vegetation consists dominantly of aspen and grasses. Runoff is slow and permeability is restricted by a water table which occurs within 60 cm of the surface in the spring and decreases gradually throughout the summer months. The texture of the soil profile grades from a silt loam on the surface down to a very fine sand on the bottom two horizons.

They are characterized by a dark gray, strongly to very strongly calcareous Ah horizon, 12 to 20 cm thick, a strongly to extremely calcareous A_{ck} or C_{ca} horizon, 12 to 25 cm thick, and underlain by a light yellowish brown to olive gray (moist) sandy textured, moderately calcareous C horizon with prominent iron mottles (Figure 6). Analytical data for the St. Claude series is presented in Table 3 below.

Table 3. *Analysis of St. Claude Silt Loam*

Horizon	Depth	%	%	%	%	%	pH
	(cm)	sand	silt	clay	moisture	org. C	
					1/3 atm		
Apk	0 - 13	23	53	24	52	8.8	7.9
A _{ck} g _j	13 - 20	33	25	42	47	4.3	7.8
C _{kg} j	20 - 55	62	13	25	-	0.3	8.1
II _{ck} g _j 1	55 - 70	93	4	3	3	<0.1	8.0
II _{ck} g _j 2	70 - 120	96	3	1	2	-	8.3



Figure 6. *St. Claude silt loam profile, 10-11-7W, from the northwest quarter in a cropped area.*

3.1.4 Skelding Fine Sand

An Orthic Regosol soil developed on recent coarse textured, weakly calcareous aeolian deposits (sand dunes); the dominant texture is fine sand. They are soils which lack profile development and have no appreciable colour difference between the surface soil and the underlying material. These grassland areas are presently sparsely wooded with scrub oak, choke cherry and scrub aspen. The topography is complex with slopes dominantly of 2 to 5 percent with occasional steeper slopes. They are excessively drained, have a very low moisture retention capacity and rapid permeability.

The soil is characterized by a weak, very thin Ah horizon of approximately 5 to 10 cm thick under wooded vegetation, but in most areas little or no organic matter is present in the surface horizon. The parent material is yellowish brown to dark yellowish brown (Figure 7). Table 4 presents the analytical data for this series.

Table 4. *Analysis of Skelding Fine Sand*

Horizon	Depth	%	%	%	%	%	pH
	(cm)	sand	silt	clay	moisture	org. C	
					1/3 atm		
Ah	0 - 10	97	2	1	-	0.4	7.1
C1	10 - 50	100	-	-	-	0.1	6.5
C2	50 - 120	99	1	0	-	-	7.0

Figure 8 illustrates the distribution of these various soil types in the study area.



Figure 7. Skelding fine sand profile, 10-11-7W, from the north side of a dune in the southwest quarter.

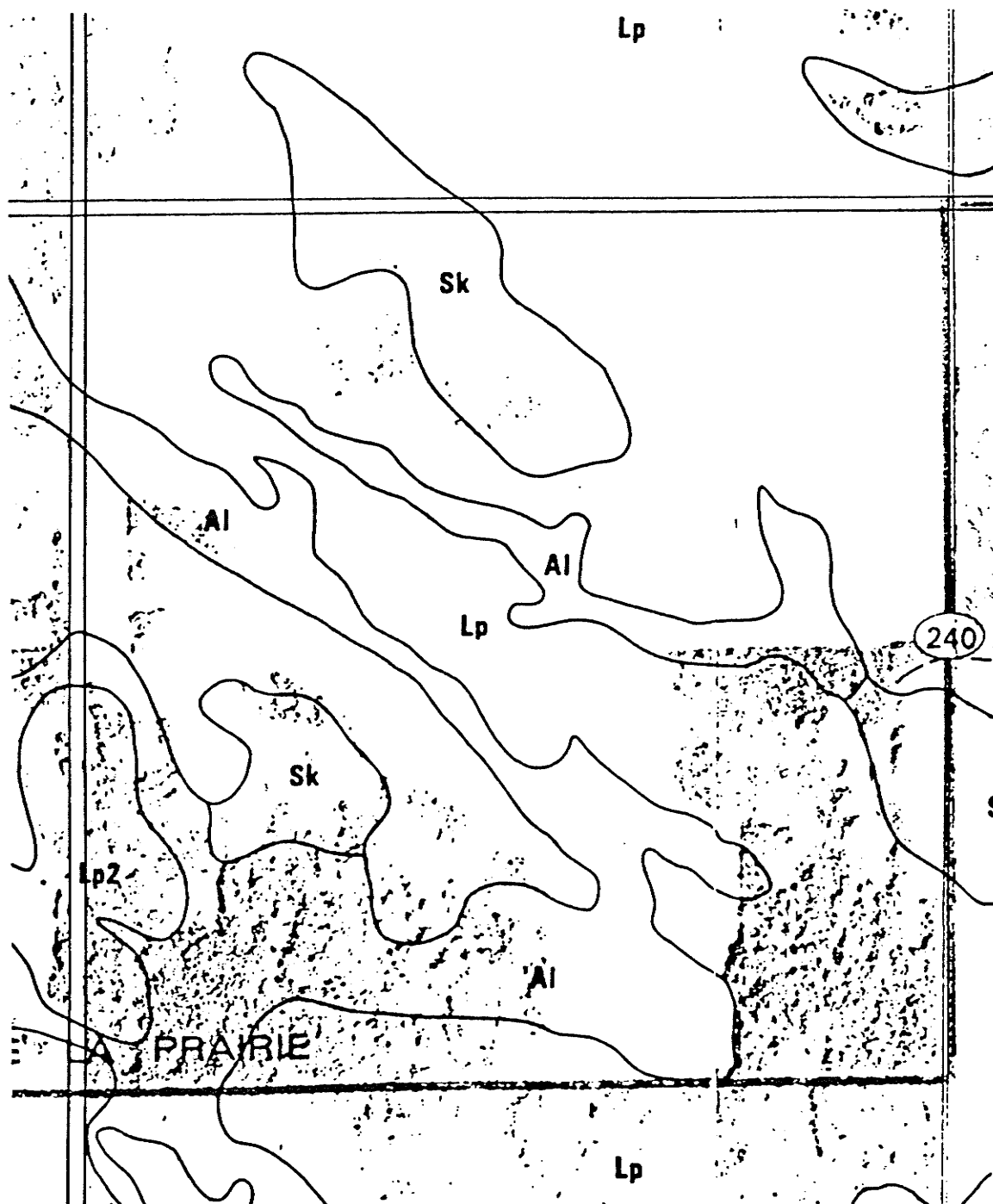


Figure 8. Distribution of the four major soil types in the study area. Al - Almasippi loamy fine sand (Gleyed Carbonated Rego Black), Lp - Long Plain loamy fine sand (Gleyed Orthic Regosol), Lp2 - Long Plain loamy fine sand, moderately eroded phase, Sk - Skelding fine sand (Orthic Regosol), Sx - St. Claude silt loam (Gleyed Carbonated Rego Black).

3.2.0 CHEMICALS

3.2.1 Pesticides

Details of the pesticide application program were obtained from the farm management for the years 1979 through 1983. Tables 5 to 9 detail the spray program for formulations used and rates. Table C.1 lists the active pesticide in the above formulations and the available toxicological data for these compounds. The Canadian Centre for Pesticide Analytical Standards, Laboratory Services Section, Production and Marketing Branch, Agriculture Canada, Ottawa, Ontario provided the following pesticide analytical standards: aldicarb (100%), azinphos-methyl (99%), bromoxynil (99.7%), bromoxynil octanoate (97%), carbofuran (99.2%), chlorothalonil (99.6%), 2,4-D acid (99+%), dicamba (99.39%), disulfoton (100%), EPTC (99.9%), mancozeb (89%), MCPA (99+%), mecoprop (99%), metribuzin (92.4%), paraquat dichloride (99.2%), propanil (99%), and zineb (96%). The following reference standards were provided courtesy of the United States Environmental Protection Agency: carbofuran (99.1%), 2,4-D (98+%), dicamba (100%), MCPA (99.65%), MCPA isooctyl ester (98.2%), and 2,4,5-T acid (98.7%). Atrazine technical standard (98.7%) was provided by Ciba-Geigy, and the trifluralin analytical standard (97%) was provided by Eli Lilly and Co.

3.2.2 Gases

Nitrogen, pre-purified helium and argon/5% methane were obtained from Welders Supplies Ltd. (Winnipeg, Manitoba).

3.2.3 Solvents

Reagent and HPLC grade 2,2,4-trimethylpentane, dichloromethane, acetonitrile, methanol, and glacial acetic acid were obtained from Fisher Scientific Ltd., Winnipeg, Manitoba and Calendon Laboratories Ltd.,

Table 5. Pesticide Application Schedule for 1983

DATE	FIELD NUMBER	PESTICIDE APPLIED	RATE
May 18	13	Eptam	5.1 L/ha
20	12	Eptam	5.5 L/ha
June 7	18	Amsol 80	0.86 L/ha
9-12	15	Sweep	2.4 L/ha
10-12	17	Sweep	2.4 L/ha
13	14,16	Hoegrass } tank mix	3.75 L/ha
		Torch	1.4 L/ha
14	11	Hoegrass } tank mix	3.75 L/ha
		Torch	1.4 L/ha
15	15	Eptam	5.5 L/ha
16	18	Amsol 80	0.86 L/ha
17	17	Eptam	5.5 L/ha
18	13	Sweep	2.5 L/ha
23	13,15,17	Sencor	0.5 L/ha
28	12	Decis } tank mix	0.13 L/ha
		Bravo	1.4 L/ha
29	13	Decis } tank mix	0.13 L/ha
		Bravo	1.4 L/ha
July 1	15,17	Decis } tank mix	0.13 L/ha
		Bravo	1.4 L/ha
12	15	Furadan } tank mix	0.85 L/ha
		Bravo	1.4 L/ha
13	17	Furadan } tank mix	0.85 L/ha
		Bravo	1.4 L/ha
14	12,13	Furadan } tank mix	0.85 L/ha
		Bravo	1.4 L/ha
27	17	Bravo	1.4 L/ha
29	15	Bravo	1.4 L/ha
August 1	12	Bravo	1.4 L/ha
5	13	Bravo	1.4 L/ha
8	17	Bravo	1.4 L/ha
10	15	Bravo	1.4 L/ha
12	12	Bravo	1.4 L/ha
16	13	Bravo	1.4 L/ha
19	17	Bravo	1.4 L/ha
20	12,15	Bravo	1.4 L/ha
26	13	Bravo	1.4 L/ha
30	17	Bravo	1.4 L/ha
September 1	15	Bravo	1.4 L/ha
2	12	Bravo	1.4 L/ha
5	17	Bravo	1.4 L/ha
11	12,15	Bravo	1.4 L/ha

Table 6. Pesticide Application Schedule for 1982

DATE	FIELD NUMBER	PESTICIDE APPLIED	RATE
May 11	18	Eptam	5.6 L/ha
12	13	Eradicane	5.6 L/ha
13	11	Eptam (potholes only)	5.5 L/ha
14	14	Eptam	5.6 L/ha
19	11/12,16	Eradicane	5.6 L/ha
June 4	12,13	Lorsban	2.8 L/ha
5	17	Lorsban	2.8 L/ha
9	11/12,16	Atrasin	8.5 L/ha
9	12,15	Pardner	1.5 L/ha
9	12,15	Hoegrass	3.75 L/ha
10	17	Pardner	1.51 L/ha
10	17	Hoegrass	4.5 L/ha
11	13	Banvel	0.7 L/ha
13	14	Lorsban	2.8 L/ha
13	16	Lorsban (Irrigation)	2.8 L/ha
14	18	Eptam (Irrigation)	5.5 L/ha
14	18	Lexone (Irrigation)	700 g/ha
14	18	Lorsban (Irrigation)	2.8 L/ha
July 2	14	Bravo	1.25 L/ha
2	14	Furadan	0.56 L/ha
2	14	Lexone (Irrigation)	700 g/ha
3	18	Bravo	1.25 L/ha
3	18	Furadan	0.56 L/ha
6	11,16	Bravo	1.25 L/ha
6	11,16	Furadan	0.56 L/ha
7	14	Lexone (Irrigation)	700 g/ha
12	14,18	Bravo	1.7 L/ha
13	11,16	Bravo	1.7 L/ha
21	14,16	Furadan	0.56 L/ha
21	14,16	Lexone	740 g/ha
22	11,18	Furadan	0.56 L/ha
22	11,18	Bravo	1.7 L/ha
26	14	Bravo	1.7 L/ha
28	16	Bravo	1.7 L/ha
August 5	16	Bravo (aerial)	1.7 L/ha
6	11,14,18	Bravo (aerial)	1.7 L/ha
15	11	Bravo (aerial)	1.7 L/ha
26	11,14,16,18	Bravo (aerial)	1.7 L/ha
September 7	11,14,16,18	Bravo (aerial)	1.7 L/ha

Potatoes - Russet Processing Fields 11,14,16,18

Corn - Pioneer 3993 Fields 11/12,13,16

Barley - Bedford Field 12 - Bonanza Field 17

Wheat - Soft White Field 15

Table 7. Pesticide Application Schedule for 1981

DATE	FIELD NUMBER	PESTICIDE APPLIED	RATE
May	12,13,15,17	Eptam	1.1 Kg/ha
May	17	Disyston 4.5 Kg @	3.7 Kg/ha
May 13	11,16	Eradicane	1.4 Kg/ha
May 13	13	Temik	3.7 Kg/ha
		Disyston	3.7 Kg/ha
June 2	11,16	Aatrex plus	340 g/ha
3	15	Sencor	0.56 L/ha
4	14,18	Stampede	1.25 L/ha
6	17	Eptam	550 g/ha
July 10	12,13,15,17	Bravo	1.25 L/ha
13	13,17	Bravo	1.25 L/ha
16	13	Sencor	0.56 L/ha
20	17	Bravo	1.25 L/ha
21	13	Bravo	1.25 L/ha
23	15	Bravo	1.25 L/ha
25	12	Bravo	1.25 L/ha
		Sencor	0.56 L/ha
31	17	Bravo	1.56 L/ha
		Furadan 4.8F	0.56 L/ha
August 1	12,13,15	Bravo	1.56 L/ha
		Guthion	140 g/ha
10	12,17	Bravo	1.7 L/ha
11	15	Bravo	1.7 L/ha
12	13	Bravo	1.7 L/ha
17	15,17	Bravo	1.7 L/ha
20	13	Bravo	1.7 L/ha
22	12	Bravo	1.7 L/ha
27	15	Bravo	1.7 L/ha
30	13	Bravo	1.7 L/ha
31	12	Bravo	1.7 L/ha
September 2	15	Bravo	1.7 L/ha

Fields 11 & 16 - Corn

Fields 14 & 18 - Barley

Fields 12,13,15 & 17 - Potatoes Netted Gems

Table 8. Pesticide Application Schedule for 1980

Date	Field #	Formulation	Crop
May 12	11	Eradicane 550 g/ha	Corn Pioneer 3994
May 12	13	Eptam 730 g/ha	Netted gems processing
	13	Eptam 1.1 Kg/ha	Netted gems processing only on sod areas.
	13	Sencor 150 g/ha	Netted gems processing
May 12	18	Eptam Gran. 5.5 Kg/ha	Netted gems processing
May 13	18	Temik 3.7 Kg/ha	Netted gems processing only on 50 acres.
	18	Disyston 2.8 Kg/ha	Netted gems processing only on 10 acres.
May 15	13	Temik 3.7 Kg/ha	Netted gems processing on fifty acres.
	13	Disyston 2.8 Kg/ha	Netted gems processing on twenty acres.
May 15	15	Eradicane 550 g/ha	Corn Pioneer 3994
May 19	16	Eptam 730 g/ha	Netted gems processing
	16	Eptam 1.1 Kg/ha	Netted gems processing only on sod areas.
	16	Sencor 150 g/ha	Netted gems processing
May 20	11	Sweep 0.6 L/ha	Corn Pioneer 3994 - only on a 5 acre test plot.
May 20	14	Treflan 140 g/ha	Regent rapeseed
	14	Furadan 370 g/ha	Regent rapeseed
May 21	16	Temik 3.7 Kg/ha	Netted gems processing
	16	Disyston 3.7 Kg/ha	Netted gems processing
June 5	12,17	Buctril M 90 g/ha	Pequis Barley

Table 9. Pesticides Applied in 1979

Field #	Crop	Pesticide Used
1	alfalfa-brome	-----
2 & 4	netted gems	Eptam Sencor Dithane M45 Polyram
3 & 7	buckwheat	-----
5	rapeseed	Furadan Treflan
6	wild hay	-----
----- no chemicals applied		

Georgetown, Ontario. Triple distilled water was obtained from the Department of Chemistry, University of Manitoba where a glass double still was operated. House distilled water was added to the first pot containing basic permanganate where it was distilled (packed column) into a second pot containing acidic dichromate where it was again distilled into a collecting flask. Dichloromethane (3%) in 2,2,4-trimethylpentane acidified with glacial acetic acid (0.5M) was used in the HPLC analysis of the pesticide residues. Acetonitrile-water (4:1) was used to elute the Sep-Paks. Dichloromethane was used in the liquid-liquid extraction of the soil column leachates. Methanol-water (triple distilled) (4:1) were used to extract the soil from the soil columns.

3.3.0 TILE DRAINAGE OUTLETS - SAMPLING

In 1981, grab samples of the tile outflow water were taken in the following manner: a clean silanized (Pierce Dri-Film SC-87 or Surfa-Sil) 4 L amber solvent bottle was placed below the outflow of the culvert and allowed to fill. The water was stored in the dark at 4°C until analysis. Tile drainage water was sampled from May 12 to August 5; a total of 41 samples were collected: 17 samples from each of the two gravity outflows and 7 samples from the sump well outlet representing a total of 14 sampling days during the season. The smaller number of samples from the sump well outlet reflects a restriction which was placed on pumping water from the sump well at the beginning of the season.

A more comprehensive sampling program was set up for 1982. Water sampling stations were set up at the two tile drainage outlets consisting of a wooden box housing either one or two (Fig. 9) amber 4 litre solvent bottles. Water was brought in via a teflon tube which had one



Figure 9. Sample box at the gravity outflow of the tile drain system, NE East corner of the farm site.

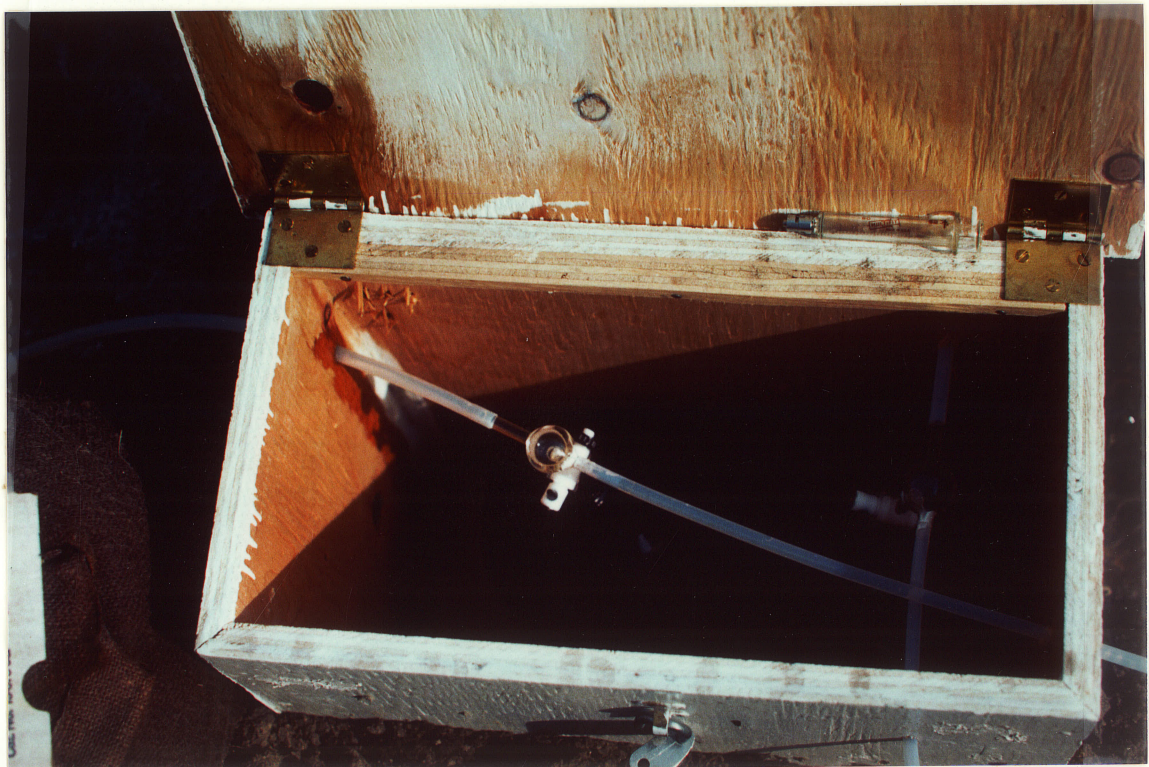


Figure 10. Flow splitter used to collect 24 & 72 h samples at the tile drain outflows.



Figure 11. *Sep-Paks attached to teflon tubing mounted in the tile drain outflows*

end placed 1.5 metres into the tile drainage outlet, through a glass flow splitter (Fig. 10) and out of the box via another teflon tube. The flow splitter was calibrated to deliver 4 L/24 h during the week and 4 L/72 h on weekends. In addition to the above form of sampling, two Waters C₁₈ Sep-Paks were affixed to a short length of teflon tubing and mounted in the tile outflow (Fig. 11); water flow through the Sep-Pak was determined to be 5 - 8 L/week. Following the above procedure a total of 177 samples were collected with the following breakdown: 66 west gravity outflow, 57 east gravity outflow, 26 sump well outflow, and 14 Sep-Pak samples from each of the gravity outflows.

During 1983 there was no further sampling of the tile outflows.

3.4.0 STAND-PIPE WELLS - SAMPLING

In 1982, two 25 cm i.d. PVC stand-pipe wells (Figs. 12 & 13) were installed in the northwest quarter to a depth of 2.5 metres in the following manner; a 1 metre deep hole was dug by hand, the pipe was placed upright in the hole and, using a water jet to flush out soil the pipe was hammered into the required depth. Each well was flushed thoroughly with water for 10 min. and allowed to equilibrate for one month before sampling was initiated. The well opening was covered with a double layer of polyethylene plastic which was held in place by a burlap bag (Fig. 14), this prevented any contamination of the well by surface deposition of either pesticide spray or contaminated soil particles.

Seven samples were collected in 1982 using an ISCO 780 Autosampler (Fig. 15). The sampler was set up to deliver a 280 mL sample every hour into a silanized 300 mL rectangular bottle. The individual samples were pooled into two 12 hour samples for the day.

In 1983, two LKB 2132 Microperspex Peristaltic pumps (Fig. 16) were used to pump water from the wells into 4 L amber solvent bottles (4 L/week). Power was supplied by a Honda EM500 Portable Generator at the side of the field (Fig. 17). Water was drawn from the wells through a four metre length of silicone rubber tubing (1.3 mm i.d.) which had a glass Pasteur pipette/glass wool filter at the end to filter out coarse particulates as well as to keep the end of the tubing below the water surface (1 metre). Each site visit produced two water samples per well; a weekly pump sample and a grab sample. The bulk grab sample was obtained by lowering a 4 litre bottle into the well and forcing it below the surface of the water with a length of pre-cleaned ABS plastic piping. This bulk sample was collected at a depth of 30 cm below water



Figure 12. Stand-pipe well established on the south side of 10-11-7NW. Ground water level about 1.25 m below ground surface.



Figure 13. Stand-pipe well established on the west side of 10-11-7NW, in this depression, water was very slow in entering the soil. Ground water was about 1 m below ground surface.



Figure 14. Stand-pipe well in the 1983 seasoning illustrating the protective covering used to prevent surface contamination. Note the sampling station in front of the well.

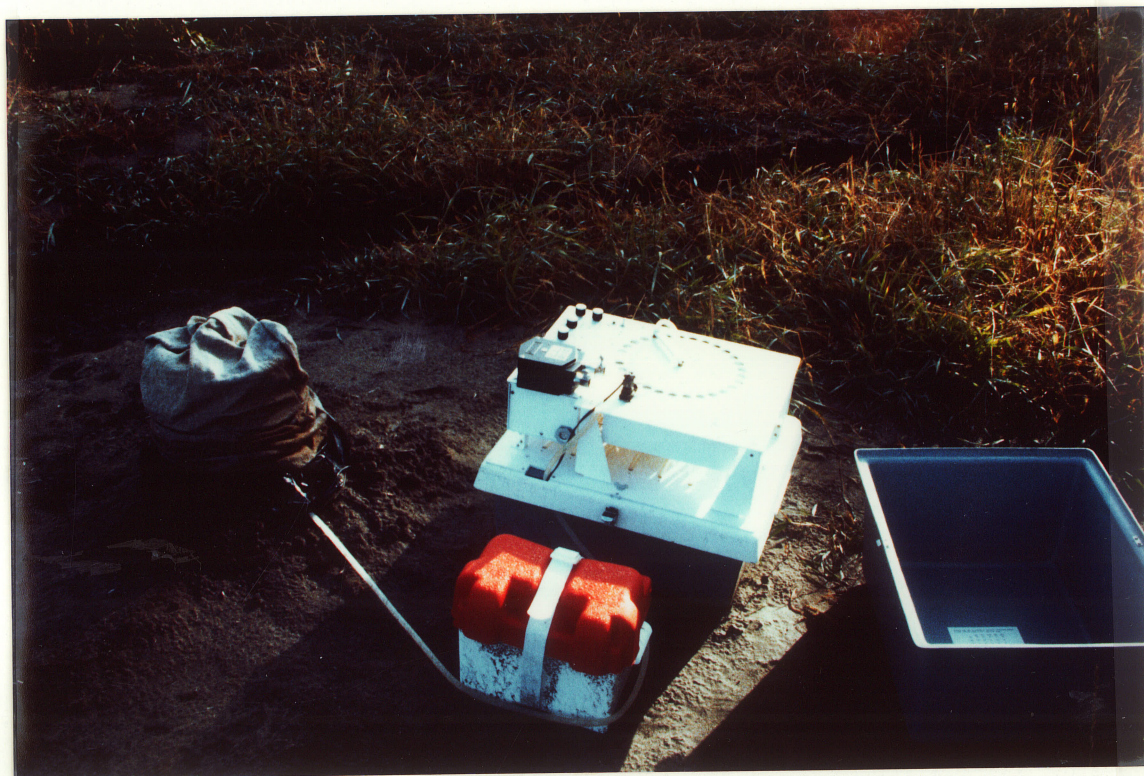


Figure 15. ISCO autosampler used in 1982 to sample water from well #1.



Figure 16. LKB Microperspex peristaltic pump used to sample wells # 1 & 2 on a continuous 168 h basis.

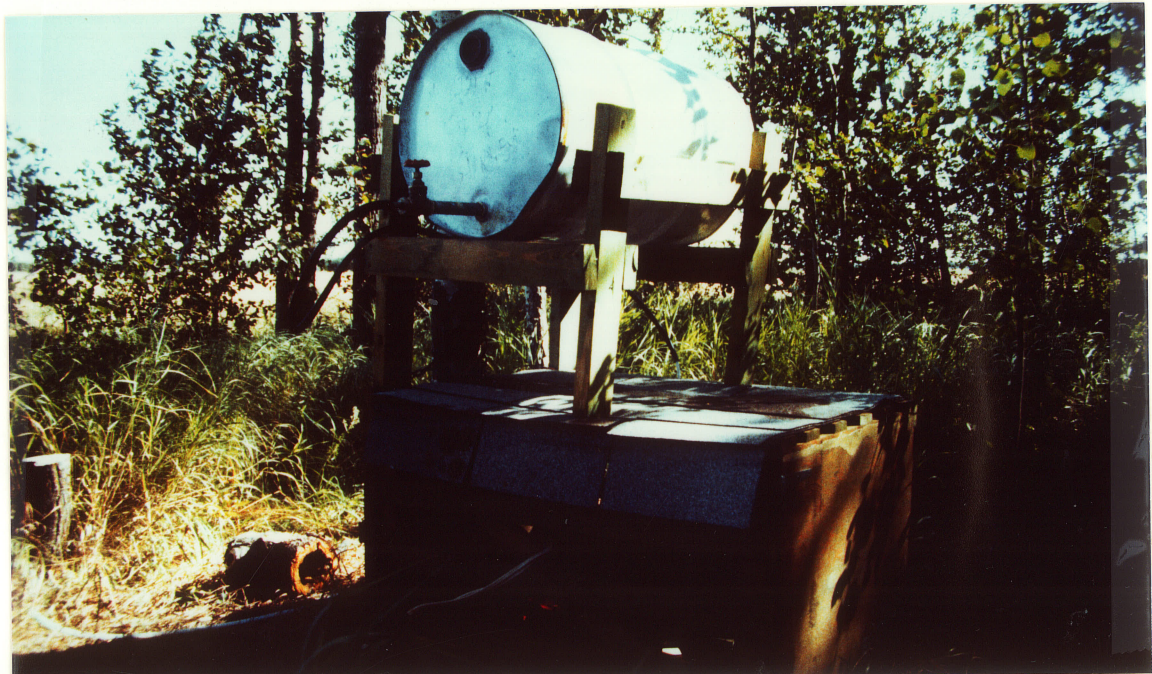


Figure 17. A Honda EM500 power generator securely housed in a wood crate powered both peristaltic pumps from a site in bush on the south side of 10-11-7NW. The white drum held a 7 day supply of fuel.

surface. To prevent contamination of the well, the clean bottle was placed on the inverted lid of the housing of the pump assembly (Fig. 18).



Figure 18. Well #2, collecting sample from pump housing, bottle for grab sampling from the stand-pipe would be placed on the inverted lid of the pump housing.

3.5.0 WATER ANALYSIS

Two 1 litre water samples were taken from the bulk water samples and filtered through Whatman 934-AH glass microfiber filters, to remove suspended particulate matter, into 1 L volumetric flasks. One flask was acidified to $\text{pH} \leq 2$ with hydrochloric acid, then each sample was aspirated through a prewashed Waters C_{18} Sep-Pak (Waters Scientific Ltd., Mississauga, Ontario) (Figs. 19 & 20). Adsorbed material was eluted from the Sep-Pak with 4 mL of 3:1 acetonitrile:water, the eluant was concentrated under nitrogen and taken up in 1 mL of the HPLC mobile phase.



Figure 19. *Modified 1 L volumetric flasks used to aspirate the water samples through a Sep-Pak.*



Figure 20. *A close-up of a Sep-Pak in the aspiration set up showing some retention of dissolved organic matter from ground water*

3.6.0 SOIL COLUMNS

3.6.1 Preparation

In the fall of 1983, 8 soil columns were prepared from three (3) different soils: Almasippi loamy fine sand (4 columns); Skelding fine sand (2 columns); and St. Claude silt loam (2 columns). The Almasippi loamy fine sand is the major soil type of the study farm as well as the immed-

iate area. The other two soils are representative of the minor soil types in the region. The columns were constructed out of 5 cm i.d. ABS plastic piping cut to lengths of 140-150 cm. One end of the pipe was closed off with a nichrome wire mesh held in place by an ABS plastic pipe coupler. The nichrome wire mesh was covered on one side, from the pipe, with a glass-fiber paper. This was to prevent any of the fine particulate matter in the pipe from passing through the wire mesh into the collecting vessels. The soil columns were made in the following manner: a 1 m by 1.5 m by 1 m pit was dug in the soil of choice. The pipe was then filled, by hand using a garden trowel, from the bottom up using soil from a side of the pit (Fig. 21). The resulting column contained the 2-3 major soil horizons common to the soils in the area. This method of construction was chosen over hydraulically pressing the column into the ground and digging it out because of the possibility that a piece of straw in the plow-layer might have caught on the edge and caused channelling within the column. The columns were returned to the laboratory and treated in the following manner: the soil column was placed within a larger sealed pipe and water was pumped into the larger pipe causing the soil column to be sub-irrigated. The soil column was sub-irrigated until surface flooding occurred, then the water was pumped out of the large pipe at the same rate it had been pumped in. The complete cycle took about 48 h; two soil columns were done at a time. This procedure settled the columns and brought them up to field capacity. In the case of the St. Claude silt loam, the procedure allowed the clay pocket to expand to normal size. The columns were mounted on a rack under which collection vessels were positioned to collect the leachates from the columns (Fig. 22). The columns were irrigated at a rate of 25



Figure 21. *Soil column under construction (see text).*



Figure 22. *The eight soil columns mounted on their rack with the leachate collecting vessels underneath.*

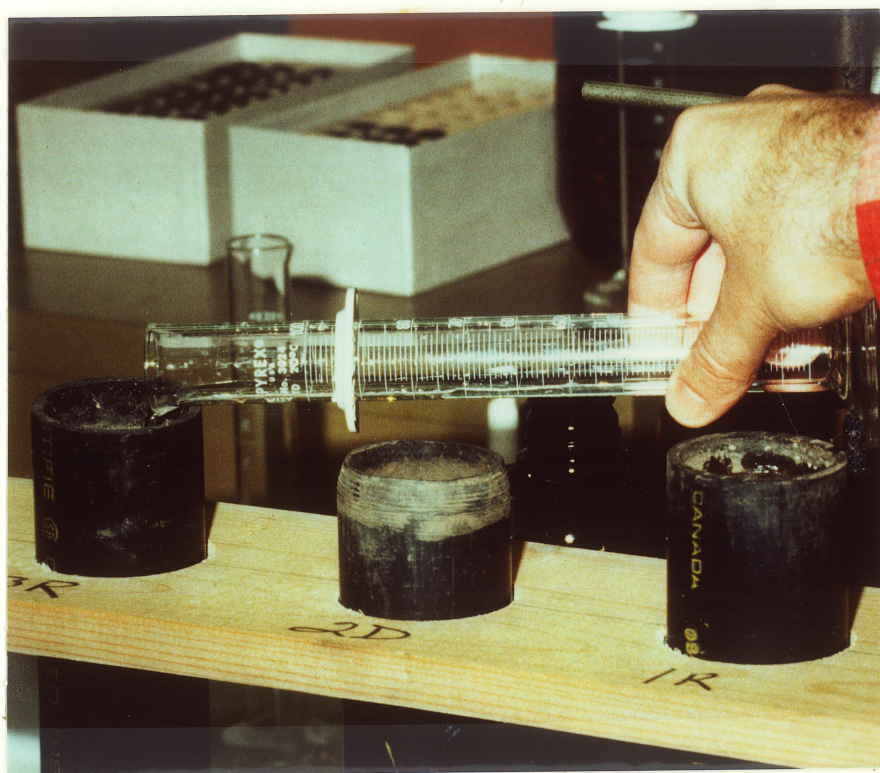


Figure 23. Manual irrigation of the soil column, 25 mL of Assiniboine River water or triple-distilled water.

mL/d (1.3 cm rainfall) for 5-6 d/wk, with occasional variation of the irrigation to simulate events such as heavier rainfall or increased irrigation (Fig. 23). (See Appendix B for the irrigation schedule and pesticide application schedule). A supply of river water was taken from the Assiniboine River at the irrigation system pump inlet and stored in the dark at 4°C this water was used to irrigate 4 of the eight columns; the other 4 were irrigated with triple-distilled water. One 4 L bottle of river water was set aside for analysis. This 4 L sample was subdivided into 4 x 1 L subsamples two of which were acidified to $\text{pH} \leq 2$ with hydrochloric acid. Each water sample was extracted using the Sep-Pak extraction system described elsewhere. The only modification to the system was the addition of a second Sep-Pak inline.

3.7.0 PESTICIDE APPLICATION TO SOIL COLUMNS

The following eight pesticides were chosen for use in this study: bromoxynil octanoate (69.2 mg/L), carbofuran (54.4 mg/L), chlorothalonil (225.2 mg/L), chlorpyrifos (242.4 mg/L), diclofop-methyl (116.4 mg/L), EPTC (1053.6 mg/L), metribuzin (296.2 mg/L), and trifluralin (110.0 mg/L). These pesticides were made up in acetone at the listed concentrations. One mL of the acetone solution was added to 25 mL of water and the mixture was applied to the head of the column. A second 25 mL irrigation of water was applied a few hours later to carry the pesticide into the soil.

EPTC was applied to the columns on days 22 (0.525 mL) and 28 (0.650 mL) for a total application of 2007.2 ug/column. After the second application a total of 5.350 L (263.95 cm) of irrigation water was added to each column over a period of 350 days. Chlorpyrifos was added to the soil columns on days 37 (0.85 L) and 40 (0.925 mL) for a total applied amount of 484.8 ug/column. After the second addition of chlorpyrifos a total of 5.075 L (250.4 cm) of irrigation water was added. Metribuzin was applied in the irrigation water at the same time as chlorpyrifos (co-application) for a total applied amount of 592.4 ug/column.

Chlorothalonil was applied to the soil columns on four occasions, days 46 (1.1 L), 52 (1.2 L), 58 (1.3 L), and 244 (4.875 L) for a total application amount of 900.8 ug/column. The fourth application on day 244 was a co-application with carbofuran. After the third application another 4.7 L (231.89 cm) of irrigation water was added during the course of the study. While after the fourth (co-application) another 1.125 L (55.51 cm) of irrigation water was added.

Diclofop-methyl was applied to the soil columns on days 113 (2.125 L)

and 117 (2.30 L) in the irrigation water for a total applied amount of 232.8 ug/column. After the second application of diclofop-methyl a total of 3.70 L (182.55 cm) of irrigation water was added to the column over the balance of the study period.

Trifluralin was applied to the columns on days 128 (2.6 L) and 135 (2.775 L) for a total application amount of 220 ug/column. After the second application another 3.225 L (159.12 cm) of irrigation water was added to each column.

Carbofuran was applied to the soil columns on days 198 (3.8 L), 211 (4.075 L), and 244 (4.875 L) for a total applied amount of 163.2 ug/column. The third application on day 244 was a co-application with chlorothalonil. After the second application carbofuran a total of 1.925 L (94.98 cm) of irrigation water was applied during the balance of the study period.

Bromoxynil octanoate was applied to the soil columns in the irrigation water on days 152 (3.175 L) and 158 (3.350 L) for a total applied amount of 138.4 ug/column. The octanoate was not expected to leach due to its hydrophobic nature and hydrolysis of the octanoate to the phenol or free bromoxynil. Therefore, bromoxynil was also monitored for in the leachate water from all columns.

Soil columns 1, 3, 5, & 7 were treated with unfiltered Assiniboine River water to represent irrigation water, while columns 2, 4, 6, & 8 were treated with triple distilled water to represent rain water. Leachate water volumes recovered, ranged from 66.7% to 70% of the irrigation water applied to the head of the column.

3.8.0 RECOVERY OF PESTICIDE RESIDUES FROM WATER

The recovery efficiency of twelve pesticides from natural water was determined for the extraction cartridge recovery procedure. A 100 mL water sample was spiked with 1 mL of the pesticide standard in methanol. The water sample was then slowly aspirated through the extraction cartridge. The cartridge was eluted with acetonitrile to recover adsorbed residues and the eluate concentrated under a stream of dry nitrogen. Residues were taken up in a quantity of the mobile phase and analyzed by HPLC with UV detection, the results are presented in Table 10. Three pesticides gave zero recoveries from the water sample. This is probably an artifact of the spiking procedure for two of these compounds as they are quite soluble in water but not in methanol. The third, a polymeric compound was not soluble in either water or methanol. Those pesticides which could assume an ionic form were found to give lower recoveries than those which could not become ionic. Modifying the pH would improve the recoveries of these compounds. As a result, two 1 L water samples were extracted from each bulk sample collected in the field; one natural and the other acidified with HCl to a pH ca. 2.

Table 10. Pesticide Recovery Efficiency from Natural & Acidified Water

Pesticide	amount added	Natural Water		Acidified Water	
		amount recovered	%	amount recovered	%
	ug	ug		ug	
Aldicarb	488	0	0	0	0
Carbofuran	445	67±4	15±1	84±10	19±3
Chlorothalonil	290	273±7	94±3	271±9	93±4
2,4-D Acid	1015	106±11	10±2	907±20	89±3
Dicamba	357	11±3	3±1	286±18	80±7
Disulfoton	977	923±23	94±3	933±21	95±3
MCPA	429	158±12	37±4	377±15	88±5
Mecoprop	190	16±3	8±2	143±10	75±7
Metribuzin	593	132±7	22±2	128±9	22±2
Paraquat Dichloride	189	0	0	0	0
Propanil	201	30±4	15±3	48±7	24±5
Zineb	325	0	0	0	0

3.9.0 LEACHATE COLLECTION AND ANALYSIS

Leachate from the bottom of the columns was collected in 100 mL volumetric flasks. The leachate was then transferred into a 250 mL separatory funnel and extracted 3 times with fresh 20 mL portions of dichloromethane. The dichloromethane extracts were combined in a 100 mL round-bottom flask and concentrated on a roto-vaporator using 2,2,4-trimethylpentane as a keeper. The concentrate was quantitatively transferred to a sample vial through a drying tube (ca. 1 g anhydrous sodium sulfate in a glass-wool plugged Pasteur pipette). The flask was rinsed with a small quantity of fresh 2,2,4-trimethylpentane and the rinse was transferred to the sample vial. The 2,2,4-trimethylpentane was concentrated under a gentle stream of dry-nitrogen with gentle warming. The residue was taken up in 1.0 mL of the HPLC mobile phase and analyzed on a silica column (uPorasil, Waters Scientific).

3.10.0 SOIL COLUMN ANALYSIS

The soil columns were sectioned by cutting the pipes at 15 cm intervals and pushing the contents into a beaker. Where a horizon division was encountered, the soil sample was further divided along the horizon line. The soil was dried at 105°C overnight then three ca. 50-60 g subsamples were placed into 250 ml flasks and 50 mL of a 4:1 methanol:water solution added. The solution was mixed and allowed to sit overnight at ambient temperature in the dark. In the morning the solutions were filtered and reduced in volume under vacuum (2,2,4-trimethylpentane used as keeper). Residues were taken up in 1 ml of 2,2,4-trimethylpentane and analyzed by HPLC.

3.11.0 HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

3.11.1 Analysis Conditions

Analysis was done using a Waters Scientific 6000A pump and model 440 UV detector with detection at 254 nm. A Waters Scientific uPorasil column was used with 3% dichloromethane in 2,2,4-trimethylpentane/0.5M acetic acid (Fisher HPLC grade, acetic acid reagent grade) as the mobile phase at a flow rate of 1.5 mL/min. The flow rate was later modified to 1 mL/min for 10 minutes then 5 mL/min for 15-25 minutes. This was done to separate some of the early eluting compounds and to resolve some of the late eluting species. Sample volume was 50 uL (autosampler-well samples 5-10 uL, column leachates 5-20 uL) using a Rheodyne 7125 injector with a 1 mL sample loop. The pesticide results were corrected for the recovery efficiency.

3.11.2 K_{ow} Determination

K_{ow} 's were determined on the above system with the following modifications: the column was a Biorad Biosil ODS-10 (25 cm X 4 mm i.d., 2 micron frits) reverse-phase column; the mobile phase was 85:15 methanol/water (Fisher HPLC grade, triple distilled organic free, respectively) and the flow rate was 1.0 mL/min. Using the method of Sarna et al. (1984) and Webster et al. (1984), K_{ow} 's were determined for 20 pesticides.

3.12.0 CAPILLARY GAS CHROMATOGRAPHY

Analysis was done using a Varian Aerograph Series 2400 gas chromatograph equipped with a 30 m X 0.254 mm i.d. J & W fused silica capillary column with SE-54 as the liquid phase. The chromatograph had been modified to

include an SGE GISS-4AK/4 inlet splitter system, an Antek model 203 ⁶³Ni electron capture detector, and an Antek model 245 electron capture linearizer. Analysis of the samples was performed under the following conditions: carrier gas flow (He) 21 cm/sec (linear velocity), injector temperature 275°C, column temperature 200°C, detector temperature 290°C, makeup gas Argon/Methane 5%. Chromatograms were recorded on a Fisher Recordall Series 5000 single pen strip chart recorder.

RESULTS AND DISCUSSION

4.1.1 FIELD WORK 1982

In 1982, from June 23rd to September 30th, tile drain water (Figs. 24 & 25) was sampled both in bulk and using extraction cartridges. The bulk water samples were both "grab" and 24/72 h samples. A number of ground water samples were taken from one of the two stand-pipe wells during August and September. Ground water from both of the stand-pipe wells was sampled from August to October on a weekly basis - both a "grab" and a weekly pump sample.

Of the twenty pesticides monitored in 1982, only one, chlorothalonil, was detected in the tile drain water on a sporadic basis. Residues of chlorothalonil were detected on only 4 of 63 sampling days, i.e., 4 times at the east culvert and 4 at the west culvert gravity outflow (Figs. 26 & 27, respectively) and once in the west culvert outflow (Fig. 28) from the sumpwell.

The first application of chlorothalonil (Bravo) was made during the period of July 2 to 6 (julian day 183 to 187) (Table 6) to the four fields planted to potatoes. This treatment was followed by 6 others: July 12 & 13 (193 & 194), July 22 to 28 (203 to 209), Aug. 5 & 6 (217 & 218), Aug. 15 (227) (1 field only), Aug. 26 (238), and Sept. 7 (250). From Aug. 5 all treatments were by aerial application. Rainfall exceeded 50 mm in a given 24 h period on two instances, July 16 & 28 (197 & 209), and exceeded 25 mm on four other occasions (Table 11). Upon comparison of the residue's time of appearance (Figs. 26, 27 & 28) in the tile outflows (grab samples, 24 h/72 h samples and extraction cartridge samples) with the water balance levels for Portage la Prairie, a rela-



Figure 24. Gravity outflow at the NE corner of 10-11-7NE, this outflow is the drainage for 3/4 of the section



Figure 25. Outflow, from the sumpwell, into the municipal ditch on the west side of the road to the west of section 10-11-7.

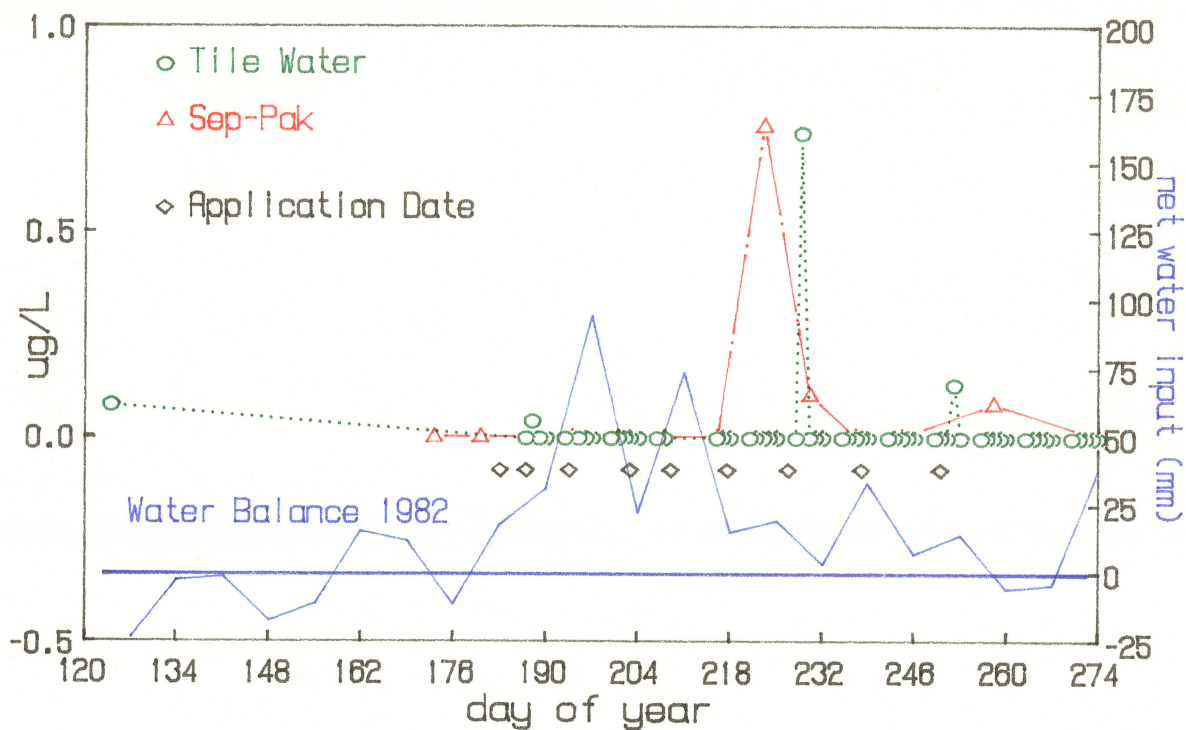


Figure 26. Chlorothalonil levels in tile drain outflow - NE East: monitored and grab water extracts and outlet Sep-Pak extracts and water balance (Dunlop, 1981)[irrigation included in precipitation input] for 10-11-7W (1982)

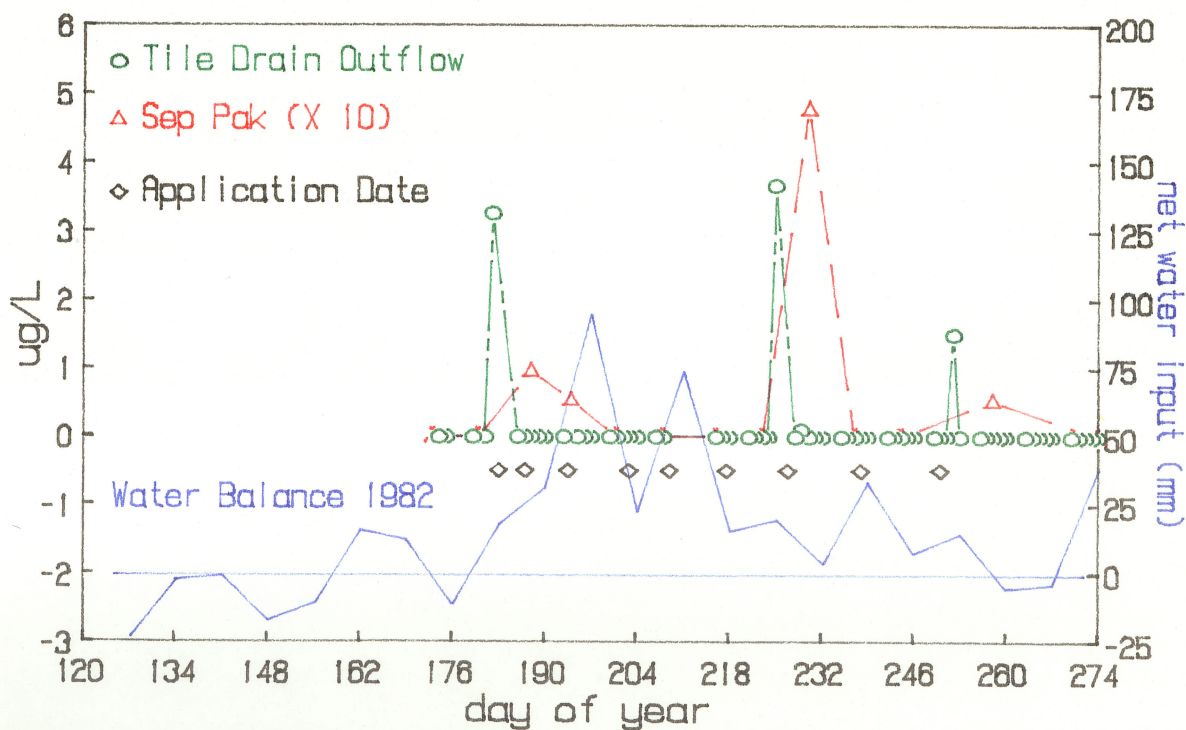


Figure 27. Chlorothalonil levels in tile drain outflow - NE West: monitored and grab water extracts and outlet Sep-Paks and water balance for 10-11-7W (1982)

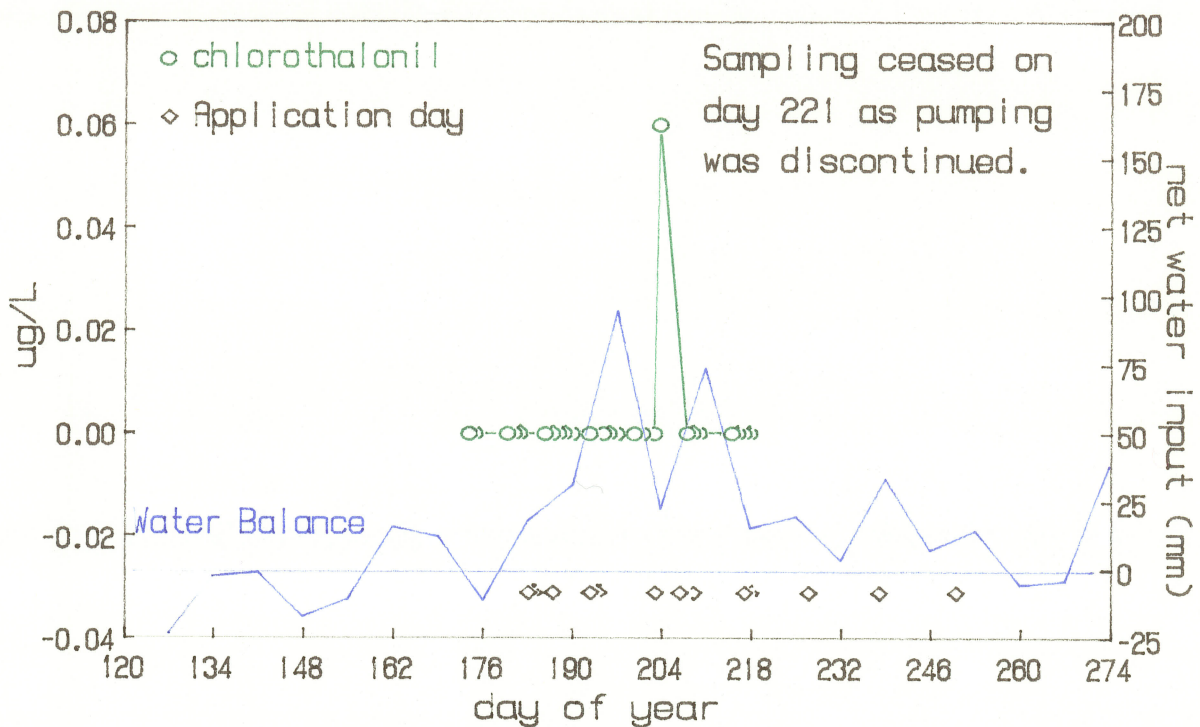


Figure 28. Chlorothalonil levels in tile drain water West Side and water balance for 10-11-7W (1982)

tionship is apparent between the precipitation pattern and appearance of chlorothalonil residues in the outflow water.

There were four occurrences of chlorothalonil residues detected in the tile outflow from the east culvert at the gravity outflow (Table 11 & Fig. 26). The first was in a sample taken on May 4 and may reflect a flush through of winter runoff as there was no major precipitation in the previous month. The second occurrence was in a sample taken on July 7, 1982 (1 to 5 days after the first 1982 application). These residues are probably a carry-over from the previous year and which could have been leached into the tile drain zone of ground water by the two moderate rainfalls in early and mid June (Table 13). The third occurrence of chlorothalonil residues, the highest level observed for the season for

Table 11. Precipitation data from CFB Portage la Prairie, 1982.
(1.6 km east of the farm site)

Day	Month											
	5		6		7		8		9		10	
	d-y	mm	d-y	mm	d-y	mm	d-y	mm	d-y	mm	d-y	mm
1	121	--	152	0.4	182	--	213	--	244	5.6	274	7.1
2		--		--		2.7		0.2		--		0.2
3		--		--		tr		--		--		tr
4		tr		0.5		5.5		0.2		--		tr
5		--		0.8		12.8		tr		tr		tr
6		3.2		25.4		tr		1.0		3.1		6.0
7		--		1.7		tr		--		--		0.9
8	128	--	159	0.3	189	--	220	3.9	251	--	281	tr
9		2.0		4.2		0.2		0.2		--		1.0
10		10.2		tr		6.9		--		--		31.7
11		tr		--		--		--		tr		1.0
12		tr		--		tr		2.0		--		0.2
13		--		2.3		4.4		--		tr		--
14		--		--		tr		18.0		--		tr
15	135	6.7	166	--	196	0.6	227	--	258	--	288	--
16		1.0		1.0		54.8		--		0.9		5.0
17		13.6		--		6.4		--		tr		0.5
18		0.6		0.2		--		7.4		1.0		tr
19		tr		26.2		--		--		1.6		2.7
20		--		1.2		--		--		--		tr
21		--		--		--		2.8		--		--
22	142	--	173	0.4	203	2.0	234	9.3	265	2.8	295	--
23		--		0.2		1.8		--		3.2		--
24		1.0		tr		--		0.7		--		--
25		--		--		--		1.3		tr		--
26		--		tr		7.6		tr		--		0.2
27		--		--		23.4		--		33.2		0.8
28		--		1.2		54.2		tr		14.8		11.6
29	149	0.2	180	--	210	--	241	--	272	--	302	0.8
30		2.6	181	--		--		--	273	--		
31	151	2.0			212	--	243	--			304	

d-y = julian day tr = trace of precipitation (<0.2 mm)

-- = no precipitation

Table 12. *Chlorothalonil Levels in Tile Drainage Water: 1982*

Date	Chlorothalonil Concentration (ug/L) in Water from the Two Gravity Outflow Culverts and the Sump Well Outflow		
yy/mm/dd	NE East	NE West	West Side
82/05/04	0.08	----	----
82/05/04	----	----	----
82/06/23	----	----	----
82/06/24	----	----	----
82/06/28	----	----	----
82/06/30	----	----	----
82/07/01	----	3.27	----
82/07/05	----	----	----
82/07/06	----	----	----
82/07/07	0.04	----	----
82/07/08	----	----	----
82/07/09	----	----	----
82/07/12	----	----	----
82/07/14	----	----	----
82/07/15	----	----	----
82/07/16	----	----	----
82/07/19	----	----	----
82/07/20	----	----	----
82/07/21	----	----	----
82/07/22	----	----	----
82/07/23	----	----	0.06
82/07/26	----	----	----
82/07/27	----	----	----
82/08/04	----	----	----
82/08/05	----	----	----
82/08/06	----	----	----
82/08/09	----	----	****
82/08/10	----	----	
82/08/11	----	----	
82/08/12	----	----	
82/08/13	----	3.66	
82/08/16	----	----	
82/08/17	0.74	0.09	
82/08/18	----	----	
82/08/19	----	----	
82/08/20	----	----	
82/08/23	----	----	
82/08/24	----	----	
82/08/25	----	----	
82/08/26	----	----	
82/08/27	----	----	
82/08/30	----	----	
82/08/31	----	----	

Table 12. *Chlorothalonil Levels in Tile Drainage Water: 1982 (continued)*

Date	Chlorothalonil Concentration (ug/L) in Water from the Two Gravity Outflow Culverts and the Sump Well Outflow		
yy/mm/dd	NE East	NE West	West Side
82/09/01	----	----	
82/09/02	----	----	
82/09/03	----	----	
82/09/06	----	1.50	
82/09/07	----	----	
82/09/08	----	----	
82/09/09	0.13	----	
82/09/10	----	----	
82/09/13	----	----	
82/09/14	----	----	
82/09/15	----	----	
82/09/16	----	----	
82/09/17	----	----	
82/09/20	----	----	
82/09/21	----	----	
82/09/22	----	----	
82/09/23	----	----	
82/09/24	----	----	
82/09/27	----	----	
82/09/28	----	----	
82/09/29	----	----	
82/09/30	----	----	
82/10/01	----	----	

**** = no water flow from this outflow from this date as pumping ceased.
 ---- = no residues detected at the 0.02 ug/L levels

Table 13. *Tile Drainage Gravity Outflow - Sep-Paks*

Date	Chlorothalonil (ug/L)	
yy/mm/dd	East Culvert	West Culvert
82/06/22	----	----
82/06/29	----	----
82/07/07	----	9.70
82/07/13	----	5.54
82/07/20	----	----
82/07/27	----	----
82/08/04	----	----
82/08/11	0.76	----
82/08/18	0.10	45.50
82/08/25	----	----
82/09/01	----	----
82/09/15	0.08	5.49

this particular tile line system was detected in a sample taken on August 17, 1982. Prior to this occurrence there had been two applications of chlorothalonil in July (Table 6) as well as two periods of heavy rainfall (Table 13), which resulted in large positive water balances during these periods. The fourth occurrence of chlorothalonil residues in tile drain water was in a sample taken on September 9, 1982 (Table 11). The data as presented in Fig. 26 suggests a direct relationship between the amount of precipitation and the appearance of chlorothalonil in the outflow of the tile drain system. Residues were detected in tile outflow water 18 to 21 days after a major series of rainstorms (usually about 7 days apart for the two tile systems).

Each precipitation event may have carried dissolved residues into the subsoil which could have been leached further by each subsequent rainfall. Sporadic heavy rainfalls may have carried larger amounts of residues into the subsoil causing a surge (faster flow) in water movement downward towards the water table. A steady level of precipitation and irrigation would have given a uniform movement of residues into ground water at a level which would not have been detected at the tile outflow because of dilution. A surge in water movement downward would have caused a "front" of higher levels of residues hitting ground water and entering the tile system. This type of movement is seen in the results obtained from the east culvert of the gravity outflow. It would have been interesting to see if this trend had continued through the balance of the year by sampling through to the end of November and seeing if the two moderately heavy rainfalls in late September and early October had carried more residues into ground water. However, funding and other time commitments terminated the field work in September.

Chlorothalonil residues were detected on four occasions in the tile drain outflow from the west culvert at the gravity outflow (Table 12). Three of these occurred 3 to 5 days prior to the appearance of residues in the east culvert; the fourth occurrence was on the same day. The pesticide concentration in water was also higher (from 2 to 5X the maximum observed in the east culvert) which was probably due to a smaller dilution factor. The earlier appearance of chlorothalonil residues in the outflow water may be a result of a smaller distance to travel to ground water and thus to the drainage tile line. Fig. 27 illustrates the pattern of appearance of residues with respect to the precipitation pattern. As in the previous case, the pattern is similar if somewhat shifted to an earlier appearance after major precipitation.

A relationship between the precipitation pattern and the time of appearance of residues in the outflow water was observed (Table 11, Fig. 26 & 27) for the tile outlet extraction cartridges. The data for the east culvert shows two peaks which correspond to two periods of rainfall, one very heavy and the other lighter, which is reflected in the amounts of residues found in the water. A similar pattern is observed for the west culvert where three peaks were observed with the same relationship to precipitation patterns.

The sump well (Figs. 29 & 30) was pumped into the municipal ditch only until the first week of August. Chlorothalonil residues were detected in the outflow water only on one occasion, July 23 (Table 11), at a low level (0.06 ppb) near the detection limit. The time of appearance of residues in the outflow water again correlates well with the precipitation pattern (Fig. 28). In this instance, three periods of heavier rainfall were required to carry an appreciable amount of residues into

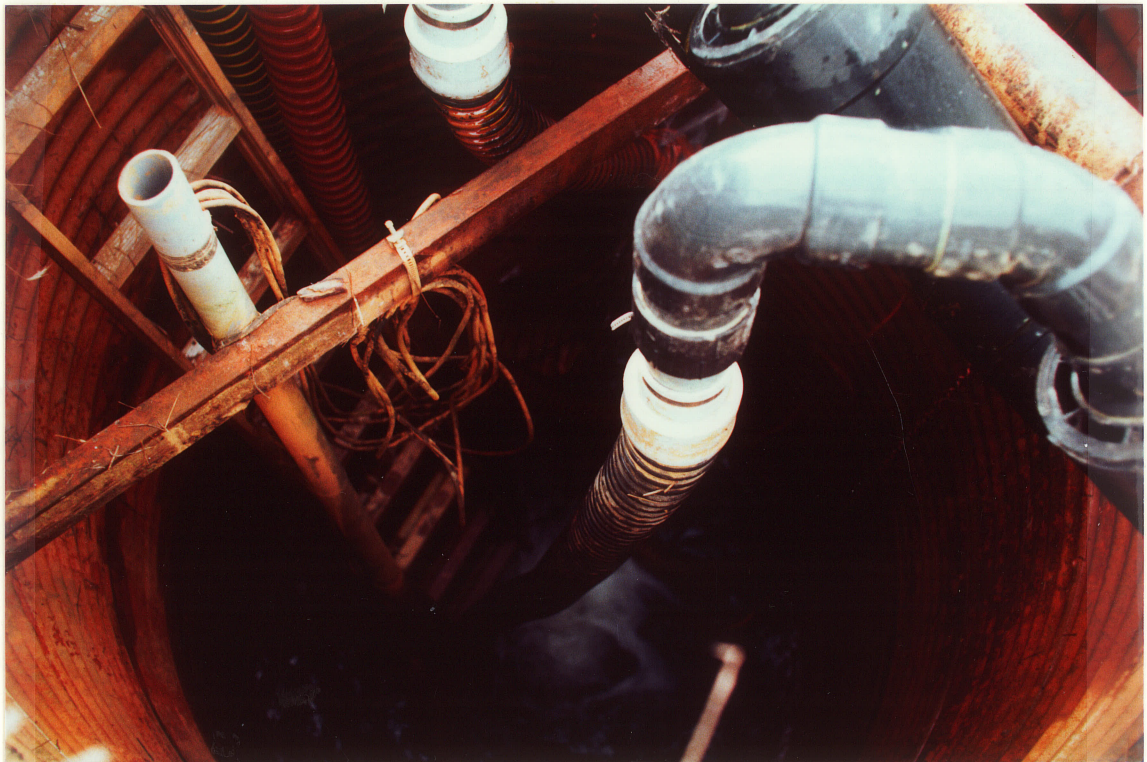


Figure 29. Sump well located at the northwest corner of 10-11-7SW, in early July under pumping condition.



Figure 30. Sump well in late August, pumping has ceased.

the tile drainage zone of ground water. The residues detected were probably carry-over from the previous year as was the case with the first appearance of residues of chlorothalonil in the outflow water from the two culverts at the gravity outflow.

Analysis of the tile drain water for 1981 indicated that there were no detectable levels (<0.02 ug/L) of residues of any of the pesticides in the tile outflow. This may have been an artifact of both the sampling schedule and the manner in which the samples were taken. Analysis of the tile drain water from 1982 found a peak which was identified as chlorothalonil on the basis of retention time and co-injection with a standard under different solvent conditions (hexane was substituted for the 2,2,4-trimethylpentane). Out of the ca. 66 sampling days, detectable amounts of chlorothalonil were found on 4 days in the outflow of both the east and west gravity outflows of the tile drain system and on one day from the sump well outflow on the west side of the site. Chlorothalonil concentrations ranged from 0.04 to 0.74 ug/L with an initial level of 0.08 ug/L observed on May 4th, the first sampling day, and subsequent levels of 0.04, 0.74, and 0.13 ug/L on July 7th, August 17th and September 9th, respectively, from the NE east culvert. The residue levels in the outflow from the NE west culvert ranged from 0.09 to 3.66 ug/L with the first occurrence of detectable residues on July 1st (3.27 ug/L), with subsequent appearances on August 13th and 17th (3.66 & 0.09 ug/L, respectively) and September 6th (1.50 ug/L). In conjunction with the monitored flow sampling and grab samples, the inline extraction cartridges (one week flow) also, indicated the presence of chlorothalonil in the tile outflow at the levels observed. It is difficult to report absolute values for chlorothalonil levels in the tile outflow for the

extraction cartridge data owing to the variation in flow volumes through each extraction cartridge. A calibration of a number of the Sep-Paks in the field indicated a flow volume ranging from 5 to 7 L/week. As the level of chlorothalonil was not constant but varied with time, averaging of the amount extracted over an average flow volume would not reflect the true occurrence pattern (Fig. 27); thus, the graphed concentration values are for the amount extracted based on a one litre flow through volume and may be much higher (5 to 7 times) than the actual case. Nevertheless the pattern is much the same between the daily data and the weekly average data (extraction cartridge).

The sump well, located in the northwest corner of 10-11-7SW was pumped from early June to mid-August. Chlorothalonil was detected in the outflow water on only one occasion, July 23, when the concentration of chlorothalonil was 0.06 ug/L.

Residues in the outflow water at the two gravity flow outlets appeared at about the same time. The difference in maximum values, 0.74 versus 3.66 ug/L was probably an effect of the area drained by that particular tile line system. The east gravity outlet drains a much larger tile system than the west gravity outlet; thus, there would be more dilution of the residues in the outflow from this outlet given the same water input ha^{-1} . Ground water flow may vary across the section creating variations in ground water pesticide residue concentrations. In addition, an examination of the application data for the fields (Table 2) shows that chlorothalonil was only applied to fields 11, 14, 16, and 18 in the 1982 crop year. The tile system (Fig. 2) emptying out of the NE east gravity outlet drains fields 13 through 16 and a portion of field 17. The tile system emptying via the west gravity outlet drains

portions of fields 11, 15, 16 and 17 and all of 18. The system emptying out of the NE west gravity outlet drains a much more extensive area to which chlorothalonil was applied and thus would be expected to have higher levels of the chemical.

The chlorothalonil detected in the initial sample taken on May 4th from the east gravity outflow is consistent with there being some carry-over of residues in the subsoil which were subsequently leached to ground water (in this case by snow melt water) once the soil had thawed. Chlorothalonil (Bravo) had been applied to fields 12, 13, 15, and 17 in the 1981 crop year. Of these fields, the first three are drained by the tile system which empties through the NE east gravity outlet where the residues were detected. In addition, the first application of chlorothalonil in 1982, to any field was not until July 2nd, thus giving greater credence to carry-over of residues from the previous crop year. Analysis of ground water in 1983 confirmed this conclusion.

The tile drain outflow from the NE west gravity outlet contained residue levels which were 50 times higher than those observed in the NE east gravity outlet water. The difference in residue levels may be attributed to the volume of water flow from each of the two tile systems. The NE east outlet tile system is much more extensive than the NE western system resulting in a higher water volume flow and a greater dilution of residues being carried into the tile system. The NE western tile system drains significant portions of fields 11 and 18 where there was extensive chlorothalonil use in 1982 while fields 14 and 16 are not as intensively drained by the NE eastern tile system which would affect the amount of residues picked up by the tile system and drained out of the area.

The significant fact here is the time of appearance of the residues. There is one instance where residues were detected in tile water early in the season prior to any chemical application, suggesting carry-over from the previous crop year and subsequent leaching once the soil had thawed down to ground water. Subsequent appearances of residues in the tile water were usually only a few days apart, with residues first appearing on the tile outflow from the NE western system, then in the NE eastern system. This time differential may be due to the distance the residues have to leach from the soil surface to ground water and the tile system. Field 18 which is extensively drained by the NE western tile system has many depressions where the distance from the soil surface to ground water is not great. Whereas, fields 13 through 16 do not have as many depressed areas, and thus do not require as extensive drainage and the distance from the soil surface to ground water is somewhat greater.

The one occurrence of chlorothalonil in the outflow from the sumpwell occurred shortly before pumping ceased and while the tile system was actively drawing water out of the field. From Fig. 2 it can be seen that only small portions of field 11 are actually drained by this tile system as there are not too many low lying areas in this field. The low level of chlorothalonil residues detected in the outflow is probably due to the relatively small drainage area as well as the greater distance to ground water in this field.

The autosampler data (Table 14) indicated the presence of two compounds, chlorothalonil and carbofuran, in the ground water sampled from the south side of 10-11-7NW. Owing to mechanical problems with the sampler, only 7 sampling days in a two month period were obtained and only

one of these was a complete 24 h day: the others were slightly over 12 h. A plot of the data for chlorothalonil and carbofuran (Fig. 31) with the precipitation data does not show any clear relationship of pesticide levels in ground water to precipitation pattern. One observation which can be made, despite this dearth of data, is that in the time period July 12 to 17 the concentration of both compounds peaked in the first 12 sampling hours of July 16th and then declined in the following 12 h period before increasing again in the 14 h sampling period of the 17th.

The last four sampling days indicate two peaks in residue concentrations in ground water for both compounds. A number of these samples were submitted for GC/MS confirmation to the RCMP laboratory. Both chlorothalonil and carbofuran were confirmed in the samples. Carbofuran phenol was also identified in a number of the samples but was not quantified. Carbofuran was identified in ground water from a stand-pipe well (W2) in the field but not in the tile drain outflow from this field. The levels observed in the ground water were low and thus the levels in the tile outflow would be expected to be even lower because of dilution. The concentration of chlorothalonil in ground water from the

Table 14. *ISCO - Autosampler - Ground Water from the South Well (W2)*

Date yy/mm/dd	Sample Description (h)	Chlorothalonil concentration (ug/L)	Carbofuran concentration (ug/L)
82/08/12	1 - 14	107.2	20.9
82/08/16	1 - 12	225.5	74.6
82/08/16	13 - 24	125.8	53.1
82/08/17	1 - 14	272.6	67.1
82/09/15	1 - 15	81.7	145.5
82/09/16	1 - 11	10.9	11.5
82/09/22	1 - 16	10.1	24.6
82/09/23	1 - 13	72.3	158.5

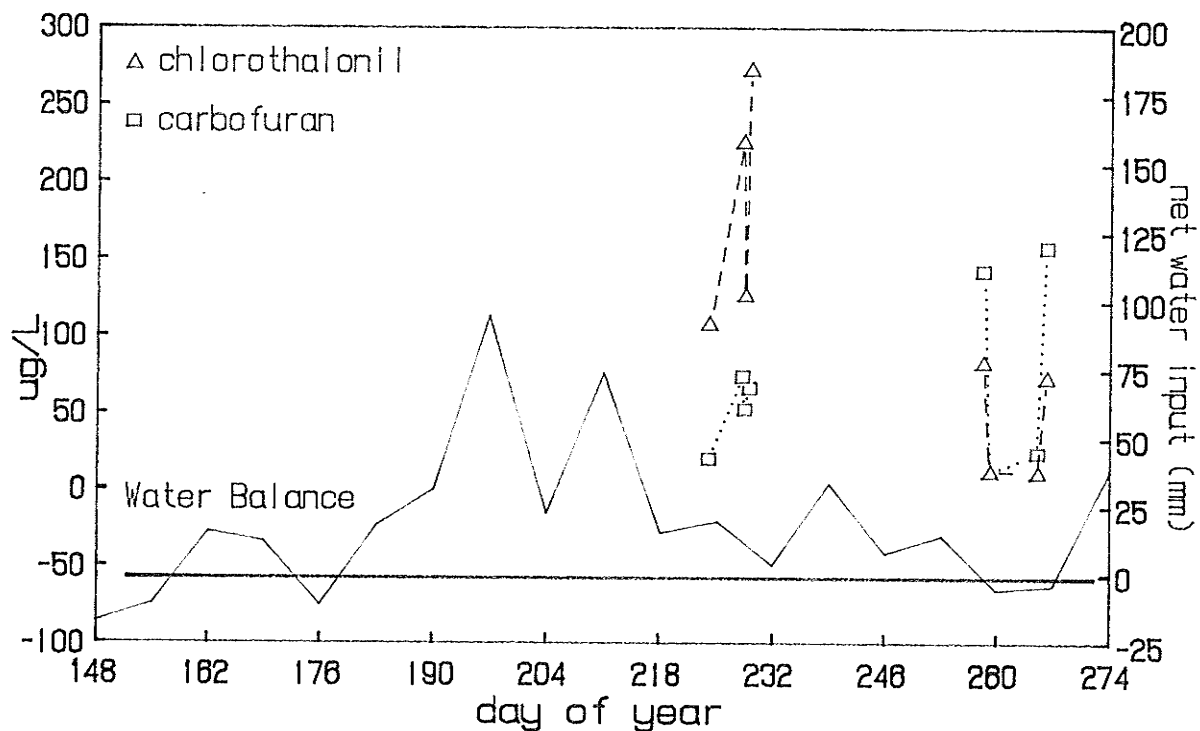


Figure 31. Chlorothalonil and carbofuran levels in ground water (Well #1) and water balance for 10-11-7W, 1982 (ISCO autosampler).

stand-pipe well was about 100x that found in the tile drain outflow. A dilution factor of about 100 would put carbofuran levels below detectable amounts for the HPLC conditions used in the analysis.

4.1.2 FIELD WORK 1983

The results from the 1983 field work is tabulated in Tables 15 & 16 for the two stand-pipe located on the south (well #1) and west (well #2) sides of 10-11-7NW. The precipitation data for 1983 (May 1 to October 31, inclusive) is presented in Table 16.

In 1983, this field (#18) was planted to barley and received two treatments of 2,4-D amine on June 7th and 16th (Table 6). No other pesticides were applied to field #18 during the growing season. Some

Table 15. Ground water from the South Well, 1983

Peristaltic Pump & Grab Samples						
Date	Chlorothalonil		2,4-D		Carbofuran	
yy/mm/dd	grab ug/L	pump ug/L	grab ug/L	pump ug/L	grab ug/L	pump ug/L
83/08/05	4.04	----	4.4	---	1.1	---
83/08/12	2.71	2.58	3.7	4.0	0.4	---
83/08/16	8.48	0.10	3.5	---	---	---
83/08/19	8.58	----	4.2	---	0.9	---
83/09/01	7.17	----	6.8	---	---	---
83/09/08	9.04	0.37	9.1	1.9	---	---
83/09/14	5.60	----	9.9	---	---	---
83/09/16	0.92	3.40	2.4	7.2	---	0.8
83/09/19	1.01	----	---	---	0.6	---
83/09/23	2.70	2.10	4.4	4.0	0.6	---
83/10/06	7.63	1.61	3.6	6.3	---	---
83/10/14	1.02	1.33	7.0	4.2	---	---
83/10/26	2.04	----	9.9	---	---	---

Table 16. Ground water from the West Well, 1983

Peristaltic Pump & Grab Samples					
Date	Chlorothalonil		2,4-D		*
yy/mm/dd	grab ug/L	pump ug/L	grab ug/L	pump ug/L	
83/08/05	----	----	---	---	
83/08/12	0.21	0.13	---	---	
83/08/16	0.02	----	0.8	---	
83/08/19	----	----	---	---	
83/09/01	----	----	---	---	
83/09/08	0.25	----	0.8	---	
83/09/14	----	----	---	---	
83/09/16	----	----	---	---	
83/09/19	2.35	----	2.5	---	
83/09/23	0.10	0.28	---	---	
83/10/06	----	----	2.1	---	
83/10/14	1.35	----	---	---	
83/10/26	0.29	----	---	---	

* Carbofuran was not detected in water samples from this well.

Table 17. *Precipitation data for CFB Portage la Prairie, 1983*
(1.6 km east of the farm site)

Day	Month											
	5		6		7		8		9		10	
	d-y	mm	d-y	mm	d-y	mm	d-y	mm	d-y	mm	d-y	mm
1	121	--	152	--	182	1.0	213	--	244	tr	274	0.2
2		tr		3.9		20.2		0.2		--		4.8
3		--		tr		0.6		--		--		0.7
4		tr		1.2		2.2		0.6		tr		0.7
5		tr		--		--		--		2.2		0.6
6		--		--		--		--		1.8		--
7		--		1.4		--		--		--		--
8	128	--	159	tr	189	--	220	--	251	7.2	281	--
9		tr		--		1.2		0.3		0.6		--
10		0.2		0.4		1.2		--		--		0.4
11		--		0.2		tr		--		0.3		4.0
12		19.2		tr		--		0.3		2.3		0.4
13		0.2		4.9		--		--		2.6		--
14		8.0		1.0		--		--		1.2		--
15	135	--	166	11.4	196	--	227	--	258	8.4	288	2.5
16		--		--		tr		0.4		--		tr
17		2.4		--		--		0.2		--		--
18		1.7		--		tr		tr		--		--
19		9.4		6.4		0.3		--		--		tr
20		tr		0.5		--		20.8		1.3		tr
21		tr		6.3		tr		0.6		tr		--
22	142	tr	173	4.9	203	--	234	--	265	--	295	--
23		3.7		0.2		--		6.8		--		5.4
24		tr		tr		--		tr		--		0.2
25		--		6.2		--		tr		--		--
26		0.6		--		tr		--		--		--
27		1.3		--		--		6.0		1.1		--
28		1.6		--		--		1.2		0.2		--
29	149	--	180	10.7	210	0.4	241	2.4	272	3.4	302	--
30		tr	181	4.5		10.2		1.6	273	20.8		--
31	151	--			212	--	243	--			304	--

d-y = day of year tr = trace of precipitation -- = no precipitation

problems were encountered in keeping the sampler pump running full-time; thus, grab samples were taken from each of the wells to supplement the pump samples.

Residues of three pesticides, chlorothalonil, carbofuran, and 2,4-D were found in the water sampled from well #1 on the south side of 10-11-7NW. Chlorothalonil levels ranged from 0.92 to 9.04 ug/L in grab samples (Fig. 32) and from 0.10 to 3.40 ug/L in pump samples (Fig. 33). Carbofuran levels ranged from 0.40 to 1.10 ug/L in the grab samples (Fig. 32) and 0.80 ug/L in the pump samples (Fig. 33). As neither of these compounds was applied to field #18 in 1983, their presence in the ground water is presumably due to carry-over from the previous year. This is supported by the findings of the previous season's work (1982), where low levels of chlorothalonil residues were detected in tile drain outflow before application and shortly after application but before it could have been leached down to the tile system depth. These low levels of chlorothalonil were attributed to carry-over residues, from 1981, in the subsoil which could have leached to ground water as a result of a number of heavy rainfalls prior to or shortly after the first application of the chemical. In 1983, chlorothalonil was not applied to this field; thus, the residues found can only be attributed to carry-over in the subsoil and subsequent leaching. In addition, the concentration of chlorothalonil in the 1983 ground water samples (about 100 times less than the previous years samples) is consistent with carry-over and subsequent leaching.

The possibility that the residues observed in 1983 in the stand-pipe samples were the result of another mechanism was examined. The wells were east of the road allowance. The sumpwell water was pumped into the

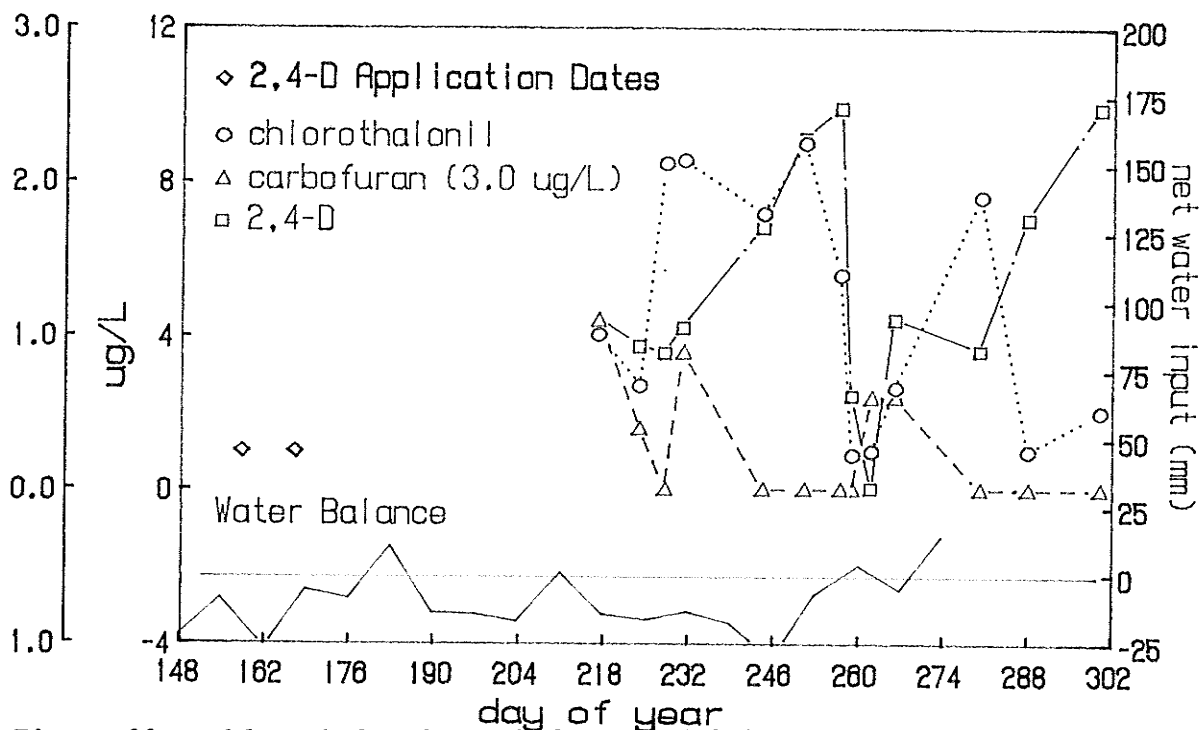


Figure 32. Chlorothalonil, carbofuran and 2,4-D levels in ground water from well #1 and water balance for 10-11-7W (1983 - grab sample)

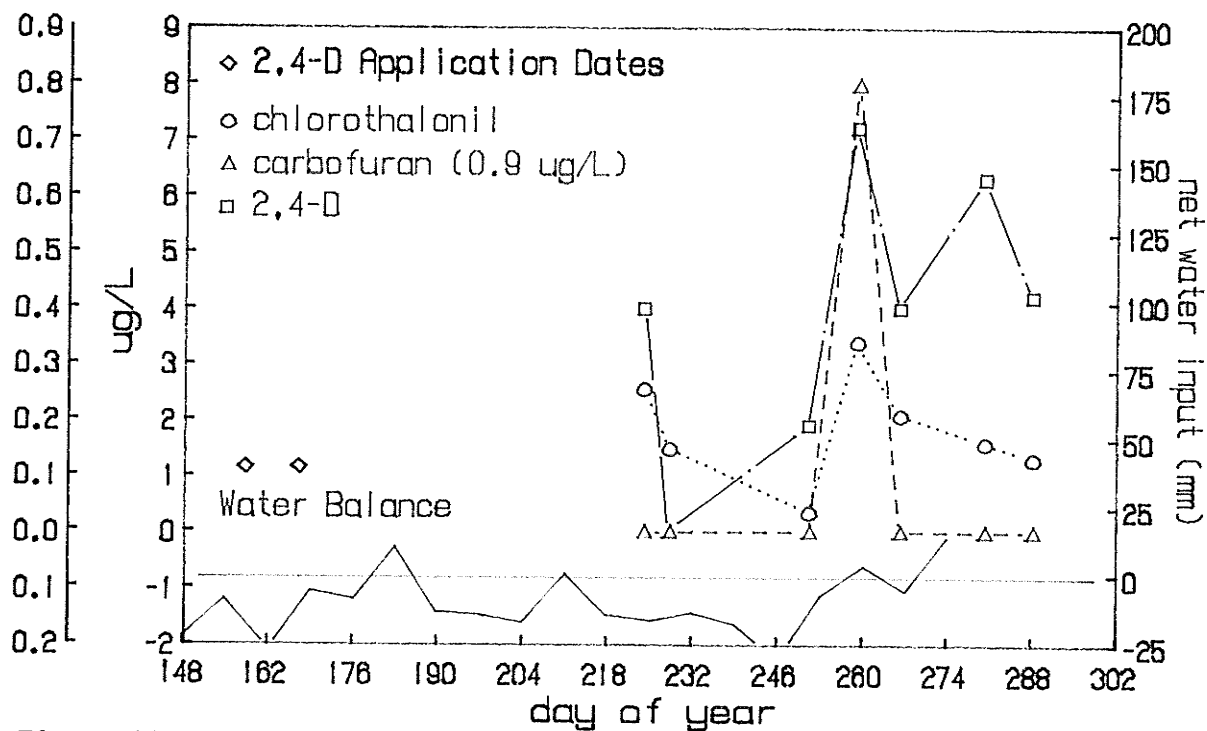


Figure 33. Chlorothalonil, carbofuran and 2,4-D levels in ground water from well #1 and water balance for 10-11-7W: (1983 - pump sample)

west ditch, and the water from the sumpwell, once it entered the ditch might have infiltrated the soil and reentered ground water and become the source of the residues observed in 1983. However, considering the extremely low residue levels detected in the tile drain outflow from the area in which the sumpwell was installed and that further dilution would occur, it was decided that this could not be the source of residues observed in the ground water sampled from the stand-pipe wells. In addition, any residues in the outflow water would be subject to additional degradation both photolytic and microbial and thus would not likely reach ground water unchanged. Examining the concentration level pattern of chlorothalonil in the grab water samples from well #1 (Fig. 32), there appears to be a direct relationship between rainfall patterns and the concentration of these pesticides in ground water. It was observed in 1982 that residue concentrations peaked about 18 days after a major rainfall or period of rainfall. This was also the pattern (Fig. 32) observed for chlorothalonil residues in the ground water from well # 1 in 1983. The chlorothalonil concentration levels in the pump samples of ground water are different from those in the grab samples (Table 15). These pump samples reflect an averaging of levels over a period of time as opposed to a level at a specific time which the grab sample would reflect. The plot of these values along with the precipitation pattern (Fig. 33) shows a similar relationship between a chemical's concentration in ground water and precipitation pattern. The first sample was taken at a time when ground concentrations had peaked and were declining after a moderate rainfall. From the third to fourth sampling, residue concentrations again peaked, this maximum being observed about 28 days after a major rainfall, then gradually decreasing as opposed to rapidly

falling off as was observed after the first maximum.

The results for carbofuran (Table 15) are similar in pattern to those for chlorothalonil. The major difference between the two compounds appears to be the leaching velocity, with carbofuran moving at a slower rate through the soil column. The grab sampling data found the ground water concentration at its maximum level on the initial sampling day with a rapid decline in concentration over the next two samplings (Fig. 32). This was followed by two periods of rapid rise and decline to give two maxima separated by a time period of 18 days where no carbofuran residues were detected in the ground water. The first of these two maxima occurred 41 days after the last heavy rainfall (20.2 mm) and 19 days after a moderate rainfall (10.2 mm); however, except for this last rainfall there was only 7.9 mm of rain fall during this 41 day period. The last maximum ground water residue concentration was observed 30 days after a heavy rainfall (20.8 mm). The difference in elapsed time between a major rainfall and a maximum concentration observed in the ground water may have been due to amount and frequency of precipitation after the major rainfall. In the first there was a total of 18.1 mm of rain of which over half was in one event midway between the major rainfall and the maximum concentration observed. In the second case, there was a total of 44.6 mm of rain over a 27 day period, with four events of between 6 to 8 mm. Thus it appears that the velocity of leaching is dependent upon water input. A heavy rainfall appears to dissolve and/or desorb and carry into the subsoil a quantity of residue from the surface layer. The constant input of water through irrigation appears to carry the residues further into the subsoil and spread them into a broad band such that they will enter ground water over a period of time and at lev-

els which will be below detection. An input of a large amount of water over a short period of time, such as a major rainfall, appears to carry the residues into ground water in a much narrower band yielding short term concentrations at detectable levels, in the case of carry-over residues.

In addition to these two carry-over residues, 2,4-D was detected in ground water samples from both well #1 and well #2 (Tables 15 & 16). The results are illustrated for both grab and pump water samples from well #1 (Figs. 32 & 33, respectively) and grab and pump water samples from well #2 (Fig. 34).

2,4-D was applied twice to this field, June 7th (158) and 16th (167) with no other pesticides being applied to this field in 1983. These two applications were just before and in the midst of a period of light rainfall which would have served to carry a portion of the applied herbicide into the subsoil where degradation would be limited. 2,4-D was detected in grab water samples from well #1 in 12 of 13 samples with concentrations ranging from 2.40 to 9.90 ug/L, for a time period beginning 50 days post-application June 2nd and ending 132 days post application. Of the seven pump water samples, 2,4-D was detected in six, with concentrations ranging from 1.90 to 7.20 ug/L. In both the grab and pump ground water samples the concentration of 2,4-D peaked about 24 d after a heavy rainfall.

In well #2, concentrations of the compounds found (chlorothalonil and 2,4-D) were much lower than those found in well #1. Carbofuran may also have been present but at levels below the detectable limit or may not have been present. The levels of chlorothalonil in grab and pump ground water samples from well #2 (Fig. 34) show a relationship to precipita-

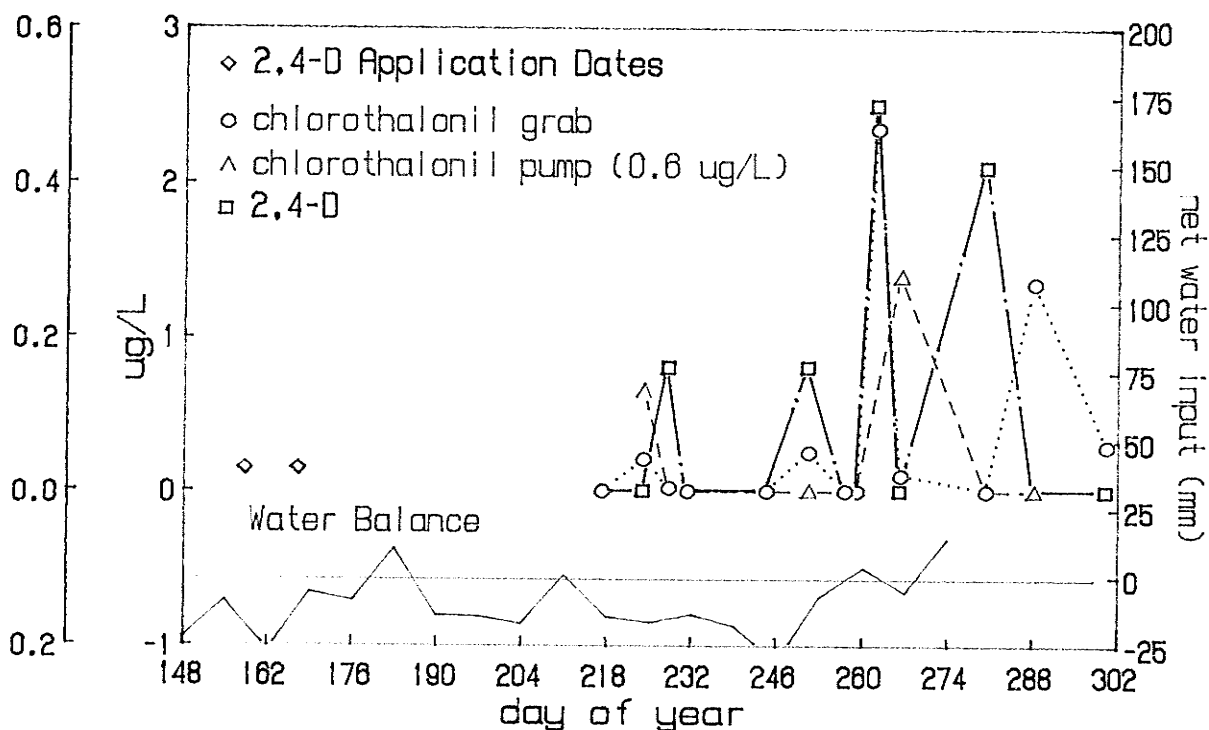


Figure 34. Chlorothalonil and 2,4-D levels in ground water from well #2 and water balance for 10-11-7W, 1983 (grab and pump samples) (2,4-D grab samples only).

tion levels similar to that observed for well #1. The concentration of chlorothalonil in these samples ranged from 0.10 to 2.35 ug/L for grab samples and 0.13 to 0.28 ug/L for pump samples. This represents residues in 7 of 13 grab samples and 2 of 7 pump samples. 2,4-D was detected in 4 of 13 grab samples at concentrations ranging from 0.80 to 2.50 ug/L and was not detected in any of the pump ground water samples.

4.1.3 COMPARISON OF 1982 AND 1983 RESULTS

Results from 1982 and 1983 indicated that at least two pesticides moved through the soil profile into ground water. Chlorothalonil (0.92 - 9.04 ug/L) and carbofuran (0.6 - 1.1 ug/L) were detected and identified in the ground water from the farm study site for sampling done in 1983. Both chlorothalonil and carbofuran were detected and identified

from the site in 1982. The degradation product carbofuran phenol was detected in a number of samples taken in 1982 (not quantified).

The significant fact here is that chlorothalonil and carbofuran, two relatively non-polar compounds are being leached through the soil into ground water. The relative amounts found in the ground water appear not to present an environmental or health hazard at the outflow because of the large dilution factor present as shown by the absence of detectable residues of carbofuran and only very low levels (<0.02 ug/L) of chlorothalonil in the tile drain outflow. Canadian guidelines for drinking water quality (Health and Welfare Canada, 1979) state that the total concentration of pesticides present should not exceed 100 ug/L and the Environmental Protection Agency in the United States of America has recently proposed a "recommended maximum contaminant level" (RMCL) of 36 ug/L for several pesticides, including carbofuran, in water. The maximum acceptable concentration for either of the above individual compounds is not documented in the Canadian Guidelines. The maximum observed combined concentration for the above two compounds, in ground water, was 9.6 ug/L in 1983 which was well below the Canadian limit of 100 ug/L and only 25% of the RMCL set forth by the U.S. E.P.A.. In 1982, the maximum combined concentration of both chlorothalonil and carbofuran were detected on August 17th at a combined concentration of 339.7 ug/L, which is three times the Canadian limit for pesticides in drinking water and an order of magnitude above the E.P.A.'s RMCL of 36 ug/L. Ground water concentrations of chlorothalonil and carbofuran fluctuated quite markedly in August, as can be seen in the data (Table 4) where, in the first 12 h sampling period the concentration of chlorothalonil peaked at 225 ug/L then dropped in the next 12 h period to a level

of 126 ug/L followed by a rise to 273 ug/L in the next 14 h period. Similarly in September, a day to day fall and rise was observed for chlorothalonil levels in the ground water. Carbofuran also followed a similar trend. There were specific occurrences where detectable levels of chlorothalonil residues were present in the tile drain outflow. The highest levels observed were from the NE west tile system which drains field 18, where the stand-pipe wells were located, plus sections of fields 11, 15, 16, and 17. There were two occurrences in 1982 where chlorothalonil levels exceeded 3 ug/L in the outflow water, viz., July 1st (3.27 ug/L) and August 13th (3.66 ug/L). In both cases, levels rapidly returned to below detectable levels in a day or two. In both cases, the level of pesticides in the water were well below both the Canadian Guidelines limit and the E.P.A.'s RMCL. The low levels of chlorothalonil in the outflow did not apparently prevent the growth of algal species in the ditch (Fig. 3, to the left of the outflows).

Of the two pesticides detected in the ground water, carbofuran is of greater toxicological significance due to its higher acute toxicity to mammalian life than chlorothalonil (8.2-14.1 mg/kg versus >10,000 mg/kg). The maximum concentration of carbofuran observed in the ground water was 158.1 ug/L. If one were to consume 1 litre of this water, the total dose would be two orders of magnitude below the lethal dose as determined for rats. The amount present would be easily detoxified by mammalian systems. Chlorothalonil, with its very low mammalian toxicity, was not present in quantities that would be of toxicological significance.

In 1982, the following pesticides were also applied to the field but were not detected in the tile outflow water: EPTC, atrazine, metribuzin,

dicamba, diclofop-methyl, bromoxynil, carbofuran, and chlorpyrifos. EPTC was not expected to appear in ground water because of both volatilization (Cliath et al., 1980) and degradation (Obrigawitch et al., 1982) especially as these soils had a history of EPTC use. On the other hand, atrazine and/or metribuzin were expected to appear in ground water as both compounds are fairly mobile in sandy soils (Bouchard et al., 1982; Nicholls et al., 1982; Smith and Hayden, 1982a; Lopez-Avila et al., 1986) and due to reports of their presence in ground water (Muir and Baker, 1978; Whetje et al., 1983; Cohen et al., 1986; Newby and Rock, 1986). Thus it was surprising that neither compound was detected in the tile outflow water, especially metribuzin which was applied a number of times. As these soils have a history of atrazine and metribuzin use, it is thought that microbial degradation probably removed significant amounts of both pesticides. In addition, the formation of bound nonextractable residues (Capriel et al., 1985) would decrease the quantity of the pesticide leaching. For both dicamba and diclofop-methyl there is little information about the mobility of these compounds in sandy soils. Both compounds are on the EPA's list for evaluation with regard to ground water contamination (Creeger, 1986). Dicamba is reported to be more mobile than 2,4-D, yet it was not detected in the tile outflow while 2,4-D was detected in ground water (in 1983) (Grover, 1977). Dilution within the tile line itself may have been the reason why dicamba was not detected in the tile outflow water. Diclofop-methyl degrades fairly rapidly in the soil under aerobic conditions and alkalinity aids in the hydrolysis of the ester bond. As the soils in this region are moderately alkaline it would be expected that very little diclofop-methyl would be available for leaching. Bromoxynil was not expected to

leach as it is rapidly degraded in the soil (Smith, 1971). The presence of carbofuran has been reported in ground water (Cohen et al., 1986; Creeger 1986) and it was thought that it might leach under these soil conditions. Even though it was detected in the ground water both in 1982 and 1983, it was not detected in the tile outflow water during 1982, probably because of dilution within the tile line itself. From the literature it was not known whether chlorpyrifos would be expected to leach. It was thought that with its low water solubility and vapour pressure that it would not leach even though its degradation under local soil conditions would be fairly slow (Chapman and Cole, 1982).

In 1983, 2,4-D was applied to the field where the two monitoring wells were located. The 2,4-D was not expected to leach to ground water in 1983 because of the low water input, both irrigation and rainfall, for this particular field (Majka et al., 1982a). In addition, the amount of organic matter in this particular field would probably have had a retarding effect on leaching as a result of adsorption of applied 2,4-D (Grover, 1977), and degradation was expected to remove significant quantities from the soil (Smith, 1980b; Stott et al., 1983). Thus it was somewhat of a surprise when 2,4-D was detected in the ground water from under this field despite the factors which should have hindered leaching.

4.2.0 SOIL COLUMNS

4.2.1 Irrigation Water from Assiniboine River

Duplicate analysis of the Assiniboine river water was performed on natural and acidified samples to determine whether co-extractives from the water would interfere in the pesticide analysis. The extraction

cartridge results indicated that one and possibly a second compound extracted from the river water may create an identification problem with some of the early eluting pesticides. To determine what, if any, interference there may be, 2 - 100 mL samples of the river water (natural) were put through the liquid-liquid extraction procedure and the extracts analyzed. The compounds extracted from the river water via the extraction cartridge method were not isolated using liquid-liquid extraction; therefore, it was concluded that the natural river water could be used without any interference in the analysis for applied pesticides by any compounds occurring in the water.

4.2.2 Simulated Rain (Triple Distilled Water)

The triple-distilled water (to simulate rain water) was also extracted to determine a background level of organic substances which might interfere in the analysis. No interfering compounds were found using both extraction methods.

4.2.3 Leachate Water Analysis

The irrigation and pesticide application schedule are tabulated in Appendix B and illustrated in Figures 35, 36 & 37 for the three soils used. Leachate volumes recovered varied from 65.0 to 83.3% of the irrigation water applied (6.0 L or 296.0 cm) and are also illustrated in Figures 35, 36, & 37 for the three soils used.

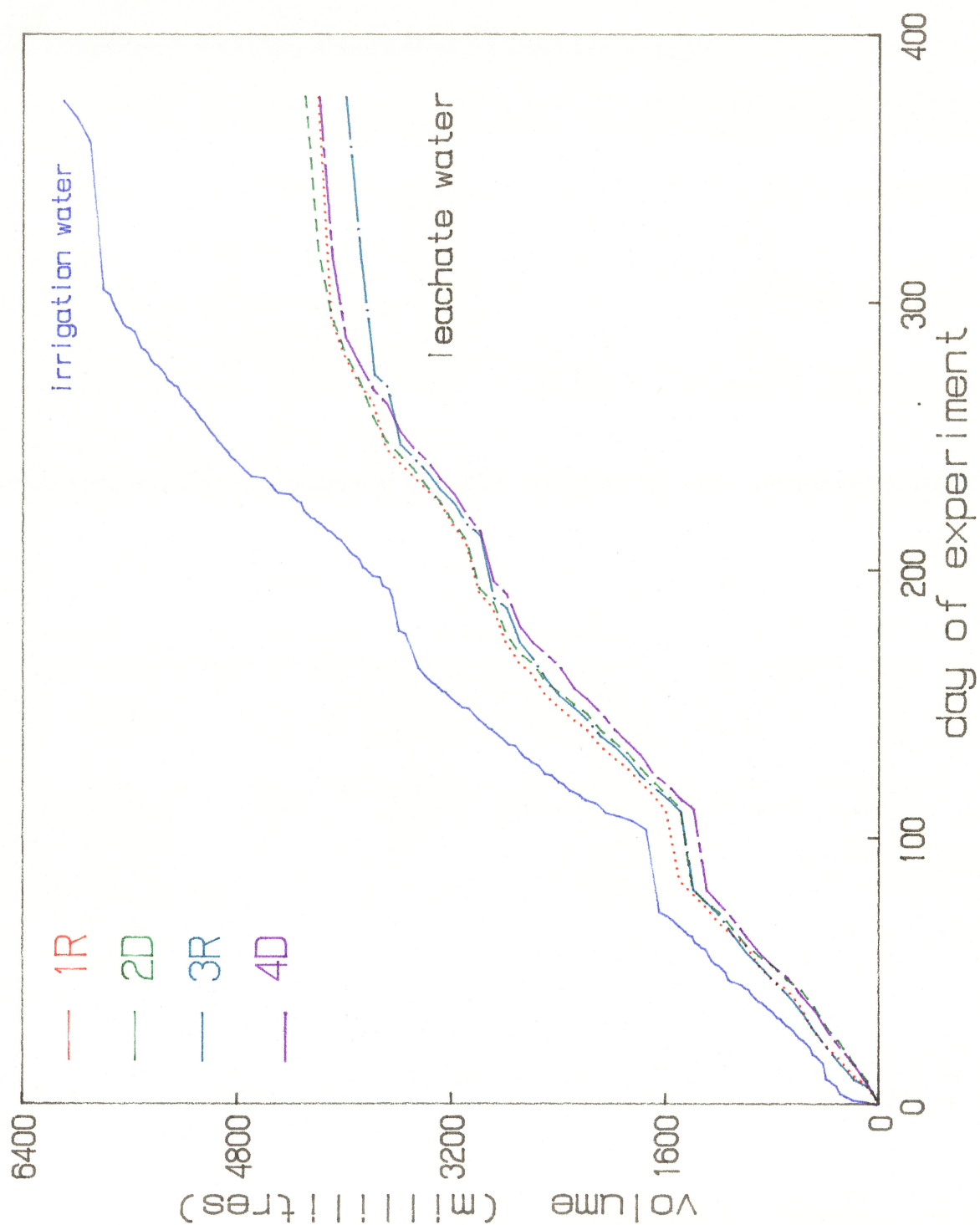


Figure 35. Plot of the input "irrigation" water and the out flowing leachate water from the Long Plain fine sand soil columns.

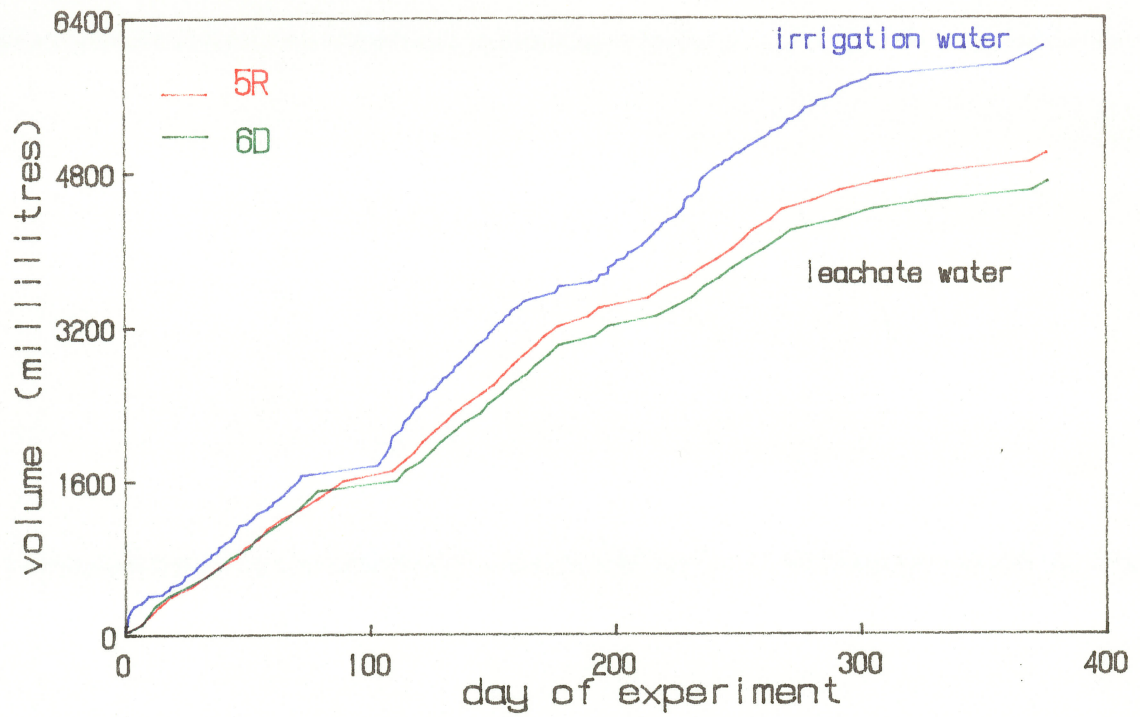


Figure 36. Plot of the input "irrigation" water and the out flowing leachate water from the Skelding fine sand soil columns.

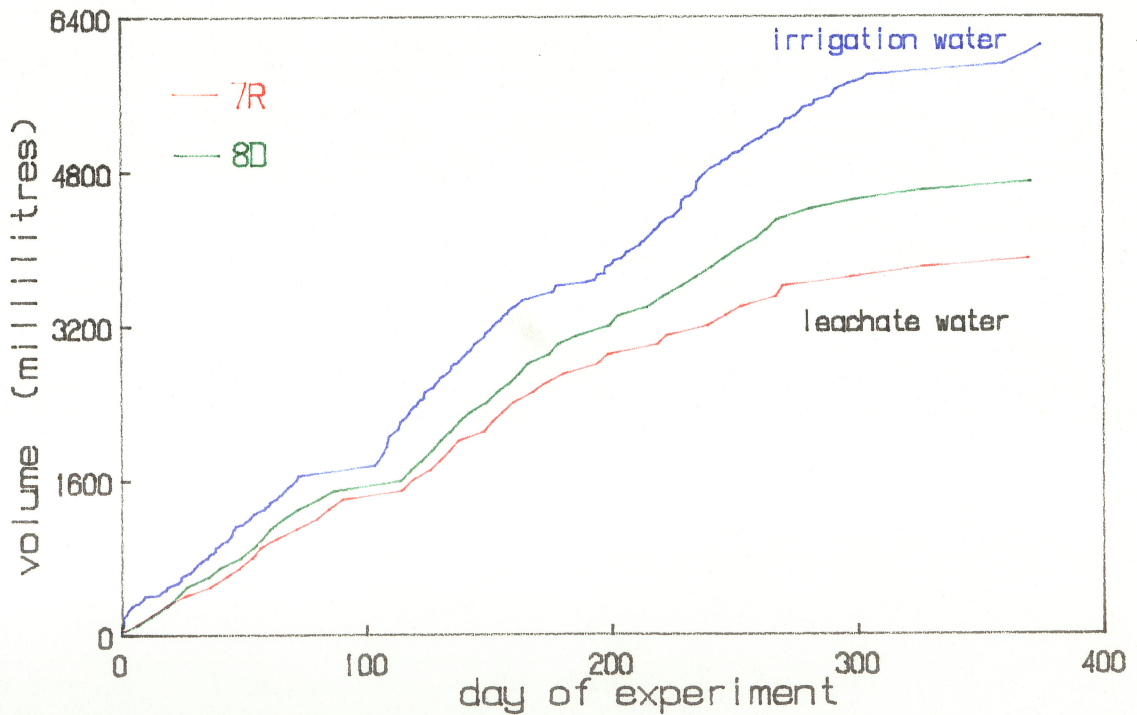


Figure 37. Plot of the input "irrigation" water and the out flowing leachate water from the St. Claude silt loam soil columns.

THE QUALITY OF THIS MICROFICHE
IS HEAVILY DEPENDENT UPON THE
QUALITY OF THE THESIS SUBMITTED
FOR MICROFILMING.

UNFORTUNATELY THE COLOURED
ILLUSTRATIONS OF THIS THESIS
CAN ONLY YIELD DIFFERENT TONES
OF GREY.

LA QUALITE DE CETTE MICROFICHE
DEPEND GRANDEMENT DE LA QUALITE DE LA
THESE SOUMISE AU MICROFILMAGE.

MALHEUREUSEMENT, LES DIFFERENTES
ILLUSTRATIONS EN COULEURS DE CETTE
THESE NE PEUVENT DONNER QUE DES
TEINTES DE GRIS.

4.2.4 Long Plain Fine Sand: Soil Columns 1R, 2D, 3R, & 4D

In this soil EPTC first appeared in the leachate water over a wide period of time for the four columns, 55 days post application for column 4 versus over 100 days for column 3 (Table 18). The difference in appearance times for the four columns does not appear to be a function of the type of water used to irrigate the columns as the distilled water treated columns were the fastest and second slowest in appearance times. Water type did affect the amount of EPTC leached through the columns. Distilled water leached more EPTC through the column than did the river water for the corresponding column. In addition, the column age affected the amount of EPTC leaching through the column; with more EPTC leaching through the "older" columns than through the "younger" columns for the corresponding water treatments. Storage of columns 1 and 2 under laboratory conditions appears to have had an affect on the amounts passed through these columns as compared to columns 3 and 4 which were used shortly after they were prepared in the field. Even though all four columns were conditioned prior to use, the microbial populations in columns 1 and 2 did not rebound to their previous levels as did those in columns 3 and 4. A similar effect can be seen in the work of Smith and Hayden (1981) and Smith (1982) where the degradation half-life doubled as a result of the use of air-dried stored soil versus air-dried "fresh" soil. Soulas and Fournier (1981) have shown that prolonged storage of soil in an air-dried state lowers the ability of metabolizing soil microflora to develop further.

For soil column 1, residues of EPTC were found in the top 60 cm of the column with the largest concentration being located in the top 15 cm of the soil (Table 19). EPTC was detected only in the top 15 cm of soil

Table 18. EPTC in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	"Older" Columns		"Younger" Columns	
	Column 1 R	Column 2D	Column 3R	Column 4D
	River Water ug	Distilled Water ug	River Water ug	Distilled Water ug
100	----	----	----	----
200	----	----	----	----
300	----	----	----	----
400	----	----	----	----
500	----	----	----	----
600	----	----	----	----
700	----	----	----	----
800	----	----	----	----
900	----	----	----	----
1000	----	----	----	11.83
1100	----	----	----	19.75
1200	28.92	----	----	9.93
1300	11.58	----	----	25.62
1400	----	109.84	----	16.86
1500	----	151.13	----	54.68
1600	----	45.43	9.93	35.11
1700	11.58	12.40	14.88	63.44
1800	45.44	17.35	12.40	43.45
1900	20.66	18.18	6.62	16.29
2000	20.66	120.99	14.06	11.83
2100	----	15.70	23.64	59.47
2200	----	35.52	9.10	27.10
2300	----	9.92	9.51	9.60
2400	21.49	14.30	5.96	14.39
2500	----	6.62	11.58	40.48
2600	----	6.12	----	14.06
2700	----	8.27	----	10.75
2800	21.90	8.27	----	----
2900	38.00	33.87	----	19.84
3000	----	11.57	----	17.61
3100	----	13.23	----	13.23
3200	20.66	35.52	18.18	38.00
3300	----	36.35	----	66.41
3400	16.53	7.94	----	58.98
3500	14.06	23.96	----	----
3600	31.81	22.31	----	----
3700	14.88	184.16	xx	----
3800	----	46.26	xx	----
3900	xx	17.77	xx	----
4000	xx	18.18	xx	xx

---- no residues detected at the 0.02 ug/L level

xx no leachate

columns 2 and 3, while in column 4 no EPTC residues were recovered from the soil column (Table 19). The soil from both river water treated columns contained more residues than from the corresponding distilled water treated columns and residues were at higher levels and distributed to a larger extent in the "older" columns than in the "younger" columns.

Chlorpyrifos appeared in the leachate water a short time after application, from 10 to 12 days for three of the columns and 27 days post application from column 3 (Table 20). This later appearance from column 3 is consistent with the results for EPTC. The pattern of appearance of chlorpyrifos from the first three columns is similar, i.e., in a small number of samples spread over a short time, whereas the pattern for the fourth column is different. The leachate water contained more chlorpyrifos residues for a longer period of time. The amounts recovered from the leachate water ranged from less than 0.5% to 6.7% of the total amount applied for the first three columns while 15.4% was recovered from the leachate water of column 4. As with EPTC, a greater amount of chlorpyrifos was leached through the column by the distilled water than by the river water (Table 20).

In the soil, no residues were recovered from the profile of column 1 while residues were detected in the profiles of the other three columns (Table 21). The distribution pattern in columns 2 and 3 were similar with the greatest amount of residues present in the Ap horizon (Fig. 38). Column 4 had a similar distribution pattern except that no residues were detected in the Ap horizon. The majority of recovered residues were recovered from the underlying C horizon. For chlorpyrifos in this soil there does not seem to be any relationship between type of water treatment or age of the column in regards to amount of residues

Table 19. EPTC Concentration in the Soil Profile for the Long Plain
Fine Sand Soil Columns: 1R, 2D, 3R, & 4D

1R		2D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	390.10 (\pm 237.88)	0 - 15	168.80 (\pm 44.54)
15 - 30	39.47 (\pm 15.46)	15 - 30	--
30 - 45	51.67 (\pm 5.54)[2]	30 - 45	--
45 - 60	73.72 (\pm 6.47)[2]	45 - 60	--
60 - 75	--	60 - 75	--
75 - 89	--	75 - 87	--

3R		4D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	11.21 (\pm 3.71)	0 - 15	--
15 - 30	--	15 - 30	--
30 - 45	--	30 - 45	--
45 - 60	--	45 - 60	--
60 - 75	--	60 - 75	--
75 - 87	--	75 - 87	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table 20. *Chlorpyrifos* in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	Old Columns		New Columns	
	Column 1R	Column 2D	Column 3R	Column 4D
	River Water ng	Distilled Water ng	River Water ng	Distilled Water ng
100	----	----	----	----
200	----	6392.40	----	1837.11
300	3102.48	----	----	2415.57
400	5633.21	7693.95	----	----
500	----	12538.49	607.90	----
600	3717.09	5958.57	463.26	----
700	1186.36	----	535.29	14056.93
800	----	----	246.37	3138.63
900	----	----	390.98	4393.77
1000	----	----	----	2581.87
1100	----	----	----	2082.96
1200	----	----	----	2054.03
1300	----	----	----	----
1400	680.21	----	----	----
1500	----	----	----	----
1600	----	----	----	9284.69
1700	----	----	----	1909.42
1800	----	----	----	5886.42
1900	----	----	----	9646.23
2000	----	----	----	8272.40
2100	----	----	----	2560.18
2200	----	----	----	----
2300	----	----	----	----
2400	----	----	----	1786.50
2500	----	----	----	----
2600	----	----	----	----
2700	----	----	----	----
2800	----	----	----	----
2900	----	----	----	----
3000	----	----	----	----
3100	----	----	----	----
3200	----	----	----	----
3300	----	----	----	----
3400	----	----	----	----
3500	----	----	xx	----
3600	----	----	xx	----
3700	xx	----	xx	----
3800	xx	----	xx	xx

---- no residues detected at the 0.02 ug/L level

xx no leachate

Table 21. *Chlorpyrifos* Concentration in the Soil Profile for the Long Plain Fine Sand Soil Columns: 1R, 2D, 3R, & 4D

1R		2D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	1269.91 (\pm 367.94)
15 - 30	--	15 - 30	292.74 (\pm 57.95)
30 - 45	--	30 - 45	254.33 (\pm 46.11)
45 - 60	--	45 - 60	--
60 - 75	--	60 - 75	--
75 - 89	--	75 - 87	--

3R		4D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	210.84 (\pm 15.34)	0 - 15	--
15 - 30	82.77 (\pm 19.79)	15 - 30	157.85 (\pm 54.94)
30 - 45	28.44 (\pm 11.23)	30 - 45	61.55 (\pm 30.50)
45 - 60	21.79 (\pm 9.88)	45 - 60	33.20 (\pm 4.23)
60 - 75	18.72 (\pm 5.87)	60 - 75	188.49 [1]
75 - 87	22.05 (\pm 11.50)	75 - 87	18.82 [1]

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

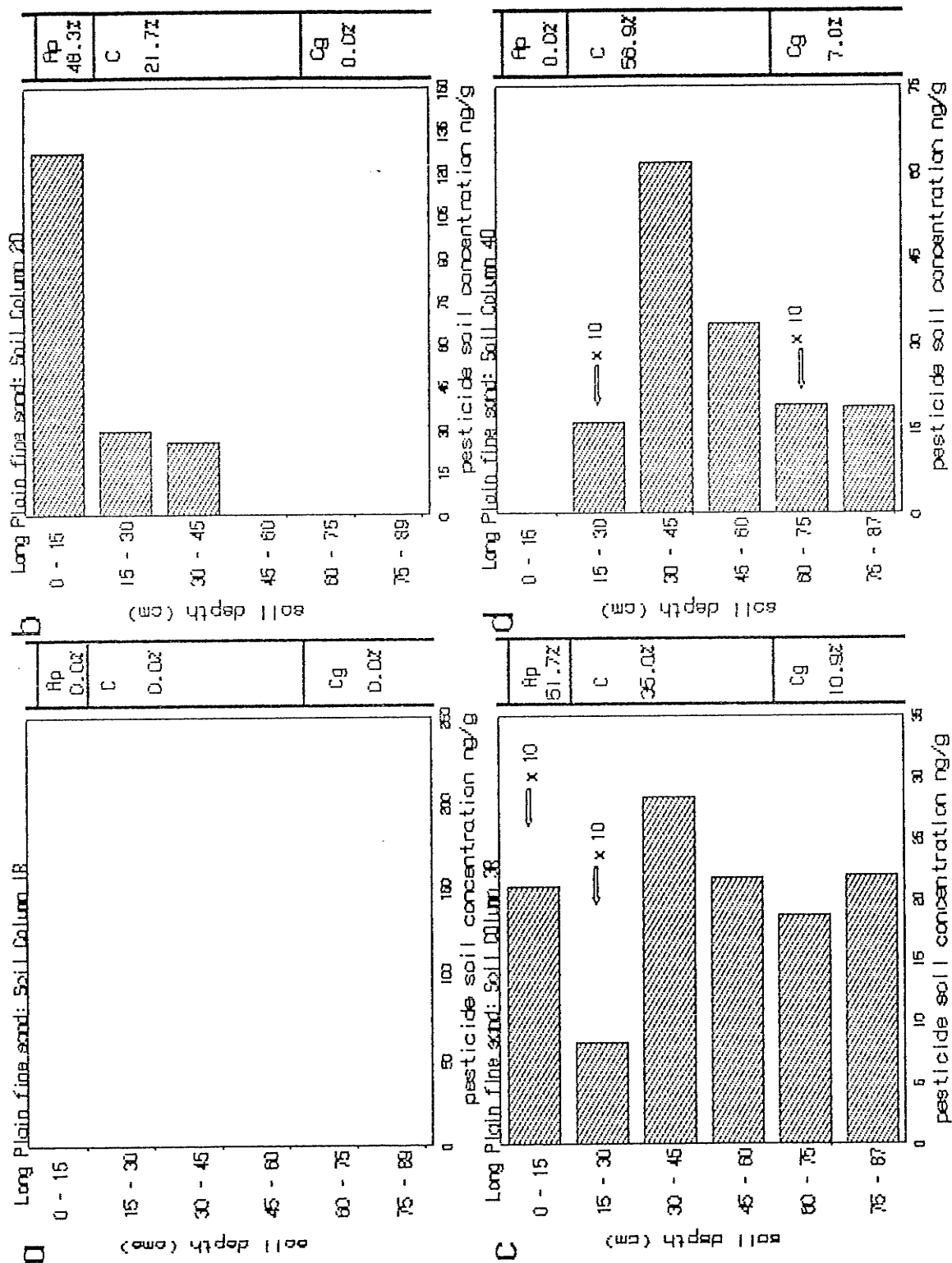


Figure 38 Chlorpyrifos concentration profile in the soil columns and on the right the percent of total recovered Chlorpyrifos present in the profile of soil columns a) 1R, b) 2D, c) 3R and d) 4D.

remaining in or the distribution of residues within the profile as was seen with EPTC.

In both columns 1 and 2 metribuzin appeared in the leachate water at about the same time 33 and 27 days post application, respectively (Table 22). In comparison to chlorpyrifos, with which it was co-applied, metribuzin appeared in the leachate water one 100 mL volume later than did chlorpyrifos, suggesting that metribuzin moves more slowly through the soil than does chlorpyrifos. The amount of metribuzin recovered from the leachate water from columns 1R and 2D were about the same, 4.6 and 6.0% of the total amount applied, respectively, while for column 3 only 0.05% was recovered and no residues were recovered from the leachate water of column 4. The pattern of appearance between the three columns is similar, with column 1 having a longer period where residues were present in the leachate water. For metribuzin, in this fine sand soil there is little difference between water treatments and movement through the soil. The greatest difference observed was between the "older" and the "younger" soil columns where the amounts of metribuzin leached through differed by a factor of 100. As for EPTC the lower recovery of metribuzin from the "younger" columns is probably due to the higher microbial activity in these columns as compared to the microbial activity of columns 1 and 2.

Metribuzin was not recovered from the soil profile from any of the four soil columns. This is not surprising as this soil has a history of metribuzin use; thus, it was expected that the degradative ability of the soil would be quite high for this herbicide. Under constant temperature, degradation would be expected to proceed rapidly based on reports of degradation in a similar Manitoba soil under field conditions

Table 22. Metribuzin in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	Old Columns		New Columns	
	Column 1 R	Column 2D	Column 3R	Column 4D
	River Water ng	Distilled Water ng	River Water ng	Distilled Water ng
100	----	----	----	----
200	----	----	----	----
300	----	4119.76	----	----
400	5941.26	4575.14	55.77	----
500	4119.76	2412.11	159.59	----
600	5030.51	8901.18	29.81	----
700	3892.08	1159.84	12.74	----
800	476.78	499.55	16.15	----
900	1250.91	1341.99	7.04	----
1000	704.46	1159.84	4.77	----
1100	----	795.54	3.40	----
1200	567.85	841.08	6.13	----
1300	476.78	795.54	3.40	----
1400	636.16	476.78	8.87	----
1500	476.78	340.16	----	----
1600	408.47	658.93	5.00	----
1700	932.15	----	----	----
1800	----	----	----	----
1900	----	----	----	----
2000	----	----	----	----
2100	----	----	----	----
2200	454.01	----	----	----
2300	----	----	----	----
2400	362.93	----	----	----
2500	454.01	----	----	----
2600	567.85	----	----	----
2700	567.85	----	----	----
2800	----	----	----	----
2900	----	----	----	----
3000	----	----	----	----
3100	----	----	----	----
3200	----	----	----	----
3300	----	----	----	----
3400	----	----	xx	----
3500	----	----	xx	----
3600	----	----	xx	----
3700	xx	----	xx	----
3800	xx	----	xx	xx

---- no residues detected at the 0.02 ug/L level

xx no leachate

(Webster and Reimer, 1976).

Chlorothalonil appeared in the leachate water within 7 days of application for the distilled water treated columns and between 28 and 35 days post application for the river water treated columns (Table 23). Of the two "older" columns, the distilled water treated column leached 10 times the amount of chlorothalonil the river water treated column leached. In the "younger" columns the same trend is observed, where the distilled water treatment leached more chlorothalonil (20X) than did the river water treatment. Within a treatment but between the older and younger columns the older columns leached more chlorothalonil than did the younger columns as has been observed already for two of the previous pesticides.

Chlorothalonil was found to be distributed throughout the soil profile of columns 1, 2, and 4 (Table 24). In column 3, chlorothalonil was recovered from the Ap horizon only. There does not seem to be an apparent relationship between type of water treatment and distribution of residues within the soil profile. The only apparent relationship is the age of the column and the relative amounts of residue remaining within the profile, as both the older columns had higher levels of residues distributed at all levels of the profile than the corresponding young column. The amount of chlorothalonil residues recovered from the distilled water treated old column was higher than from the corresponding distilled water treated younger column.

Diclofop-methyl was present in the leachate water 8 days post application for columns 1, 2, and 3 and some 33 days post application in the leachate water from column 4 (Table 25). The pattern of appearance of diclofop-methyl in the leachate water was not similar for the four col-

Table 23. Chlorothalonil in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	Old Columns		New Columns	
	Column 1 R	Column 2D	Column 3R	Column 4D
	River Water ng	Distilled Water ng	River Water ng	Distilled Water ng
100	----	----	----	----
200	----	368.56	----	137.19
300	----	959.08	----	115.55
400	----	722.29	----	661.53
500	66.44	1119.29	----	4.02
600	62.28	572.06	----	18.17
700	53.96	182.96	4.85	----
800	12.34	249.55	0.27	41.47
900	17.34	266.19	4.02	----
1000	11.93	45.64	8.18	----
1100	8.18	----	0.27	----
1200	34.81	----	----	20.67
1300	----	----	----	----
1400	----	----	----	----
1500	----	----	----	----
1600	----	----	----	----
1700	----	----	----	----
1800	----	----	----	----
1900	----	----	----	----
2000	----	----	----	4.02
2100	20.67	----	----	----
2200	17.34	----	----	----
2300	----	----	----	----
2400	45.63	----	----	----
2500	----	----	----	----
2600	----	----	----	----
2700	----	----	----	----
2800	----	----	----	----
2900	4.02	----	----	----
3000	----	----	----	----
3100	----	12.34	----	8.18
3200	12.34	15.26	32.32	----
3300	49.80	24.83	53.96	8.18
3400	49.80	----	xx	----
3500	xx	70.60	xx	74.76
3600	xx	157.99	xx	18.59
3700	xx	257.87	xx	xx

---- no residues detected at the 0.02 ug/L level

xx no leachate

Table 24. Chlorothalonil Concentration in the Soil Profile for the Long Plain Fine Sand Soil Columns: 1R, 2D, 3R, & 4D

1R		2D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	87.37 (\pm 45.10)	0 - 15	202.48 (\pm 140.42)
15 - 30	82.65 (\pm 21.98)	15 - 30	74.51 (\pm 31.19)
30 - 45	48.14 (\pm 34.25)	30 - 45	80.63 (\pm 21.54)
45 - 60	111.53 (\pm 35.72)	45 - 60	57.93 (\pm 30.61)
60 - 75	66.78 (\pm 10.34)	60 - 75	47.04 (\pm 33.07)
75 - 89	51.98 (\pm 9.31)	75 - 87	130.20 (\pm 27.47)

3R		4D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	11.34 (\pm 5.06)	0 - 15	50.88 (\pm 22.72)
15 - 30	--	15 - 30	6.34 (\pm 1.76)
30 - 45	--	30 - 45	0.34 (\pm 0.12)
45 - 60	--	45 - 60	4.94 (\pm 7.99)
60 - 75	--	60 - 75	13.76 (\pm 5.65)
75 - 87	--	75 - 87	5.51 (\pm 3.83)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table 25. *Diclofop-methyl* in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	Old Columns		New Columns	
	Column 1 R River Water ng	Column 2D Distilled Water ng	Column 3R River Water ng	Column 4D Distilled Water ng
100	----	----	----	----
200	45.61	85.25	22.81	----
300	26.78	106.07	26.78	----
400	39.66	101.11	43.63	----
500	34.71	----	363.75	----
600	31.73	65.43	190.31	101.11
700	715.58	487.63	81.29	71.38
800	180.40	150.66	----	81.29
900	41.65	111.02	----	----
1000	----	58.49	----	368.70
1100	824.60	229.95	----	34.71
1200	86.24	78.32	----	497.54
1300	85.16	39.66	----	65.43
1400	41.65	309.24	----	----
1500	47.59	79.31	----	41.65
1600	140.75	133.82	----	884.06
1700	990.11	67.41	----	41.65
1800	31.73	91.20	----	72.37
1900	----	150.66	----	1206.16
2000	32.73	195.26	----	547.10
2100	22.81	195.26	----	101.11
2200	25.79	284.46	----	191.30
2300	25.79	1201.21	----	295.36
2400	35.70	1002.99	----	210.13
2500	----	138.77	xx	220.04
2600	----	299.33	xx	120.93
2700	xx	81.29	xx	51.56
2800	xx	81.29	xx	xx

---- no residues detected at the 0.02 ug/L level

xx no leachate

umns (Fig. 39). In each case, the distilled water treatment leached a greater amount of diclofop-methyl through the soil columns than the river water treatment as has been observed for three of the previous four pesticides. Similarly, the amount leached through the "older" was greater than that leached through the corresponding "younger" column probably because of the lower microbial activity in the "older" columns.

Diclofop-methyl was found to be throughout the profile in only 2 of the 4 columns, columns 1 and 4 (Table 26). In column 1 the results did not indicate that the residues were disperse uniformly throughout each layer but may have been concentrated along a vertical channel. For column 4 diclofop-methyl appeared to be uniformly dispersed horizontally within a layer. However, in both cases the greatest concentration of residues was in the top 15 cms of the soil (Ap horizon). For column 2, all of the recovered residues were from this top layer while no residues were recovered from column 3. Where comparisons could be made the older soil columns retained more residues then did the younger columns. In this instance it is difficult to compare the effect of water treatments on residue retention in the soil as in the older column set the river water treated column retained more residues while in the younger column set the distilled water treated column retained more residues. The age of the column and its affect on microbial activity was not as clear cut in this instance as it was for EPTC and chlorothalonil. The two river water columns , 1 and 3, showed a marked difference in the amounts leached, where the older column 1 leached 5 times more diclofop-methyl than did the younger column 3. There was very little difference between columns 2 and 4, with column 2, the older column, leaching slightly more diclofop-methyl than column 4, 5.83 ug versus 5.20 ug. The differences

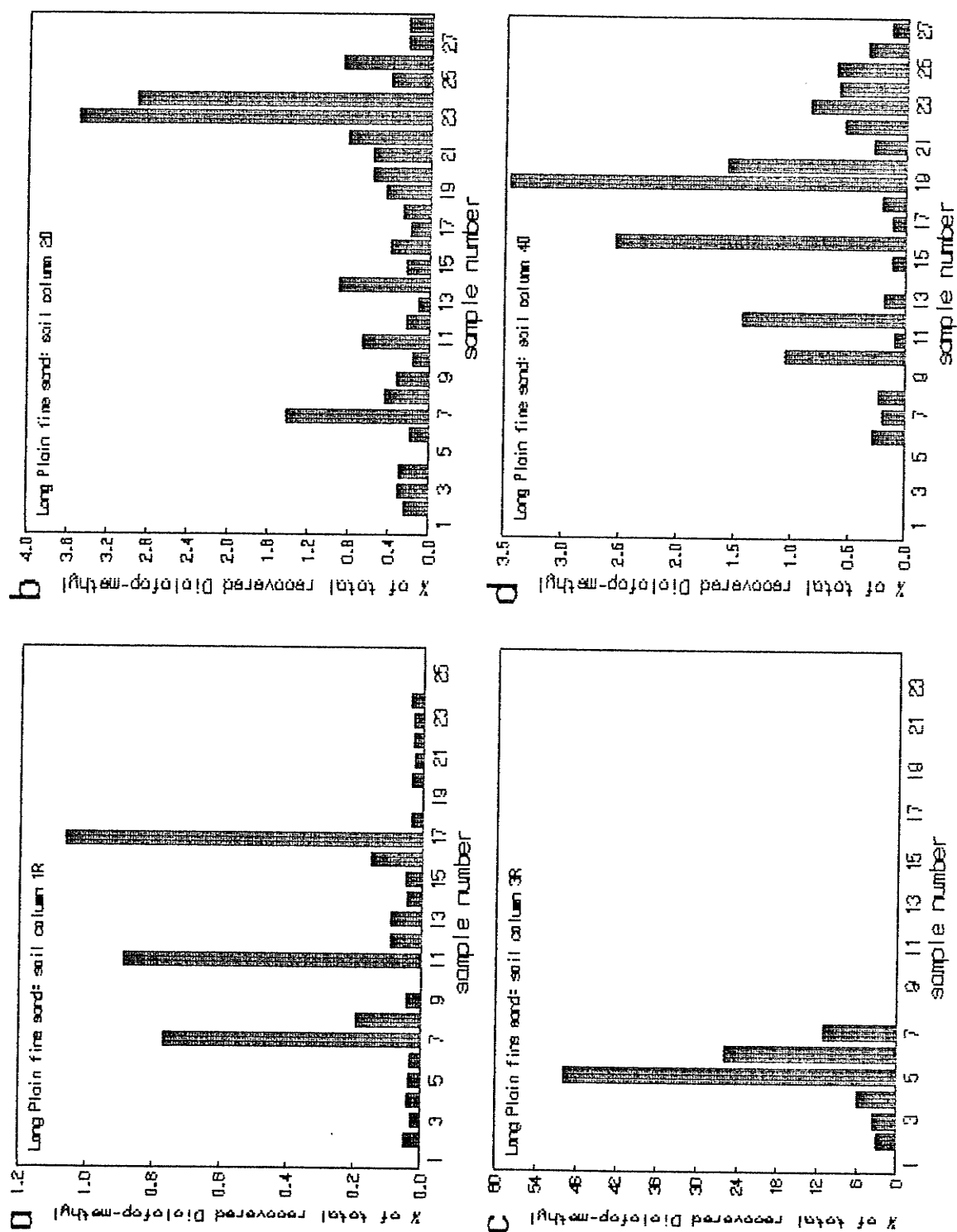


Figure 39 Percentage of total recovered Diclofop-methyl residues found in the leachate water from soil column: a) 1R, b) 2D, c) 3R, and d) 4D

Table 26. Diclofop-methyl Concentration in the Soil Profile for the Long Plain Fine Sand Soil Columns: 1R, 2D, 3R, & 4D

1R		2D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	781.77 [1]	0 - 15	61.81 (\pm 12.10)
15 - 30	35.05 [1]	15 - 30	--
30 - 45	121.85 [1]	30 - 45	--
45 - 60	85.87 [1]	45 - 60	--
60 - 75	43.05 (\pm 36.59)	60 - 75	--
75 - 89	21.19 (\pm 19.26)	75 - 87	--

3R		4D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	29.55 (\pm 8.94)
15 - 30	--	15 - 30	26.26 (\pm 1.16)
30 - 45	--	30 - 45	3.09 (\pm 2.57)
45 - 60	--	45 - 60	1.61 (\pm 0.21)
60 - 75	--	60 - 75	2.83 (\pm 1.20)
75 - 87	--	75 - 87	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

in the results between the two treatments may indicate that the dissolved organic matter or some other component of the river water may have an effect on the degradation of diclofop-methyl either by chemical or microbial means. Low amounts of the parent compound were expected to be found as diclofop-methyl degrades rapidly in soil via hydrolysis of the ester bond to give the free acid (Martens, 1978) under both aerobic and anaerobic conditions. In some soils the degradation is slower under both aerobic and anaerobic conditions due in part to soil properties (i.e., soil pH). This slower degradation rate in some soils may enable significant amounts to be leached into the anaerobic zone where degradation is further slowed down allowing a small portion of the applied parent material to reach ground water.

Trifluralin has been termed immobile as it had been found not to move beyond the 20 cm mark in a number of soils (Duseja and Holmes, 1978), thus it was thought that little to no movement would occur in the soil columns. However, with the large water input movement through the soil column was found to occur. Movement through the columns was slow with neither water treatment affecting the rate of movement. It is difficult to evaluate which water treatment carried more trifluralin through the soil as sampling ceased while trifluralin was emerging from the columns (Table 27). In the "older" columns the distilled water treatment carried trifluralin through the column in a shorter time and in greater amounts while in the "younger" columns it was the river water treatment. There appears to be little difference between the two types of treatments, river water versus distilled water, as each yielded similar results for the movement of trifluralin through this soil. The amounts leaching were less than 1% of the total amount applied for three of the

Table 27. Trifluralin in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	Old Columns		New Columns	
	Column 1 R	Column 2D	Column 3R	Column 4D
	River Water ng	Distilled Water ng	River Water ng	Distilled Water ng
100	----	----	----	----
200	----	----	----	----
300	----	----	----	----
400	----	----	----	----
500	----	----	----	----
600	----	----	----	----
700	----	----	----	----
800	----	----	----	----
900	----	----	----	----
1000	----	----	----	----
1100	----	----	----	----
1200	----	----	----	----
1300	----	----	----	----
1400	----	----	----	----
1500	----	----	----	----
1600	----	----	----	----
1700	----	161.98	357.29	----
1800	----	169.80	833.85	----
1900	----	255.73	1107.29	----
2000	----	509.63	616.66	----
2100	255.73	----	81.90	----
2200	60.41	----	x	----
2300	x	529.16	x	----
2400	x	158.07	x	439.32
2500	x	72.13	x	64.32

---- no residues detected at the 0.02 ug/L level

x no leachate

four columns and less than 1.5% for the fourth column.

In the soil columns, trifluralin was found to be distributed throughout the length of the column (Fig. 40) with the highest concentration in the top 15 cm section (Ap horizon) of the soil column (Table 28). It would appear that trifluralin under increased water input conditions (over a short time) can be leached through the Ap horizon into the underlying C and Cg horizons in this coarse textured soil. The effect of column age was reflected in the concentrations of trifluralin remaining in the various depths of the soil columns. In the "older" soil columns the levels of trifluralin were higher than in the corresponding "younger" soil column. As has been noted previously for a number of pesticides, the reduced soil microbial activity due to drying of the soil resulted in a greater residual amount in the soil.

Duseja and Holmes (1978) reported considerable movement of trifluralin to the 20 cm mark but little past that in a loam and a clay soil, with the greater proportion of the trifluralin residing in the top 10 cm of the soil. Rainfall during the period of movement totaled 18.3 cm whereas the column study applied 8x that amount. Thus the greater movement observed in the present study can be attributed to the larger amount of water flowing through the column. At the farm site rainfall during the period June to September inclusive ranges from 19.62 to 36.9 cm with irrigation adding another 12 to 20 cms. In the field, trifluralin would not be expected to move through this soil to ground water to any great degree.

Bromoxynil octanoate was not detected in any of the leachate samples as was expected (short soil half-life), and bromoxynil was detected in only one sample. It appeared in one sample from column 3, ca. 85 days

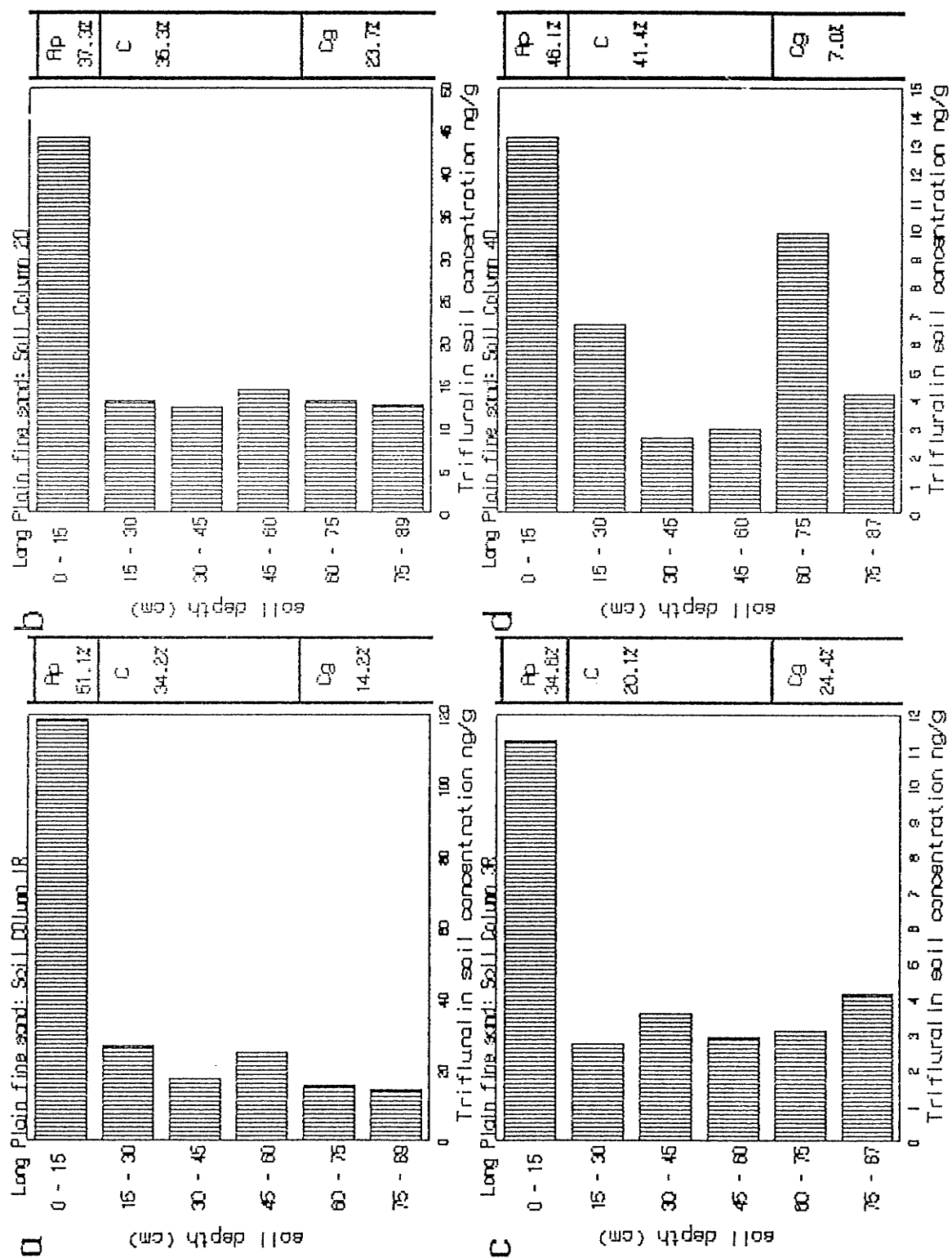


Figure 40. Trifluralin concentration profile in the soil columns and on the right the percent of total recovered Trifluralin present in the profile of the soil columns: a) 1R, b) 2D, c) 3R, and d) 4D.

Table 28. Trifluralin Concentration in the Soil Profile for the Long Plain Fine Sand Soil Columns: 1R, 2D, 3R, & 4D

1R		2D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	118.79 (\pm 59.85)	0 - 15	44.32 (\pm 17.06)
15 - 30	26.66 (\pm 10.74)	15 - 30	13.25 (\pm 3.02)
30 - 45	17.44 (\pm 7.18)	30 - 45	12.40 (\pm 2.48)
45 - 60	25.10 (\pm 11.15)	45 - 60	14.48 (\pm 2.82)
60 - 75	15.83 (\pm 2.48)	60 - 75	13.25 (\pm 2.00)
75 - 89	14.50 (\pm 4.00)	75 - 87	12.80 (\pm 3.03)

3R		4D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	11.27 (\pm 4.42)	0 - 15	13.26 (\pm 4.90)
15 - 30	2.71 (\pm 1.43)	15 - 30	6.65 (\pm 3.41)
30 - 45	3.61 [1]	30 - 45	2.65 (\pm 1.40)
45 - 60	2.92 (\pm 0.82)	45 - 60	2.96 (\pm 0.08) [2]
60 - 75	3.12 (\pm 0.13)	60 - 75	9.92 [1]
75 - 87	4.14 (\pm 0.54)	75 - 87	4.23 [1]

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

after the initial application. The amount of bromoxynil recovered represented only 0.2% of the total amount applied. Bromoxynil is very susceptible to microbial degradation especially under moist conditions (Smith, 1971), and as the columns were irrigated on a regular basis post application, the conditions in the columns were favourable for microbial degradation to occur.

Bromoxynil (from bromoxynil octanoate) was not detected in the extracts from any of the sections of soil columns 1R, 2D, 3R and 4D indicating that the applied bromoxynil octanoate is completely degraded.

Carbofuran appeared in leachate water from three of the four columns 12 to 14 days post application (Table 29). Twice as much carbofuran was recovered from the leachate of the distilled water treated "older" column as from the river water treated column (Table 29). The amounts recovered in the leachates from columns 1, 2 and 3 were 0.26, 0.61 and 0.03%, respectively, of the amount applied. The distilled water treatment leached more carbofuran through the older column than did the river water treatment, while in the younger columns no carbofuran was leached by the distilled water treatment. This pattern follows that which was observed for EPTC, chlorothalonil, and diclofop-methyl in that the "older columns" passed more material through them intact. The lower level of microbial activity in the soil, due to drying of the soil, increased the amount of a pesticide available for leaching through the soil.

Carbofuran was present throughout the profile of both the "older" soil columns, with the maximum concentration present in the 0 to 15 cm soil layer. The amount of carbofuran residues recovered from the soil in the river water water treated column was 16 times that of the distilled water treated column. This may be an effect of the dissolved

Table 29. Carbofuran in Leachate Water from Long Plain Fine Sand Soil Columns

Sample Volume mL	Old Columns		New Columns	
	Column 1 R	Column 2D	Column 3R	Column 4D
	River Water ng	Distilled Water ng	River Water ng	Distilled Water ng
100	----	----	----	----
200	26.61	21.77	15.97	----
300	22.74	34.36	----	----
400	23.71	17.90	----	----
500	12.09	15.00	12.09	----
600	15.97	13.06	20.81	----
700	75.99	9.19	----	----
800	----	----	----	----
900	----	24.68	----	----
1000	----	33.39	----	----
1100	----	120.52	----	----
1200	72.11	333.49	----	----
1300	75.99	72.11	xx	----
1400	xx	62.43	xx	xx

----- no residues detected at the 0.02 ug/L level

x no leachate

Table 30. Carbofuran Concentration in the Soil Profile for the Long Plain Fine Sand Soil Columns: 1R, 2D, 3R, & 4D

1R		2D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	59.24 (\pm 13.44)	0 - 15	4.76 (\pm 3.07)
15 - 30	25.96 (\pm 9.48)	15 - 30	1.00 (\pm 0.37)
30 - 45	10.92 (\pm 1.75)	30 - 45	1.02 [1]
45 - 60	10.74 (\pm 1.49)	45 - 60	--
60 - 75	16.01 (\pm 9.26)	60 - 75	0.93 (\pm 0.04)[2]
75 - 89	12.35 (\pm 11.95)[2]	75 - 87	0.57 (\pm 0.16)[2]

3R		4D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	--
15 - 30	--	15 - 30	--
30 - 45	--	30 - 45	--
45 - 60	--	45 - 60	--
60 - 75	--	60 - 75	--
75 - 87	--	75 - 87	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

organic matter in the river water. Neither of the "younger" soil columns contained any carbofuran in any segment of the soil profile. A small amount of carbofuran leached through column 3R while none leached through column 4D showing that microbial activity may remove all or nearly all the carbofuran applied to the soil where the microbe population is at its normal levels. Where microbial activity has been reduced by drying or storage of the soil more carbofuran is retained in the profile and/or leached through the profile.

4.2.5 Skelding Fine Sand: Soil Columns 5R & 6D

The results from these soil columns are discussed in the following section and are recorded in Appendix D.

In comparison with the Long Plain fine sand EPTC eluted much later from the river water treated column, and at about the same time from the distilled water treated column. The total amount recovered was also much lower for each treatment in comparison to the amounts recovered from the "younger" Long Plain fine sand columns. The total amounts recovered from the leachate water follow the same pattern observed for trifluralin and chlorpyrifos for this soil. In this soil, as in the previous soil, the distilled water treatment leached more EPTC through the soil than the river water treatment. It is not known why EPTC was slowed in leaching through column 5 as this column had the fastest flow through rate of the eight soil columns.

In the soil, residues were only found in the river water treated column, at lower levels than were found in the Long Plain fine sand column. In this instance, the residues were not in the top 15 cm of the soil but were contained in a broad band extending from the 15 cm to the 60 cm

depth. However the total amount of residues recovered was lower for this soil indicating a greater efficacy of degradation and other mechanisms of pesticide removal.

Chlorpyrifos first appeared in the leachate water some 23 days post application for both water treatments. This was somewhat slower than what was observed for the Long Plain fine sand. The total amount leached was higher in the distilled water treated column (16.70% of the total amount applied) than for the river water treated column (5.86% of the total amount applied). The amounts leached through these two columns is comparable to the amounts leached through the "older" Long Plain fine sand columns which would indicate that this soil has a lower microbial activity than the Long Plain soil.

As in the Long Plain fine sand "older" soil column no chlorpyrifos residues were detected in the column treated with river water. For the distilled water treated column chlorpyrifos residues were distributed in a similar pattern to that found for the distilled water treated Long Plain "younger" soil column except that the 0 - 15 cm layer (containing organic matter) was shifted to the bottom of the column. In both cases, soil columns 4D and 6D, the soil section, 0 to 15 cm (Ap horizon) and 75 to 89 cm (buried A horizon), respectively, which had a higher organic matter content did not contain any measurable amounts of chlorpyrifos. The residues recovered from the soil from column 6D represented 51.9% of the total amount of chlorpyrifos applied to the soil. This soil gave both the lowest (river water treatment) and the highest (distilled water treatment) combined recoveries of chlorpyrifos from the leachate water and the soil profiles.

Metribuzin appeared in the leachate water from the river water treat-

ed column 35 days post application and 23 days post application for the distilled water treated column. These times are similar to those observed for chlorpyrifos with which metribuzin was co-applied. The time for the river water sample is slightly slower. Both the duration of residues in leachate water and the amounts found (0.9% and 1.0% of the total amount applied to columns 5R and 6D, respectively) were similar between the two treatments with no residues detected in the water 120 days post application.

No residues of metribuzin were recovered from the soil profile for either treatment. Thus all the residues recovered from these two columns were those which leached through the column. As observed in the "younger" Long Plain fine sand soil columns only a very small amount of metribuzin leached through the soil. The majority of the applied metribuzin must either have been degraded quite rapidly or strongly bound by soil organic matter reducing the amount available for leaching.

Chlorothalonil's behavior in the Skelding fine sand is the opposite of what was observed in the Long Plain fine sand. In the river water treated column chlorothalonil appeared in the leachate within ten days post application while in the the distilled water treated column it did not appear until some 20 days post application. The actual amounts leached by the river water were 8 times greater than those leached by the distilled water, 0.59% versus 0.07% of the total amount applied. This is the opposite leaching pattern from the Long Plain soil where the distilled water leached more chlorothalonil through the soil than the river water. The amount leached through this fine sand is slightly higher than what was leached by the distilled water through the "older" Long Plain fine sand soil indicating that microbial activity (capable of

degrading chlorothalonil) in this soil may be lower than normally found in the Long Plain fine sand. On the basis of total chlorothalonil residues recovered from the columns (water and soil), the amount present in the leachate water from column 5R was about 33.5% of the total recovered. For column 6D the residues recovered from the leachate water amounted to less than 1.0% of the total recovered.

Chlorothalonil was distributed at a fairly uniform concentration in the top 60 cm of the soil with no residues detected below the 60 cm level in the river water treated Skelding fine sand soil column. The amount recovered from this soil column represented about 1.2% of the total amount applied. In the distilled water treated column, 6D, chlorothalonil residues were distributed through the entire length of the column with the maximum concentration in the top 15 cms of the soil profile. The pattern observed in the Long Plain fine sand columns where the concentration rose in the lower sections of the column was observed in this column in the bottom two sections from 60 cms to 89 cms. Though the amount of chlorothalonil leached under the distilled water irrigation treatment was a factor of 10 less than that leached under the river water irrigation treatment, the amount of chlorothalonil remaining in the soil profile was much larger (10X) for the distilled water treated column.

Diclofop-methyl exhibited the same behavior as chlorothalonil in this soil, it emerge earlier and in a larger amount under the river water treatment than the distilled water treatment which is the opposite of its behavior in the Long Plain fine sand under the same irrigation conditions. Under the river water treatment diclofop-methyl appeared in the leachate within 6 days of treatment, while under the distilled water

treatment it was 32 days post application before diclofop-methyl appeared in the leachate water. The pattern of appearance under the two treatments is different, with diclofop-methyl appearing in the leachate water over a broader time span for the river water treatment than for the distilled water treatment. As already stated the river water treatment leached a larger amount, 1.32% of the total applied, than the distilled water treatment did, 0.42% of the total applied. In addition, of the total amounts recovered from each column the proportion of diclofop-methyl recovered in the leachate water was higher for the river water treated column than for the distilled water treated column.

In the river water treated Skelding fine sand soil column diclofop-methyl was detected in 3 of the six sections. There were no detectable residues of diclofop-methyl in the 0 to 15 cm or the 30 to 60 cm sections of the profile. A low concentration (3.91 ng/g) was found in the 15 to 30 cm depth of this soil. Then in the 60 to 74 cm depth a concentration of 17.1 ng/g was found which increased to 52.2 ng/g in the 74 to 88 cm depth (buried A horizon). In the distilled water treated soil column diclofop-methyl was found to be distributed throughout the soil profile with maximum concentrations at the top (0-15 cm) and the bottom (75 to 89 cm) with intermediate values in between. The soil concentration of diclofop-methyl was higher throughout the profile for the distilled water treated soil than those observed for the river water treated soil. The amount of diclofop-methyl retained in the soil column was higher for the distilled water treated column than for the river water treated column even though a larger amount (3x) of diclofop-methyl was leached through the river water treated column.

Trifluralin was found in the leachate water from column 5 (river wa-

ter treatment) on two occasions, the first, 31 days post application, and the second, was in the last two samples obtained in the last two weeks of the study (150 days post application). The amount recovered from this column's leachate was 0.34% of the total amount applied. Trifluralin was slower in appearing in the leachate from column 6 (distilled water treatment) than it was in the leachate from column 5. The first appearance was 126 days post application. It was present in all samples from this point to the end of the study. The amount carried through the soil column was also much larger than that carried through column 5, 1.38% versus 0.34% of the total amount applied. Of the amount recovered, the proportion in the leachate for column 6D was less than it was for column 5R, 2.0% versus 5.9% indicating more residues remained in the soil profile under the distilled water treatment. In comparison with the Long Plain fine sand columns the amounts leached through the Skelding fine sand followed the same trend as in the "older" columns with more trifluralin leaching under the distilled water treatment than under the river water treatment. The amounts leached were also of the same order of magnitude for these two particular sets of columns with the Skelding leaching twice the amount of the corresponding "older" Long Plain column.

As in the Long Plain soil columns trifluralin residues were distributed throughout the Skelding soil columns. In the river water treated column trifluralin was distributed at a fairly uniform concentration down the soil profile. The majority of residues recovered from this soil column were from the soil, the amount recovered from the soil represented 5.4% of the total amount applied. For the distilled water treated column, a much larger portion of the applied trifluralin was

recovered from the soil profile, 67.5% of the total applied. In the distilled water treated column trifluralin was distributed throughout the soil profile with the largest concentrations in the 0 to 15 cm and the 60 to 75 cm depths with the latter section having the maximum concentration observed. Overall, the concentrations of trifluralin in the soil under the distilled water irrigation treatment were higher than those under the river water irrigation treatment. This is a departure from what was observed for the Long Plain fine sand where the soil concentrations of trifluralin were comparable between treatments for both the "older" and "younger" columns. The results from the river water treated Skelding soil column are comparable to the the results from the river water treated Long Plain "younger" soil column. While the results of the distilled water treated soil column are comparable to the distilled water treated Long Plain "older" soil column. For the Skelding fine sand the distilled water treated column both leached and contained more residues of trifluralin than the river water treated column.

Bromoxynil was detected in only one of 23 100 mL leachate samples collected post application from the river water treated column covering a period of over 100 days. The first appearance of bromoxynil in the leachate water from the distilled water treated soil was likewise over 100 days post application with a second appearance in the final sample some 120 days latter. Bromoxynil leaching through the soil column accounted for 0.29% and 0.67% of the total applied to the two columns under the river water and distilled water treatments, respectively. This is slightly higher than what was observed for the one case where bromoxynil was detected leaching from the Long Plain soil.

In the river water treated column bromoxynil was distributed through

the soil column from the 15 cm depth to the bottom of the column. No bromoxynil residues were recovered from the 0 to 15 cm section of this column. The maximum concentration was in the 15 to 30 cm depth and it decreased in the next two sections before it rose and held at a steady concentration for the final 28 cm of the column. This is the first instance where substantial amounts of bromoxynil are found within the soil profile of the columns as no bromoxynil was recovered from the Long Plain soil columns. In the distilled water treated column bromoxynil was only found in the last soil section, 75 to 89 cms (buried A horizon), at a concentration level much higher than that observed in the river water treated column. This concentration level was such that, this single section contained twice the residue amount of bromoxynil than the entire river water treated column 5R contained. The large amount recovered from the bottom organic rich sections of the columns may indicate that bromoxynil tends to be concentrated by the organic matter in this layer and that in an aerobic, microbially active environment may be completely degraded, as may have been the case in the Long Plain soil.

Carbofuran followed the pattern set in columns 1 to 4 with a larger amount leaching through the column with the distilled water treatment than with the river water treatment. Under the river water treatment a total of 40 ng of carbofuran leached through the soil into the leachate samples some 70 days after the initial application (0.025% of the total amount applied). Whereas under the distilled water treatment 0.56% of the total amount applied leached through the soil beginning 26 days after the initial application and continuing to be present in the leachate until the end of the study.

The distilled water not only leached a greater amount of carbofuran

through the soil but also a greater proportion of material into the soil. This last observation was inconsistent with what was observed for the Long Plain soil. In the Long Plain soil, more carbofuran residues were present in the river water treated "older" soil column than in the distilled water treated column. In the "younger" columns no carbofuran residues remained in the soil under either water treatment. In the Skelding soil columns the largest concentration of carbofuran was associated with the organic matter rich layer, for this soil at the bottom of the column, as in the Long Plain soil columns.

The pattern observed for the following pesticides: trifluralin, diclofop-methyl and carbofuran, where the bottom section of the column had the highest concentration as opposed to the top section can be attributed to the structure of the soil profile where the bottom section had the highest organic matter content of any part of the soil column.

4.2.6 St. Claude Silt Loam: Soil Columns 7R & 8D

The results from these soil columns appear in Appendix D and are presented in the following section.

EPTC was leached in a larger overall quantity by the river water treatment than the distilled water treatment and over a longer period of time. This was a reversal of the trend observed in the other two soils. In the St. Claude silt loam soil EPTC first appeared ca. 120 days post application from the river water treated column and was present, in varying amounts, to the end of the study. Leachate from the distilled water treated column contained EPTC in only 2 samples, 44 and 219 days post application. The leaching time was comparable to the other two soils and any differences were due to differing flow rates through the various

columns. The total amount of EPTC leached through this silt loam soil differed by a factor of 3 between the two treatments, 3.31% and 9.76% for the river water and distilled water treatment, respectively.

In the river water treated soil column, the distribution pattern of EPTC residues in this soil is similar to that observed in the Long Plain soil under the same water treatment. In the distilled water treated column EPTC was present in the top 39 cm of the silt loam column roughly the same depth as with the river water treated column, but in greater concentrations. Under both treatments the organic matter rich (8.8%) Apk layer of this silt loam soil contained the largest percentage of the residues recovered from the soil profile while the AC and C layers held smaller amounts. Like the other two soils, the distilled water irrigation treatment leached more EPTC than the river water through the silt loam soil, 195.9 ug versus 66.49 ug. As well, there was less EPTC retained in the soil under the distilled water irrigation treatment which was consistent with what was observed for the Long Plain and Skelding fine sand soil.

EPTC has a much higher water solubility than either of the previous two compounds, thus connoting that a larger amount would be leached through the soils. Actual results from the 8 soil columns confirm this prediction with the largest amounts recovered from the distilled water treated Long Plain fine sand in the leachate water and in the soil profile and leachate water of the river water treated St. Claude silt loam soil. The smallest recoveries of residues was from the Skelding fine sand where 6.0 and 10.8% of the total applied amount was recovered under the two treatments, river water and distilled water, respectively. For both the fine sand soils, distilled water leached a larger amount

through the soil column with a smaller amount remaining in the soil profile than the river water. The silt loam soil's result were the inverse with respect to amount leached, in that the river water treated silt loam soil leached more EPTC through the column than did the distilled water treated soil. From the literature and the physical properties (vapour pressure), EPTC was expected to be short lived in the soil environment especially where the soil was not subjected to daily fluctuations in temperature or water content. So it was a great surprise when large amounts of EPTC was recovered from the soil columns especially from the surface layers. As some of these soils (silt loam) had a previous history of EPTC application it was expected that EPTC would be degraded rapidly in these soils. However this was not observed as some of the highest soil concentrations of EPTC was observed in these soils.

Chlorpyrifos appeared in the leachate water 20 days post application from column 7, the river water treatment, which was of the same time frame as the Skelding soil and slightly slower than the Long Plain soil. Chlorpyrifos first appeared in the leachate 77 days post application from the distilled water treated column. In comparison to the other 7 columns, chlorpyrifos was delayed on this column more than any of the others under both treatments. The distilled water treated column leached a slightly greater amount of chlorpyrifos, even though it was delayed, than the river water treated column, 3.7% versus 3.1% of the total amount of chlorpyrifos applied to the columns. The difference in the two treatments is not as evident in this soil as the other two on the amount leached. For both treatments this represented 100% of the residues recovered from the soils. Residues of chlorpyrifos were not recovered from any of the sections of the silt loam soil columns unlike the

other two soils where residues were recovered from the soil profiles.

Chlorpyrifos leached through all three soils rapidly with residues appearing in the leachate water a short time after application. The only exception to this was the silt loam soil under the distilled water treatment where it was some time before chlorpyrifos appeared in the leachate unlike the river water treated column where residues were recovered from the leachate water a few days post application. Of the two treatments, distilled water irrigation both leached more chlorpyrifos through the soils as well as into the soil profile. The largest amounts leached through the soil was in the fine sand soils under the distilled water irrigation. In the silt loam silt lower amounts of chlorpyrifos were recovered from the leachate and no residues were recovered from the soil profile indicating that degradation gives rapid clearing of residues. This degradation may be related to contact time, the longer the pesticides are in contact with the microbially active portion of the soil the lower the amounts available for leaching out of this layer into the subsoil. The chemical hydrolysis of chlorpyrifos in these soils would be a minor contributor to the total losses as degradation by this pathway is only significant above a pH of 8.0. As no chlorpyrifos was detected in the ground water or the tile drain outflow it can be stated that under normal precipitation and irrigation levels that large amounts of chlorpyrifos are not leached through the soil column into ground water. For 7 of the 8 columns the amount leached was under 10% of the amount applied, with a much lower water input into the columns one would expect much less material to be carried through the column. With a water solubility greater than that of trifluralin it was expected that more chlorpyrifos would leach in comparison to trifluralin.

Metribuzin appeared in the leachate water 12 days post application from the distilled water treated soil and 35 days post application from the river water treated soil. This was consistent with the observation of the other two soils where residues emerged from the distilled water treated column before they emerged from the river water treated column. In this instance, St. Claude silt loam, the time between emergences for the two treatments is greater than that observed for the other two soils. The total amount leached through each of the two columns was less than 0.1% of the total amount applied with more leached through the distilled water treated column than through the river water treated column. This last observation was consistent with the behaviour observed for metribuzin in the previous two soils. The amounts emerging from the columns was comparable to the amounts emerging from the other two soils.

For both water treatments, metribuzin was not detected in the silt loam soil at any point in the profile of either column, as was the case for the other two soils.

Residues of metribuzin were not detected on the soil profile at any depth for all three soils. The amounts leached through the three soils were similar for both water treatments ranging from 0.0% to 0.1% of the total amount applied. Only in the "older" Long Plain fine sand were larger amounts (4.6 and 6.0% of the total amount applied) of metribuzin recovered from the leachate water which is probably due to lower microbial activity on these two columns. In general, the distilled water leached a slightly greater amount of metribuzin through the soil than did the river water, except in column 4D where no metribuzin was recovered.

Chlorothalonil did not appear in the leachate water from the river

water treated silt loam soil column until over 250 days post initial application or 54 days after the last application, unlike the other two soils where chlorothalonil appeared in the leachate water a short time after application. The amount leached was low, only 0.012% of the total amount applied or less than 1% of the total amount recovered. The distilled water treated column exhibited two periods where chlorothalonil was present in the leachate water. The first period began 8 days after the initial application of chlorothalonil and extended over a 17 day period, and the second period was towards the end of the study where chlorothalonil was found in 3 of the last 4 leachate samples taken. A larger amount of chlorothalonil was leached through this column, 0.38% of the total amount applied or 8.6% of the total amount recovered. Here as in the other two soils, the distilled water leached more chlorothalonil through the soil than the river water (3.42 ug versus 0.11 ug) and in a shorter period of time.

In the river water treated silt loam soil column chlorothalonil was found to be distributed in the soil profile in a corresponding pattern to EPTC but at different soil concentrations which reflected the amounts applied. Under the distilled water treatment chlorothalonil was found to be distributed throughout the silt loam soil's profile. For both treatments the maximum concentration of chlorothalonil were recovered from the organic matter rich Apk horizon. The under lying clayish layer (ACkgj horizon) contained only 2.0% of the recovered residues while the Ckgj horizon yielded the balance of the recovered residues from one section in the middle of the layer. The amount recovered from the soil profile represented less than 1.5% (river water treatment) and 4.0% (distilled water treatment) of the total amount applied to the soil col-

umn. In the distilled water treated column there was a slight increase in the soil chlorothalonil concentration in the 54 to 69 cm depth from the previous 39 to 54 cm section, which may indicate a concentration wave front passing through the profile. The amount of chlorothalonil remaining in the soil was also greater under the distilled water irrigation treatment than under the river water treatment, 36.26 ug versus 13.20 ug as was the case in the other two soils.

Chlorothalonil was present in the leachate water from all soil columns as well as remaining in the soil profiles. For the Long Plain fine sand and St. Claude silt loam soils, distilled water carried more chlorothalonil into the soil profile and through into the leachate water than the river water. River water leached more chlorothalonil through the Skelding fine sand than the distilled water did, even though more chlorothalonil was carried into the soil profile by the distilled water. Chlorothalonil breakdown in soil is dependent upon moisture content, temperature and pH of the soil (Ballee et al., 1976) with a half-life of 6 to 12 weeks in temperate zone soils. As chlorothalonil is stable towards hydrolysis at pH's less than 9.0 (Ballee et al., 1976; Szalkowski and Stallard, 1977), hydrolysis was not have every indication of being a major degradative pathway in these soils, as the pH of these soils did not come close to 9.0 at any depth. Even though photolysis has been shown to remove chlorothalonil from solution (Binkley et al., 1977; Loeffler, 1978; Satoh, 1979; Khan and Akhtar, 1983) it was not a major degradative pathway in the column study as the lighting in the study area would not produce significant amounts of photons of sufficient energy. The major contributor to degradation of chlorothalonil would be the microbial populations in the soil, as is evidenced by the recovery

results for columns 1R through 4D. Columns 1R and 2D were prepared 35 days prior to columns 3R and 4D and stored at ambient conditions in the laboratory. The temporary drying of these columns reduced the microbial activity as much more chlorothalonil was leached through the fine sand soils and retained in them as compared to the fresh columns which were used immediately after construction. The amount of chlorothalonil leaching through the soil profile is very small ($< 1.0\%$) of the total applied amount. It was noted that in the Long Plain fine sand soil, which is the major soil type in the immediate area of the field study, that distilled water leached more chlorothalonil through the soil than the river water. In the field this would indicate that precipitation in the form of rain would influence the amount leached more than the river water applied through the irrigation system. An examination of the field results from 1982 and 1983 shows a definite correlation between the precipitation pattern and the appearance of chlorothalonil in the tile drainage outflow and ground water. The appearance of residues in the column leachate water was in a shorter period of time when compared to the field results due to the larger amount of water applied to the columns. In addition, the carry-over of chlorothalonil residues in the soil validates the appearance of chlorothalonil residues in the tile drainage water at the beginning of the season. Spring melt waters would flush some of these residues through the soil into the ground water and subsequently into the tile outflow. The amounts would be low as the carry-over amounts in the field would be lower than those observed in the laboratory due less being carried into the subsoil because of lower water input (precipitation and irrigation combined).

Under both water treatments diclofop-methyl appeared in the leachate

water at about the same time, 25 and 21 days post application for the river and distilled water treatments, respectively, which was later than in the other two soils. The pattern of appearance for diclofop-methyl in the leachate water from the two treatments is roughly similar for the period where it appeared in the leachate water at the same time. Diclofop-methyl was present in the leachate water under the river water treatment for 10 of 11 consecutive samples (2 sequences of 5 consecutive samples) disappearing from the leachate well before the end of the study. Whereas, the distilled water treated soil column had diclofop-methyl in the leachate water in a sporadic basis (in groups of 3 to 6 consecutive samples) through to the end of the study. The total amount of diclofop-methyl leached through the soil was higher for the distilled water treated soil column than for the river water treated column, 2.14% versus 0.52% of the total amount applied, as was observed in the Long Plain soil but not the Skelding soil.

In the river water treated soil column diclofop-methyl was not present at all in the organic soil layer (Apk) or the clay layer (ACkgj) or even in the upper part of the underlying sand (Ckgj). It only appeared in the last 30 cms of the column and only in the last portion of the 50 to 65 cm section. Under the distilled water irrigation treatment, diclofop-methyl was distributed throughout the profile of the silt loam soil column with three peak concentrations evident as the depth increases. Actually there was an alternating drop-rise pattern to the concentrations observed as depth increased. Each succeeding maximum was always less than the preceding by ca. 20 ng/g beginning at the second maximum. The majority of recovered residues was from the Apk horizon (top 20 cm) where 54.2% of the recovered residues were held. The sandy

Ckgj horizon was the next source of recovered residues mainly due to the volume of this layer with respect to the others. Overall, the distilled water treatment leached more diclofop-methyl into and through the silt loam soil than did the river water treatment.

The behaviour of diclofop-methyl in the Long Plain fine sand is not entirely evident. The distilled water treatment leached more diclofop-methyl through the soil than did the river water as has been observed for other pesticides. There was little or no difference in the amounts leached or retained on the columns under the distilled water treatment between the "older" and "younger" columns. Whereas, under the river water treatment, more diclofop-methyl was leached and retained in the soil profile for the "older" column than for the "younger" column. The recoveries of diclofop-methyl were identical from the two distilled water treated columns (14.8 to 14.9% of the total amount applied), but the recovery from the "older" river water treated column was two orders of magnitude greater than for the "younger" column (39.9% versus 0.3% of the total amount applied). In the other fine sand soil (Skelding), the river water leached more diclofop-methyl through the profile than the distilled water, although the distilled water carried more diclofop-methyl into the soil profile where it was later recovered. In the silt loam soil the distilled water treatment leached and carried more diclofop-methyl through and into the soil profile than the river water. There was significant retention of diclofop-methyl in two of the soils, Skelding and St. Claude, under the distilled water treatment where a large proportion of the retained residues were recovered from the surface layer of the soil. Under the river water treatment it appears that a larger proportion of the residues are either degraded or fixed within

the soil matrix in a form which was unextractable (unavailable?).

Trifluralin residues appeared only in the last leachate water sample obtained from the river water treated column. The distilled water treated column had an initial appearance of trifluralin 30 days post application. However, it did not appear in a regular basis until latter on and from there appearing in 9 of 12 samples. The pattern of appearance of trifluralin in the leachate water with the series of 4 peaks is different from the previous 7 columns. The amount carried through this soil follows the pattern observed in 2 of the 3 previous pairs of columns. Where the distilled water treatment carried more trifluralin through the soil than the river water treatment, 0.90% and 0.16% of the total amount applied, respectively.

In the river water treated column trifluralin was not found in the very organic matter rich (8.8% versus < 1.0% for the other two soils) Apk horizon of the St. Claude silt loam soil. Trifluralin first appeared in the 20 to 30 cm depth, a clay soil pocket (AC horizon) lying between the organic rich A horizon and the organic poor C horizon. The maximum concentration (149.6 ng/g) of trifluralin for this silt loam soil column was observed in the top of the C horizon, the 30 to 35 cm depth. The level of trifluralin dropped sharply (15.9 ng/g) in the underlying section, then rose to 40 ng/g and 47.9 ng/g for the last two sections of the column. As in the river water irrigated silt loam soil column trifluralin was not detected in the Apk horizon of the distilled water treated soil but was present in the last 60 cms of the profile. In the 24 to 28 cm and the 28 to 39 cm sections the concentration ranged from 47.9 to 49.9 ng/g before jumping to 172.8 ng/g in the 39 to 54 cm section of the soil column. The concentration decreased in the last two

sections. The amount remaining in the soil under the distilled water treatment was nearly twice the amount remaining in the soil under the river water treatment.

The behaviour of trifluralin in the Long Plain fine sand is difficult to comment on as the results from the four soils do not form any definite trend. Between columns 1R and 2D, the river water irrigated column leached less trifluralin and held more trifluralin within the soil profile than the distilled water irrigated column. On the other hand, for columns 3R and 4D, the river water irrigated column leached more trifluralin and held slightly less trifluralin within the soil profile than the distilled water irrigated column. Of the material remaining on the soil column the majority of it was in the top 15 cms of each soil column. In the Skelding fine sand and the St. Claude silt loam, the distilled water irrigation leached more trifluralin into and through the soil than the river water irrigation. In the Skelding fine sand the trifluralin was found to be distributed throughout the profile without there being any particular buildup of levels at any specific depth. In the St. Claude silt loam, trifluralin was present in the subsurface layers but not in the organic rich surface layer where it is either rapidly degraded or bound so tightly that it is unextractable (unavailable). In the field trifluralin was not detected in the ground water so was thought to be relatively immobile or degraded before any residues could reach ground water. Trifluralin was seen in the leachate water from the soil columns mainly due to the large amount of water be put through each of the columns. In the field, the soil may receive up to 36.9 cm of rain and 10.8 cm of river water as irrigation for a total of about 47.7 cm of input water (from June to September inclusive). The column study

inputted 296.0 cm of water to each column which is in the order of 6x the normal amount of water the soil would receive in an average growing season. Therefore, under normal precipitation and irrigation levels trifluralin would be immobile in all three soils, remaining in the top 15 to 20 cms of the soil, and in the silt loam being either totally immobilized or degraded totally within a short time.

Bromoxynil made a more pronounced appearance in the leachate water from the silt loam soil than it did from either of the fine sands. Whereas in the Skelding fine sand, bromoxynil appeared in one or two leachate samples, in the St. Claude silt loam column leachate water samples bromoxynil appeared in 8 and 9 consecutive samples (river and distilled water treatments, respectively). Bromoxynil appeared first in the river water treated silt loam soil leachate some 16 days after the columns had initially been treated with bromoxynil octanoate. It appeared six days later in the leachate from the distilled water treated silt loam column. The pattern of appearance of the residues in the leachate water was roughly the same for both treatments. The total amounts leached through each of the two columns was roughly the same (1.18% and 1.02% of the total amount applied) with the river water treated silt loam leaching the greater amount. These amounts represent 100% of the amounts recovered as residues of bromoxynil were not detected in the soil profile of the silt loam for both water treatments. This last observation was consistent with the other two soils where residues of bromoxynil were not recovered from the soil profile.

Bromoxynil octanoate was not expected to appear in any of samples and did not, bromoxynil on the other hand appeared in a number of samples. In the Long Plain fine sand the only appearance of bromoxynil was in the

leachate water from column 3R at a very low level (0.2% of the total amount applied). In the Skelding fine sand and the St. Claude silt loam larger amounts were recovered from the leachate water. The Skelding fine sand also contained large amounts of bromoxynil within the soil profile. In the river water treated column the residues were distributed fairly evenly through the bottom 73 cms of the column, while in the distilled water treated column all of the residues were localized in the bottom 14 cms of the column. In this fine sand 36% and 76% of the applied pesticide (as bromoxynil) was recovered from the river water and distilled water treated columns respectively. In the other two soils little to none of this compound was recovered under either irrigation treatment. Under field conditions, little to none of the applied bromoxynil would be expected to reach ground water from any of these soils due to degradation, distance to travel, and the amount of input water is much less.

Carbofuran appeared in the leachate water from the distilled water treated column 16 days earlier than from the river water treated column. This difference may be due to a difference flow rates through the two columns as column 7 appeared to have a slower flow rate as well as greater losses of moisture through evapotranspiration than any of the other columns. The pattern of carbofuran appearance in the leachate water is similar for both treatments differing only in amounts and duration. For this soil, silt loam, the river water treatment leached more carbofuran through the soil coil than did the distilled water treatment, 0.66% versus 0.38% of the total amount applied, even though there was a greater volume of water passing through the distilled water treated column. This was a reversal of the trend seen in the other two soils, and

the amounts leached through the column was also larger than previously seen for this water treatment in the other two soils. The pattern of appearance from the distilled water treated column was similar to the other two soils, except the "younger" Long Plain soil. In both cases the largest amounts of carbofuran were leaching out in the last few samples collected indicating that even though a small amount of carbofuran leached through the soil quickly the bulk of the material moves much more slowly in this soil (observed in all three soils).

As in the other soils, the highest concentrations of carbofuran were observed in the organic matter rich Apk horizon for both treatments. There were little to no residues of carbofuran in the sand horizon below the clay. The major difference was concentration, much more carbofuran was recovered from the top three sections of the distilled water treated soil than from the river water treated soil. Proportionally the three horizons held similar percentages of material with the bulk of the retained carbofuran being recovered from the Apk horizons under both water treatments.

In the Long Plain fine sand very little carbofuran was leached or remained in the soil profile of the younger columns under either water treatment. But there were significant residues leached through the column and remaining in the soil profile for the older columns. The river water treated older column had a large amount (39.7% of the total amount applied) remaining in the soil profile with the highest concentration in the top 15 cm of the soil profile. The distilled water treated older column leached twice the amount of carbofuran through the column (1.00 ug versus 0.43 ug) but retained less than a sixteenth the amount on the soil profile (3.92 ug versus 64.62 ug). In the younger columns no car-

bofuran was recovered from the soil profiles for either treatment and only a very small amount was recovered (0.03% of the total amount applied) from the leachate water of the river water treated soil column. For the other fine sand soil and the silt loam soil significant amounts of carbofuran were recovered from the soil profiles of the columns with more present in the distilled water treated columns than the river water treated columns. The amounts recovered from the soil profile and the leachate water were higher for the silt loam than for the corresponding fine sand soil. The distribution pattern for the two soils was different for the same water treatment, in the fine sand the majority of residues were located in the bottom 30 cms of the columns while in the silt loam the majority of the residues were in the top 24 cms of the columns. In both cases this is where the largest amounts of organic material was present.

In the field, where carbofuran was found in the ground water, it was in an area where there were substantial areas of the silt loam soil. Both sampling wells were located either next to or within a silt loam soil area in the NW quarter of 10-11-7. This may explain why carbofuran was detected in the ground water sampled from one of these wells (not in the other due to position with respect to the area and direction of ground water flow) as it appears from the column study that carbofuran is leached more readily through the silt loam than through either of the fine sands. Moreover, distance from the surface to ground water in the silt loam areas is generally less than for the fine sand areas, especially the Skelding fine sand.

4.2.7 Summary of Soil Column Work

In summary, it was found that in general distilled water leached larger amounts of the eight pesticides through the three soils studied with only a few exceptions, than the river water (Table 31). Therefore, it is concluded that the river water applied to the fields through the irrigation system will have little or no effect on the leaching of any pesticides applied to the fields. A heavy rainfall, a short time after application of a pesticide will hasten leaching of that compound through the soil. The microbial activity of the surface layer (0 to 15 cm) of the soil will affect the amount of pesticide leached through it. Where microbial activity has been reduced, the amount available to be leached increases. The leachability of a compound applied in this area is dependent upon a number of factors: amount applied, amount of rainfall and how soon after application, the microbial activity of the soil, the chemical activity of the soil, and the adsorption/desorption interaction with various soil constituents. From the field results it appears that time after application and amount of rainfall is the major contributing factor for pesticide leaching to ground water. Based on the time it took to appear in the leachate water after application and its final distribution on the soil columns trifluralin would not leach to ground water under field conditions; even though its half-life (Table C.3) in the soil is such that substantial amounts would be available for leaching. It would remain in the surface horizon associated with the soil organic matter as indicated by its large K_{ow} (Table C.3), where it would be degraded by a number of pathways (microbial and chemical). Small amounts of chlorpyrifos might be expected to leach to ground water in

Table 31. Pesticide Recovery from Soil Columns: Leachate Water & Soil

Column		Trifluralin ug	Chlorpyrifos ug	EPTC ug	Chlorothalonil ug
	amount applied	220.0	484.8	2007.2	900.8
1R	leachate	0.32	14.32	318.17	0.47
	soil extract	103.90	0.00	261.02	224.01
	flask	0.20	0.00	0.00	0.20
	total	104.42	14.32	579.19	224.68
	% applied	47.5	3.0	28.9	24.9
2D	leachate	1.86	32.58	1074.94	5.02
	soil extract	52.77	84.91	77.91	283.64
	flask	0.19	3.90	0.00	0.19
	total	54.83	121.39	1152.85	288.85
	% applied	24.9	25.0	57.5	32.1
3R	leachate	3.00	2.24	135.86	0.10
	soil extract	11.86	182.69	51.85	5.20
	flask	0.13	2.31	0.00	0.00
	total	14.95	187.24	187.71	5.31
	% applied	6.8	38.6	9.4	0.6
4D	leachate	0.59	74.43	698.71	1.28
	soil extract	13.09	131.56	0.00	39.20
	flask	0.17	0.00	0.00	0.01
	total	13.84	205.99	698.71	40.49
	% applied	6.3	42.5	34.8	4.5

Table 31. Pesticide Recovery from Soil Columns: Leachate Water & Soil
(continued....)

Column		Trifluralin ug	Chlorpyrifos ug	EPTC ug	Chlorothalonil ug
	amount applied	220.0	484.8	2007.2	900.8
5R	leachate	0.74	12.89	88.44	5.27
	soil extract	11.80	0.00	31.05	10.46
	flask	0.00	0.00	0.00	0.00
	total	12.54	12.89	119.49	15.73
	% applied	5.7	2.7	6.0	1.7
6D	leachate	3.04	36.75	216.36	0.64
	soil extract	148.49	295.95	0.00	139.29
	flask	0.76	0.00	0.00	0.31
	total	152.29	332.70	216.36	140.24
	% applied	69.2	68.6	10.8	15.6
7R	leachate	0.35	15.26	66.49	0.11
	soil extract	69.08	0.00	57.01	13.20
	flask	0.00	0.00	0.00	0.00
	total	69.44	15.26	123.49	13.31
	% applied	31.6	3.1	6.2	1.5
8D	leachate	1.98	18.10	195.90	3.42
	soil extract	121.74	0.00	98.32	36.26
	flask	0.16	0.00	0.00	0.00
	total	123.88	18.10	294.22	39.68
	% applied	56.3	3.7	14.7	4.4

Table 31. *Pesticide Recovery from Soil Columns: Leachate Water & Soil*
(continued...)

Column		Diclofop-methyl ug	Carbofuran ug	Metribuzin ug	Bromoxynil ug
	amount applied	232.8	163.2	592.4	95.1 *
1R	leachate	3.49	0.43	27.32	0.00
	soil extract	89.46	64.62	0.00	0.00
	flask	0.00	0.00	0.00	0.00
	total	92.95	65.05	27.32	0.00
	% applied	39.9	39.9	4.6	0.0
2D	leachate	5.83	1.00	35.52	0.00
	soil extract	28.53	3.92	0.00	0.00
	flask	0.00	0.00	0.00	0.00
	total	34.36	4.92	35.52	0.00
	% applied	14.8	3.0	6.0	0.0
3R	leachate	0.73	0.05	0.31	0.19
	soil extract	0.00	0.00	0.00	0.00
	flask	0.00	0.00	0.00	0.00
	total	0.73	0.05	0.31	0.19
	% applied	0.3	0.03	0.05	0.2
4D	leachate	5.20	0.00	0.00	0.00
	soil extract	29.51	0.00	0.00	0.00
	flask	0.05	0.00	0.00	0.00
	total	34.76	0.00	0.00	0.00
	% applied	14.9	0.0	0.0	0.0

Table 31. *Pesticide Recovery from Soil Columns: Leachate Water & Soil*
(continued...)

Column		Diclofop-methyl ug	Carbofuran ug	Metribuzin ug	Bromoxynil ug
	amount applied	232.8	163.2	592.4	95.1 *
5R	leachate	3.07	0.04	0.54	0.28
	soil extract	37.67	5.68	0.00	33.92
	flask	0.00	0.00	0.00	0.00
	total	40.74	5.71	0.54	34.20
	% applied	17.5	3.5	0.09	36.0
6D	leachate	0.98	0.92	0.63	0.64
	soil extract	134.11	19.11	0.00	71.35
	flask	0.56	0.00	0.00	0.00
	total	135.65	20.03	0.63	71.99
	% applied	58.3	12.3	0.1	75.7
7R	leachate	1.22	1.22	0.21	1.12
	soil extract	22.60	32.29	0.00	0.00
	flask	0.00	0.00	0.00	0.00
	total	23.82	33.52	0.21	1.12
	% applied	10.8	20.5	0.04	1.2
8D	leachate	4.98	3.21	0.38	0.97
	soil extract	156.97	69.17	0.00	0.00
	flask	0.00	0.00	0.00	1.34
	total	161.94	72.38	0.38	2.31
	% applied	73.6	44.4	0.06	2.4

* as the octanoate (138.4 ug)

the Long Plain fine sand based on the column work, however under field conditions the applied chlorpyrifos may be held in the surface horizon's organic matter (large K_{ow}) where it is degraded. It would appear that time after application and amount of rainfall would determine if any chlorpyrifos would be carried into the subsoil even though the half-life of chlorpyrifos is fairly long. Even though large amounts of EPTC were recovered from the leachate water from the soil columns, this compound would not be expected to appear in ground water under field conditions. This is based on the length of time it took EPTC to appear in the leachate water after application and it's relatively short half-life. The distribution in the soil profile also suggests that this compound would be retained in the surface horizon where it would be subject to a number of degradative processes. In addition, with it's relatively high vapour pressure substantial losses would occur through vaporization. The soil column and K_{ow} results suggest that very small amounts of chlorothalonil would reach ground water and that the amount of rainfall and time after application would be the major contributing factors. Diclofop-methyl would not be expected to move through the soil to any great degree under field conditions based on the laboratory column results and diclofop-methyl's water solubility and K_{ow} . A heavy rainfall may move residues further into the surface horizon but little to none should be transported to the subsurface horizons. Carbofuran would not be expected to appear in the ground water under field conditions based on the column results when compared to diclofop-methyl. However, a higher water solubility and a lower K_{ow} than a number of the other compounds tested may enable small amounts of carbofuran to leach through the soil. This then would make leachability of carbofuran a function of amount of rainfall

and time after application. As well, the half-life indicates that carbofuran would be available for leaching over a longer period of time. Bromoxynil octanoate or bromoxynil would not be expected to leach to ground water under field conditions based on the soil column results and it's half-life. Under normal precipitation levels bromoxynil would not move out of the surface horizon before being degraded and in those soils where enhanced movement was observed the distance to ground water would be an additional factor which would further reduce the amount if any that would reach ground water.

4.3.0 LOG K_{ow} AND PESTICIDE MOVEMENT

The partition coefficient, K_{ow} , has been correlated with the environmental and soil behaviour parameters of pesticides (Karickhoff et al., 1979; Kenega and Goring, 1980; Mackay et al., 1980; Chiou, 1981; McCall et al., 1983; Geyer et al., 1984; Hawker and Connell, 1985). The partition coefficient can not only be determined experimentally but can also be calculated from the experimentally determined value of a similar compound if the molecular fragment values are known. Leo et al. (1971) have tabulated the experimental value of a large group of chemicals in a variety of solvents and from these other $\log K_{ow}$'s can be calculated for similar compounds. $\log K_{ow}$ can be calculated from molecular fragment data (fractal constant method) (Leo and Hansch, 1979; Rekker, 1977; Rekker and de Kort, 1979) either by hand or on a microcomputer (LogP Program, Labsware Programs, CompuDrug Limited). The LogP microcomputer program utilizes Rekker's method of calculating the partition coefficient. The experimentally determined values for $\log K_{ow}$ will be compared to the literature values and the calculated values, using a number of

different methods and discussed with respect to the experimental results of the field and laboratory work for the pesticides monitored for and worked with in the laboratory.

The results of the $\text{Log } K_{ow}$ determination are summarized in Table 32 along with the values obtained from the literature. Using these experimentally determined $\text{Log } K_{ow}$ values, the partition coefficient for the soil organic matter, K_{oc} , was calculated using a number of equations from the literature (Table 33, equations 4 to 10). The results are tabulated in Table 34 and graphically depicted in Fig. 41, in which it can be seen that the data fits one of two trends. In one, the data from five of the seven equations fit close together with similar slopes while the other two equations (4 and 9) yield results with a similar slope but different from the first five. An average $\text{Log } K_{oc}$ was calculated from the data obtained from the five line grouping (Fig. 41) and is presented in Table 35 along with an average $\text{Log } K_{oc}$ value obtained from the literature (see Table C.3 for a listing of literature values and references) and is plotted in Fig. 42 along with the standard deviation. For comparison purposes, $\text{Log } K_{oc}$ was calculated from literature (The Royal Society of Chemistry, 1983) data for water solubility using equation 1 (Table 33). Along with $\text{Log } K_{oc}$, water solubilities were calculated from the $\text{Log } K_{ow}$ data, Rt data from the $\text{Log } K_{ow}$ determination, and calculated K_{oc} using three equations from the literature (Table 33). The calculated water solubilities for the three equations, 12 to 14, is also included in Table 35. The results of the field and laboratory work will be discussed with respect to these three parameters for the pesticides identified in the tile/ground/leachate water and the soil columns.

The experimentally determined value of $\text{log } K_{ow}$ for trifluralin (Table

Table 32. Results of Pesticide K_{ow} Determination

Compound	Rt' (min)	log K_{ow}		
		quadratic	linear	literature
Bromoxynil	0.594	-0.106	-0.181	0.49 [1a]
Dicamba	0.707	0.271	0.208	0.477 [3]
2,4,5-T Acid	0.932	0.869	0.825	0.845 [3] 0.851 [4] 2.99 [5] 0.602 [6]
Mecoprop	1.016	1.056	1.017	2.83 [5]
MCPA	1.087	1.204	1.169	2.30 [5]
2,4-D Acid	1.241	1.491	1.464	2.81 [1] 2.619 [3] 2.646 [3] 2.810 [3] 2.22 [5] 1.56 [6]
Carbofuran	1.479	1.876	1.858	2.316 [3] 1.60 [6]
Aldicarb	1.466	1.856	1.837	0.699 [3]
Metribuzin	1.704	2.186	2.174	1.39 [1] 1.70 [1]
Atrazine	2.092	2.635	2.631	2.71 [2] 2.326 [3] 2.354 [3] 2.05 [5] 2.17 [6]
Azinphos-methyl	2.218	2.672	2.669	

Table 32. Results of Pesticide K_{ow} Determination (continued....)

Compound	Rt' (min)	log K_{ow}		
		quadratic	linear	literature
Chlorothalonil	2.530	3.052	3.055	
Propanil	2.543	3.063	3.067	2.025 [3]
EPTC	3.405	3.707	3.719	
Disulfoton	3.986	4.055	4.070	
Diclofop-methyl	5.130	4.614	4.634	
Chlorpyrifos	6.037	5.123	5.144	5.04 [2] 3.314 [3] 4.820 [3], [4] 5.110 [3] 4.99 [6]
Trifluralin	6.711	5.212	5.233	5.28 [2] 3.061 [3] 5.34 [6]
Bromoxynil octanoate	9.975	6.097	6.118	
MCPA isooctyl ester	12.995	6.691	6.709	
Zineb	18.947	7.541	7.550	

- [1] Leo et al. (1971)
- [2] McDuffie (1981)
- [3] Rao and Davidson (1981)
- [4] Kenega (1975)
- [5] Braumann et al. (1983)
- [6] Kenega and Goring (1980)

Table 33. Regression equations used for the estimation of K_{oc}

Equation 1	$\log K_{oc} = -0.55 \log S + 3.64$	(S in mg/L)	[1]
Equation 2	$\log K_{oc} = -0.54 \log S + 0.44$	(S in mole fraction)	[1]
Equation 3	$\log K_{oc} = -0.557 \log S + 4.277$	(S in umoles/L)	[1]
Equation 4	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$		[2]
Equation 5	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$		[1]
Equation 6	$\log K_{oc} = 1.00 K_{ow} - 0.21$		[2]
Equation 7	$\log K_{oc} = 0.94 \log K_{ow} + 0.02$		[1]
Equation 8	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$		[1]
Equation 9	$\log K_{oc} = 0.524 \log K_{ow} + 0.855$		[1]
Equation 10	$\ln K_{oc} = \ln K_{ow} - 0.7301$	(converted to log)	[4]
Equation 11	$\log K_{om} = 0.52 \log K_{ow} + 0.62$		[3]
Equation 12	$\log WS = 4.184 - 0.922 \log K_{ow}$		[2]
Equation 13	$\ln WS = -7.618 \ln R_t - 0.01 (MP - 25) + 18.328$		[5]
Equation 14	$\ln WS = -1.7288 \ln K_{oc} - 0.01 (MP - 25) + 15.1621$		[4]

Solubilities for the calculation of K_{oc} for Eq. 1 were taken from from The Agrochemicals Handbook, Royal Society of Chemistry

[1] Lyman (1982), [2] Kenaga and Goring (1980), [3] Briggs (1981),
[4] McCall *et al.* (1983), [5] Swann *et al.* (1983)

Table 34. Calculation of K_{oc} based on Experimental K_{ow}

Pesticide Name	Log K_{oc}							
	Eq. 1	Eq. 4	Eq. 5	Eq. 6	Eq. 7	Eq. 8	Eq. 9	Eq. 10
Bromoxynil	2.48	1.30	-0.14	-0.35	-0.12	-0.33	0.78	-0.46
Dicamba	1.50	1.51	0.22	0.03	0.25	0.07	0.98	-0.08
2,4,5-T Acid	2.30	1.84	0.79	0.64	0.82	0.69	1.30	0.53
Mecoprop	2.10	1.94	0.97	0.83	0.99	0.89	1.40	0.72
MCPA	1.89	2.02	1.11	0.98	1.14	1.04	1.48	0.87
2,4-D Acid	2.11	2.18	1.38	1.27	1.41	1.34	1.63	1.16
Aldicarb	1.56	2.38	1.72	1.64	1.76	1.72	1.82	1.53
Carbofuran	2.17	2.39	1.74	1.66	1.78	1.74	1.83	1.55
Metribuzin	1.94	2.56	2.04	1.97	2.07	2.06	2.00	1.86
Atrazine	2.63	2.81	2.46	2.42	2.50	2.53	2.24	2.32
Azinphos-methyl	2.83	2.83	2.50	2.46	2.53	2.57	2.25	2.35
Chlorothalonil	3.76	3.04	2.86	2.84	2.89	2.96	2.46	2.74
Propanil	2.37	3.04	2.87	2.86	2.90	2.97	2.46	2.75
EPTC	2.22	3.40	3.47	3.50	3.51	3.64	2.80	3.40
Disulfoton	2.87	3.59	3.80	3.85	3.84	4.00	2.98	3.75
Diclofop-methyl	2.71	3.89	4.33	4.41	4.37	4.58	3.28	4.31
Chlorpyrifos	3.47	4.17	4.80	4.92	4.85	5.10	3.55	4.82
Trifluralin	3.64	4.22	4.89	5.01	4.93	5.19	3.59	4.91
Bromoxynil								
Octanoate	4.74	4.70	5.72	5.90	5.76	6.11	4.06	5.79
MCPA Isooctyl								
ester	4.74	5.02	6.27	6.49	6.32	6.71	4.37	6.38
Zineb	3.09	5.48	7.06	7.34	7.11	7.58	4.81	7.23

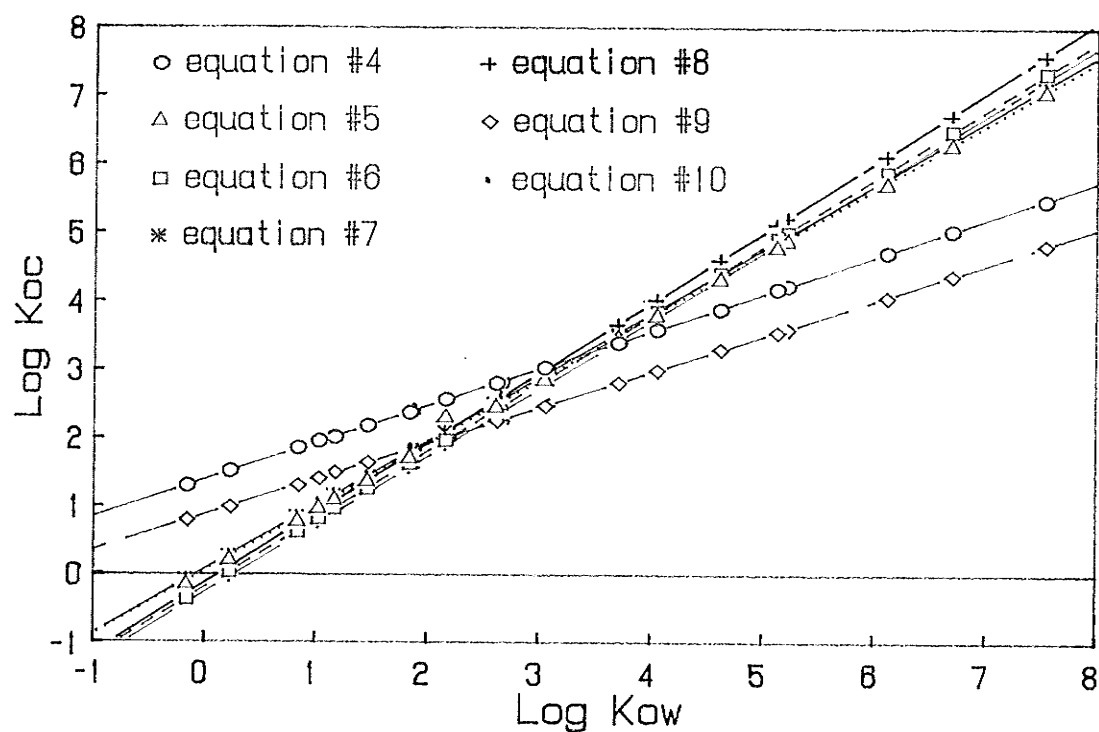


Figure 41. A plot of $\log K_{oc}$ values (calculated from the regression equations in Table 37) versus $\log K_{ow}$.

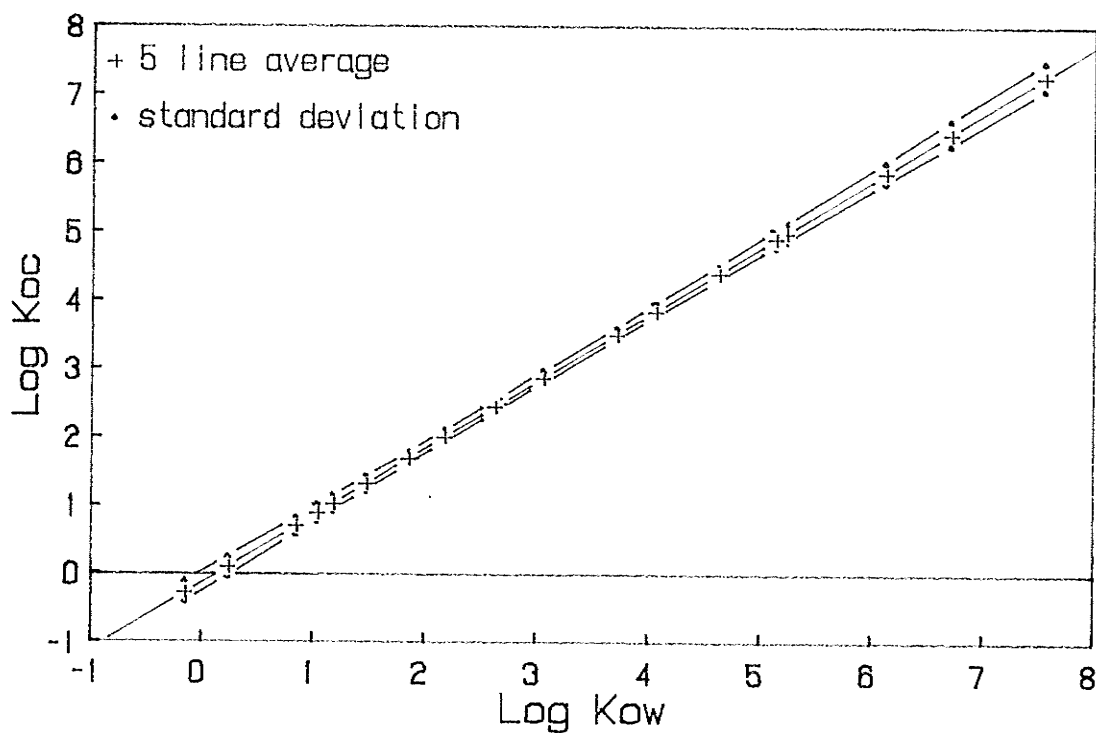


Figure 42. A plot of the five line average K_{oc} versus K_{ow}

Table 35. Environmental parameters calculated from K_{ow}

Pesticide	log K_{ow}	log K_{oc}	log K_{oc}	Water Solubility			
	exp.	calc. ¹	lit. ²	calc. ³ mg/L	calc. ⁴ mg/L	calc. ⁵ mg/L	lit. ⁶ mg/L
Bromoxynil	-0.144	-0.279		2.07E+04	3.67E+04	2.15E+06	130
Dicamba	0.240	0.096	-0.03	9.19E+03	5.72E+04	1.06E+06	7990
2,4,5-T Acid	0.847	0.692	1.81	2.53E+03	1.99E+04	6.65E+04	278
Mecoprop	1.037	0.878		1.69E+03	2.86E+04	5.81E+04	620
MCPA	1.187	1.026		1.23E+03	1.88E+04	2.55E+04	1500
2,4-D Acid	1.478	1.311	1.30	6.63E+02	1.01E+04	6.55E+03	600
Aldicarb	1.847	1.673	1.00	3.03E+02	5.16E+03	1.36E+03	6000
Carbofuran	1.867	1.693	1.46	2.90E+02	8.53E+03	2.15E+03	250-700
Metribuzin	2.180	2.000	1.98	1.49E+02	3.97E+03	4.88E+02	1220
Atrazine	2.633	2.445	2.22	5.71E+01	1.08E+03	5.04E+01	70
Azinphos- methyl	2.671	2.482		5.27E+01	2.81E+03	1.21E+02	30
Chloro- thalonil	3.054	2.857		2.34E+01	2.27E+02	4.63E+00	0.6
Propanil	3.065	2.869		2.28E+01	1.04E+03	2.15E+01	200
EPTC	3.713	3.505	1.92	5.76E+00	6.82E+02	4.31E+00	375
Disulfoton	4.063	3.848	3.22	2.74E+00	3.04E+02	1.10E+00	25
Diclofop- methyl	4.624	4.398		8.33E-01	5.16E+01	8.23E-02	50
Chlorpyrifos	5.134	4.898	3.96	2.82E-01	1.33E+01	1.10E-02	2
Trifluralin	5.223	4.986	4.00	2.34E-01	9.86E+00	7.28E-03	< 1
Bromoxynil Octanoate	6.108	5.854		3.57E-02	8.57E-01	2.37E-04	
MCPA Isooctyl ester	6.700	6.435		1.02E-02	2.37E-01	3.70E-05	
Zineb	7.546	7.265		1.69E-03	1.54E-02	1.36E-06	10

- ¹ - Average value for equations 5, 6, 7, 8, & 10
- ² - Average of literature values where more than one value found, see Table C.2 for references.
- ³ - Equation 12 (Table 33)
- ⁴ - Equation 13 (Table 33)
- ⁵ - Equation 14 (Table 33)
- ⁶ - The Royal Society of Chemistry (1983) (The Agrochemicals Handbook)

32) corresponds to that reported by Kenaga and Goring (1980) and McDuffie (1981) and is higher than the value reported by Rao and Davidson (1981). With a $\log K_{ow}$ value of 5.22 (average of the linear and the quadratic function values) trifluralin would be expected to partition more into the soil organic matter (hydrophobic) than into the hydrophilic portions. Thus, little to no movement would be expected of trifluralin in the soil (McCall et al., 1981). The field study found no detectable levels of trifluralin in the ground water or the tile outflow. The laboratory soil column study found small amounts (1 to 2% of the total amount applied) of trifluralin in the leachate water from the soil columns for all three soil types. This is probably more a function of the amount of water put through each column (5x normal precipitation levels in this area). The average calculated value of $\log K_{oc}$ corresponds to the literature values (Tables 35 and C.3). The magnitude of this partition coefficient also indicates that trifluralin would partition strongly into soil organic matter. The water solubilities calculated for trifluralin (Table 35) are within the range tabulated in the literature (Table C.2) with the value calculated from $\log K_{oc}$ being a little on the low side (two orders of magnitude). With the low water solubility and the high partition coefficients, trifluralin would not be very mobile in the soil. In the Long Plain fine sand the majority of the residues remaining in the soil profile were associated with the surface 10 to 15 cm of the soil where organic matter levels were higher than the rest of the soil profile. In the Skelding fine sand, trifluralin was found to be distributed through out the profile at fairly uniform concentrations except for the lowest layer which had a higher concentration due in part to the higher organic matter content of this lay-

er of soil (buried surface layer). In the silt loam soil with its organic matter rich surface layer no trifluralin was extracted from this surface layer while some was extracted from the depths beneath. This lack of extractable residues may be due to either complete microbial degradation of trifluralin residues held in this layer or that the trifluralin held in this layer is unextractively bound in the organic matter. As stated earlier, the reason why trifluralin was found in the leachate water, as well as distributed through out all of the soil columns (beyond the expected 10 to 20 cms) was due to the large volume of water added to each column. Thus it could be expected that a heavy rainfall shortly after application could possibly carry trifluralin deeper into the soil profile than would normally be the case. However, significant amounts would not be expected to reach ground water, and the amounts that might actually reach ground water would be further diluted in the flow that they would be undetectable.

Chlorpyrifos had an experimentally determined $\log K_{ow}$ which was slightly less than that of trifluralin, with a similarly lower $\log K_{oc}$. Both of the partition coefficients obtained for chlorpyrifos are similar to those reported in the literature (Tables 35 and C.3) while the calculated water solubilities are either an order of magnitude higher or lower. Based on these three chemodynamic properties, chlorpyrifos would be expected to behave similarly to trifluralin as the magnitude of the three parameters is similar between the two compounds. A larger amount of chlorpyrifos (based on percent of amount applied) leached through the soil columns than trifluralin. This may be due to the difference in solubilities, but as the literature values vary so widely it is difficult to definitely conclude that this is the sole reason that a larger

percentage of chlorpyrifos leached through the soil columns. With the partition coefficients being so similar chlorpyrifos would have been expected to leach in about the same time frame as trifluralin, however chlorpyrifos was detected in leachate waters a very short time after application unlike trifluralin. This rapid appearance of chlorpyrifos in the leachate waters is contrary to what both the K_{ow} and K_{oc} parameters suggest should be happening. The time of appearance is similar to that of metribuzin a compound with much lower partition coefficients and a high water solubility. The fact that chlorpyrifos was co-applied with metribuzin to the columns may or may not be a factor at this time for the earlier than expected appearance of chlorpyrifos. In the soils where residues of chlorpyrifos was still present the majority of the residues were in the surface layer as might be expected. In the two fine sand soils there was an unexpected concentration peak in the lower depths of the soil columns which may be related to the K_{ow} and K_{oc} properties of this compound. Under normal field conditions, chlorpyrifos would be expected to remain in the surface horizon of the soil where it would be degraded in a short period of time. However, the column study shows that a large amount of water, a heavy rainfall (5 cms) shortly after application, could leach significant amounts into the subsoil where it may remain for sometime unchanged and be further leached through the soil with similar large influxes of water.

The $\log K_{ow}$ was experimentally found to be 3.71 for EPTC which is more than an order of magnitude lower than the $\log K_{ow}$'s for either trifluralin or chlorpyrifos. As well, the calculated $\log K_{oc}$ was lower by a similar factor but higher than the value in the literature (Tables 35 and C.3). The calculated water solubilities were either less than or

greater than the literature value (Tables 35 and C.2). The lower partition coefficients would suggest that EPTC should move through the soil faster than either of the previous two compounds, and the higher water solubility (literature) would indicate that larger amounts would be leached. The soil column results did show that EPTC moved through the column in greater amounts than either trifluralin or chlorpyrifos and faster than trifluralin but not as fast as the anomalous chlorpyrifos. Remaining residues of EPTC were concentrated in the top 15 cms of the soils except in the Skelding fine sand where they were found lower in the profile, as there was very little organic matter in the upper 60 cms of the soil profile. In addition, there was greater penetration into the soil profile of the silt loam soil. This deeper penetration is probably due to the higher water solubility of EPTC as well as the large amount of water added to the columns, which also carried a significant amount through the soil into the leachate water. Under field conditions, EPTC would not be expected to move appreciably to ground water due to its rapid removal from the soil by degradation and other physico-chemical losses (vaporization). Its soil half-life varies from 4 to 30 days (Table C.2) under field conditions and longer where the soil microbial activity has been reduced. A heavy rainfall after application may carry significant amounts into the subsoil from where it might be subsequently leached to ground water. Its toxicity (LD_{50}) is such that the quantities reaching ground water would not pose a health hazard to mammalian life due to further dilution. In addition, EPTC in field use was only spot applied where needed or in the irrigation water which was noted in the column study to reduce the amounts leached into and through the soil.

Chlorothalonil with an experimental $\log K_{ow}$ of 3.05 and a calculated $\log K_{oc}$ of 2.86 (Tables 32, 34, and 35) would be expected to be more mobile in the soil than any of the previous three compounds discussed. The low water solubility (literature) would indicate that lower amounts of chlorothalonil would be leached through the soil. The calculated water solubilities (Table 35) were all much higher than the literature value (one to two orders of magnitude). The leaching velocity on the soil columns appears to conform to the expectations based on the lower partition coefficients. In addition, the amounts leached through the soil columns were similar to those of trifluralin (similar solubilities) and lower than either chlorpyrifos or EPTC. In the field, chlorothalonil was detected both in the tile outflow water (at low ppb levels) and in the ground water beneath a field (at slightly higher levels) treated with chlorothalonil, both in the year of treatment and in the following year (at lower levels). Based on the findings from field water monitoring work and the partition coefficients of these four compounds, the first two, trifluralin and chlorpyrifos would be virtually immobile under field conditions, while EPTC would be slightly mobile with possibly trace amounts leaching to ground water under favourable conditions.

Diclofop-methyl's experimental $\log K_{ow}$ and calculated $\log K_{oc}$ were higher than for chlorothalonil which was evidenced in the soil column work by a longer transit time through the soil columns. The higher water solubility caused a greater amount to leach through and into the soil profile. The calculated water solubilities were much lower in two cases (Table 35) than the literature values while the third agreed quite closely. The larger partition coefficients and the soil column results indicate a slower movement of diclofop-methyl through the soil in com-

parison to chlorothalonil which would enable greater microbial activity on both it and the free acid. Therefore, diclofop-methyl would not be expected to leach through the soil to any great degree under normal field conditions.

Of the applied compounds, carbofuran had the lowest experimental $\log K_{ow}$ and calculated $\log K_{oc}$ (Tables 32, 34 and 35) of the eight compounds applied to the soil columns. In addition, the water solubility was high in comparison to the previous compounds (second highest of the eight compounds). The experimental $\log K_{ow}$ fell within the range recorded in the literature and the $\log K_{oc}$ agreed closely with the literature values. The calculated water solubility based on $\log K_{ow}$ was within the literature range while the other two calculations were an order of magnitude greater. With a $\log K_{ow}$ of 1.87, a $\log K_{oc}$ of 1.69 and a water solubility of 250 to 700 mg/L, carbofuran would be expected to leach through the soil faster than chlorothalonil and in larger quantities. The soil column study found that carbofuran leached through the soil columns at a much slower rate than what was expected, and the quantities leached through the fine sand soil were less than expected. In the silt loam the amounts leached were also less than what might have been expected based on the differences in water solubilities. This behaviour was also observed in the field results which leads to the consideration that there is another parameter in the soil which is affecting (retarding) the leaching of carbofuran. This slowing down of the leaching of carbofuran would also cause greater exposure to degradative activity which would reduce the amounts of carbofuran being leached both in the field and in the column study. The amounts actually leached in the column study were similar to the amounts leached for diclofop-methyl a com-

pound with a much lower water solubility and higher partition coefficients. The field work only detected carbofuran in the ground water under a field where it had been applied (both in the year of application and the following year at lower levels) in one of two wells. No carbofuran residues were detected in the outflow water from the tile system which may indicate that the carbofuran present in the ground water is either diluted below detectable amounts or that it is degraded before the water enters the municipal ditch.

Metribuzin's experimental $\log K_{ow}$ of 2.18 and calculated $\log K_{oc}$ of 2.00 were slightly greater than the values obtained for carbofuran and substantially lower than those for chlorothalonil. The experimental $\log K_{ow}$ determined for metribuzin is higher than the value in the literature (Table 32) while the calculated $\log K_{oc}$ is comparable to the literature value (Table 35). The calculated water solubilities bracket the literature value (Table 35) with no one equation giving a good agreement to the literature value. Based on the partition coefficients obtained for metribuzin it would be expected that this compound would leach through the soil fairly rapidly in comparison to chlorothalonil or trifluralin. In actual observations from the soil column study, metribuzin did leach through the soil fairly quickly, though not as rapidly as was expected in comparison to some of the compounds with higher partition coefficients. The literature water solubility of metribuzin (1220 mg/L) was the highest solubility of the compounds applied to the soil columns thus it would have been expected that the amounts leached through to the leachate water would be the highest. In actuality the amounts of metribuzin leached through the columns were very low, generally less than 0.1% of the total amount applied, except in the case of the two older fine sand

columns where between 4 to 6% of the total amount applied was leached through the columns. In all cases no residues were extracted from the soil profile. The lower than expected amounts recovered from the leachate water was attributed to rapid microbial degradation in the soil as was evidenced by the higher amount recovered from the older columns where microbial activity was reduced by a period of storage (drying of the column below natural field levels). Under normal precipitation levels in the field the amount of metribuzin actually leaching into the subsoil would be very low due to its rapid metabolism by soil microbes. Thus metribuzin would not be expected to leach through the soil profile, in the field, into ground water under any condition.

Bromoxynil Octanoate had a high $\log K_{ow}$ (6.11) which was expected due to the octanoate portion of the molecule. The calculated $\log K_{oc}$ was correspondingly high (5.85), as a result this molecule was expected to be very immobile on the soil column partitioning strongly into the soil organic matter. The free acid, bromoxynil, on the other hand had a very low $\log K_{ow}$ (-0.14) and a correspondingly low $\log K_{oc}$ (-0.28) which would indicate that the free acid would be very mobile (susceptible to leaching) in the soil profile. The calculated water solubilities were all very high in comparison to the literature values which would indicate that all three equations can not handle hydrophilic compounds adequately. The octanoate hydrolyses in the soil rapidly into the free acid under moist conditions thus only the free acid was expected to leach through the soil, quite rapidly as indicated by the partition coefficients and in large quantities (water solubility). The column results did not confirm these expectations for one of the fine sand soils. Only a trace amount leached through one of the Long Plain soil columns

and no residues were recovered from the soil profile of this fine sand soil as well as from the silt loam soil. The amount that leached through the silt loam soil was slightly larger than what was recovered from the Long Plain leachate water but still not in the amounts expected. The amount leached through the Skelding fine sand was again low, but there were substantial amounts distributed through the lower portion of the profile in both columns with the higher amount in the distilled water treated column in the bottom layer which had the highest organic matter content of any portion of these soil columns. The extremely low value of both of the partition coefficients would indicate that the free acid should be leached quickly through the columns but this does not seem to be the case as there were substantial amounts retained in the Skelding fine sand and little to no residues leached through or retained in either of the other two soils. This rapid disappearance of bromoxynil would indicate that under field conditions bromoxynil, regardless whether applied as the octanoate or the free acid would not persist long enough in the soil to leach to ground water in the major soils from this area. In the fine sand in which persistence was noted, distance to ground water would be a major inhibiting factor as well as the buried organic layer which seems to act as a filter in these soils.

CONCLUSION

The fungicide, chlorothalonil, was detected in the tile water outflowing into the municipal ditch on a total of 4 days during 1982 from each of the gravity outflows at the NE corner, and once in the outflow water from the sumpwell tile system. The maximum concentration observed in the outflow water was 3.66 ug/L which is well below both the Canadian Drinking Water Guides (100 ug/L) for maximum allowable amounts of pesticides and the the U.S. E.P.A. recommended maximum contaminant level (36 ug/L). Overall the amounts observed in the outflow water were below 1 ug/L and did not appear to affect the plant growth in or along the ditch. The appearance of detectable amounts of chlorothalonil in the tile outflow appeared to be a function of the input water (water balance), in this instance the rainfall, as the peak pattern seemed to follow the precipitation pattern which created periods where there was a large positive water balance in 1982.

Ground water sampled from one of two standpipe wells in 10-11-7NW was found to contain chlorothalonil and carbofuran in 1982 and chlorothalonil, carbofuran and 2,4-D in 1983 from one of the wells. Ground water sampled from the other well was found to contain chlorothalonil and 2,4-D in 1983. The amount of chlorothalonil detected in the ground water in 1982 was two orders of magnitude greater than the maximum observed in the ground water outflowing from the tile system. Concentrations of chlorothalonil ranged from 10 to 272 ug/L and seemed to fluctuate almost on a daily basis. In 1983 these concentrations were greatly reduced (by a factor of 100) as there was no input into this field of chlorothalonil. The carbofuran concentration range also was reduced in level bet-

ween the two years falling from 11.5 to 158 ug/L to 0.4 to 1.0 ug/L. Both compounds were found to follow the same rise and fall pattern in concentration levels indicating a common influencing factor in the environment. The concentration levels were greatly reduced in 1983 when there was no new input of carbofuran to this field. A third pesticide was detected in the ground water sampled from under this field in 1983. 2,4-D applied to this field in the first part of June appeared in the ground water sporadically in both wells from August through October. The combined concentrations of the pesticides detected in the ground water from the wells in 1982 were well above both of the limits set by Canada and the United States. However, the low levels found in the out-flow water indicates that there is a considerable amount of dilution occurring which reduces these levels well below the limits. The observed rise and fall of the pesticide levels appeared to follow the precipitation pattern (water balance) and appeared not be affected to any great degree by the irrigation input water. The only contributing factor to the water balance which varied markedly from 1982 to 1983 was the precipitation for the area, which was much less in 1983 creating a negative water balance for much of the growing season.

The soil column leaching study using 8 pesticides: trifluralin, chlorpyrifos, EPTC, chlorothalonil, diclofop-methyl, carbofuran, metribuzin and bromoxynil octanoate found that all of the pesticides would leach through the three soils; two fine sands and a silt loam. Even those compounds which are considered to be relatively immobile (i.e., trifluralin) were found to leach in small quantities through the soil as well as deeper into the soil profile than had been previously reported. This apparent leaching ability appeared to be more a function of the a-

mount of water added to the column than to the the compounds ability to leach. Distilled water (the equivalent of rain water) was found to have a greater leaching effect on all eight compounds than river water (irrigation water). Thus, it was concluded that the peak concentrations of pesticides detected in the ground water from 10-11-7 both from the tile outflow as well as the standpipe wells are due to the leaching of these compounds through the soil by precipitation. And, that the river water added via the irrigation system has little to no effect on the leaching of any of the applied pesticides on this farm site. Under field precipitation conditions, trifluralin, chlorpyrifos, diclofop-methyl would not move out of the top 20 cm of soil with an organic matter content greater than 1%. In a soil with very little organic matter these compounds may penetrate deeper into the profile. EPTC, chlorothalonil, carbofuran, metribuzin and bromoxynil all appear to have the ability to leach readily through the soil; however, the soil's degradative ability may limit the amounts leached. Of these five compounds only chlorothalonil and carbofuran were detected in the ground water.

Based on the field and laboratory (soil column leaching) results, the following observations were made. $\log K_{ow}$ and $\log K_{oc}$ give an indication of the leachability of a compound, i.e., the higher the value of K_{ow} and K_{oc} the less leachable the compound will or it will leach but will take a longer time to do so and may require more water to flow through the soil. A number of the pesticides examined were anomalous in their behaviour, chlorpyrifos which based on the partition coefficient should have had limited leaching, leached readily. Carbofuran which was expected to leach readily was slower than expected. In addition, the compound's water solubility determined how much of the compound leached

through the soil while the soil microbial activity level determined the amount which was available for leaching. A reduced microbial activity level enabled greater amounts to leach through the soil.

Based on the results of this study the following conclusions were reached:

- 1) pesticides with a log Kow of 3.0 and below have a greater potential to leach in these soils under field conditions than pesticides with log Kow's greater than 3.0
- 2) the actual movement in the soil may be influenced by factors other than partitioning with the soil organic matter (as was shown in the case of carbofuran and chlorpyrifos)
- 3) the water solubility of the compound will determine how much will be available to leach
- 4) the microbial activity level of the soil will actually determine what amount of the chemical available in 2) will actually leach to the subsoil. In that, a compound with a low partition coefficient and a high water solubility which would favour rapid transport of large amounts, may have only a small percentage of the amount applied actually reaching the subsoil due to the level of microbial activity.
- 5) river water added as irrigation does not increase the amount leached through the soil; however, the amounts leached into and retained in the soil may be higher for some compounds.
- 6) precipitation in the form of rain is the main impetus for leaching. Normal precipitation levels (<20 mm) appear to have little effect on leaching. Higher amounts are required to carry the residues through the surface soil layer into the subsoil. Chlorothalonil concentration maxima appeared in tile outflow after heavy rainfalls (>50 mm).

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APPENDIX A

Soil Analysis

Particle Size Analysis - Pipette Method

Two subsamples of each soil horizon were weighed (ca. 10 grams) into 400 mL beakers, 25 ml of distilled water was added, followed by 25 mL of 30% hydrogen peroxide, in 5 mL increments. Once the frothing had ceased (about 2 hours) the samples were heated gently to decompose any residual organic matter and to remove any remaining peroxide. The sample was allowed to cool to room temperature, then the contents of the beaker was quantitatively transferred into the metal container of a mechanical stirrer, volume was brought up to about 300 mL with distilled water and 10 mL of Calgon dispersing agent was added, then the sample was stirred for 15 minutes.

The sample was allowed to settle for 10-15 seconds then, was filtered through a 270 mesh sieve into a 1000 mL cylinder, the sand in the metal container was washed with 5x100 mL portions of distilled water with the washings passed through the sieve. The remaining sand was washed onto the sieve and any remaining silt and clay was washed through the sieve using a stream of distilled water. The volume of the cylinder was made up to the 1000 mL mark and then it was placed in the water bath (30°C) and allowed to come to thermal equilibrium.

The sand remaining on the sieve was washed back into a 400 mL beaker and dried at 105°C and then weighed to determine the sand portion of the soil.

Once the cylinder with the silt and clay portions of the soil had thermally equilibrated, it was stirred for 1 minute to evenly distribute the silt and clay particles throughout the column. Upon cessation of stirring a 25 mL aliquot was taken from the 10 cm depth and placed in

a pre-weighed 50 ml beaker, the pipette was rinsed into the beaker to dislodge any adhering particles. This 25 mL sample was dried at 105°C and the silt and clay portion of the soil was determined.

After the appropriate settling time for 2 micron particles (6 hrs 20 min at 30°C) a second 25 aliquot was taken from the 10 cm depth and treated as before. From this second aliquot the clay content was determined and by difference the silt content was calculated. The weight of the Calgon dispersent added was determined and it was taken into account in the determination of the soil fraction.

Data and results for the three soils analyzed are presented in the following three tables.

Table A.1 Data and Results for the Particle Size Determination of a Long Plain Loamy Fine Sand

	Ap Horizon		C Horizon	
BEAKER #	1	2	3	4
EMPTY	135.04020	134.73436	143.51184	140.92267
with soil	149.71044	144.48340	153.75686	150.99316
NET SOIL	14.67024	9.74904	10.24502	10.07049
BEAKER #	1a	2a	3a	4a
EMPTY	36.41213	26.59427	28.14848	30.48592
i silt/clay	36.44791	26.62156	28.16897	30.50740
NET SILT/CLAY*	0.02494	0.01645	0.00965	0.01064
BEAKER #	1b	2b	3b	4b
EMPTY	28.04585	27.89655	26.19295	30.79018
with clay	28.06803	27.91549	26.20813	30.80545
NET CLAY*	0.01134	0.00810	0.00434	0.00443
BEAKER #	1	2	3	4
with sand	148.36684	143.64868	153.27553	150.52742
NET SAND	13.32664	8.91432	9.76369	9.60475
NET SILT()	0.54400	0.33400	0.21240	0.24840
NET CLAY()	0.45364	0.32404	0.17364	0.17724
% SAND	93.04	93.12	96.20	95.76
% SILT	3.79	3.49	2.09	2.47
% CLAY	3.17	3.39	1.71	1.77
% ORGANIC MATTER	2.36	1.81	0.93	0.40

* - corrected for the Calgon dispersant

() - corrected for total volume (25 mL to 1000 mL)

Table A.2 Data and Results for the Particle Size Determination of a Skelding Fine Sand

	Ap Horizon		C Horizon	
BEAKER #	5	6	7	8
EMPTY	125.51495	127.65040	132.47743	130.18511
with soil	136.05333	138.59155	143.20979	140.90560
NET SOIL	10.53838	10.94115	10.73236	10.72049
BEAKER #	5a	6a	7a	8a
EMPTY	27.15375	38.44833	27.57592	28.11079
i silt/clay	27.16974	38.46449	27.60279	28.13688
NET SILT/CLAY*	0.00515	0.00532	0.01603	0.01525
BEAKER #	5b	6b	7b	8b
EMPTY	26.36385	27.97724	29.23269	28.92351
with clay	26.37843	27.99162	29.25152	28.94208
NET CLAY*	0.00374	0.00354	0.00799	0.00773
BEAKER #	5	6	7	8
with sand	135.79249	138.29689	142.39338	140.10092
NET SAND	10.27754	10.64649	9.91595	9.91581
NET SILT()	0.05640	0.07120	0.32160	0.30080
NET CLAY()	0.14964	0.14164	0.31964	0.30924
% SAND	98.03	98.04	93.93	94.20
% SILT	0.54	0.66	3.05	2.86
% CLAY	1.43	1.30	3.02	2.94
% ORGANIC MATTER	0.52	0.75	1.63	1.82

* - corrected for the Calgon dispersant

() - corrected for total volume (25 mL to 1000 mL)

Table A.3 Data and Results for the Particle Size Determination of a St. Claude Silt Loam

	Ap Horizon		C Horizon	
BEAKER #	9	10	11	12
EMPTY	147.99252	143.30352	133.33005	141.62756
with soil	158.39960	153.96737	146.21797	153.74808
NET SOIL	10.40708	10.63217	12.88792	12.12052
BEAKER #	9a	10a	11a	12a
EMPTY	37.01499	28.60416	27.47097	37.98263
i silt/clay	37.15052	28.74776	27.65861	38.15298
NET SILT/CLAY*	0.12469	0.13276	0.17680	0.15951
BEAKER #	9b	10b	11b	12b
EMPTY	29.05526	28.24267	28.25525	27.27188
with clay	29.09760	28.29821	28.34217	27.35484
NET CLAY*	0.03150	0.04470	0.07608	0.07212
BEAKER #	9	10	11	12
with sand	153.08933	148.33534	138.99566	147.22455
NET SAND	5.09681	5.03182	5.66561	5.59699
NET SILT()	3.72760	3.52240	4.02880	3.49560
NET CLAY()	1.26004	1.78804	3.04324	2.88484
% SAND	50.54	48.65	44.48	46.73
% SILT	36.96	34.06	31.63	29.18
% CLAY	12.50	17.29	23.89	24.09
%ORGANIC MATTER	3.10	2.73	1.17	1.18

* - corrected for the Calgon dispersant

() - corrected for total volume (25 mL to 1000 mL)

APPENDIX B

Soil Column Pesticide Application and Irrigation Data

Column Description and Use

The eight soil columns were set up in a wooden stand such that the leachate from the base of the column would be collected in a 100 mL volumetric flask. Columns 1, 2, 3, and 4 were representative of the Long Plain loamy fine sand, columns 5 and 6 were representative of the Skelding fine sand, and columns 7 and 8 were representative of the St. Claude silt loam. Columns 1, 3, 5, and 7 were irrigated with natural Assiniboine river water. Columns 2, 4, 6, and 8 were irrigated with triple-distilled water (rain). The eight pesticides to be applied were made up in acetone solution (Table B1). For application, 1 mL of the acetone stock solution was mixed with the irrigation water and then applied to the head of the column.

Table B.1 *Irrigation Pesticide Data*

Pesticide	Concentration	Number of Applications	Total Amount Applied (ug)
EPTC	1003.6 ppm	2	2007.2
Chlorpyrifos	242.4 ppm	2	484.8
Metribuzin	296.2 ppm	2	592.4
Chlorothalonil	225.2 ppm	4	900.8
Diclofop-methyl	116.4 ppm	2	236.8
Trifluralin	110.0 ppm	2	220.0
Bromoxynil Octanoate	69.2 ppm	2	138.4
Carbofuran	54.4 ppm	3	163.2

Table B.2 Irrigation and Pesticide Application Schedule

Date	Quantity	Pesticide	Date	Quantity	Pesticide
05/07/84	2 x 50 mL		07/16/84	1 x 50 mL	
05/08/84	2 x 50 mL		07/17/84	1 x 50 mL	
05/09/84	1 x 50 mL		08/17/84	1 x 100 mL	
05/10/84	1 x 50 mL		08/20/84	2 x 50 mL	
05/13/84	1 x 25 mL		08/22/84	2 x 50 mL	
05/14/84	1 x 25 mL		08/23/84	1 x 100 mL	
05/15/84	1 x 25 mL		08/27/84	3 x 25 mL + 1 mL #5	
05/16/84	1 x 25 mL		08/28/84	3 x 25 mL	
05/22/84	1 x 25 mL		08/29/84	1 x 25 mL	
05/23/84	1 x 25 mL		08/30/84	1 x 25 mL	
05/24/84	1 x 25 mL		08/31/84	2 x 25 mL + 1 mL #5	
05/25/84	1 x 25 mL		09/01/84	1 x 25 mL	
05/28/84	1 x 25 mL + 1 mL #1		09/02/84	1 x 25 mL	
05/29/84	1 x 25 mL		09/03/84	1 x 25 mL	
05/30/84	1 x 25 mL		09/04/84	1 x 25 mL	
05/31/84	1 x 25 mL		09/05/84	1 x 25 mL	
06/01/84	1 x 25 mL		09/06/84	1 x 25 mL	
06/03/84	1 x 25 mL + 1 mL #1		09/07/84	1 x 50 mL	
06/04/84	1 x 25 mL		09/10/84	1 x 50 mL	
06/05/84	1 x 25 mL		09/11/84	2 x 25 mL + 1 mL #6	
06/06/84	1 x 25 mL		09/12/84	1 x 25 mL	
06/07/84	1 x 25 mL		09/13/84	1 x 25 mL	
06/08/84	1 x 25 mL		09/14/84	1 x 25 mL	
06/10/84	1 x 25 mL		09/17/84	1 x 50 mL	
06/11/84	1 x 25 mL		09/18/84	2 x 25 mL + 1 mL #6	
06/12/84	1 x 25 mL + 1 mL #2 & 3		09/19/84	1 x 25 mL	
06/13/84	1 x 25 mL		09/20/84	1 x 25 mL	
06/14/84	1 x 25 mL		09/22/84	2 x 25 mL	
06/15/84	1 x 25 mL + 1 mL #2 & 3		09/23/84	1 x 25 mL	
06/16/84	1 x 25 mL		09/24/84	1 x 25 mL	
06/18/84	1 x 25 mL		09/25/84	1 x 25 mL	
06/19/84	1 x 25 mL		09/27/84	1 x 50 mL	
06/20/84	1 x 25 mL		10/01/84	1 x 75 mL	
06/21/84	3 x 25 mL + 1 mL #4		10/02/84	1 x 50 mL	
06/22/84	1 x 25 mL		10/03/84	1 x 25 mL	
06/25/84	1 x 25 mL		10/05/84	2 x 25 mL + 1 mL #7	
06/26/84	1 x 25 mL		10/06/84	1 x 25 mL	
06/27/84	1 x 25 mL + 1 mL #4		10/07/84	1 x 25 mL	
06/28/84	1 x 25 mL		10/08/84	1 x 25 mL	
06/29/84	1 x 25 mL		10/09/84	1 x 25 mL	
07/03/84	2 x 25 mL + 1 mL #4		10/10/84	1 x 25 mL	
07/04/84	1 x 25 mL		10/11/84	1 x 25 mL + 1 mL #7	
07/05/84	1 x 25 mL		10/12/84	1 x 25 mL	
07/06/84	1 x 25 mL		10/13/84	1 x 25 mL	
07/08/84	1 x 25 mL		10/16/84	1 x 50 mL	
07/09/84	1 x 25 mL		10/29/84	1 x 100 mL	
07/10/84	1 x 25 mL		10/30/84	1 x 50 mL	
07/12/84	1 x 50 mL		11/12/84	1 x 50 mL	
07/13/84	1 x 25 mL		11/15/84	1 x 25 mL	
07/14/84	1 x 25 mL		11/16/84	1 x 50 mL	

Table B.2 Irrigation and Pesticide Application Schedule (continued ...)

Date	Quantity	Pesticide	Date	Quantity	Pesticide
11/19/84	1 x 25 mL		01/09/85	1 x 25 mL	
11/20/84	2 x 25 mL + 1 mL #8		01/11/85	1 x 25 mL	
11/21/84	1 x 25 mL		01/12/85	1 x 25 mL	
11/22/84	1 x 25 mL		01/14/85	1 x 25 mL	
11/23/84	1 x 25 mL		01/16/85	1 x 25 mL	
11/26/84	1 x 25 mL		01/17/85	1 x 25 mL	
11/27/84	1 x 25 mL		01/19/85	1 x 25 mL	
11/28/84	1 x 25 mL		01/21/85	1 x 25 mL	
11/29/84	1 x 25 mL		01/22/85	1 x 25 mL	
12/03/84	2 x 25 mL + 1 mL #8		01/24/85	1 x 25 mL	
12/04/84	1 x 25 mL		01/25/85	1 x 25 mL	
12/05/84	1 x 25 mL		01/26/85	1 x 25 mL	
12/06/84	1 x 25 mL		01/29/85	1 x 25 mL	
12/07/84	1 x 25 mL		01/30/85	1 x 25 mL	
12/08/84	1 x 25 mL		01/31/85	1 x 25 mL	
12/09/84	1 x 25 mL		02/01/85	1 x 25 mL	
12/10/84	1 x 25 mL		02/03/85	1 x 25 mL	
12/11/84	1 x 25 mL		02/05/85	1 x 25 mL	
12/12/84	1 x 25 mL		02/06/85	1 x 25 mL	
12/13/84	1 x 25 mL		02/07/85	1 x 25 mL	
12/14/84	1 x 25 mL		02/08/85	1 x 25 mL	
12/17/84	1 x 25 mL		02/11/85	1 x 25 mL	
12/18/84	1 x 25 mL		02/12/85	1 x 25 mL	
12/19/84	1 x 25 mL		02/13/85	1 x 25 mL	
12/20/84	1 x 25 mL		02/19/85	1 x 50 mL	
12/21/84	1 x 100 mL		02/20/85	1 x 25 mL	
12/22/84	1 x 25 mL		02/21/85	1 x 25 mL	
12/24/84	1 x 25 mL		02/22/85	1 x 25 mL	
12/26/84	1 x 25 mL		02/25/85	1 x 25 mL	
12/27/84	2 x 50 mL		02/27/85	1 x 25 mL	
12/28/84	1 x 25 mL		03/01/85	1 x 25 mL	
01/02/85	4 x 25 mL		03/05/85	1 x 25 mL	
01/03/85	1 x 25 mL		03/07/85	1 x 50 mL	
01/05/85	1 x 25 mL + 1 mL #4 & 8		05/01/85	1 x 100 mL	
01/06/85	1 x 25 mL		05/10/85	1 x 100 mL	
01/08/85	1 x 25 mL		05/16/85	1 x 100 mL	

#1 - EPTC	#2 - Chlorpyrifos	#3 - Metribuzin
#4 - Chlorothalonil	#5 - Diclofop-methyl	#6 - Trifluralin
#7 - Bromoxynil Octanoate		#8 - Carbofuran

APPENDIX C

Additional Pesticide Data

Table C.1 Pesticide Toxicological Data

TRADE NAME	COMMON/CHEMICAL NAME	LD50
Eptam	EPTC / S-Ethyl dipropylthiocarbamate	1631 mg/kg rats
Eradicaine	EPTC plus a crop protectant	"
Lorsban	Clorpyrifos / O,O-diethyl-O(3,5,6-trichloro-2-pyridyl)phosphorothioate	135-163 mg/kg rats
Atrazine	Atrazine / 2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine	1869 mg/kg rats
Pardner	Bromoxynil / 3,5-Dibromo-4-hydroxybenzo-nitrile	190 mg/kg rats
Hoegrass	Diclofop-methyl / 2-[4-(2,4-dichloro-phenoxy)phenoxy]propionic acid	563 mg/kg rat(F)
Banvel	Dicamba / 2-Methoxy-3,6-dichloro-benzoic acid	2900 mg/kg rats
Lexone	Metribuzin / 4-Amino-6-(1,1-dimethyl-ethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one.	2200 mg/kg rats
Bravo	Chlorothalonil / Tetrachloroisophthalo-nitrile	>10,000 mg/kg rats
Furadan	Carbofuran / 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate	10 mg/kg rats
Temik	Aldicarb / 2-Methyl-2-(methylthio)-propionaldehyde O-(methylcarbamoyl)oxime	10 mg/kg rats 10% formulation
Disyston	Disulfoton / O,O-Diethyl S-2(ethylthio)-ethyl phosphorodithioate	12.5 mg/kg rat (M)
Aatrex plus	Atrazine + petroleum oil	
Sencor	Metribuzin (see Lexone)	
Stampede	Propanil / 3,4-dichloropropionanilide	1400 mg/kg rats
Guthion	Azinphos-methyl / O,O-Dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl]phosphorodithioate.	16.4 mg/kg rat (F)
Sweep	Paraquat / 1,1'-Dimethyl-4,4'-bipyridinium ion	150 mg/kg dichloride in rats

Table C.1 Pesticide Toxicological Data (continued...)

TRADE NAME	COMMON/CHEMICAL NAME	LD50
Buctril M	Bromoxynil Octanoate / 2,6-Dibromo-4-cyanophenyl octanoate MCPA Ester / 4-Chloro-2-methylphenoxy-acetic acid ester	420 mg/kg rats 700 mg/kg
Treflan	Trifluralin / 2,6-Dinitro-N,N-dipropyl-4-trifluoromethylaniline	>10,000 mg/kg rats
Dithane M45	Mancozeb / [(1,2-Ethanediybis(carbamodithioato))(2 ⁻)]manganese mixture with [(1,2-ethanediybis(carbamodithioato))(2 ⁻)]zinc	>8,000 mg/kg rats
Polyram	Metiram / Tris(amine(ethylenebis(dithiocarbamato)))zinc (2+)) (tetrahydro-1,2,4,7-dithiadiazocine-3,8-dithione), polymer	>10,000 mg/kg rats
Decis	Decamethrin / (S)- -Cyano-3-phenoxybenzyl (IR)-cis-3-(2,2-dibromovinyl)-2,2-dimethyl-cyclopropanecarboxylate	135 mg/kg for rats
Torch	see Buctril M	
Amsol 80	2,4-D / 2,4-Dichlorophenoxyacetic acid	375 mg/kg for rats

Table C.2 Physical Properties of Monitored Pesticides

Name	Ionization Constant (pK _a)	Water Solubility (mg/L)	Vapour Pressure (mPa @ 20-25°C)	Reference
Aldicarb	nonionic	6000	13	[3],[4], [5]
		0.017	6650	[6]
		6000		[15]
		9000	13	[17]
Atrazine	1.7	35	0.04	[1]
		33-70		[2]
		70	0.04	[3],[5]
	1.7	30	0.04	[4]
		33	0.04	[6]
		33		[8]
	1.7	33	0.04	[10]
		32	0.04	[17]
Azinphos-methyl		33		[2],[5]
		30	< 1	[3]
		33	< 1	[4]
		33	< 5	[6]
		29		[8]
		30		[15]
Bromoxynil		130	< 1	[3]
	4.06	130		[4],[5], [6]
	4.08	130		[13]
Bromoxynil Octa.		insol.		[3],[5], [6]
Carbofuran	nonionic	700	2.7	[1],[4], [5],[6]
		415-700		[2]
		250-700	2.6	[3]
		700		[8]
		320	2.7	[17]
Chlorothalonil		0.6	1300 (40°)	[3],[4], [5],[6]
		0.6		[8]

Table C.2 Physical Properties of Monitored Pesticides (continued...)

Name	Ionization Constant (pK _a)	Water Solubility (ppm)	Vapour Pressure (mPa @ 20-25°C)	Reference
Chlorpyrifos		2 2 0.4 2	2.4-2.5 2.49 2.5	[2],[8] [3],[4], [5],[6] [7] [17]
2,4-D salt	2.8	650	1.1	[1]
2,4-D acid		620-900 600 620 al.insol. 620 890 600 50-900 900	< 0.01 5300 (160°) 0.08	[2] [3] [4] [5] [6] [7] [8] [9] [17]
Decamethrin/ deltamethrin		< 0.1 < 0.002	0.002 0.002	[3] [4],[5]
Dicamba	1.9	4550 4500-7900 7990 6500 v.sl.sol. v.sl.sol. 4500	< 13 500 (100°) 4.5 500 (100°) 498.75	[1] [2] [3] [4] [5] [6] [13]
Diclofop-methyl		50 3 3	0.034 0.0344 0.399	[3] [4],[5] [6]
Disulfoton		15-66 25 insol. 25	24 24	[2] [3],[4], [6],[17] [5] [8]

Table C.2 *Physical Properties of Monitored Pesticides (continued...)*

Name	Ionization Constant (pK _a)	Water Solubility (ppm)	Vapour Pressure (mPa @ 20-25°C)	Reference
EPTC		370-375 375 365 365 375 370	4500-4700 4522 20,600 4540 4500	[2] [3],[4], [6] [5] [8] [11] [16] [17]
Mancozeb		v.sl.sol. insol.	< 1	[3],[4] [6]
MCPA	3.07 2.90/3.40	825 1500 825 insol. 550-1600	non-volatile 0.2	[2],[8] [3] [4] [5],[6] [9]
Mecoprop		620 v.sl.sol. 620	< 0.01	[3],[4] [6] [8]
Metiram		insol.	< 0.01	[3],[4], [6]
Metribuzin	1.1	1220 1220 1200	< 0.13 < 1 < 1.3	[1] [3],[6] [4],[5]
Paraquat dichloride		sol.	< 0.01	[3],[4],[5], [6],[8]
Propanil		268-500 200 225 130 500	12 12 (60°) 12 (60°)	[2] [3] [4],[5] [6] [14]
2,4,5-T salt	2.8	238	< 0.13	[1],[5]

Table C.2 *Physical Properties of Monitored Pesticides (continued...)*

Name	Ionization Constant (pK _a)	Water Solubility (ppm)	Vapour Pressure (mPa @ 20-25°C)	Reference
2,4,5-T	3.14/3.46	238-280		[2]
		278	< 0.01	[3],[6]
		150	0.0007	[4]
		280	< 0.859	[7]
		278		[8]
		200-280		[9]
Trifluralin	nonionic	0.05	2.9	[1]
		0.05-24		[2]
		< 1	26	[3]
		< 1	13.7	[4]
		24		[5]
		4	26.5	[6]
		< 1		[8]
		0.1-0.3	26.5	[12]
			32.2	[16]
Zineb		0.3	14	[17]
		10	< 0.01	[3],[4],
		insol.		[6] [5]

[1] Weber et al. (1981), [2] Willis & McDowell (1982), [3] Royal Society of Chemistry (1983), [4] British Crop Protection Council (1983), [5] Merck & Co., Inc. (1983), [6] Agriculture Canada Research Branch (1982), [7] Kenega (1975), [8] U.S. Environmental Protection Agency (1982), [9] Loos (1975), [10] Esser et al. (1975), [11] Fang (1975), [12] Probst et al. (1975), [13] Frear (1975), [14] Still and Herrett (1975), [15] Matsumura (1975), [16] Nash (1983), [17] Rao et al. (1985)

Aldicarb: is a soil-applied systemic pesticide that has demonstrated excellent control of many species of insects, mites and nematodes attacking plants. Seed furrow, band or overall treatments (either pre-plant or at planting) as well as post-emergence sidedress treatments are used. Soil moisture is required to release the active chemical from the granules, so irrigation or rainfall should follow application. Uptake by the roots is rapid and residual protection against various sucking and piercing pests lasts from 70 to 84 days in many cases. Mode of action is inhibition of cholinesterase activity and it was specifically designed to resemble *O*-acetylcholine structurally. It is non-phytotoxic at the recommended application rates. Degradation and metabolism in plants, animals, and soil, the sulphur atom is oxidized to the sulfoxide and sulphone groups. Various oximes, nitriles, amides, acids, and alcohols are also formed. Usual formulation is 10% granular.

Atrazine: is a selective pre- and post-emergence soil and leaf herbicide used on many crops including maize, sorghum, sugarcane, pineapple, asparagus at 1 - 4 kg a.i./ha. Higher rates are used for general weed control. Mode of action - interference with photosynthesis and other enzymatic processes in the plant. Degradation and metabolism - hydroxy-atrazine is formed in the soil and microbially degraded by splitting the heterocyclic ring. Usual formulations are 50 and 80% active ingredient, as well it is often formulated in combination with other herbicides.

Azinphos-methyl: is a non-systemic insecticide and acaricide of long persistence marketed for the control of many insect pests on a wide range of crops. It exhibits residual activity which is significantly

longer than that of other non-systemic organic phosphate insecticides. It has given control of insects known to be resistant to chlorinated hydrocarbon insecticides. Mode of action - cholinesterase inhibitor with stomach and contact action. Degradation and metabolism - follows the usual pattern of dithiophosphate degradation: oxidation to the phosphate (oxon) and thiol phosphate, demethylation of one or both methyl groups, and hydrolysis finally to phosphoric acid. Benzazimide is a metabolic by-product. Elimination of >95% in the urine and faeces within 2 days. Formulations available are spray concentrates, 1.5 and 2.0 lb/U.S. gal, and wettable powders, 20, 25, 40 & 50%, and a 20% emulsifiable concentrate.

Bromoxynil: is a selective contact herbicide with some systemic activity which when applied under field conditions causes necrotic and blistered areas on the leaves of susceptible species, followed by death of the plants. Speed of action varies, but usually death of the weed occurs in 2 to 7 days after spraying. Graminaceous plants are not killed but occasionally may suffer local leaf scorch when treated with high rates or at late stages of growth. Bromoxynil itself is the toxicant which inhibits photosynthesis at the second light reaction and uncouples oxidative phosphorylation in respiration. As a post-emergence herbicide it is used to control seedling broadleafed weeds in cereal crops, flax, garlic, maize, onions, sorghum, and newly sown turf. Degradation and metabolism - in soil, the nitrile group is converted in the first instance to the acid amide, then to the carbonic acid. The benzene ring is debrominated and hydroxylated. The half-life in soil (heavy clay) is ca. 14 days. The octanoyl ester formulation has been found to be more

useful under Canadian conditions. Usual formulation is a 25% (w/v) solution of the potassium salt in aqueous tetrahydrofurfuryl alcohol. It is also commercially available as mixtures with phenoxyalkanoic acids or formulations with the octanoyl ester.

Bromoxynil Octanoate: is a selective herbicide generally more effective than bromoxynil potassium salt, although this depends upon local factors, such as the weeds present. In Canada it has been found to be active against a number of troublesome broadleafed weeds, particularly those resistant to 2,4-D and MCPA. It is hydrolyzed in plants and animals to the phenol and degraded further. Usually formulated as a 2 lb./gallon emulsifiable concentrate.

Carbofuran: is a systemic and contact acaricide, insecticide and nematocide which is absorbed and translocated by the plant. It is a short residual toxicant which is effective against a number of mites. Mode of action - cholinesterase inhibition through ingestion and inhalation. Degradation and metabolism - oxidation occurs at C-3 via hydroxylation and ketone formation; there is hydroxylation of the N-group and hydrolysis of the ester bond. Half-life in soil is 30 to 60 days. Formulated as either granules, 10, 5, 3, 2% active material or flowable 4 lb. active/gal.

Chlorothalonil: is a broad spectrum foliage protectant fungicide effective against pathogens of vegetables, agronomic, ornamental tree and small fruit crops and turf. Degradation and metabolism - in plants, 4-hydroxy-2,5,6-trichloroisophthalonitrile has been found as a metabolite.

Half-life in soil is 45 to 90 days depending on moisture content and temperature. It is formulated as a wettable powder (75%), flowable (54%) and a thermal dust 20 & 90%).

Chlorpyrifos: is a broad spectrum insecticide, and is effective by contact, ingestion, and vapour action, but is not systemic. It is absorbed through leaves and roots with slight translocation. It is particularly active against mosquitoes, household pests, chinchbugs, cutworms and other soil insects. It is moderately residual on plant surfaces and quite residual on inert surfaces - wood. It is volatile enough to form residues on nearby surfaces, and it is stable except under vigorous conditions of alkalinity or acidity. It is non-phytotoxic at insecticidal concentrations and is degraded in the soil with a persistence ranging from 60 to 120 days. Degradation and metabolism - following oral intake (rats) 90% is excreted in the urine. The metabolites are monoethyl chlorpyrifos, the P=O oxidation product, and trichloropyridinol. In soil, there is a slow hydrolysis, a low level of bacterial degradation.

2,4-D: is a widely used systemic, translocatable, herbicide for the control of weeds in cereals and other crops. Its phytotoxic action is due to an effect on plant growth which is more pronounced in broadleafed plants than in cereals. It is used as a post-emergent herbicide in cereals, corn, pasture and lawn. Soil persistence is about 30 days at the highest recommended rate. Degradation and metabolism - in soil and plants, degradation of the side chain, i.e. the acetic acid ester, with the formation of 2,4-dichlorophenol. Ring hydroxylation at position 6 and ring opening. It is formulated as a 98% concentrate or in a solid

mixture with alkali to facilitate solution.

Deltamethrin: is a very potent insecticide effective as a contact and stomach poison against a wide variety of insects. Its toxicity to houseflies is about 1000x and to the American cockroach 30x that of pyrethrins. It has very good residual activity also for outdoor uses (cattle dip, field crops, mosquito control) and for indoor uses (crawling and flying insects, stable flies and stored products insects). Degradation and metabolism - about 10 days after use, there are no residues on plants. In soil, degradation occurs within 1 to 2 weeks. It is formulated as an emulsifiable concentrate (25 g a.i./L), wettable powder (25 and 50 g/kg), dusts (0.5 and 1.0 g/kg), and granules (0.5 and 1.0 g/kg).

Dicamba: is a selective foliar- or soil-applied post-emergence herbicide which is readily absorbed by leaves and roots and is translocated throughout the plant. It effectively controls many annual and perennial broadleafed weed species in asparagus, cereals, grain, maize, perennial seed grasses, sorghum, sugarcane, and turf between cropping systems. It is also used for woody brush and vine control in pasture, rangeland and cropland. Degradation and metabolism - following uptake by grasses, dicamba is degraded within a few days, in the course of which the 2-methoxy group is presumably converted to a hydroxyl group. In other plants, the compound remains stable over weeks. In warm-blooded animals elimination of dicamba is rapid through the urine partly as the glycine conjugate. Residual activity in the soil is about 90 days (at 4 kg/ha). Usually formulated with another herbicide usually one of the phenoxyal-

kanoics.

Diclofop-methyl: is a selective, post-emergence, systemic herbicide effective against wild oats, wild millets and other annual grassy weeds. It is effective after uptake by foliage and roots and is selective to barley, carrots, celery, clover, cucumbers, field and dwarf beans, groundnuts, lettuces, lucerne, peas, potatoes, rape-seed, soyabeans, spinach, sugar beet, tomatoes and wheat. Both diclofop-methyl and diclofop are herbicidal but with different sites of action, primary action is inhibition of root growth. Degradation and metabolism - in warm-blooded animals it is metabolized via hydroxylation and elimination as the conjugate is complete within 96 hours. In soil, 4-(2,4-dichlorophenoxy)-phenol is found as well as the hydroxylated free acids. It is formulated as either a 36% or 28% emulsifiable concentrate.

Disulfoton: is a systemic insecticide and acaricide recommended for use on cotton, beets, potatoes, hops, vegetables, and ornamentals against a wide range of insects and mites. It also exhibits some nematocidal action that may persist for 6 to 12 weeks. It is particularly effective against sucking insects with control lasting 6 to 12 weeks. When applied to soil it is taken up by the roots and translocated thus not destroying predators and pollinating insects. Mode of action - cholinesterase inhibitor. Degradation and metabolism - in plants, the thioester sulphur atom is oxidized to the sulfoxide and sulphone, and the dithiophosphate moiety to thiophosphate. Subsequent hydrolysis to diethyl phosphate and to the mercaptan residue. In rats, there is rapid absorption and elimination, the latter being in the urine, mostly in the

oxidized and hydroxylated forms. It is formulated as a seed dressing (50% a.i.), as granules (2 & 5% a.i.) and as an emulsifiable concentrate (8 lb./US gal).

EPTC: is a selective, translocating soil-herbicide which is used in preplant, pre-emergence and post-emergence control of crabgrass, fox-tails, barnyard grass, wild oats and volunteer grain. It is also effective against nutsedges and certain other perennial grass species with proper application, morningglory, chickweed, lambsquarters, redroot pigweed, and others are some of the broadleafed weeds controlled by *EPTC*. It kills germinating weed seeds and inhibits bud development from underground portions of some perennial weeds. It is tolerated by alfalfa, clovers, white potatoes, dry and snap beans, and other crops. Incorporation into the soil mechanically or by irrigation is necessary to avoid loss by volatilization. Degradation and metabolism - in plants, degradation is accompanied by carbon dioxide liberation. In soil, decomposition to a mercaptan residue, carbon dioxide, and an amino acid residue. Formulations available include an emulsifiable concentrate (6 lb./US gal.) and granules (1% a.i.)

Mancozeb: is a protective leaf fungicide effective against many diseases, particularly blights of tomatoes and potatoes at strengths of 1.5 to 2 lbs per 100 gallons. It is used, in combined formulation, with zineb, against a wide range of foliage fungal diseases on pome fruits and against various rust diseases. It is also used in combination with some systemic fungicides to increase the duration of protection given to the crop. It is also used as a seed treatment. It is essentially non-

phytotoxic. Degradation and metabolism - the major metabolite in plants is ethylene thiourea; also formed are ethylene thiuram monosulphide and presumably also ethylene thiuram disulphide and sulphur. It is usually formulated as a wettable powder (80% active ingredient).

MCPA: is a selective, systemic hormone-type selective herbicide, readily absorbed by leaves and roots. It is an effective weedkiller and growth-regulating compound closely resembling 2,4-D in its properties. Its uses include the post-emergence control of annual and perennial weeds in cereals, grassland, grass-seed crops, peas, linseed, non-cropped areas, and turf. Degradation and metabolism - in plants and soil, side-chain degradation to 2-methyl-4-chlorophenol, ring hydroxylation at position 6, and ring opening. Residual activity in the soil is in the order of 90 to 120 days. Formulations include a solution containing 15 to 25% of the active sodium salt, and a dust (0.75 to 1.5% active ingredient).

Mecoprop: is a selective, systemic, growth regulating herbicide for post-emergence weed control in seedling grasses, established turf and cereals. It is particularly effective against cleavers and chickweed. Absorption is via the leaves. It is mainly used in combination with other herbicides to extend the range of weeds controlled. Degradation and metabolism - in soil and plants, degradation of the side chain to 2-methyl-4-chlorophenol, ring hydroxylation (presumably at position 6), and ring opening. Residual activity in the soil is ca. 60 days (at 4 kg/ha)

Metribuzin: is a selective asymmetrical triazine herbicide used pre- and post-emergence to control annual small-seeded grasses and broad-leaved weeds in soyabeans, potatoes, sugar beet, tomatoes, sugarcane, and other crops. Mode of action - uptake via leaves and roots, inhibiting photosynthesis. Degradation and metabolism - in warm blooded animals, 90% elimination occurs within 96 hours, about equally in urine and faeces. In soil and plants, degradation is via desamino-diketometribuzin. Further metabolism occurs by glycoside formation or binding to soil particles. Sunlight promotes degradation. Residual activity in the soil is ca. 90 days. Formulations include wettable powder, liquid suspension, and water dispersible granules.

Paraquat: is a contact herbicide with a relatively short duration of activity, which destroys green plant tissue with some translocation. It is rapidly inactivated on contact with soil due to its ionic nature. Its uses include stubble cleaning; pasture renovation; inter-row weed control in vegetable crops; desiccation of various crops; and weed control in plantation crops. Degradation and metabolism - photochemical decomposition occurs. In plants, presumably demethylation at one N atom followed by degradation of the ring concerned, accompanied by methylamine and 1-methyl-4-carboxypyridinium ion formation. No residual activity in soil due to the immediate inactivation upon contact with soil.

Propanil: is a post-emergence contact herbicide with a short duration of activity, used for the control of mono- and dicotyledonous weeds in rice fields, spring wheat, barley, oats, flax, and potatoes. It is selective and fast acting and at recommended dosages it is non-phytotoxic.

If applied to some crops that have been treated with organophosphorus insecticides, severe phytotoxicity may result. Degradation and metabolism - presumably ring hydroxylation, degradation to the aniline derivative, and ring opening. In resistant plants, it is rapidly broken down. In warm, damp conditions residual activity is ca. 3 days. It is usually formulated as an emulsifiable concentrate (250 & 360 grams/L).

Trifluralin: is a selective pre-emergence herbicide with little post-emergence activity for the control of annual grasses and broadleaved weeds, affects the germination of the seed, in cotton, soybeans, peanuts, snapbeans, safflower, sweet potatoes, turf and ornamentals. Degradation and metabolism - in soil, plants, and animals, dealkylation of the amino group, reduction of the nitro group to an amino group, partial oxidation of the trifluoromethyl group to a carboxy group, and subsequent degradation to smaller fragments. Residual activity in the soil is ca. 6 to 8 months. It is formulated as both an emulsifiable concentrate (4 lb./US gal) and granular (5%).

Zineb: is a protective leaf fungicide used to protect foliage and fruit of a wide range of crops against diseases such as tomato and potato blight, downy mildews, and rusts. It is non-phytotoxic except to zinc sensitive plants. Degradation and metabolism - ethylene thiourea is the major metabolite in plants, also formed are ethylene thiuram monosulphide and presumably ethylene thiuram disulphide and sulphur. It is formulated as a wettable powder (75% active ingredient).

Table C.3 Chemodynamic Properties of Several Pesticides

Pesticide	S (mg/L)	Log K_{oc}	K_h	V (Pa)	$t_{1/2}$ (days)	u (day ⁻¹)
Aldicarb	9.00E+03	1.00	1.00E-04	1.30E-02 1.30E-02	28 ¹	
					0.9 ⁶	0.80
					1.3 ⁶	0.55
					175 ⁷	
					266 ⁷	
					245 ⁷	
					16 ¹¹	
					40 ¹¹	
					61 ¹¹	
					9 ¹⁴	0.078
					2 ¹⁴	0.35
Atrazine	3.20E+01	2 ^{2.20}	1 ⁴	2.50E-07	4.00E-05	71 ¹
	3.30E+01	12 ^{2.28}	12 ¹²			70 ²
	3.30E+01					48 ⁴
						6900 ⁴
						20 ⁴
Azinphos- methyl	2.90E+01				80 ²	
					13 ²¹	
					29 ²¹	
					88 ²¹	
					135 ²¹	
Bromoxynil					6 ¹⁵	
					14 ¹⁵	
					<7 ¹⁹	
Carbofuran	3.20E+02	1 ^{1.45}	1 ⁴	3.10E-07	2.70E-03	40 ¹
	7.00E+02	2 ^{1.47}	23 ²³			60 ²
	4.15E+02	12 ^{2.02}	24 ²⁴			37 ⁴
			2.78 ²⁴			535 ⁴
			2.20 ²⁴			44 ⁴
						68 ⁴
						1190 ⁷
						4830 ⁷
						57 ⁷
						7 ⁹
						21 ⁹
						350 ⁹

Table C.3 Chemodynamic Properties of Several Pesticides (continued...)

Pesticide	S (mg/L)	Log K_{oc}	K_h	V_p (Pa)	$t_{1/2}$ (days)	u (day ⁻¹)
Chlorpyrifos	2.00E+00 3.00E-01	12	3.78 ¹ 4.13 ¹² 3.78 ²³ 3.70 ²⁴ 3.86 ²⁴	1.80E-04	2.50E-03	63 ¹ 77 ⁷ 49 ⁷ 29 ⁷ 19 ⁷
2,4-D	9.00E+02 >5.00E+03 9.00E+02	2 12	1.30 ¹ 1.29 ⁴ 1.30 ¹² 1.76 ²³ 1.68 ²⁴ 1.88 ²⁴	5.60E-09	5.30E+01	15 ¹ <10 ² 16 ⁴ 15 ⁴ 5 ⁴ <7 ¹⁷ 12 ¹⁷ 0.0462 ³ 0.066 0.051 3.6
Decamethrin					35 49	10 10
Dicamba	4.50E+03 4.50E+02	2 12	0.34 ⁴ -0.40 ¹²		14 ² 14 ⁴ 309 ⁴ 147 ⁴ 8 ⁴ 16 ¹⁹ 50 ¹⁹ 20 ¹⁹	0.022 0.0022 0.0044 0.093
Diclofop-methyl					21 28 70	16 16 16
Disulfoton	2.50E+01 2.50E+01	12	3.20 ¹ 3.20 ⁴ 3.25 ¹²	1.10E-04	2.40E-02	5 ¹
EPTC	3.70E+02 3.65E+02	1 12	1.45 ¹ 2.38 ¹²	5.90E-04	4.50E+00	30 ¹ 4 ¹³ >15 ¹³ 6 ¹³ >45 ¹³

Table C.3 Chemodynamic Properties of Several Pesticides (continued...)

Pesticide	S (mg/L)	Log K_{oc}	K_h	V (Pa)	$t_{1/2}$ (days)	u (day ⁻¹)
MCPA					13 ¹⁸ 5 ²⁰ 7 ²⁰	
Mecoprop					7 ²⁰ 9 ²⁰	
Metribuzin	1.22E+03 ¹²	1.98 ¹²			18 ⁵	
Paraquat	1.00E+06 ¹²	4.19 ¹²			487 ⁴ 4747 ⁴	0.0016 0.00015
Propanil					<7 ¹⁹	
2,4,5-T	2.38E+02 ¹²	1.90 ⁴ 1.72 ¹²			33 ⁴ 16 ⁴	0.029 0.035
Trifluralin	3.00E-01 ¹² 6.00E-01	3.86 ¹ 4.14 ¹² 3.64 ²³ 3.47 ²⁴ 3.73 ²⁴	6.70E-03	1.40E-02	132 ¹ 132 ⁴ 28 ⁴ 544 ⁴ 46 ⁴ 36 ⁸ 26 ⁸ 34 ²² 54 ²²	0.008 0.025 0.0013 0.02 0.0194 0.0270

1 - Rao et al., 1985; 2 - Neary, 1985; 3 - Jury et al., 1983; 4 - Rao and Davidson (1981); 5 - Bouchard et al. (1982); 6 - Bromilow et al. (1980); 7 - Chapman and Cole (1982); 8 - Duseja and Holmes (1978); 9 - Getzin (1973); 10 - Hill (1983); 11 - Jones (1985); 12 - Kenaga and Goring (1980); 13 - Lee et al. (1984); 14 - Smelt et al. (1978); 15 - Smith (1971); 16 - Smith (1977); 17 - Smith (1980b); 18 - Smith (1982a); 19 - Smith (1984); 20 - Smith and Hayden (1981); 21 - Yaron et al. (1974); 22 - Zimdahl and Gwynn (1977); 23 - McCall et al. (1980); 24 - Swann et al. (1981).

APPENDIX D

Additional Soil Column Data

for

Columns 5R & 6D

Skelding Fine Sand Soil

and

Columns 7R & 8D

St. Claude Silt Loam Soil

Table D.1 EPTC in Leachate Water from Skelding Fine Sand Soil Columns

Sample Volume mL	Column 5R River Water mcg	Column 6D Distilled Water mcg
100	----	----
200	----	----
300	----	----
400	----	----
500	----	----
600	----	----
700	----	----
800	----	----
900	----	80.94
1000	----	79.29
1100	----	----
1200	----	----
1300	----	----
1400	----	----
1500	----	19.84
1600	----	24.30
1700	----	11.99
1800	----	----
1900	----	----
2000	----	----
2100	----	----
2200	----	----
2300	----	----
2400	----	----
2500	----	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	----
3200	----	----
3300	15.71	----
3400	18.18	----
3500	3.32	----
3600	----	----
3700	----	----
3800	44.61	----
3900	6.62	----
4000	----	----
4100	----	----
4200	----	----
4300	----	xx
4400	----	xx
4500	----	xx
4600	----	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.2 EPTC Concentration in the Soil Profile for the Skelding
Fine Sand Soil Columns: 5R & 6D

5R		6D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	--
15 - 30	5.55 [1]	15 - 30	--
30 - 45	4.96 (\pm 1.95)	30 - 45	--
45 - 60	5.24 [1]	45 - 60	--
60 - 74	--	60 - 75	--
74 - 88	--	75 - 89	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.3 Chlorpyrifos in Leachate Water from Skelding Fine Sand Soil Columns

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	2,111.88	3,186.77
500	2,162.49	6,565.97
600	4,922.13	9,646.23
700	2,090.19	14,201.54
800	390.98	----
900	535.60	3,153.09
1000	680.21	----
1100	----	----
1200	----	----
1300	----	----
1400	----	----
1500	----	----
1600	----	----
1700	----	----
1800	----	----
1900	----	----
2000	----	----
2100	----	----
2200	----	----
2300	----	----
2400	----	----
2500	----	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	----
3200	----	----
3300	----	----
3400	----	----
3500	----	----
3600	----	----
3700	----	----
3800	----	----
3900	----	----
4000	----	----
4100	----	xx
4200	----	xx
4300	----	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.4 Chlorpyrifos Concentration in the Soil Profile for the
Skelding Fine Sand Soil Columns: 5R & 6D

5R Column Section cm	Concentration ng/g	6D Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	130.72 (\pm 44.34)
15 - 30	--	15 - 30	60.40 (\pm 19.60)
30 - 45	--	30 - 45	18.96 (\pm 8.15)
45 - 60	--	45 - 60	84.98 (\pm 86.45)
60 - 74	--	60 - 75	17.16 [1]
74 - 88	--	75 - 89	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.5 Metribuzin in Leachate Water from Skelding Fine Sand Soil
Columns

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	----	9.85
500	----	4.02
600	298.13	2.36
700	120.89	----
800	44.16	----
900	20.71	39.39
1000	7.04	----
1100	11.60	----
1200	6.36	----
1300	5.00	----
1400	----	----
1500	12.96	----
1600	7.96	----
1700	----	----
1800	----	----
1900	4.77	4.02
2000	5.22	----
2100	----	----
2200	----	----
2300	----	----
2400	----	----
2500	----	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	----
3200	----	----
3300	----	----
3400	----	----
3500	----	----
3600	----	----
3700	----	294.49
3800	----	141.35
3900	----	149.26
4000	----	xx
4100	----	xx
4200	----	xx
4300	----	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.6 Chlorothalonil in Leachate Water from Skelding Fine Sand
Soil Columns

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	1,905.67	----
300	101.40	----
400	886.25	9.85
500	2,204.16	4.02
600	16.50	2.36
700	24.83	----
800	1.52	----
900	----	39.39
1000	----	----
1100	----	----
1200	----	----
1300	----	----
1400	----	----
1500	----	----
1600	----	----
1700	----	----
1800	----	----
1900	----	4.02
2000	----	----
2100	----	----
2200	----	----
2300	----	----
2400	----	----
2500	20.67	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	----
3200	----	----
3300	----	----
3400	----	----
3500	----	----
3600	8.60	----
3700	14.84	294.49
3800	18.59	141.35
3900	6.10	149.26
4000	57.70	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.7 Chlorothalonil Concentration in the Soil Profile for the Skelding Fine Sand Soil Columns: 5R & 6D

5R		6D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	5.99 (\pm 1.93)	0 - 15	211.46 (\pm 136.40)
15 - 30	6.11 (\pm 1.18)	15 - 30	18.08 (\pm 18.75)[2]
30 - 45	4.49 (\pm 0.07)[2]	30 - 45	8.29 (\pm 0.64)
45 - 60	5.05 (\pm 0.65)	45 - 60	3.77 (\pm 0.11)[2]
60 - 74	--	60 - 75	18.16 (\pm 19.59)
74 - 88	--	75 - 89	26.13 (\pm 2.29)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.8 Diclofop-methyl in Leachate Water from Skelding Fine Sand
Soil Columns

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	81.29	----
200	1,040.65	----
300	247.79	----
400	41.65	----
500	101.11	----
600	376.63	28.76
700	51.56	31.73
800	63.45	35.70
900	51.56	----
1000	26.78	----
1100	----	----
1200	----	113.00
1300	----	----
1400	81.29	636.29
1500	289.42	53.54
1600	126.88	----
1700	71.38	81.29
1800	24.80	----
1900	25.79	----
2000	22.81	----
2100	51.56	----
2200	----	----
2300	81.29	----
2400	189.32	----
2500	25.79	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	xx
3200	----	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.9 *Diclofop-methyl Concentration in the Soil Profile for the Skelding Fine Sand Soil Columns: 5R & 6D*

5R		6D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	86.88 (\pm 11.86)
15 - 30	3.91 (\pm 0.85) [2]	15 - 30	43.16 (\pm 9.51)
30 - 45	--	30 - 45	24.05 (\pm 2.80)
45 - 60	--	45 - 60	28.38 (\pm 2.06)
60 - 74	17.10 (\pm 8.58)	60 - 75	28.43 (\pm 6.56)
74 - 88	52.23 (\pm 0.28)	75 - 89	60.63 (\pm 15.47)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.10 *Trifluralin in Leachate Water from Skelding Fine Sand Soil Columns*

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	----	----
500	----	----
600	----	----
700	318.23	----
800	99.48	----
900	----	----
1000	----	----
1100	----	----
1200	----	----
1300	----	----
1400	----	----
1500	----	----
1600	----	----
1700	----	----
1800	----	----
1900	----	165.88
2000	----	158.07
2100	----	279.95
2200	----	220.57
2300	----	140.10
2400	----	97.91
2500	----	576.04
2600	----	826.04
2700	----	576.04
2800	181.51	xx
2900	138.54	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.11 *Trifluralin Concentration in the Soil Profile for the Skelding Fine Sand Soil Columns: 5R & 6D*

5R		6D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	3.98 (± 1.54)	0 - 15	63.00 (± 14.12)
15 - 30	4.64 (± 1.82)	15 - 30	22.45 (± 5.92)
30 - 45	3.16 (± 0.22)	30 - 45	14.60 (± 3.63)
45 - 60	3.44 (± 0.75)	45 - 60	11.27 (± 4.94)
60 - 74	3.49 (± 0.98)	60 - 75	177.49 (± 143.11)
74 - 88	5.17 (± 0.49)	75 - 89	10.06 [1]

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.12 *Bromoxynil in Leachate Water from Skelding Fine Sand Soil Columns*

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	----	----
500	----	----
600	----	----
700	----	----
800	----	----
900	----	----
1000	----	----
1100	----	----
1200	----	----
1300	----	----
1400	----	336.55
1500	275.41	----
1600	----	----
1700	----	----
1800	----	----
1900	----	----
2000	----	----
2100	----	----
2200	----	302.39
2300	----	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.13 *Bromoxynil Concentration in the Soil Profile for the Skelding Fine Sand Soil Columns: 5R & 6D*

5R		6D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	--	0 - 15	--
15 - 30	18.53 (\pm 4.66)	15 - 30	--
30 - 45	12.91 (\pm 6.14)	30 - 45	--
45 - 60	8.29 (\pm 1.70)	45 - 60	--
60 - 74	14.17 (\pm 6.75)	60 - 75	--
74 - 88	14.57 (\pm 1.70)	75 - 89	154.21 (\pm 73.79)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.14 *Carbofuran in Leachate Water from Skelding Fine Sand Soil Columns*

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	----	45.01
300	----	23.71
400	----	15.00
500	----	43.07
600	----	----
700	----	38.23
800	----	21.77
900	----	85.67
1000	21.77	33.39
1100	15.00	23.71
1200	----	24.68
1300	----	129.31
1400	----	134.07
1500	275.41	299.61
1600	----	xx

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.15 Carbofuran Concentration in the Soil Profile for the
Skelding Fine Sand Soil Columns: 5R & 6D

5R		6D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 15	0.98 (\pm 0.27)[2]	0 - 15	--
15 - 30	--	15 - 30	--
30 - 45	--	30 - 45	--
45 - 60	--	45 - 60	7.31 (\pm 6.56)
60 - 74	3.00 (\pm 0.38)	60 - 75	6.84 (\pm 3.81)
74 - 88	7.14 (\pm 2.74)	75 - 89	25.37 (\pm 15.35)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.16 EPTC in Leachate Water from St. Claude Silt Loam Soil
Columns

Sample Volume mL	Column 7R River Water mcg	Column 8D Distilled Water mcg
100	----	----
200	----	----
300	----	----
400	----	----
500	----	----
600	----	----
700	----	----
800	----	184.16
900	----	----
1000	----	----
1100	----	----
1200	----	----
1300	----	----
1400	2.51	----
1500	1.02	----
1600	1.27	----
1700	5.59	----
1800	5.94	----
1900	8.42	----
2000	6.10	----
2100	0.85	----
2200	4.80	----
2300	2.79	----
2400	1.36	----
2500	3.64	----
2600	1.41	----
2700	1.90	----
2800	----	----
2900	3.47	----
3000	----	----
3100	2.06	----
3200	6.48	----
3300	1.24	----
3400	3.06	11.74
3500	1.41	----
3600	1.18	----
3700	xx	----
3800	xx	----
3900	xx	----
4000	xx	----
4100	xx	----
4200	xx	----
4300	xx	----
4400	xx	----

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.17 EPTC Concentration in the Soil Profile for the St. Claude
Silt Loam Soil Columns: 7R & 8D

7R		8D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 5	83.18 (\pm 27.45)	0 - 12	142.88 (\pm 14.47)
5 - 20	57.52 (\pm 10.75)	12 - 24	115.98 (\pm 16.06)
20 - 30	23.18 (\pm 2.58)	24 - 28	79.34 (\pm 6.04)
30 - 35	31.88 [1]	28 - 39	39.97 (\pm 3.93)
35 - 50	--	39 - 54	--
50 - 65	31.71 (\pm 10.73) [2]	54 - 69	--
65 - 80	--	69 - 84	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.18 Chlorpyrifos in Leachate Water from St. Claude Silt Loam
Soil Columns

Sample Volume mL	Column 7R River Water ng	Column 8D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	3,572.47	----
500	3,186.77	----
600	969.44	----
700	463.29	----
800	3,572.47	----
900	2,328.80	----
1000	340.38	969.44
1100	----	1,547.89
1200	----	535.60
1300	----	354.83
1400	824.82	----
1500	----	----
1600	----	----
1700	----	----
1800	----	----
1900	----	2,328.80
2000	----	1,649.12
2100	----	----
2200	----	----
2300	----	6,392.43
2400	----	3,174.79
2500	----	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	----
3200	----	----
3300	----	----
3400	----	----
3500	xx	----
3600	xx	----
3700	xx	----
3800	xx	----
3900	xx	----
4000	xx	----
4100	xx	1,142.97
4200	xx	----

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.19 Metribuzin in Leachate Water from St. Claude Silt Loam
Soil Columns

Sample Volume mL	Column 7R River Water ng	Column 8D Distilled Water ng
100	----	----
200	----	41.20
300	----	54.86
400	----	38.62
500	----	34.37
600	50.31	82.18
700	43.02	38.92
800	20.71	29.81
900	10.92	8.18
1000	9.78	4.77
1100	6.59	6.59
1200	----	4.77
1300	7.04	3.63
1400	7.27	----
1500	9.32	----
1600	10.69	----
1700	5.00	----
1800	4.31	----
1900	5.00	----
2000	5.00	27.54
2100	10.46	7.04
2200	9.32	----
2300	----	----
2400	----	----
2500	----	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	----	----
3100	----	----
3200	----	----
3300	----	----
3400	xx	----
3500	xx	----
3600	xx	----
3700	xx	----
3800	xx	----
3900	xx	----
4000	xx	----
4100	xx	----

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.20 Chlorothalonil in Leachate Water from St. Claude Silt
Loam Soil Columns

Sample Volume mL	Column 7R River Water ng	Column 8D Distilled Water ng
100	----	----
200	----	1,755.86
300	----	806.77
400	----	403.52
500	----	----
600	----	----
700	----	----
800	----	----
900	----	----
1000	----	----
1100	----	----
1200	----	----
1300	----	----
1400	----	----
1500	----	----
1600	----	----
1700	----	----
1800	----	----
1900	----	----
2000	----	----
2100	----	----
2200	----	----
2300	----	----
2400	----	----
2500	----	----
2600	----	----
2700	----	----
2800	----	----
2900	----	----
3000	11.93	----
3100	53.96	----
3200	41.47	----
3300	xx	----
3400	xx	----
3500	xx	----
3600	xx	----
3700	xx	4.85
3800	xx	----
3900	xx	62.28
4000	xx	41.47

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.21 Chlorothalonil Concentration in the Soil Profile for the
St. Claude Silt Loam Soil Columns: 7R & 8D

7R		8D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 5	26.76 (± 1.41)	0 - 12	65.94 (± 7.63)
5 - 20	7.22 (± 5.15)	12 - 24	42.57 (± 8.15)
20 - 30	1.09 (± 0.85)	24 - 28	10.01 (± 3.33)
30 - 35	--	28 - 39	5.14 (± 2.08)
35 - 50	--	39 - 54	1.14 (± 1.50)
50 - 65	9.95 (± 4.71)[2]	54 - 69	2.83 (± 2.03)
65 - 80	--	69 - 84	0.24 (± 0.19)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.22 *Diclofop-methyl in Leachate Water from St. Claude Silt Loam Soil Columns*

Sample Volume mL	Column 5R River Water ng	Column 6D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	----	----
500	31.73	55.52
600	41.65	111.02
700	132.82	834.51
800	161.57	109.04
900	81.29	----
1000	----	66.42
1100	219.05	----
1200	104.08	----
1300	246.80	----
1400	82.28	143.73
1500	120.93	65.43
1600	----	408.34
1700	----	180.40
1800	----	61.47
1900	----	65.43
2000	----	----
2100	----	----
2200	----	101.11
2300	----	39.66
2400	----	22.81
2500	xx	----
2600	xx	----
2700	xx	----
2800	xx	96.15
2900	xx	31.73
3000	xx	114.99

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.23 *Diclofop-methyl Concentration in the Soil Profile for the St. Claude Silt Loam Soil Columns: 7R & 8D*

7R		8D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 5	--	0 - 12	272.72 (\pm 16.06)
5 - 20	--	12 - 24	29.29 (\pm 18.17)
20 - 30	--	24 - 28	75.70 (\pm 26.96)
30 - 35	--	28 - 39	36.18 (\pm 4.49)
35 - 50	--	39 - 54	52.41 (\pm 37.63)
50 - 65	35.22 [1]	54 - 69	31.37 (\pm 1.15)
65 - 80	43.51 (\pm 21.34)	69 - 84	33.98 (\pm 3.50)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.24 Trifluralin in Leachate Water from St. Claude Silt
Loam Soil Columns

Sample Volume mL	Column 7R River Water ng	Column 8D Distilled Water ng
100	----	----
200	----	----
300	----	----
400	----	----
500	----	----
600	----	128.77
700	----	----
800	----	----
900	----	----
1000	----	----
1100	----	----
1200	----	----
1300	----	----
1400	----	----
1500	----	40.88
1600	----	----
1700	----	29.16
1800	----	206.12
1900	----	150.26
2000	----	----
2100	353.38	----
2200	xx	193.62
2300	xx	236.20
2400	xx	360.80
2500	xx	36.98
2600	xx	368.23
2700	xx	232.29

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.25 *Trifluralin Concentration in the Soil Profile for the St. Claude Silt Loam Soil Columns: 7R & 8D*

7R		8D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 5	--	0 - 12	--
5 - 20	--	12 - 24	--
20 - 30	39.32 (\pm 3.10)	24 - 28	47.86 (\pm 8.80)
30 - 35	149.58 (\pm 29.92)	28 - 39	49.88 (\pm 13.65)
35 - 50	15.92 [1]	39 - 54	172.76 (\pm 44.74)
50 - 65	40.09 (\pm 1.57)[2]	54 - 69	33.34 (\pm 2.01)
65 - 80	47.90 (\pm 8.69)	69 - 84	24.10 (\pm 0.19)

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

Table D.26 *Bromoxynil in Leachate Water from St. Claude Silt
Loam Soil Columns*

Sample Volume mL	Column 7R River Water ng	Column 8D Distilled Water ng
100	----	----
200	----	----
300	599.10	----
400	104.58	176.51
500	45.24	96.59
600	95.59	113.57
700	70.41	77.61
800	79.40	23.66
900	41.64	41.64
1000	84.80	77.61
1100	----	68.62
1200	----	41.64
1300	----	----
1400	----	----
1500	----	----
1600	----	----
1700	----	----
1800	xx	----
1900	xx	----
2000	xx	----
2100	xx	----
2200	xx	257.43

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.27 Carbofuran in Leachate Water from St. Claude Silt
Loam Soil Columns

Sample Volume mL	Column 7R River Water ng	Column 8D Distilled Water ng
100	54.69	23.71
200	33.39	24.68
300	23.71	37.26
400	62.43	27.58
500	----	23.71
600	52.75	33.39
700	48.88	14.03
800	91.47	----
900	378.99	----
1000	333.49	14.03
1100	xx	23.71
1200	xx	62.71
1300	xx	38.23
1400	xx	149.56
1500	xx	159.56

---- no residues detected at the 0.02 ug/L level xx no leachate

Table D.28 Carbofuran Concentration in the Soil Profile for the
St. Claude Silt Loam Soil Columns: 7R & 8D

7R		8D	
Column Section cm	Concentration ng/g	Column Section cm	Concentration ng/g
0 - 5	76.13 (\pm 37.19)	0 - 12	136.86 (\pm 6.27)
5 - 20	19.26 (\pm 9.55)	12 - 24	61.02 (\pm 12.68)
20 - 30	11.66 (\pm 1.68)	24 - 28	40.33 (\pm 21.08)
30 - 35	11.07 (\pm 5.31)[2]	28 - 39	19.50 (\pm 1.14)
35 - 50	11.82 (\pm 0.49)[2]	39 - 54	--
50 - 65	--	54 - 69	8.85 [1]
65 - 80	--	69 - 84	--

-- no residues detected (<0.02 ng/g) () - standard deviation

[] number of samples - if no number then 3 samples

APPENDIX E

Supplementary Gas Chromatographic/Mass Spectral Data

Table E.1 Gas chromatographic and mass spectrometer conditions

1/13/84 9:47:58
ACQ STARTED
RUN: 0:JK6

SCAN 113 OF 1200

SAMPLE: SAMPLE #6
SUBMITTED BY: BK
ANALYST: JK
COMMENTS: 2UL

GC PARAMETERS:

275 DEG = ZONE TEMP.
100 DEG = INITIAL TEMP.
290 DEG = FINAL TEMP.
1 MIN = INITIAL TIME
12.0 D/M = RAMP RATE
18 MIN = FINAL TIME
250 DEG = SEP. SET PT.
80 DEG = MANIF. SET PT.
INJ. MODE: CAP.
30 SEC = SPLIT/SWEEP VALVE TIME
120 SEC = FIL./MULT. OFF TIME
FIL/MUL MODE: AUTO.

SCAN FROM 41 AMU TO 450 AMU IN 1.0 SEC.

1/13/84 10:07:22
ACQUISITION COMPLETED

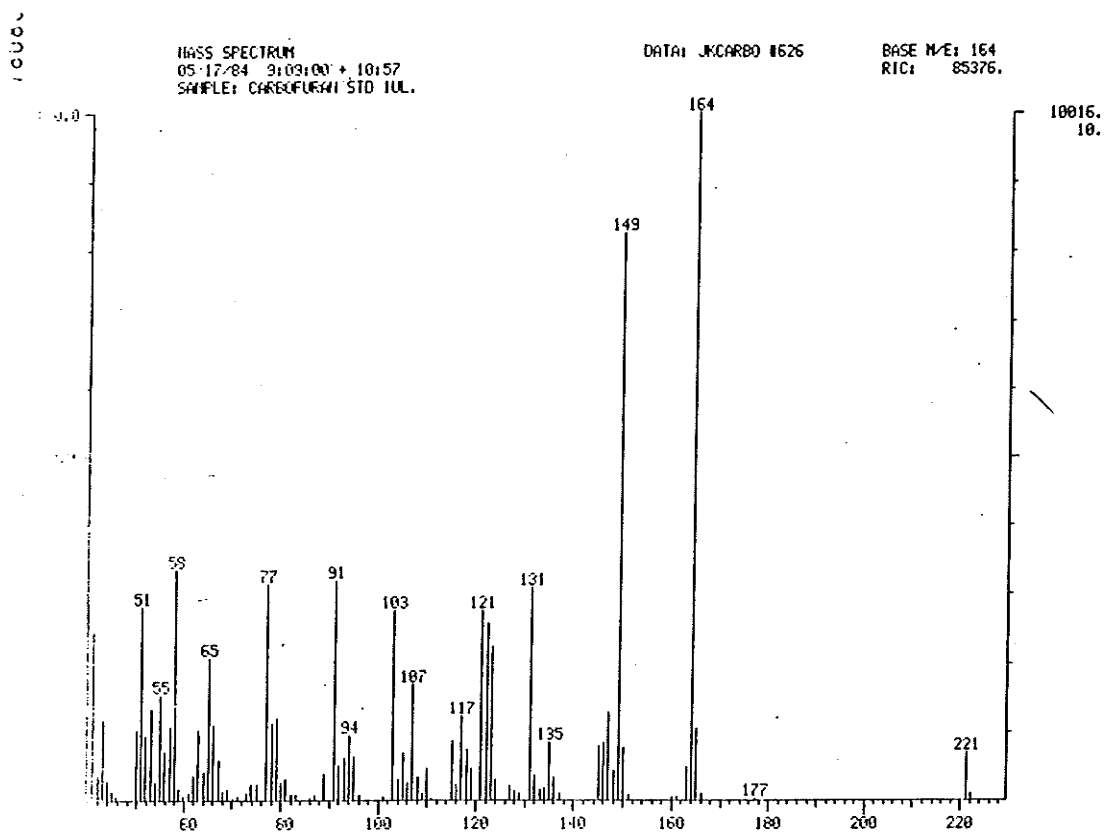


Figure E.1 Mass spectrum of standard carbofuran

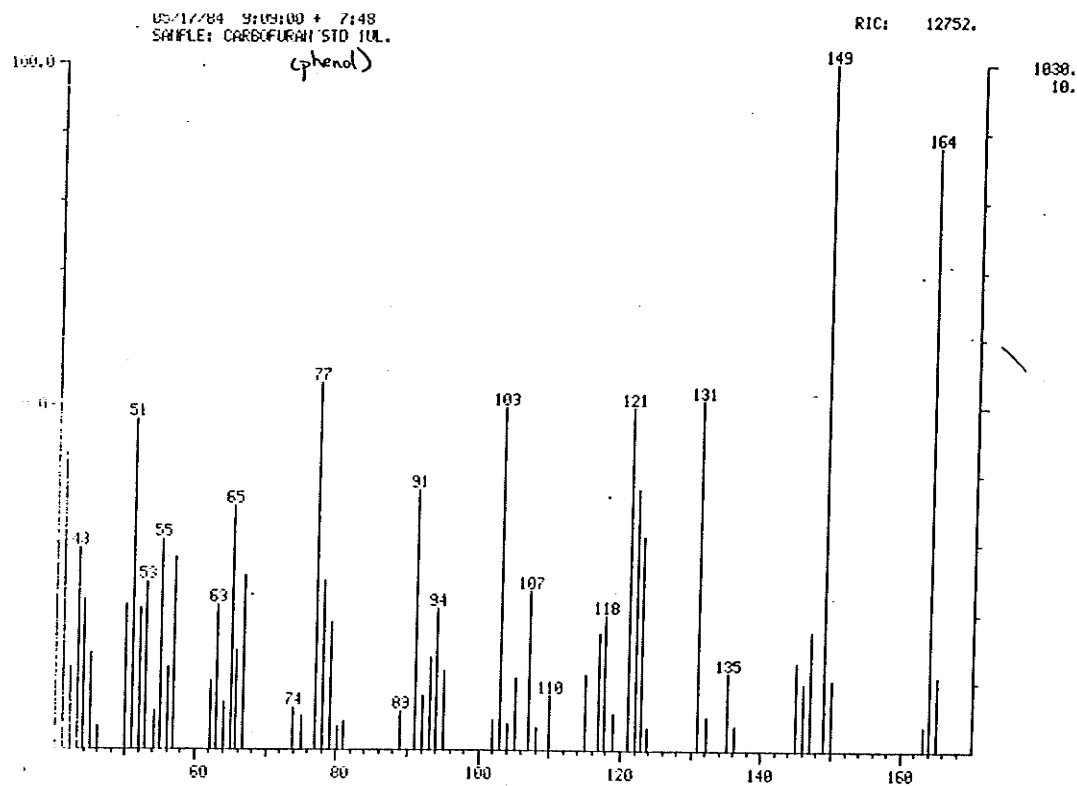


Figure E.2 Mass spectrum of carbofuran phenol in carbofuran standard

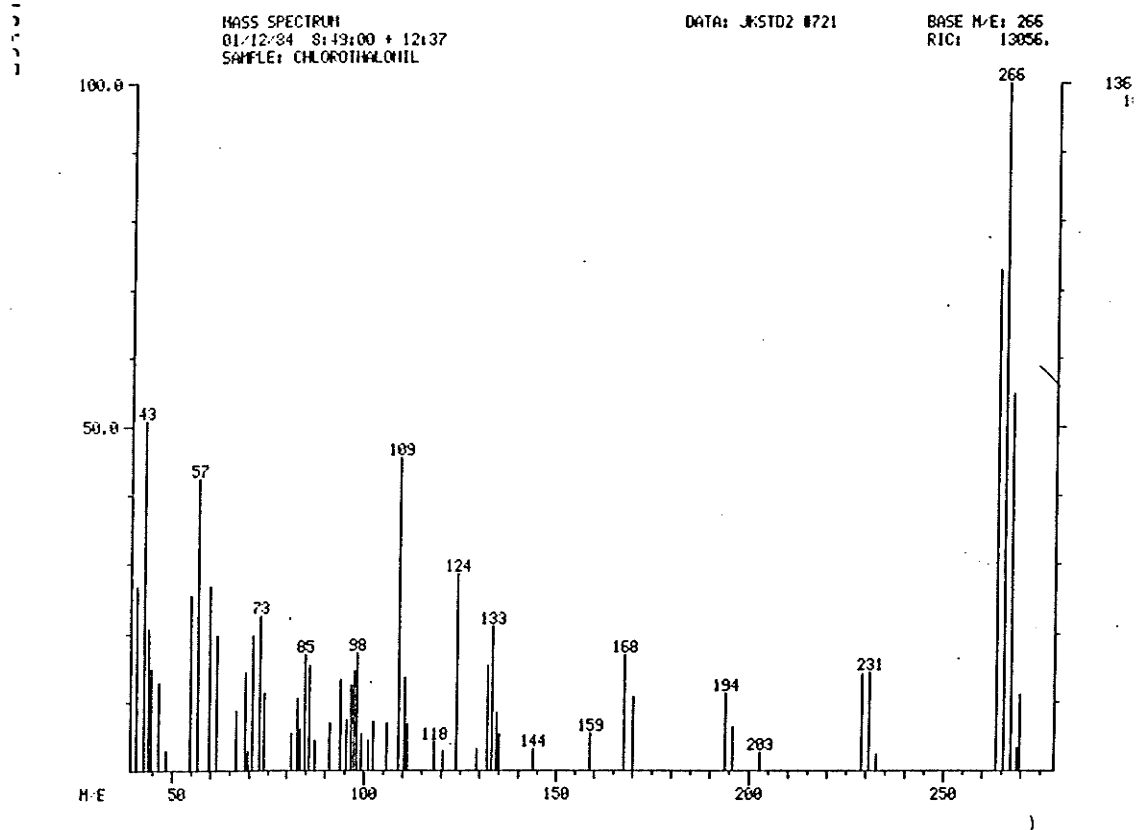


Figure E.3 Mass spectrum of chlorothalonil standard

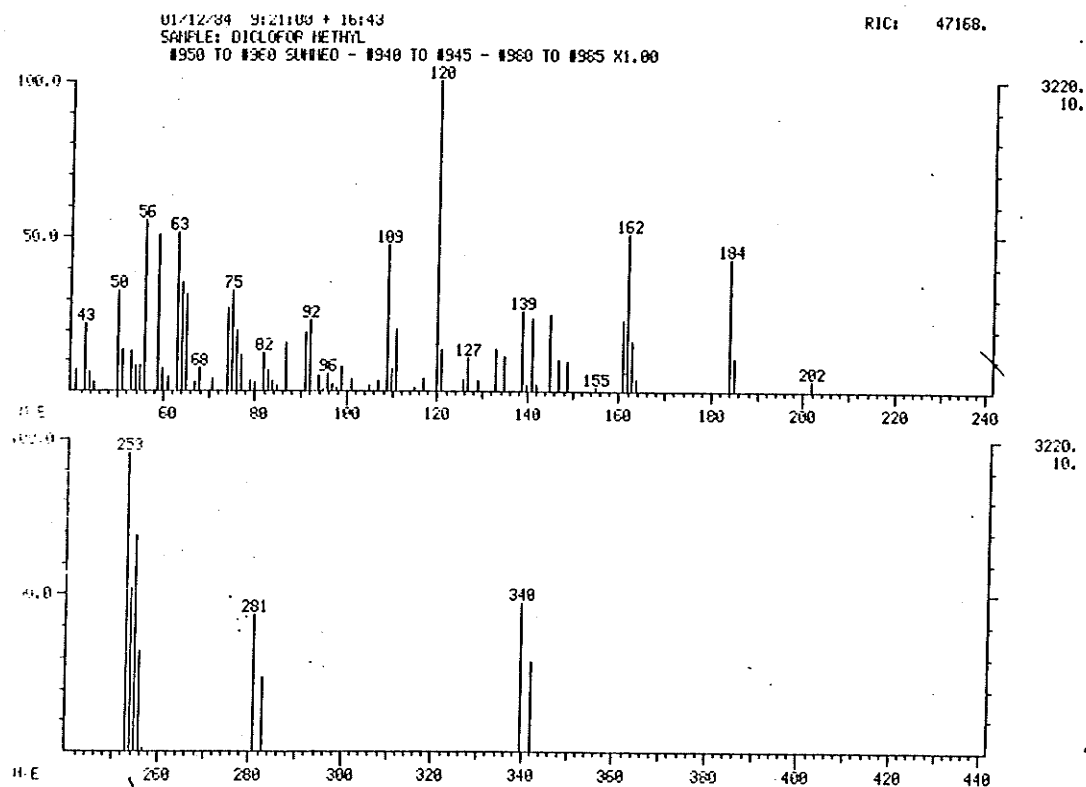


Figure E.4 Mass spectrum of diclofop-methyl standard

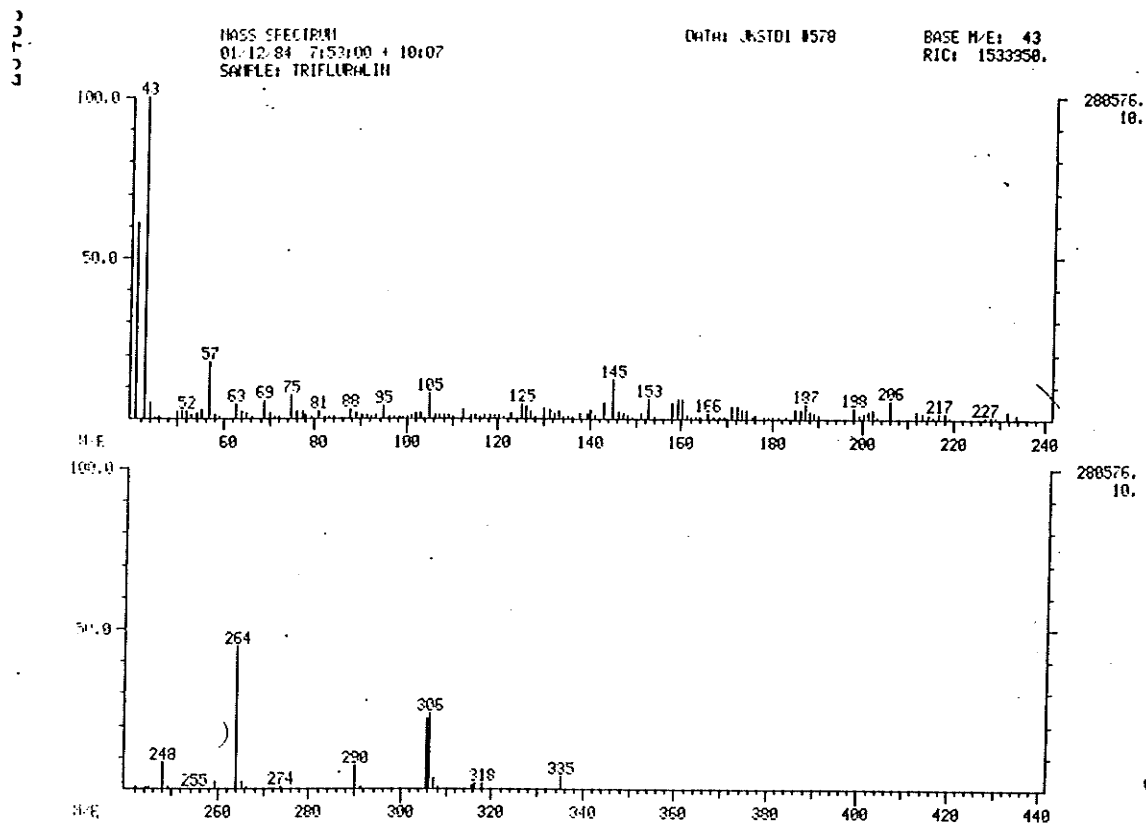


Figure E.5 Mass spectrum of trifluralin standard

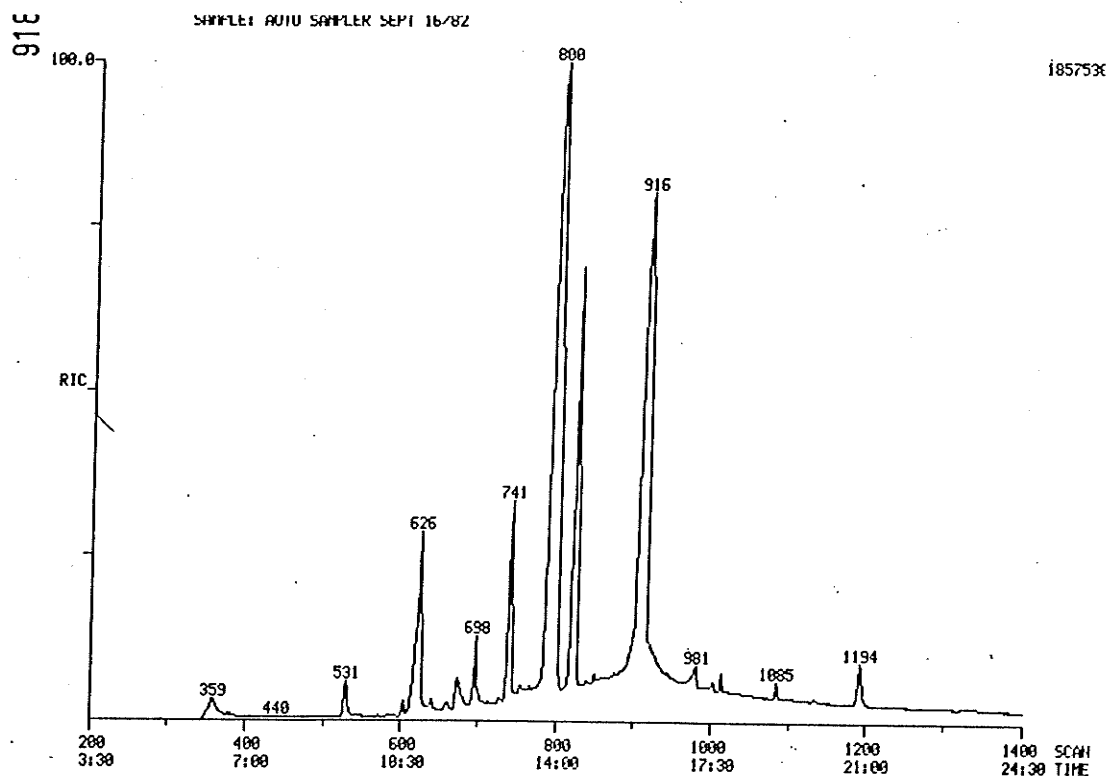


Figure E.6 Reconstructed ion chromatograph of an autosampler water extract from September 16, 1982

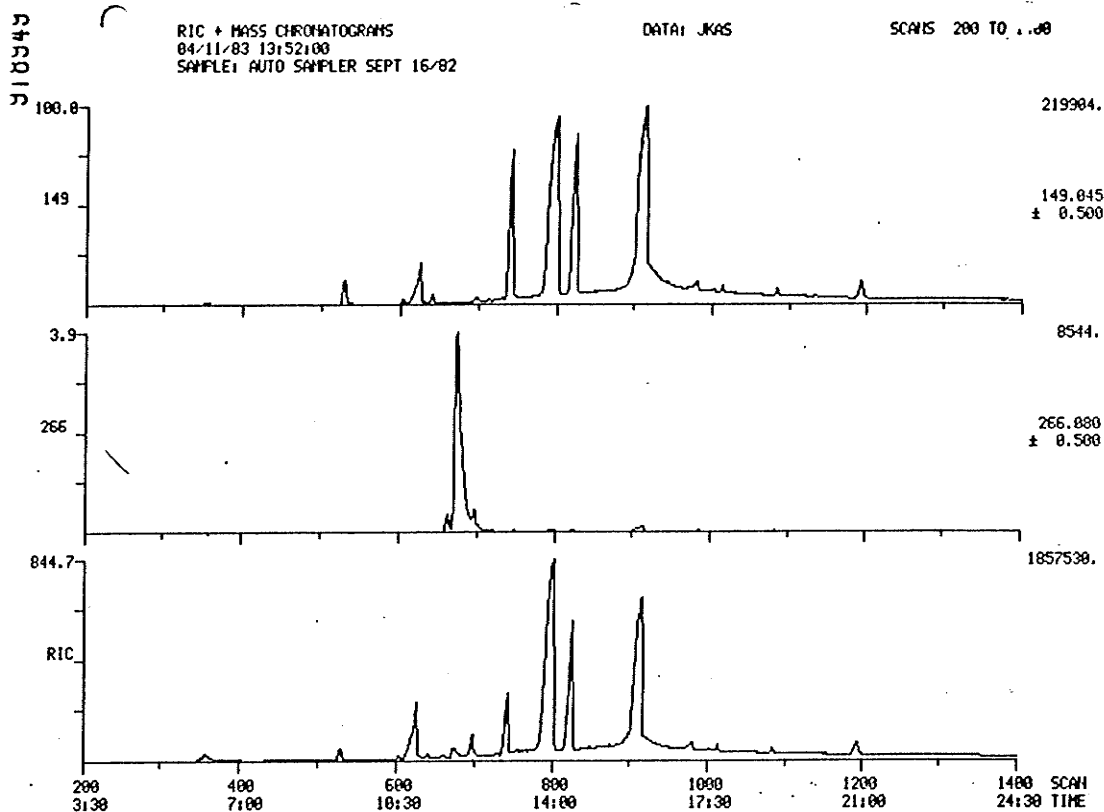


Figure E.7 Reconstructed ion chromatographs of the total scan (lower), for chlorothalonil (center), and for phthalates (top).

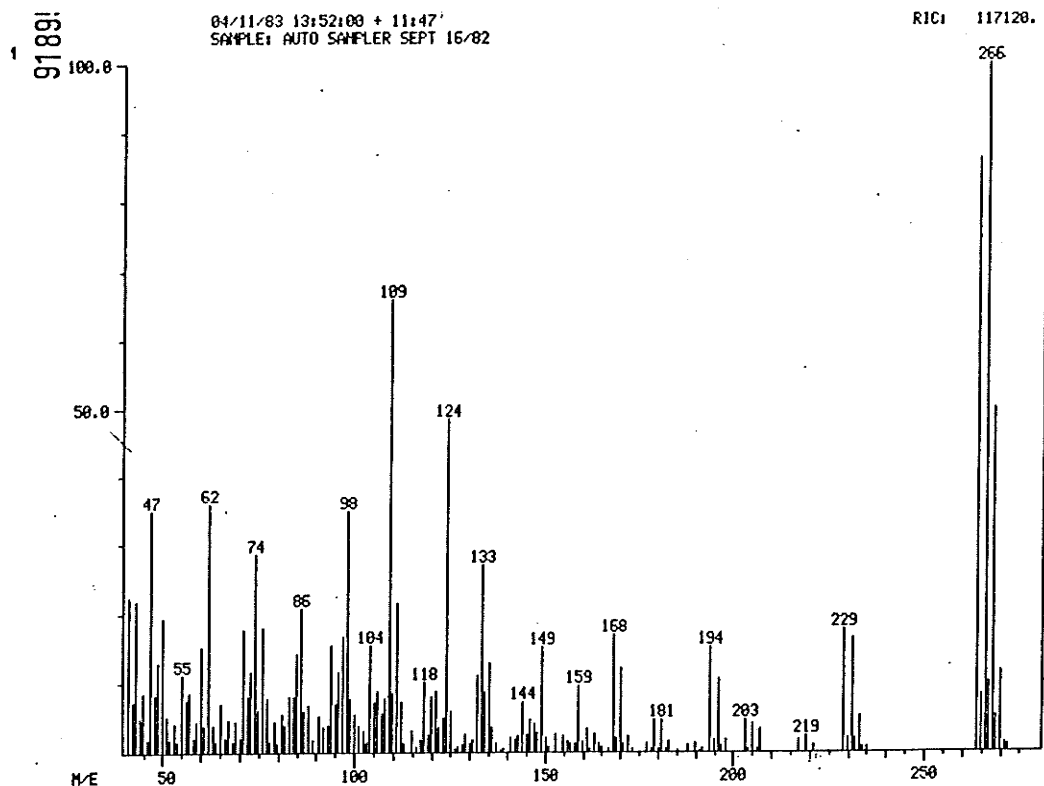


Figure E.8 Mass spectrum of the peak at scan 673. This pattern corresponds to that of the standard chlorothalonil.

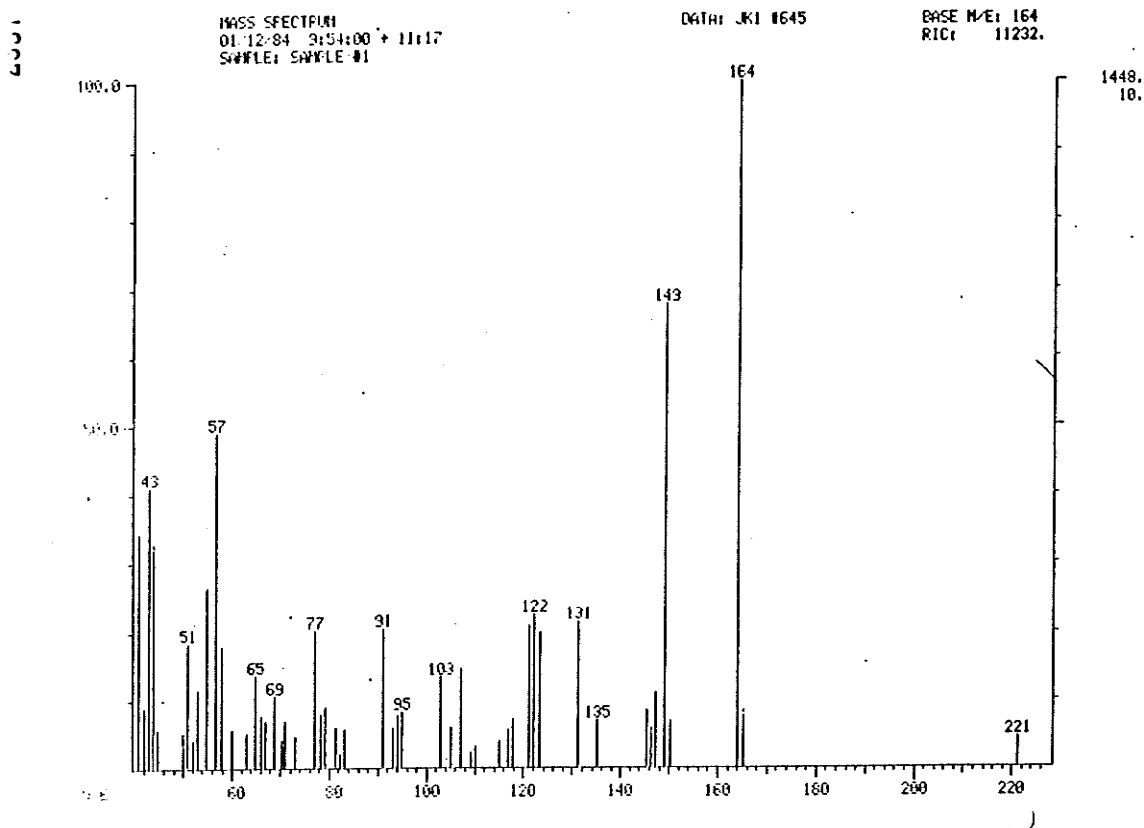


Figure E.9 Mass spectrum of a compound, identified as carbofuran in water extract from a grab water sample from the south well, August 5, 1983.

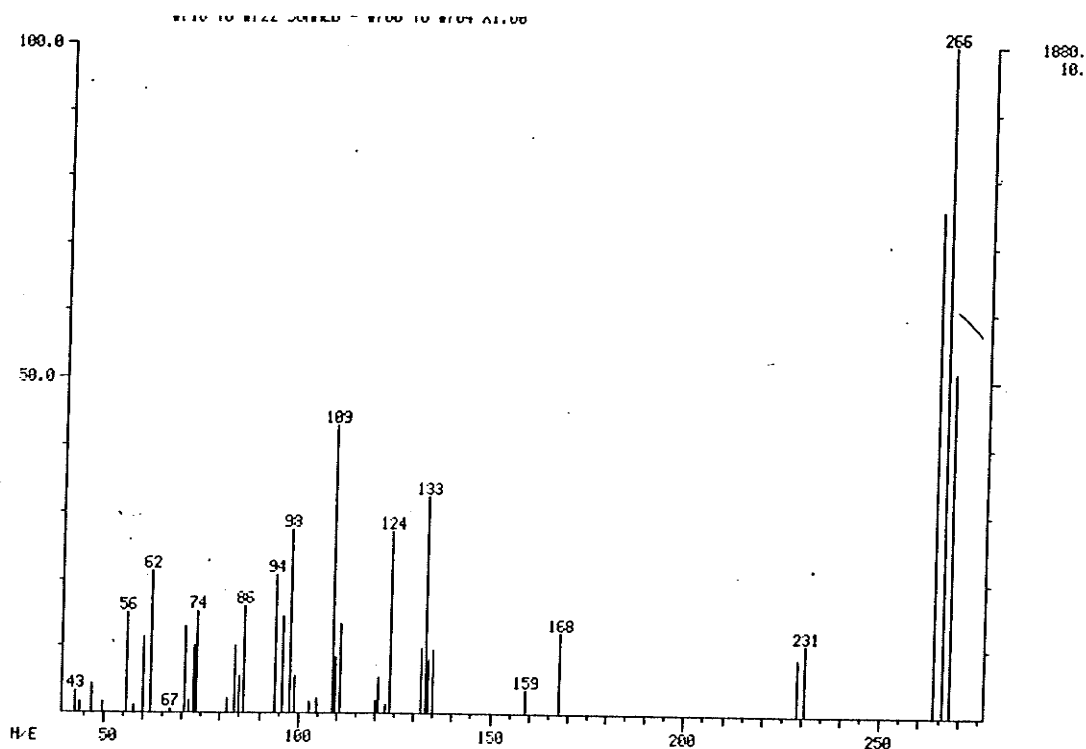


Figure E.10 Mass spectrum of a compound, identified as chlorothalonil which was extracted from a grab water sample taken from the south well on August 16, 1983.