

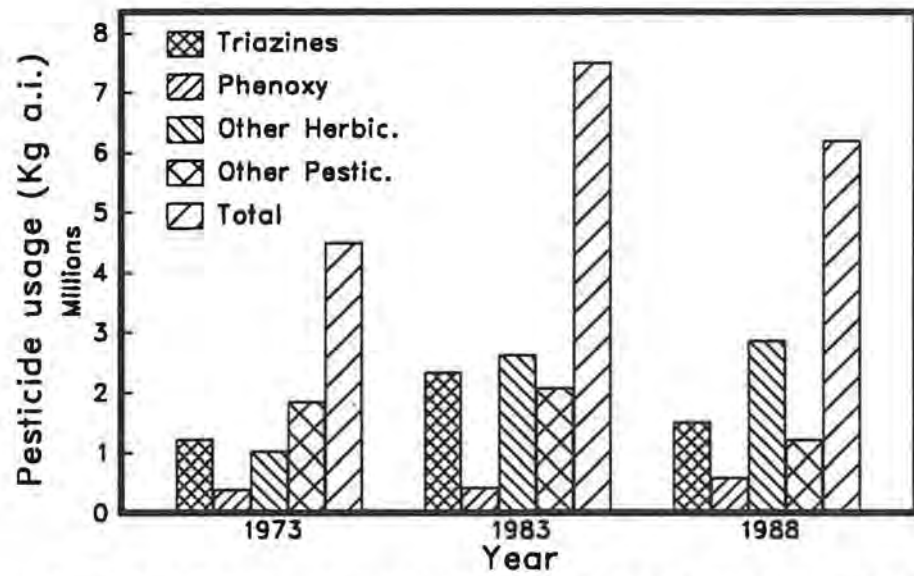
4. INTENTIONAL ANTHROPOGENIC ADDITIONS TO SOILS: PESTICIDES

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4.1 INTRODUCTION

Although agricultural pesticide usage in Canada began to increase following World War II, its rate did not increase rapidly until the early 1970's. From 1971 through 1976, pesticide sales in Canada more than tripled from approximately \$200 M to almost \$700 M (Hall 1981). By 1981, over 400 pesticides, based on active ingredient, were registered for use in Canada, appearing in over 3000 registered formulations. In Ontario, the total pesticide usage was 4.5 M kg in 1973 (Roller 1975), increasing to 7.5 M kg in 1983 (McGee 1984), and decreasing to 6.2 M kg (Moxley 1989) in 1988 (Figure 1). The non-herbicide component (insecticides, fungicides, growth regulators) has steadily decreased from 41.2% (1973) to 27.8% (1983) to 19.6% (1988). Canada's Research/Development in the pesticide industry has been rather minuscule, forcing us to use products developed in other countries, primarily in the U.S.A. We have developed our own set of registration protocols which, although often a subset of American protocols, usually steered a middle course between U.S. Environmental Protection Agency and European Organization of Economic Cooperation and Development (O.E.C.D.) protocols, with additional testing specific for Canadian conditions, such as for regional climatic and soil differences.

In the late 1950's and early 1960's, the widespread availability of commercially formulated pesticides ushered in a new era in which farmers were able to increase greatly both the yield and quality of their agricultural products, as well as improving their profitability. Application recommendations were often based on amounts necessary to prevent, or greatly suppress, a pest problem throughout the production season, rather than simply controlling it when the particular pest was a problem (the definition of "pest" in this context is broadly based, including any unwanted species, including plants and fungi as well as insects). The perception existed that farmers were now able to "control" or "manage" their production environment in a way never before possible in the history of agriculture. This led to the



Note: Other Pesticides includes insecticides, fungicides, growth regulators
Source: Economics Information, O.M.A.F., Prov. of Ontario

Figure 1. Pesticide usage trends in Ontario, 1973, 1983, and 1988.

concept that large-scale monoculture practices for crops, such as corn and soybeans, were not only possible, but the economical and logical way to proceed.

Little attention was paid to the effects of pesticides upon non-target organisms (pests or plants), nor the long-term consequences of such practices upon soil and water quality. By the late-60's the "miracle" herbicides, such as the triazines, combined with a new generation of larger agricultural equipment made it possible for farmers to convert quickly considerable acreages of idle pastureland into productive cornland. Those practices often resulted in moderate-to-severe soil erosion where excessive and careless herbicide application severely damaged grassed waterways and fence bottoms. By 1973 in Ontario, almost 1.8 million kg of herbicides were used on corn, while approximately 355000 kg were applied to soybeans (Roller 1975).

In the early 1970's, an awareness began to develop of negative side-effects of organochlorine insecticides upon non-target species, especially in those avian species which preyed upon those lower in the food chain. Biomagnification of these fat-soluble, hydrophobic pesticides in these species manifested itself in the form of gross abnormalities, and in lowered survivability of the egg hatch and of the remaining young (Peakall 1970). Most of the organochlorine insecticides were banned from the marketplace by the latter part of that decade, to be largely replaced with another class of pesticide, the carbamates. Although this group of pesticides did not tend to exhibit the adverse biomagnification effects of their predecessors, they were actually much more toxic to a wide variety of species, including earthworms, honeybees and, in general, mammals (Broadbent and Tomlin 1982; Harris and Miles 1975). However, the negative side effects of pesticide usage were now better recognized, and integrated pest management techniques became more widely accepted and used. Instead of applying blanket pesticide applications throughout the production season, attention was focussed on the most susceptible period for the target species (Harris 1972), and on how much pesticide was required to suppress, but not necessarily totally wipe them out.

During the 1980's, environmental issues grew rapidly in importance, and more sophisticated modelling scenarios were developed as an aid in predicting the transport and persistence behaviour of pesticides in various ecosystems. In most of the pesticide transport models, two particular parameters are of prime importance: a parameter to describe the partitioning between soil and water, the soil-water partitioning coefficient (K_d); and a parameter to describe the time required for one-half of the applied pesticide to disappear ($T_{1/2}$) based on first-order kinetics, where $T_{1/2} = 0.693/k$, and k is the first-order disappearance rate constant. Much of the discussion that follows deals with issues and techniques surrounding the use of these key parameters, and problems associated with accurately measuring and correctly using them.

4.2. PHYSICAL, BIOLOGICAL AND CHEMICAL REACTIONS WITH SOIL

4.2.1 Soil Sorption of Pesticides

The bonding mechanisms responsible for pesticide retention by soil components include most of the classical physical (and some chemical) bonding forces, which have been reviewed elsewhere (Chesters et al. 1989). "Sorption" is a general term used to describe solute or vapour uptake by soil without being specific about the mechanism. "Adsorption" onto a solid refers to condensation of solute or vapour on the surface of the adsorbent, and depending on the definition, usually includes interior pores of a porous adsorbent such as soil aggregates, or the interlamellar surfaces of clay minerals. Mingelgrin and Gerstl (1983) defined "adsorption" as the "excess of solute concentration at the solid-liquid interface over the concentration in the bulk solution, regardless of the nature of the interface region or of the interaction between the solute and the solid surface causing the excess".

The sorption of nonionic pesticides by soils is influenced by a wide range of both chemical and soil factors, including solute and solvent properties, soil organic and mineral properties, and soil moisture content. Chiou (1990) stated that a wide range of organic sorption behaviour can be accounted for by considering the soil as a dual sorbent, in which the

mineral fraction functions as a conventional solid adsorbent and the organic matter functions as a partition medium. In aqueous systems, adsorption on mineral matter is suppressed by water, and soil uptake consists primarily of solute partitioning into the organic matter. Chiou suggested that the presumed partition with organic matter was supported by several facts, including: (1) observed linearity of soil-water isotherms, (2) absence of competitive effects between solutes, (3) low equilibrium heats, and (4) difference in limiting sorption capacity for liquid and solid compounds.

In an earlier paper, Mingelgrin and Gerstl (1983) argued that linear isotherms, per se, were not evidence of a partitioning process rather than an adsorption process if the surface concentrations were low. They further stated that correlations between solubilities, liquid-liquid partitions and soil uptake were insufficient proof for a partition process, as had been previously proposed (Chiou et al. 1979). Many pesticides exhibit predominantly non-linear adsorption isotherms (Freundlich slope, $N < 0.95$ or $N > 1.05$) on soils and clays (Bowman 1973; 1981). Reference smectitic clays saturated with divalent or trivalent cations often result in pesticide adsorption isotherms with slopes greater than 1.05, whereas mineral soils with varying amounts of organic matter usually produced slopes less than 0.90 (Bowman 1981; 1989). Chiou's concept of organic matter acting as a partitioning medium would be at odds with that of Gamble and Khan (1992) and Wang et al. (1991) who have related atrazine sorption by soil to carboxyl-group sites on the organic matter.

Pesticide adsorption by soils has most frequently been described using the empirical Freundlich adsorption isotherm (Chesters et al. 1989), although there are some instances, such as organo-cations (paraquat, diquat) where the theoretically-based Langmuir adsorption equation is more appropriate (Singh et al. 1989). The Freundlich isotherm equation can be expressed as:

$$X/M = K_d C_e^N \quad (1)$$

where the defined parameters (with examples of units) are:

$$X/M = \text{unit mass of adsorbate adsorbed/unit mass of adsorbent} \\ \mu\text{g/g (mass); } \mu\text{mole/g (molar)}$$

- C_e = equilibrium concentration of solute, $\mu\text{g/mL}$ (mass); $\mu\text{mole/mL}$ (molar)
 K_d = Freundlich constant, $\mu\text{g}^{(1-N)} \text{g}^{-1} \text{mL}^N$ (mass); $\mu\text{mole}^{(1-N)} \text{g}^{-1} \text{mL}^N$ (molar)
 N = unitless Freundlich constant, a measure of curvature of the isotherm,
 $N > 1$, convex downwards; $N < 1$, convex upwards; $N = 1$, linear

The Freundlich constants are obtained by performing linear regression on the log-transformed adsorption data and the Freundlich equation in Log format is given by:

$$\text{Log } X/M = \text{Log } K_d + N \text{ Log } C_e \quad (2)$$

The Freundlich K_d value, commonly referred to as the soil-water partitioning coefficient, is the most frequently-used means of reporting pesticide adsorption by soils and is extensively used by modelling algorithms to predict pesticide mobility in soils. Sensitivity analysis conducted for a number of transport models has shown that relatively small variations in K_d values used to calculate pesticide movement can have a major influence upon their predicted movement (Boesten 1991; Boesten and Van Der Linden 1991; Jernlas 1990). The K_d value is therefore one of the most important environmental parameters used to assess pesticide behaviour, and top priority should be given to its accurate determination. Adsorption isotherms for a number of nonionic pesticides at low solution concentration ranges often approach linearity (N within 5% of unity). Consequently a considerable number of researchers (Karickhoff and Brown 1979; Tim and Mostaghimi 1989) have calculated partitioning coefficients based on a linear modification of the Freundlich isotherm (assuming $N = 1$) given as:

$$X/M = K_p C_e \quad (3a)$$

The linear partitioning coefficient is shown as K_p , since its units will be different than K_d , and re-arranging Equation (3a) we obtain:

$$K_p = \frac{X/M}{C_e} \quad \text{Units :} \quad \frac{\mu\text{g/g}}{\mu\text{g/mL}} \equiv \text{mL/g} \quad (3b)$$

When calculating the K_p , linear regression is forced through the origin since all isotherms must converge at that point. The downside of using linear isotherms is the introduction of a less precise version of the partitioning coefficient, with its own set of units. The magnitude of K_p is somewhat different from K_d values calculated for the same data set, therefore creating a

consistency problem in their use in models. There is no convention recommending when isotherm data would be better plotted in Freundlich form to properly account for nonlinearity.

The presence of N (Freundlich slope), in the units of K_d complicates its use. When N is not unity, the magnitude of K_d does not change by factors of 1000 when changing sets of units (e.g., μg to mg , or μmole to nmole , etc.) (Bowman 1981). Thus, great care must be exercised in converting literature K_d values into another unit set for comparison or modelling purposes. By definition, the K_d value is always evaluated at $\text{Log } C_e = 0$, $C_e = 1.0$, in whatever set of units is being used. Therefore K_d is not a numerical constant unless $N = 1$, and consequently, modellers should be very aware that the units of K_d are consistent with the requirements of their model. The proper way to set up an adsorption isotherm experiment is to ensure that $C_e = 1.0$ always falls within the equilibrium concentration range of that data set.

In a previous study (Bowman and Sans 1977) we found that the adsorption of the insecticide fenitrothion by Fe^{3+} -saturated montmorillonite was quite nonlinear, giving a Freundlich slope (N) of 1.772. If the adsorption data were plotted in nanomolar units (nanomole/mL, nanomole/g) as shown in Figure 2, then $\text{Log } K_d = 2.87$ ($K_d = 741 \text{ nmole}^{(1-N)} \text{ g}^{-1} \text{ mL}^N$). However, if the same data set was plotted in either micromolar or picomolar units, K_d would have been $153460 \mu\text{mole}^{(1-N)} \text{ g}^{-1} \text{ mL}^N$, or $3.58 \text{ pmole}^{(1-N)} \text{ g}^{-1} \text{ mL}^N$, respectively. Of the three plots, only the nanomolar plot included $C_e = 1.0$ within the data range. The concentration at which K_d was calculated in micromolar units ($\text{Log } C_e = 0$; $C_e = 1.0$) occurred far above the water solubility limit of 0.092 nmole/mL ($\text{Log solubility} = -1.04$) for fenitrothion - a physical impossibility. Unfortunately there is no means for making K_d values totally consistent because of the wide water solubility ranges involved in the various classes of pesticides, and the impossibility of conducting all adsorption isotherm experiments within the same solution concentration range. The next best step is always to ensure that K_d falls within the experimental data range.

Over a decade ago, there was a keen interest to find a means for rating "pesticide adsorption potential" that would be independent of soil parameters, equivalent to a

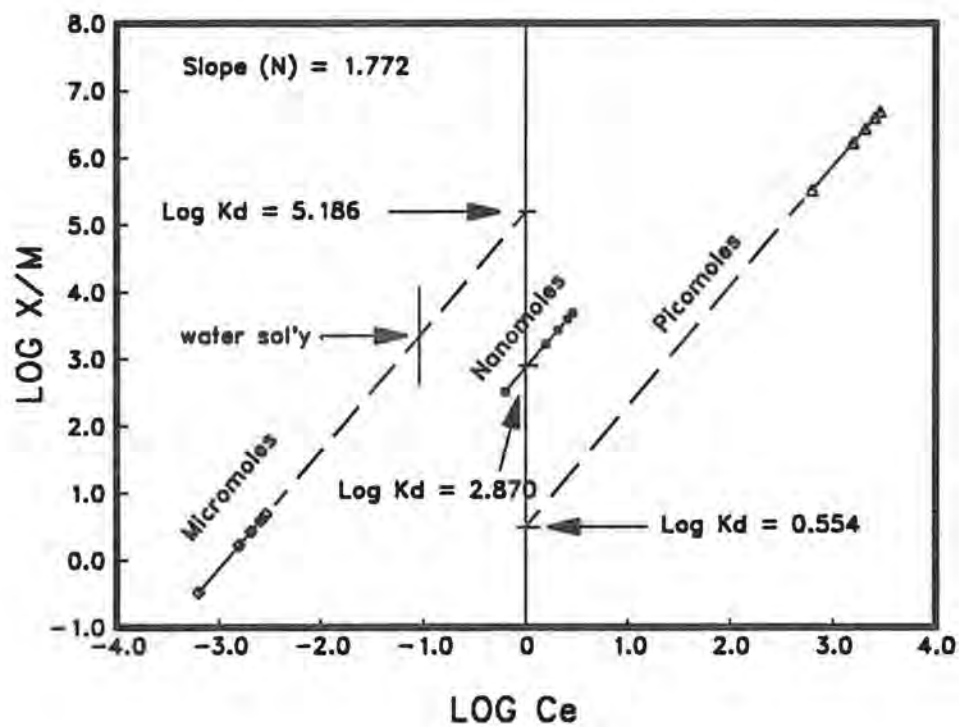


Figure 2. Log-log Freundlich isotherm of fenitrothion-Fe-montmorillonite plotted in three sets of units; X-axis - "x"mole/mL; Y-axis, "x"mole/g, where "x" = micro, nano, or pico.

universal adsorption constant for each pesticide. The closest that anyone has come to that constant was the derivation of a K_{OC} value which was a K_d value normalized for soil organic carbon (Karickhoff et al. 1979; Karickhoff 1981). However, there was not universal agreement on the implementation of K_{OC} and some researchers instead based their normalized K_d on organic matter content (K_{OM}) (Briggs 1981). The definitions are as follows:

$$K_{OC} = K_d / f_{OC} \quad (4a)$$

or $K_{OM} = K_d / f_{OM} \quad (4b)$

where f_{OC} = organic carbon fraction of the soil,
 f_{OM} = organic matter fraction of the soil.

Since soil organic matter contains approximately 58% organic carbon (Nelson and Summers 1982), then

$$f_{OC} = 0.58 f_{OM} \quad (5a)$$

and $K_{OC} = K_{OM} / 0.58 \quad (5b)$

The presence of both of these terms in the literature, as well as in modelling scenarios led to unnecessary confusion, especially for less technical personnel who could easily interchange the terms. The usefulness of the normalized K_d value (we'll use K_{OC}) lies in the fact that adsorption by soil of nonionic pesticides can be largely attributed to the organic matter fraction in soil. However, this simple relationship starts to fall apart in soils with organic matter contents less than 1 to 2 %, at which time the clay mineral contribution to adsorption accounts for an increasing proportion of the adsorption capacity. K_{OC} values increasingly underestimate the sorptive capacity of the soil for a given pesticide as the organic matter content falls below the 1 to 2% range (Sanchez-Martin and Sanchez-Camazano 1991). Von Oepen et al. (1991) found that there was a large variation in adsorption behaviour for polar compounds between soils, and that K_{OC} values were of no use in predicting their adsorption.

Gustafson (1989) developed a useful relationship called the Groundwater Ubiquity Score (G.U.S.), for predicting pesticide leachability using the relationship between the logarithm of K_{OC} and the logarithm of the pesticide half-life in soil ($T_{1/2,soil}$). Two semi-empirical hyperbolic curves generated by the following equation for two numerical G.U.S.

values, 2.8 and 1.8, divided the Log K_{OC} vs Log $T_{1/2}$ graph into three leachability zones (high, transition, low):

$$G.U.S. = \text{Log}_{10} (T_{1/2}\text{soil}) \times (4 - \text{Log}_{10}(K_{OC})) \quad (6)$$

This relationship, although not foolproof, was certainly a very good initial screening step in trying to predict whether a given pesticide would be a leacher, recognizing that compounds with low K_{OC} values are not necessarily leachers if they have short $T_{1/2}$ values, and conversely, compounds having moderate K_{OC} values can be leachers if they are very persistent. Compounds falling into the "transition" and "high" leachability zones would require more detailed investigations before registration.

4.2.2. Soil-bound Residues and Sorption Nonequilibrium

The subject of soil-bound pesticide residues has become a focal point for much attention in recent years because of the wide-spread implications it has for environmental as well as efficacy issues. Khan (1991) defined bound herbicide residues as "chemical species, originating from herbicide usage, that cannot be extracted by methods commonly used in residues analysis". This definition can be broadened to include almost all pesticide residues in soil. Extraction in this context refers to the exhaustive removal of the chemical species from a soil or plant matrix by a selected mixture of solvents. Khan's definition of bound residues excluded fragments of the chemical species possessing no pesticidal activity, and which are recycled into natural polymeric products through metabolic pathways of a biological system. The rates and extent of bound residue formation vary widely, depending on factors including properties of the specific chemical, soil type, amount and quality of organic matter, microbial activity and climatic factors (temperature, moisture). There is an indication that there is some association between chemical structure and the tendency to be bound by soil (Klein and Scheunert 1982; Roberts 1984). Chlorinated compounds appear to exhibit less binding tendencies than other structural groups, such as triazine, carbamates, phenols, anilines, or organophosphorus compounds. Khan (1991) reported that from 7% to 90% of a diverse group of soil-applied herbicides became soil-bound over periods ranging from several months to more than a year.

Sorption nonequilibrium of pesticides by soils is a different approach to describing soil-binding, emphasizing the kinetics (dynamics) of sorption processes, usually in aqueous media, as compared with soil-binding processes which were defined in terms of maximum extractability by various solvent systems. Pignatello and Huang (1991) defined nonequilibrium processes as "sorptive processes that are slow compared with concurrent transport or degradation reactions". Rao (1990) grouped these processes into two general classes, transport-related and sorption-related. Transport-related processes occur when sorption at the sorbent-solvent interface is instantaneous, but access to sorptive sites is rate-limited by solute diffusion rates within pore sequences in immobile domains. This process is of significance in aggregated or macroporous soils as well as in fissured/fractured aquifers, and in heterogeneous aquifers with layers and inclusions. Sorption-related nonequilibrium occurs in rate-limited solute interactions with specific sorption sites, including solute diffusion within the organic matter matrix.

The sorption dynamics of pesticides in soil-water systems influence their accessibility to microorganisms, which are greatly restricted in assimilating or transforming sorbed species relative to those molecules in solution (Steen et al. 1980). Sorption can also influence chemical reactions, such as base-catalyzed hydrolysis which is much slower for sediment-associated molecules than for dissolved molecules (Macalady and Wolfe 1985). There are other reactions, such as those involving humic materials or surface-catalyzed reactions on clays, which may occur only in the sorbed state.

Sorptive uptake processes appear to be biphasic, consisting of both rapid and slow phases. Pignatello (1989), in a review of sorption dynamics, stated that desorption processes are also biphasic in nature. The overall sorptive process, while initially quite rapid for freshly-applied pesticides, decreases in a multiphase exponential fashion over periods of hours, days, months, and even years, depending upon the compound and the soil. Scribner et al. (1992) found that field-aged simazine residues produced apparent sorption coefficients that were approximately 15-fold greater than freshly added simazine residues. Similarly, Pignatello and Huang (1991) reported that apparent soil-water partitioning coefficients for field-aged (2 to

14 mo.) atrazine and metolachlor residues were 2.3 to 42 times greater than for 24-hour equilibrium K_d values. Under these experimental conditions, 5.6% to 60% of the herbicides were considered to be labile.

Solute partitioning onto soil (sediment) adsorbents has been classified into "reversible" (labile) and "resistant" fractions (DiToro et al. 1982). Pignatello carried the classification one step further by subdividing the "resistant" fraction into a second "irreversible" fraction. In his definition, "resistant" refers to that portion of the adsorbed solute which has not desorbed within the time frame of the experiment, but given sufficient time eventually will desorb in its original form. The "irreversible" fraction was defined as that fraction that cannot be recovered in its original form, indicating that the compound has undergone a chemical or biological transformation. Pignatello pointed out that while some sorption processes may technically be "resistant", they will effectively be "irreversible" in environmentally relevant situations. This raises an interesting scenario for soil-bound pesticides, such as atrazine, which have been transported on eroded soil particles in runoff into streams. Given the very extensive, long-term usage of atrazine combined with the fact that the parent molecule may still comprise a considerable portion of soil-bound residues (Khan 1991), there may be a very large reservoir of eroded, soil-bound parent atrazine which has the potential to be slowly released into water courses. Perhaps this is a contributing factor as to why trace levels of atrazine are so widely detected in various bodies of water.

In the earlier discussion on sorption processes, it was noted that pesticide transport models tend to be quite sensitive to relatively small variations in K_d (or K_{OC} or K_{OM}) values. As an example, Boesten and Van der Linden (1991) reported that changing the K_{OM} or transformation rate by a factor of two typically changed the dose leached by a factor of 10. Under some circumstances, existing transport models may considerably overestimate the amounts of soil-aged chemicals predicted to leach, especially for extended time frames. There have been a number of recent efforts to incorporate sorption nonequilibrium processes into pesticide transport models (Brusseau 1991; Brusseau et al. 1991; Pignatello and Huang 1991). Brusseau (1991) reported that the multiprocess nonequilibrium (MPNE) model provided a good

description of breakthrough curves at different flow velocities, and seemed to yield a valid representation of sorption dynamics and solute transport for layered systems influenced by sorption capacity heterogeneity and multiple sources of nonequilibrium.

4.2.3 Enhanced Microbial Degradation

Microbial degradation has long been recognized as a major route by which pesticides are dissipated in soil and water ecosystems. The balance between pesticide dissipation and leaching rates in the soil profile determines their potential to reach groundwater. Ideally, the suitability of a pesticide for a given application would be based upon its ability to persist sufficiently long to perform its task, and then to degrade before it leached to groundwater. Most microbial activity in soil resides in the organic matter-rich surface layer, where there is an abundance of carbon and nutrients necessary for their activities. Hence most pesticide degradation processes occur in this surface layer, and residual pesticides which migrate to lower horizons have an increased probability of reaching groundwater before completely disappearing.

Enhanced microbial degradation in soil refers to the increase in decomposition rate of a pesticide in a soil that has been previously treated with the same or a chemically-related compound, compared to that pesticide's decomposition rate in an identical medium not previously treated (Roeth 1986). Although enhanced herbicide degradation was first reported by Audus (1949) for 2,4-D (2,4-dichlorophenoxy acid), the phenomenon did not attract much attention nor was perceived to be of economic importance at that time. In the case of foliar herbicides, such as 2,4-D, enhanced degradation in the soil was not a serious problem since they were not targeted for soil application. Later studies showed that the monochloro analog of 2,4-D, MCPA (2-methyl-4-chlorophenoxyacetic acid) was also susceptible to enhanced degradation in the field (Kirkland and Fryer 1966). In the early 1970's, enhanced biodegradation began to be associated with insect control failures (Sethunathan 1971).

Of all the classes of pesticidal compounds reported to be susceptible to enhanced degradation, the methyl carbamate insecticides and the thiocarbamate herbicides have been the most thoroughly investigated (Felsot 1989). One of the first reported carbamate control failures was for carbofuran (2,3-dihydro-2,2-diethylbenzofuran-7-yl methylcarbamate) on grape phylloxera (Williams et al. 1976). During the 1970's in the mid-western cornbelt of the U.S.A., reported failures of carbofuran to control corn rootworm damage quickly grew from only 6% during 1969 to 1974, to 28% during 1976 to 1980 (percent of test plots exceeding economic injury levels; Kuhlman and Steffey 1981). Initially it was believed that the corn rootworms had developed an increasing resistance to carbofuran, although western corn rootworm beetles collected in Illinois exhibited continuing low resistance levels (Felsot 1981). Felsot et al. (1981) suggested enhanced degradation as an alternative to the resistance theory for carbofuran control failures, based on: (1) the fact that poorest control occurred on fields where carbofuran had been repeatedly applied and, (2) the ample time for significant degradation to occur between carbofuran application and corn rootworm egg hatches.

There are a number of factors influencing the development and longevity of enhanced microbial degradation in soils, in addition to the nature of the chemical classes of pesticide involved. Chapman and Harris (1990) found that the degree of developed enhanced activity was greater when pure chemicals rather than formulated products were used, and that granular formulations presented a heterogeneous system with respect to the micro-location and accessibility of the insecticide to the microbial population. They also found that there was no enhancement of carbofuran degradation in soils maintained at 3°C following initial treatment, but that enhancement increased by 16 and 41 fold (first-order half-life ratios) at 15 and 28°C, respectively. Moisture contents for enhanced carbofuran degradation in their soils had a broad optimum range from about 9 to 36%, with enhancement factors reaching 54 fold at 27% moisture. At low soil moisture contents, enhanced carbofuran degradation failed to develop. Once enhanced microbial populations for carbofuran degradation had developed, they appeared relatively insensitive to temperature and moisture changes, even in the more extreme portions of the above-discussed ranges. Carbofuran soil concentrations of 1.0 µg/g were sufficient to trigger enhanced activity in mineral soils, but 10 µg/g levels were required in organic soils.

Cross-enhancement is the enhanced degradation of a chemical in a soil in which enhanced microbial activity was initially generated by a different chemical (Chapman and Harris 1990). Both Felsot (1989) and Roeth (1986) have cited numerous instances of cross-enhancement in their reviews. Cross-enhancement studies can provide valuable information on the nature of the adaptation process since the occurrence of cross-enhancement is a test of specificity for microbial adaptation. The incidence of cross-enhancement is much greater within chemical classes (e.g.; carbamates, organophosphorus compounds), although the degree of enhanced activity is often less than with a repeat application of the same chemical (Roeth 1986).

Despite the fact that soils are very heterogeneous in nature, most theoretical descriptions of pesticide dissipation kinetics have been based on models assuming various degrees of soil homogeneity. Gustafson (1990) developed a nonlinear pesticide dissipation model using the concept of a spatially-variable first-order rate constant to deal with the issue of heterogeneous domains in the soil. This model recognizes the fact that although most pesticide degradation processes probably follow first-order rates, there are many factors that can spatially vary on a micro-scale in the soil including microbial population density, temperature, amount and intensity of precipitation, solar intensity, soil properties (moisture, organic matter, texture, sorptive capacity), tillage and cropping practices. Gustafson found that the relative variability in rate constants was similar for both laboratory and field experiments, suggesting that the repeating scale for spatial variability may well be on the order of pore-size dimensions.

The trend towards monoculture cropping practices in many regions of North America over the past two decades may have hastened the more widespread development of enhanced degradation, since repeated soil applications of the same pesticide appear to be the most common means for its development. There has been a very intensive scientific effort during the past decade to characterize the processes involved in the development of enhanced microbial degradation and to identify the most susceptible classes of compounds. These efforts have been thoroughly covered in several excellent reviews published elsewhere (Felsot 1989; Racke and Coats 1990; Roeth 1986).

4.2.4 Adsorbent Concentration Effects on Sorption Partitioning

During the past two decades there has been an ongoing controversy regarding the influence that adsorbent concentration appears to have upon the partitioning of nonionic organic compounds between aqueous and solid phases (soil, sediments). The phenomenon has commonly been referred to by many terms, including soil (solid)-solution (water, liquid) ratio effects (Boesten 1990), solids (particle, (ad)sorbent) concentration effects (Bowman and Sans 1985; DiToro et al. 1982; Van Hoof and Andren 1991; Voice and Weber 1985), or third-phase effects (Gschwend and Wu 1985; Mackay and Powers 1987; Schrap and Opperhuizen 1989). The range of reported K_d shifts with changing adsorbent concentration can span several orders of magnitude, which would have very significant implications for use in modelling. In this discussion, factors contributing to observed adsorbent concentration effects in solute partitioning experiments are grouped into two categories, Experimental Design, and Experimental Technique.

4.2.4.1 Experimental Design

4.2.4.1.1. Solute Removal and Measuring Errors When setting up a solute partitioning experiment, one must carefully examine the quantities being measured, including their associated errors. Partitioning coefficients are obtained from adsorption isotherm experiments in which the adsorbed concentration is derived from the difference between initial and equilibrium solute concentrations, and therefore the measuring errors of the difference are additive. To demonstrate this effect (Table 1), a scenario was set up for three different percentage solute removals (5%, 10%, 50%) by a hypothetical adsorbent, with an initial solute concentration of 10 $\mu\text{g/mL}$, a 100 mL solution volume, and assuming a 3% error in determining solution concentrations (typical analytical error for gas/liquid chromatographic analyses). The "Range" columns beside the initial and equilibrium concentration columns show predicted analytical ranges, based on the 3% error. For a 5% solute removal, it would be possible to observe a negative adsorption because of measuring errors. Maximum measuring errors in the adsorbed amounts occur when the difference between initial and

Table 1. Effect of analytical measuring errors in the determination of adsorbed amounts in adsorption isotherm experiments as a function of percent solute removal.

Percent Solute Removal	Initial		At Equilibrium		Adsorbed Amount ^c		Range/ Mean
	C _e ^a	Range ^b	C _e	Range	Mean	Range	
5	10.0	9.7 to 10.3	9.5	9.2 to 9.8	50	-10 to 110	2.40
10	10.0	9.7 to 10.3	9.0	8.7 to 9.3	100	40 to 160	1.20
50	10.0	9.7 to 10.3	5.0	4.7 to 5.3	500	440 to 560	0.24

Assume constant 3% measuring error based on initial concentration of 10 µg/mL = 0.3 µg/mL

^a solution concentration, µg/mL.

^b measured range, based on 3% error

^c adsorbed solute, µg

equilibrium concentrations are small, most likely to occur for weakly adsorbed species in an adsorption system using low adsorbent concentrations. This type of error increases rapidly as solute removal from solution drops below 10% of the total. Boesten (1990) performed a detailed mathematical analysis of random and systematic experimental errors associated with sorption coefficients. He recommended that to minimize experimental errors, the adsorbent concentration should be kept as large as possible, unless this results in an equilibrium concentration too low to measure accurately. In practice it was found that designing adsorption experiments to remove from 10% to 90% of initial adsorbate from solution would generally minimize this type of error.

Measuring errors also become significant for sorption systems having very low solution concentrations, or which approach detection limits for that particular solute (more likely for very hydrophobic, low water solubility compounds). Under such circumstances, the uncertainty in measured values increase, compounded by interferences (chemical or electronic), and become increasingly significant as the detection limit is approached for that compound.

4.2.4.1.2. Sorption Nonequilibrium Failure to achieve equilibrium in sorption partitioning experiments may lead to nonsingularity in adsorption-desorption branches of the isotherm, and may be a major source of apparent adsorbent concentration effects. Before sorption experiments are conducted, equilibrium-time studies should be conducted to determine appropriate equilibration times. Van Hoof and Andren (1991) reported that partitioning coefficients for a chlorinated biphenyl congener-polystyrene system became independent of adsorbent concentration after 96 days, and suggested that the effects of particle concentration on solute partitioning requires a kinetic rather than a thermodynamic explanation.

4.2.4.2 Experimental technique. There are numerous pitfalls in sorption techniques which can result in anomalous partitioning coefficients, especially for those experimental setups discussed above which are already quite sensitive to additive measuring errors.

4.2.4.2.1 Incomplete Phase Separation Failure to completely separate the solid and liquid phases in sorption studies can produce anomalous partitioning coefficients, especially for strongly adsorbed solutes (hydrophobic, low water solubility) in sorption systems with low equilibrium concentrations and very fine particle-size sediments. Under such conditions, amounts of solute associated with unseparated adsorbent may represent a significant fraction of the amount in the solution phase (Voice et al. 1983). In our experience, centrifugation times and speeds of at least 0.5 to 1.0 hr and 40000 x g are necessary to ensure complete phase separation. Careful attention must also be paid to the deceleration phase of centrifugation as well as to post-centrifugation handling of the samples. Improperly balanced high-speed centrifuge rotors frequently experience strong vibration nodes during deceleration, resulting in resuspension of very fine materials. Samples of the supernatant solution should be withdrawn from the centrifuge tube without removing it from the rotor to minimize the possibility of resuspension. Occasionally, light mineral or organic debris in the form of a thin film will remain floating on the surface of centrifuged samples, which can be avoided when sampling by keeping a finger over the pipette as it is lowered into the tube.

Some researchers have invoked a "third-phase" effect to explain K_d -adsorbent concentration effects (Gschwend and Wu 1985; Voice et al. 1983; Voice and Weber 1985). This theory contends that dissolved concentrations are essentially in error because a portion of the measured solute in solution is actually sorbed to colloidal or non-filterable matter. Mackay and Powers (1987) stated that the magnitude of the K_d shifts, in their opinion, were too large to be completely accounted for by the "third-phase" explanation. When filtering techniques are employed for primary phase separation, it should be followed by a secondary high-speed centrifugation of the filtrate to ensure complete separation. Rigorous centrifugation techniques may well minimize or eliminate the occurrence of "third-phase" effects.

4.2.4.2.2 Strong Solute Adsorption by Adsorption Vessels. When conducting adsorption partitioning studies, caution must be taken in selection of the materials used in handling, equilibrating and storing the solutes. In general, avoid the use of plastics for storing, equilibrating or transferring aqueous solutions of the test solute. Recent studies have clearly

shown that soft plastics, such as Tygon® or Nalgene®, can quickly adsorb a large fraction of moderately hydrophilic compounds, such as the herbicides atrazine or metolachlor, from aqueous solution, whereas some harder plastics such as low or high density polyethylene remove considerably lesser amounts (Topp and Smith 1992). It would be prudent to check possible sorption by teflon stir bars in experiments using very hydrophobic compounds.

Hydrophobic compounds such as dieldrin, an organochlorine insecticide, can be strongly adsorbed from aqueous solution by certain types of glass surfaces, and removed only by organic solvents such as acetone (Bowman and Sans 1985). Dieldrin adsorption by glass was concentration-dependent, precluding the use of standard adsorption blanks to correct for a constant amount of depletion by adsorption vessels. Glass adsorption of dieldrin was also bottle-specific for certain types of glass, such as flint. A sequential blank-sample equilibration procedure should be used for very hydrophobic compounds (such as polychlorinated biphenyls (PCB) or polyaromatic hydrocarbons (PAH)) in which the different concentrations of aqueous solute solutions are initially equilibrated in their respective adsorption vessels. A sub-sample of that equilibrated volume is analyzed to determine the "actual initial concentration". An appropriate amount of adsorbent is then weighed into the remaining glass-equilibrated solution for the isotherm experiment. As a further precaution, replace plastic liners, which come in screw-capped glass bottles used in sorption studies, with tin foil-lined caps. In general, the two best materials for minimizing unexplained solute losses in sorption studies are Pyrex® glass and stainless steel.

4.2.4.2.3 Radiochemical impurities. Radioisotopes are a very convenient means for detecting very small amounts of solute in sorption systems and for maintaining mass balance calculations. However, radioisotope detection is specific only for the tagged entity and does not distinguish between the primary tagged compound and any tagged metabolites or impurities present in the system. McCarthy et al. (1986) found that minute amounts of radiolabelled impurities in sorption systems using low adsorbent concentrations (100 mg/L) resulted in anomalous partition coefficients, leading to erroneous conclusions regarding the reversibility of

the sorption process for that solute. They presented a list of five criteria which should be followed in validating solute partitioning when using radioisotopes.

4.2.4.2.4 Adsorbent/Adsorbate Losses and Measuring Errors. Errors in measuring adsorbent weights used in generating partitioning coefficient data are usually not significant when using adsorbent concentrations exceeding 100 mg/L. This type of measuring error or loss does become increasingly important with decreasing adsorbent concentrations. Baker et al. (1986) reported uncertainties in the order of 2% (0.1 mg/L at 5 mg/L) for filtering suspended solids through tared glass fibre or membrane filters. Such errors, while nominally small, compound analytical measuring errors of the same order of magnitude. Glass microfibre filters also have a small adsorptive capacity for insecticides such as parathion, which could further augment the above-mentioned measuring errors for more hydrophobic compounds.

In situations where adsorbent concentration effects have been reported, the partitioning coefficient (K_d or K_p , the linear partitioning coefficient) frequently decreases linearly at a slope of -1.0 (Log partition coefficient vs Log adsorbent concentration plot) with increasing adsorbent concentration at low adsorbent concentrations (< 100 mg/L) (Lodge and Cook 1989). In some cases the partition coefficient approached constancy at higher adsorbent concentrations (DiToro et al. 1982; O'Connor and Connolly 1980). In the linear region at lower adsorbent concentrations, a given increase in adsorbent concentration would be completely offset by the decrease in partitioning coefficient, meaning that a 1-L volume of 1 mg/L suspension would remove the same amount of solute as a 10 mg/L or 100 mg/L suspension - in other words, the total solute adsorbed is independent of adsorbent concentration in this region. These results are consistent with a secondary source of solute removal, such as glass or plastic surfaces which, while removing a constant amount, would gradually become the dominant source of removal at very low adsorbent concentrations. For studies using adsorbent (soil) concentrations exceeding 1.0 g/L, there were no consistent conclusions as to whether adsorbent concentration influenced partitioning (Farmer and Aochi 1974; Karickhoff et al. 1979; Koskinen and Cheng 1983; Lotse et al. 1968).

4.2.4.3. The Law of Mass Action: Experimental Consequences. Consider the case of a nonionic pesticide that is distributed between aqueous solution and suspended soil phases. The soil adsorbent will generally have a sorption capacity for the pesticide in the same sense that it has an ion exchange capacity for metal ions and thus the sorption capacity can be defined and measured as a saturation limit, expressed fundamentally as θ_C , the (moles/g) of sorption sites in the solid soil, or operationally as C_C , the (moles/L of slurry). When the system is at equilibrium, the pesticide distribution is governed by the law of mass action, expressed by Equation (7) (Gamble and Khan 1988; 1992; D.S. Gamble, personal communication 1992).

$$P_{\text{solution}} + S_O \xrightleftharpoons{\bar{K}_1} S_A \quad (7a)$$

$$\bar{K}_1 = \theta_A / \theta_O M_A = C_A / C_O M_A \quad (7b)$$

where P = pesticide molecules \bar{K}_1 = weighted average equilibrium constant

S_A = occupied sorption sites S_O = empty sorption sites

M_A = aqueous pesticide concentration (mole/L) (equivalent to Freundlich C_e)

θ_A = adsorbed pesticide concentration (moles/g; equivalent to Freundlich X/M)

θ_O = concentration of unoccupied sites on soil (moles/g soil)

C_A = adsorbed pesticide concentration (moles/L suspension)

C_O = concentration of unoccupied sites on soil (moles/L suspension)

The empty sorption sites (θ_O or C_O) cannot be ignored in the most general case, because if the number of empty sites changes then this will change the equilibrium distribution (θ_A/M_A) between the two phases. This can be seen by examining the behaviour of the distribution coefficient, K_p (assuming a linear isotherm) which is defined by Equation (8), and which is equivalent to Equation (3b)

$$K_p = (\theta_A / M_A) \quad (8)$$

Note that K_p defined in this scenario has the units, (L/g). Combining Equations (7b) and (8) gives the relationship between K_p and \bar{K}_1 , in Equation (9).

$$\bar{K}_1 = K_p / \theta_O \quad \text{or} \quad K_p = \bar{K}_1 \theta_O \quad (9)$$

The total concentration of sorption sites, θ_C , is

$$\theta_C = \theta_O + \theta_A \quad (10)$$

Combining (9) and (10)

$$K_p = \bar{K}_1(\theta_c - \theta_A) \quad (11)$$

Equation (12) gives a useful units conversion

$$\theta_A/C_A = V/W \quad \text{or} \quad \theta_A = (V/W) C_A \quad (12)$$

where W = Adsorbent weight (g), and V = Solution volume (L)

and W/V = Soil/water ratio (adsorbent concentration, g/L)

Substituting for θ_A in Equation (11)

$$K_p = \bar{K}_1(\theta_c - C_A/(W/V)) \quad (13)$$

For a given soil-pesticide system, the sorption capacity, θ_c , is a constant. K_p is not inherently a rigorous constant in Equation (13), and approaches constancy only for certain special limiting conditions. Pesticide sorption by soils usually exhibits limited surface coverage because of low application rates and water solubility limitations on solution concentration, and therefore $C_A \ll \theta_c$. The ratio $C_A/(W/V)$ usually increases only slightly for a several order of magnitude change in (W/V) (from 10 g/L to 10 mg/L, for example), and thus changes in K_p , as a function of (W/V) , would be small compared to experimental errors. In heterogeneous soil systems, \bar{K}_1 might decrease modestly with increasing coverage of sorption sites since the most energetic sites are occupied first. Thus K_p would also change as sorption increased under this scenario, but not in the order of magnitudes that has been ascribed to adsorbent concentration effects.

Precautions should be taken to ensure that a possible experimental anomaly is not misinterpreted as a real equilibrium phenomenon. If the system has started with all of the pesticide in solution and has not attained equilibrium, then increasing the adsorbent concentration (g/L of solution), (W/V) , will put the system farther away from equilibrium. In such a case K_p would not only not represent true equilibrium values, but would decrease as the (W/V) ratio increased. The reason is that the (θ_A/M_A) ratio in Equation (8) would be below the equilibrium value.

In general, K_d - adsorbent concentration interactions are reported most frequently under one or a combination of the following circumstances:

1. when the solute is a highly adsorbed (hydrophobic) nonionic organic compound which would tend to have low water solubility, leading to low equilibrium concentrations,
2. in presence of low adsorbent concentrations (< 100 mg/L) which result in minimal removal of the solute from solution, making it difficult to accurately measure the removal by difference between initial and equilibrium solution concentrations,
3. when systematic, technical errors or unaccounted-for losses of adsorbent or adsorbate dominate solute removal under either or both of the above two situations.

If technique- and design-related sorption errors were minimized, would one expect to observe real K_d dependence on adsorbent concentration? If so, there are some rather far-reaching consequences for partitioning studies. Consider the scenario of suspended stream sediments carrying a load of PCB's, PAH's or hydrophobic pesticides. If K_d decreases with increasing adsorbent concentration, then one should expect a portion of the sorbed organics to desorb as the sediments settle out on the stream floor (increase in adsorbent concentration in the local domain). Should turbulent water re-suspend some of this sediment, then the adsorbent concentration would once again decrease, supposedly resulting in a re-sorption of organics, reflecting the increased K_d . Or, consider the fact that if K_d values were a function of adsorbent concentration, we would not be able to use centrifugation, or any other phase separation technique, to separate phases in order to analyze solution concentrations. As in the stream scenario, the separation process would, in itself, result in changes in the very solution concentration which was to be measured. Sorption of organics by soil and sediments are in fact driven by "intensive" type of processes (kinetics) rather than by "capacity" type of processes (volume), and if there are observed dependencies between K_d and adsorbent concentration, there are likely to be some unaccounted-for physical processes influencing the sorption processes.

4.3. ENVIRONMENTAL IMPLICATIONS

4.3.1 Preferential Water and Solute Transport in Soils

Preferential flow of water with accompanying solutes through cracks, fissures, or channels formed by soil fauna or by decaying plant roots, is now a widely recognized phenomenon, which under appropriate conditions can result in rapid non-equilibrium solute transport to considerable depths in a soil profile (Beven and Germann 1982; Ehlers 1975). This phenomenon was first reported by Lawes et al. in 1882 during studies at Rothamstead when they noticed "channel" drainage preceding the regular drainage in their soil. The first arrival of applied solute at any given depth in the soil profile may occur considerably before one pore volume has been displaced (Thomas and Phillips 1979; White 1985). The phenomenon has also been referred to by a number of other terms, including "channeling", "bypassing", "partial displacement", "sub-surface storm flow" and "short-circuiting" (Andreini and Steenhuis 1990; Bouma et al. 1981; Brusseau and Rao 1990).

Beven and Germann (1982) provided an in depth discussion of what constitutes a macropore, the various types of macropores, and experimental means for determining macroporosity in soils. At the microscopic scale, storage and flow of water in any particular soil void is related to the size and geometry of that void, and flow rates will be controlled by the void of smallest size in any continuous flow path (a pore neck). The most common means of classifying pore space in soil has been the soil moisture retention curve, in terms of pore sized classes. Although macropores may constitute only a small percentage of the total pore space, they may account for the bulk of water movement through the soil. Watson and Luxmore (1986) found that under ponded conditions on a forest floor, 90% of the water flux was through 0.32% of the soil volume. In agricultural soils, macropore space is in the order of 0.5% to 5% (Germann and Beven 1981; Kneale 1985).

Since macropores may permit spatial concentrations of water flow through unsaturated soil that can not be described by Darcy's Law, current physically-based flow

models do not properly cope with the transient nature of preferential flow under field conditions. There are many researchers currently developing models for preferential water and solute flows using approaches which incorporate multi-domain concepts for the hydraulic properties of the soil (Brusseau and Rao 1990; Jarvis et al. 1991 a, b; Chen and Wagenet 1992 a, b).

Steenhuis et al. (1990) reviewed a number of modelling approaches for preferential flow that have been used either in the laboratory or in the field, including the transfer function model (Jury et al. 1986) and a deterministic mathematical approach which was solved using analytical or numerical techniques (Rao et al. 1980 a, 1980 b). Although many computer models, such as PRZM (Carsel et al. 1985), GLEAMS (Leonard et al. 1987), CMIS (Nofziger and Hornsby 1986), or LEACHEM (Wagenet and Hutson 1986) have been based on the convective-dispersive equation, it now appears from tracer and dye studies (Addiscott et al. 1978; Andreini and Steenhuis 1990; Parlange et al. 1988) that it may fail to properly describe bulk-flow processes with accompanying dispersion under field conditions. An improved approach to this problem was to distinguish between mobile and immobile water as suggested by Van Genuchten and Wierenga (1976) and by Addiscott (1977) by dividing liquid water into two distinct pore size groups. Although this approach is superior to the convective-dispersive equation, it is still rather unrealistic to divide soil water into two arbitrary groups. A preferential flow model developed by Steenhuis et al. (1990) improved upon this by considering soil water to move with a range of velocities. In their review, Brusseau and Rao (1990) noted that the phenomena attributed to transport nonequilibrium (TNE) (constrained solute access to portions of the porous medium by diffusive mass transfer) are exhibited by both nonadsorbing and adsorbing solutes. Thus the mechanism influencing this nonequilibrium is transport- and not sorption-related.

Nonideality of a soil-water system usually increases as the soil-water content is reduced from saturation, and is dependent upon the pore-size distribution of the soil. Dispersive effects steadily increase with the degree of unsaturation because an increasing portion of the pores no longer easily transmit water, thereby creating immobile water domains.

Andreini and Steenhuis (1990) used a grid lysimeter to study the spatial variability of water flow through undisturbed soil blocks from conservation and conventional tillage practices (35 cm square, 34 to 46 cm in depth). They observed large spatial variations in both unsaturated water and solute (bromide, dye) flows through these soil blocks over extended periods (10 to 30 days) using a modest input rate of only 20 mm/day. Of the 52 collector cells below the blocks, water flowed from only 16 cells under the no-till block and 21 cells under the conventional tilled block. Selected horizontal slices through the blocks following the experiment showed that there were large areas apparently untouched by the dye. In current grid lysimeter studies using large undisturbed soil blocks (48 cm cube), we have found similar, very large spatial variations in water flow under unsaturated conditions (15 mm/hr input), which should not even involve the larger macropores (worm channels) in the system. Less than 20% of the collector cells transmitted the bulk of the water flow, and often full collector tubes (50 mL) were surrounded by empty or near-empty neighbouring tubes.

Rapid movement of pesticides may occur in soil profiles having a highly conducting, coarser horizon underlying a finer horizon (such as the A/B horizon interface), during periods when surface ponding exists. Under such conditions, unstable water flow (fingering or streaming) is enhanced whenever the lower layer's water entry is very low (controlled by the surface horizon hydraulic conductivity) while having a very high hydraulic conductivity at that suction (Baker and Hillel 1990; Hillel and Baker 1988). Essentially tension-free water accumulates at the interface and periodically streams down any available pore channels, carrying with it any dissolved solutes. In field lysimeter studies using medium-textured soil cores packed with an A and B horizon, rapid movement (up to 20 cm) has been repeatedly observed for various pesticides (terbuthylazine, a triazine herbicide; Bowman 1989; isazofos, a soil insecticide; Bowman 1990) following surface ponding of water. These chemicals moved only half as far (10 cm) in adjacent lysimeters uniformly packed with a much less adsorptive, coarser-textured Plainfield sand under the same water application conditions.

In recent laboratory studies, Baker and Hillel (1991) reported that in infiltration tests when the sublayer particle size was made smaller (closer to the texture of the surface

layer), or the sublayer particle size distribution was made wider (by addition of fines), or increasing amounts of water were uniformly mixed with the sublayer prior to infiltration, then the fractional wetted volume increased until fingering was no longer observed. Recently Steenhuis and Parlange (1991) reported that layered soils are not necessarily required to produce water flow instabilities (fingering), and that it can occur in a relatively homogeneous sandy soil at rainfall rates substantially below the saturated hydraulic conductivity. In a homogeneous sand profile, the fingers are quite vertical, but deviate more from their vertical paths as the sand becomes more heterogeneous. Similar preferential flow behaviour has been described by Jury (1991) in unstructured sandy soils in California. It therefore seems apparent that water flow and solute transport in unsaturated soils is a much more complex process than earlier-held concepts of relatively-uniform matrix flow, and that observed hydraulic conductivities in unsaturated soils may be very dependent upon input rates and antecedent moisture levels as well as upon the heterogeneous nature of the soil itself.

4.3.2 Effect of Tillage Practices on Pesticide Transport in Soils

The portion of farmland in the U.S.A. employing some sort of conservation tillage has increased about 24 fold from 1963 (1.5×10^6 ha; Mannering et al. 1987) to 1987 (35.6×10^6 ha; Thornton 1987). In this discussion, "conservation tillage" practices include both "no-till" and "reduced tillage", which includes any practice leaving at least 30% crop residue on the soil surface (Allmaras and Dowdy 1985; Wauchope 1987). Conservation tillage has gained in popularity not only because it reduces soil erosion, but also because field operations can be significantly reduced, lessening input costs. There are ongoing arguments as to whether adoption of conservation tillage practices leads to increased pesticide use to compensate for lack of tillage. Wauchope (1987) stated that herbicide use would probably increase under conservation tillage, but not necessarily other pesticide usage. In many cases the development of conservation tillage practices has led to the development of different kinds and combinations of herbicide use patterns, but not necessarily greater total amounts applied.

Depending on the type of conservation tillage practiced, water infiltration may be significantly higher than on conventional tillage (Radcliffe et al. 1988), raising the potential for increased pesticide transport to groundwater. In some rainfall simulation studies on 1 m² plots (silt loam) using the Guelph Rainfall Simulator (Tossell et al. 1987), it was consistently observed that there was greater water infiltration on no-till plots compared to adjacent conventional tillage practices, and conversely, lesser runoff volumes. Edwards et al. (1988) and Dick et al. (1989) likewise reported much lower runoff volumes from no-till relative to conventional tillage, leaving more water for percolation. Much lower soil erosion losses can be expected from conservation tillage, which in turn translates into lower surface losses of strongly soil-adsorbed pesticides (nonionic pesticides of low water solubility (<1 µg/mL) and organic cations such as paraquat) (Wauchope 1987). Difference in pesticide runoff losses between the two tillage types are less distinct for more water soluble nonionic pesticides which tend to be transported in the aqueous phase. In field-plot rainfall simulation studies, it was found that about 85% to 95% of herbicides, such as atrazine and metolachlor (K_{oc} values about 50 to 100 µg^{1-N} g⁻¹ mL^N; N = Freundlich slope), were partitioned into the water phase in surface runoff. Leonard (1988) stated that the distribution of pesticide between solution and adsorbed phases can be assumed to follow relationships such as the Freundlich equation, and this has been found to be the case in these rainfall simulation studies.

The considerable amounts of crop residues remaining on the soil surface under conservation tillage increase the likelihood of significant washoff losses of freshly-applied herbicide (Felsot et al. 1990). Freshly-applied foliar pesticides are also quite susceptible to washoff losses but the hazard decreases substantially with time (Willis et al. 1992). In recent rainfall simulation studies at our research centre, substantial washoff losses of freshly-applied atrazine and metolachlor occurred on plots with high corn stover residue cover. It appeared that the herbicides did not strongly adhere to the crop residues, and a heavy rain following application quickly washed chemicals off the crop residue onto the wet soil surface, then transported them away in surface runoff water.

Isensee et al. (1990) found in their field studies that four to five times (unconfined aquifer) and 20 to 50 times (confined aquifer) as much atrazine leached into shallow groundwater under no-till than under conventional tillage. The amounts found far exceeded the level expected from piston-type displacement, which was strong presumptive evidence for preferential flow. Rainfall amounts, storm profiles and their timing following pesticide application greatly influence whether, and to what extent preferential transport of those chemicals is likely to occur. Shipitalo et al. (1990) found that a 1-hr, 5-mm rain followed by a 0.5 hr, 30 mm-rain one day later on no-till soil blocks (30 cm cubes) reduced atrazine transport through the blocks by 2-fold relative to replicate soil blocks receiving only the 30-mm rain. Light rain on herbicide-treated soil following application moved the chemicals slightly into the soil matrix, greatly reducing their susceptibility to preferential transport during subsequent storms. Even larger reductions in preferential flow of bromide ion (7 times) and strontium ion (10 times) were recorded for the same two rain scenarios. In subsequent water flow studies with the 30-cm cube no-till soil blocks they (Edwards et al. 1992) found very heterogeneous flow patterns as a result of the macroporous structure of the soil, and that average atrazine concentrations in the percolate did not seem to be influenced by rainfall intensity. Transport of the chemicals appeared to be dominated by percolate volumes rather than by rainfall intensity.

4.4. CONTINUING RESEARCH PROBLEMS

In some respects there are less serious environmentally-related problems with agricultural pesticide usage than was the case a decade ago. There tends to be a much greater public awareness and sensitivity towards environmental issues today and as a result pesticides are now used more judiciously. Extensive well-water surveys taken here in Southwestern Ontario have found declining amounts of pesticides over the past several years (unpublished report, Agriculture Canada, 1992). There is also a growing interest in the agricultural community towards more holistic forms of farming which take a more balanced view of the ecosystem. Some of the ongoing research challenges facing agriculture through the next decade range from theoretical modelling of pesticide transport and dissipation to on-farm

related research problems, such as selecting the best management practices for an individual operation.

4.4.1 Experimental Design and Data Quality

From a research viewpoint, efforts at modelling pesticide behaviour in agricultural systems have become increasingly sophisticated and complex. With this sophistication comes an increasing demand for better quality inputs, such as partitioning coefficients and dissipation rate constants. For more accurate long-term modelling scenarios, there is a need to include time-dependent K_d parameters in models that reflect the slow binding processes taking place in the soil. In the preceding discussion we have dealt in some detail with the numerous pitfalls that can and do occur in the generation of critical parameters such as partitioning coefficients. In setting up an experimental design it is of critical importance to the quality of the data generated that the researcher be aware of the errors associated with the measurements being made, and to minimize them as much as possible.

4.4.2 Modelling Preferential Flow in Heterogeneous Media

As conservation tillage practices gain acceptance throughout this decade, the influence of preferential flow behaviour on pesticides, nutrients and manure bacteria will receive increasing scrutiny. Unsaturated water flow patterns in soil exhibit great spatial variability making it difficult to simulate in modeling scenarios. Extreme spatial variability in unsaturated water flow has been observed in soil block studies (includes A/B horizon interface) which suggests that both rainfall rate as well as the antecedent moisture status of the block determines which suite of pores conduct water for a given event. In successive rainfall simulations on the same block, different combinations of highly-conducting pores (not identified macropores or worm channels) may be involved in water conduction; the only change between simulations was the moisture status of the block. It would therefore appear that unsaturated hydraulic conductivity in a given soil block could vary greatly throughout domains within that block, depending on its "moisture history" as well as the current rainfall

rate. Unsaturated water flows in soil often seem to follow along "fracture planes" which may not appear evident until dye tracers are used to visualize the flow patterns. Such heterogeneous behaviour will prove to be a great challenge for modellers to deal with, and it is evident that preferential flow is a reality in unsaturated, as well as in saturated porous heterogeneous media.

4.4.3 Farm Management Systems

Although conservation tillage practices in general are rapidly gaining acceptance, there remain lively ongoing discussions as to whether no-tillage or some form of reduced tillage is superior. While no-tillage practices have many supporters who correctly argue that no-tillage can greatly reduce soil erosion and improve soil quality, there remains the as yet-unresolved issue of the significance of rapid solute transport through the macroporous channels in the soil. In contrast, proponents of minimum tillage argue that light tillage at planting disrupts the surface access of preferential channels sufficiently long to permit pesticides to dissipate or move just below the soil surface where preferential flow is no longer a problem. The answer to these and other cropping and tillage practices may be found by developing more comprehensive approaches to farm management from an ecosystems viewpoint. In Ontario, and probably in many other jurisdictions, there is a rapidly growing movement among a broad-based coalition of farm organizations to develop environmentally-sustainable farm plans in cooperation with research and extension personnel. In Canada, this process is being stimulated by Environmental Greenplan funding, a joint Federal/Provincial program being currently put into place.

With new crop and tillage practices being tried by innovative farmers comes different requirements for pest management techniques. In some cases this may require new pesticides, improved formulations, new combinations of existing registered pesticides, or perhaps more holistic approaches to crop management which do not employ pesticides. Pesticide registration guidelines in Canada appear to be considerably more conservative and perhaps restrictive than their counterparts in the U.S.A., especially for the use of new tank mix combinations for already-registered pesticides. Often the market for such tank mixes will be

relatively small, especially for those required for new crop management techniques, and therefore there is no economic incentive for the agrichemical industry to do the necessary field efficacy studies required for registration. This fact, combined with the close proximity to, and the pressures of competition with the much freer U.S. market has driven some Canadian farmers to quietly use non-registered tank mixes. The access to new types of tank mixes is certainly an essential step for innovative farmers in successfully adapting to improved management practices.

The type of research issues involving pesticide use through the next decade will represent a cross-section of activities from the theoretical laboratory-based studies to the on-farm types of research activities alluded to above. Much more than ever before, there will be strong incentives for the research community to work closely with innovative farming groups, and to employ an ecosystems-based approach to solving and implementing new sustainable farming technologies for the next century. Pesticides, rather than being relied on as a means of controlling the production environment will instead become one of many tools available to the farmer in developing more comprehensive pest management strategies.

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AND

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AND

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C.B. Powter, S.A. Abboud and W.B. McGill

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Y.A. Kalra and W.W. Pettapiece

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PREFACE

The Environmental Soil Science conference was held August 8-13, 1992 at the University of Alberta, Edmonton, AB. It was sponsored jointly by the Canadian Land Reclamation Association (CLRA) and the Canadian Society of Soil Science (CSSS). The objective of the conference was to share theoretical and applied aspects of soil science. It also served to get participants from the sponsoring groups together to find areas of mutual interest. There were 330 participants from Austria, Bangladesh, Canada, England, France, Germany, India, Japan, New Zealand, Norway, Spain, the Netherlands, and USA.

Abstracts of the oral and poster papers were published in the Canadian Journal of Soil Science (Vol.72, No.3, August 1992. (p.299-353). Volunteer papers covered all aspects of land reclamation, soil science, and public participation in the environmental review process. Seventy six of the 164 volunteer papers were presented as posters.

The invited papers presented in the plenary sessions focused on soil quality and interaction of soils with anthropogenic chemicals, and are published in this proceedings. Publication of the proceedings has taken an unduly long time due to unavoidable circumstances and we apologize for the delay.

Grateful acknowledgement is expressed to our colleagues on the organizing committee (J.A. Robertson, Chair) for their contributions to the success of the conference.

Y.P. Kalra and W.W. Pettapiece, Compilers

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