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POTENTIAL CONTAMINATION OF GROUND WATER BY PESTICIDES

Prepared for publication by

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Potential contamination of ground water by pesticides

Abstract- The objectives of this review are to summarize existing information on the occurrence of pesticides in groundwater and processes resulting in their detection; to identify existing technologies, and to describe missing information needed to make assessments and predictions. Validated data on the occurrence of pesticides in groundwater are still limited. Pesticides can reach groundwater following normal agricultural usage and improper disposal and handling. Three frequently detected pesticides, aldicarb, atrazine, and DBCP, are considered in detail, while other reported occurrences are summarized. Mobility and transformation processes that determine the amount of a pesticide actually reaching groundwater are described. Transformation processes include microbial metabolism and chemical reactions. While these processes are well researched for the root zone, less data are available on the subsoil and saturated zone. Other factors influencing the rate and amount of pesticide infiltration include the soil-subsoil-groundwater structure, depth of groundwater, macropore flow, and rainfall or water management practices. An attempt is made to quantify the pesticide properties and field conditions to predict their potential for leaching. Experimental and mathematical models are described and the importance of well designed field studies is emphasized.

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INTRODUCTION

For many years the likelihood of contamination of ground water by synthetic organic chemicals was largely ignored. The assumption that the soil profile always serves as an efficient purifying filter led to the conclusion that extensive penetration of pollutants into ground water was unlikely. Recent reports on ground water contamination, however, aroused public and government concern about a potential threat to the quality of drinking water. Indeed, in 1981 experts (Ref. 1) speculated that in the U.S.A. almost 1% of ground water resources contain detectable amounts of foreign organic chemicals. This figure may be misleading, however, since the contamination is usually associated with populated areas and therefore probably has a proportionally greater impact on drinking water supplies.

In contrast to previous assumptions, ground water quality may be affected by human activities, particularly by the widespread use of organic chemicals. Under certain soil and climatic conditions, some organic compounds exhibit sufficient soil mobility and persistence to allow them to reach ground water; the recent discovery of aldicarb and other carbamates, as well as some halogenated hydrocarbons and triazines, in some ground water has been confirmed. The extent of occurance of pesticides in ground water is still unknown, however, and the magnitude of the problem has to be defined. Preliminary findings indicate a need for more monitoring to determine the extent of the problem and interdisciplinary research to elucidate the processes governing the transport and fate of organic chemicals in subsoil and ground water.

Description of the problem

To assess the potential for chemicals to reach ground water, the nature of soil–subsoil– ground water system and the kind of physical and chemical processes that occur in the various zones must be understood. Figure 1 indicates the hydrologic zones involved. The vadose zone, i.e. the area below the root zone and above the water table, is important in all subsequent discussions.
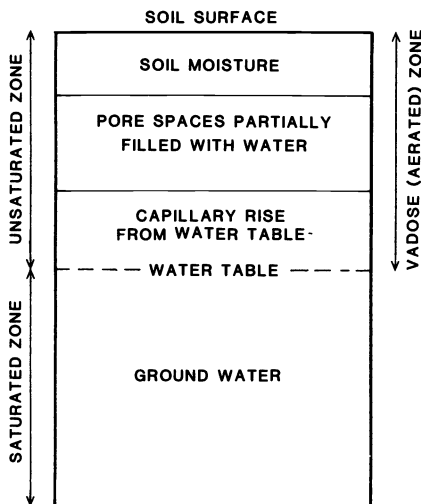

Fig 1. Hydrologic zones in a soil–subsoil–groundwater profile

A broad description of the factors influencing potential contamination of ground water by pesticides has been given by Pacenka and Porter (Ref. 2) and McCarty et al. (Ref. 3). A number of questions must be evaluated in a pesticide/ground water situation. These may be summarized as follows:

1. How will the pesticide be used?

   How much pesticide will be used? Where, when, and how will it be applied? What agricultural practices are involved, particularly water management?

2. How will the pesticide move within the vadose zone?

   What fraction of the pesticide is likely to leach out of the root zone? How much of this is lost due to microbial or chemical action below the root zone, and at what rate is the remaining pesticide likely to reach the water table?

3. How will the soil–subsoil type influence the fate of the pesticide?

4. If a pesticide reaches ground water, what is the subsequent fate?

   What are the directions and velocity of ground water flow, and how is the associated pesticide distributed? How far below the water table does the pesticide penetrate? Does the pesticide degrade in the ground water?

Objectives

The objectives of this review are to describe the nature and scope of the problem by reviewing the reported cases by considering the processes affecting the fate of a pesticide in soil, subsoil, and ground water and by identifying existing technologies and missing information necessary to determine the extent and limits of the problem. This information can be used in various risk assessments.

REPORTED CASES

Growing concern about ground water contamination by xenobiotic chemicals has fostered monitoring programs to explore the extent, type, and distribution of chemicals. Lehr (in Josephson (Ref. 1)) estimated that less than 1% of the total U.S. ground water is "badly degraded" by chemicals; the remainder is either in good condition or is manageable. The U.S. EPA also estimated that about 1% of the U.S. usable ground water contains detectable amounts of organic chemicals based on an evaluation of contamination from primary and secondary sources (Ref. 4). Others (Ref. 1), however, suggest that at least 5 years will be needed just to define the magnitude of the problem. Whether the true value is 1% or some other value does not reflect the possibility that actual human exposure may be much higher, i.e., the water is mostly contaminated where people live.

To explore the relationship between land use and hazardous substances in ground water, Greenberg et al. (Ref. 5) observed that the presence of organic pesticides in ground water was associated with agriculture, forestry, and horticulture. Cohen et al. (Ref. 6) reported the detection of a total of 12 different pesticides in 18 states of the U.S.A. The most updated values in 1985 show a total of 17 different pesticides in a total of 23 different states (Table 1:Ref. 7). According to a report to the Committee on Environmental and Public Works of the U.S. Senate (Ref. 4), 201 wells have been closed due to ground water contamination with insecticides. Since this work was published, the actual number of wells in the U.S.A. in which pesticides have been detected has increased. Based on actual analytical measurements--not statistical extrapolations--roughly 6500 wells in the U.S. contain pesticide residues arising from normal agricultural use. This has resulted in exposure to roughly 800,000 people nationwide. These numbers represent a fraction of the 13 million wells in the United States. (S. Cohen, personal communication).

The following paragraphs review reports on the presence and fate of pesticides in ground water. The emphasis is on pesticides in ground water as a result of normal use, as opposed to ground water occurrence as a result of improper disposal and poor industrial practice. Table 2 lists the structure, common name, chemical name, and solubility of the pesticides discussed in the following sections.

Aldicarb

The insecticide aldicarb was used on potato crops in eastern Suffolk County, Long Island, mainly during the 4-year period 1976-1979. Its use in Long Island was discontinued in 1980 due to accumulation of its oxidation metabolites in the upper aquifer layer. Aldicarb metabolites were detected in the shallow ground water (at a depth of 1 to 2 m) in concentrations of 20-30 µg/L and in some instances even at levels of 50-400 µg/L (Ref. 8). Pacenka and Porter (Ref. 2) prepared a preliminary regional assessment of the environmental fate of aldicarb in Long Island. The assessment of degradation, plant uptake, and leaching showed that aldicarb has considerable potential to leach. Even with the most optimistic values for uptake by plants, microbial degradation and dilution in ground water, the higher concentrations could not be reduced to safe levels.

Conditions on Long Island which are somewhat extreme, albeit not unique, lead to a very efficient downward transport. The conditions include sandy soil, a shallow water table, and low spring temperatures (at the time of pesticide application), which suppress microbial degradation and plant uptake of aldicarb.

Total aldicarb residues (aldicarb plus its sulfoxide and sulfone metabolites) have now been reported in the ground water of 15 states (Ref. 7).

The occurrence and movement of aldicarb in ground water in the Central Sand Plain of Wisconsin during the period 1980-1981 showed that most of the aldicarb was detected in shallow wells, located immediately below the water table. Aldicarb was not detected in any of the deep monitoring wells, situated roughly 60 feet below the water table. Marked seasonal fluctuations in aldicarb concentrations occurred in several wells (Ref. 9).

Snegaroff and Jamet (Ref. 10) applied aldicarb (5 times, 5 kg/ha) on 2-m-deep lysimeters containing an undisturbed calcareous soil. Aldicarb sulfoxide was detected in the percolating water 3 months after the first application and up to 6 months after the last application. Aldicarb sulfone (aldoxycarb) appeared in the percolate 2 months after the last application and 9 months after the first. It remained detectable for about 3 months. Maximum concentrations were of the order of 16 µg/L for the sulfoxide and 12 µg/L for the sulfone. The metabolites of aldicarb have a high tendency to leach to the ground water, since both are persistent and highly water-soluble and exhibit a limited absorption to soil.

TABLE 1. Typical positive results of pesticide ground-water monitoring in the U.S.[1]

Pesticide	Use[2]	State(s)[3]	Typical positive, (µg/L)	Pesticide	Use[2]	State(s)[3]	Typical positive, (µg/L)
Alachlor	H	IA, MD, NE, PA	0.1-10	1,2-Dichloro-propane	N	CA, MD, NY, WA	1-50
Aldicarb (sulfoxide & sulfone)	I, N	AR, AZ, CA, FL, MA, ME, NC, NJ, NY, OR, RI, TX, VA, WA, WI	1-50	Dinoseb	H	NY	1-5
				EDB	N	AZ, CA, CT, FL, GA, SC, MA, WA	0.05-20
Atrazine	H	IA, MD, NE, PA, WI	0.3-3	Fonofos	I	IA	0.1
Bromacil	H	FL	300	Metolachlor	H	IA, PA	0.1-0.4
Carbofuran	I, N	MD, NY, WI	1-50	Metribuzin	H	IA	1.0-4.3
Cyanazine	H	IA, PA	0.1-1.0	Oxamyl	I, N	NY, RI	5-65
DBCP	N	AZ, CA, HI, MD, SC	0.02-20	Simazine	H	CA, MD, PA	0.2-3.0
DCPA (and acid products)	H	NY	50-700	1,2,3-Trichloro-ropropane	N (impurity)	CA, HI	0.1-5.0

[1]Total of 17 different pesticides in a total of 23 different states.

[2]H = herbicide, I = insecticide, N = nematicide.

[3] States are identified by initials, e.g., AZ=Arizona, AR=Arkansas, CA=California, CT=Connecticut, FL=Florida, IA=Iowa, GA=Georgia, HI=Hawaii, ME=Maine, MD=Maryland, MA=Massachusetts, NE=Nebraska, NJ=New Jersey, NY=New York, NC=North Carolina, OR=Oregon, PA=Pennsylvania, RI=Rhode Island, SC=South Carolina, TX=Texas, VA=Virginia WA=Washington, WI=Wisconsin.

TABLE 2. Structure, common name, chemical name and solubility of selected pesticides
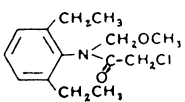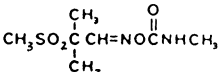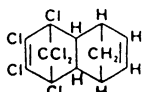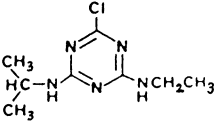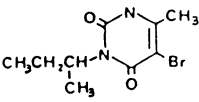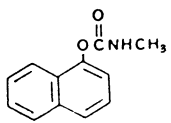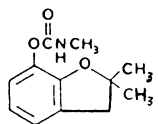
Structure	Common Name	Chemical Name	Solubility in water (ppm)
	alachlor	2-chloro-2',6'-diethyl-N-(methoxy=methyl)acetanilide	242 (25°C)
	aldicarb	2-methyl-2-(methylthio)propionaldehyde O-(methylcarbamoyl)oxime	6000 (25°C)
	aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo-exo-5,8-dimethano=naphthalene	0.027 (27°C)
	atrazine	2-chloro-4-(ethylamino)-6-(isopropyl=amino)-s-triazine	33 (33°C)
	bromacil	5-bromo-3-sec-butyl-6-methyluracil	815 (25°C)
	carbaryl	1-naphthyl methylcarbamate	120 (30°C)
	carbofuran	2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate	700(25°C)

TABLE 2 (contd.)

TABLE 2. (Continued)

Structure	Common Name	Chemical Name	Solubility in water (ppm)
	cyanazine	2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylpropionitrile	171 (25°C)
	1,2-D	1,2-dichloropropane	42700 (20°C)
ClCH=CH—CH₂Cl	1,3-D	1,3-dichloropropene	41000 (20°C)
BrCH₂CHBrCH₂Cl	DBCP	1,2-dibromo-3-chloropropane	41000
	DCPA	dimethyl tetrachloroterephthalate	0.5 (25°C)
	DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane	0.0012 (27°C)
	dinoseb	2-sec-butyl-4,6-dinitrophenol	50 (20°C)
BrCH₂CH₂Br	EDB	1,2-dibromoethane	4300 (30°C)
	fonofos	O-ethyl S-phenyl ethylphosphonodithioate	13.0 (25°C)
	lindane	1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer of not less than 99% purity	10 (20°C)
	metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide	530 (20°C)
	metribuzin	4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)-one	1220 (20°C)
	oxamyl	methyl N',N'-dimethyl-N-[(methylcarbamoyl)oxy]-1-thiooxamimidate	280,000 (25°C)
	picloram	4-amino-3,5,6-trichloropicolinic acid	430 (25°C)
	prometryn	2,4-bis(isopropylamino)-6-(methylthio)-s-triazine	48 (20°C)
	simazine	2-chloro-4,6-bis(ethylamino)-s-triazine	3.5 (20°C)

Atrazine

Atrazine is a pre-emergence herbicide used internationally in corn production. In Nebraska, atrazine is the most extensively used pesticide and it has been detected in ground water. The widespread low-level contamination suggests a non-point source of origin, namely the result of direct leaching from the surface into the aquifer.

Wehtje et al. (Ref. 11 & 12) detected atrazine in 41 monitored wells, both on terraced land (depth to ground water 5-9 m) and on bottom land (depth to ground water 0.6-1.8 m) in Buffalo and Hall counties, Nebraska. Concentrations ranged from 0.01 to 8.29 µg/L but generally were between 0.2 and 0.8 µg/L. The wells were used for land irrigation, but atrazine levels are well below the levels that would damage even the most sensitive crops. Over a 1-year period, concentrations fluctuated sufficiently in a seasonal pattern to indicate that atrazine dissipates.

With the aid of soil extractors Wehtje et al. (Ref. 11) showed that 0.07% of the atrazine applied to the soil surface leached to 1.5 m below the surface by the end of the growing season. A mathematical model indicated that trace amounts of atrazine seasonally entering the aquifer are not accumulating, since degradation is effectively keeping the level of contamination well below the level at which phytotoxicity can occur.

During the 1978 irrigation season, Spalding et al. (Ref. 13) investigated 14 Nebraska ground water samples for the presence of atrazine, alachlor, 2,4-D, EPTC, silvex, lindane, endrin, dieldrin, DDT, heptachlor, and methoxychlor. Atrazine levels ranged from 0.06 ug/L to 3.12 ug/L, with an average of 0.75 µg/L. An estimated 1% of the applied atrazine was detected in ground water. Alachlor was detected in only two samples. The other pesticides were not found.

Leaching of atrazine from corn plots had been observed previously by Von Stryk and Bolton (Ref. 14), who found 0.5-3.5 µg/L in drainwater at 70-cm depth. The discharge of atrazine monitored over a 4-year period ranged from 2.75 to 8.69 g/ha annually. Drinking water from Iowa cities using wells as their source of raw water contained small amounts of pesticides (Ref. 15). Water was contaminated with atrazine in Cedar Rapids, Marshalltown, Oskaloosa, and Waterloo. Atrazine levels ranged from 4-483 ng/L. Atrazine was the most frequently occurring pesticide in a recent series of ground water studies in northern Iowa (Ref. 16-18).

Two other critical reviews summarize atrazine findings in five U.S. states: Iowa, Maryland, Nebraska, Pennsylvania, and Wisconsin (Ref. 6 & 7). The Maryland and Pennsylvania reports were most recent. In central Pennsylvania, the U.S. Geological Survey reported atrazine in 21 of approximately 82 observation and residential wells sampled (Ref. 19). Atrazine was reported in three public wells out of over 30 public and private wells sampled in eastern and central Maryland (Ref. 20).

DBCP (1,2-dibromo-3-chloropropane)

Liquid 1,2-dibromo-3-chloropropane (DBCP) was used as a soil nematicide in California from the late 1950's through early August 1977, when the state registration was cancelled because DBCP was identified as a potential carcinogen. Usage elsewhere in the United States and in the world continued beyond that time. The major application in California had been in the sandy soil areas of the east side of the San Joaquin Valley, the valleys of Ventura County, and the irrigated desert areas of Riverside County. Application rates of DBCP ranged from about 20-90 kg/ha annually to once in 5 years (Ref. 21).

Peoples et al. (Ref. 21) tested 32 fields that had been treated with DBCP 2 to 4 years before and found the topsoil contained only about 2 to 5 µg/kg; however, DBCP appeared in well water sampled in districts where it had been used previously. Well water samples found to contain DBCP were mostly from the San Joaquin Valley. About half the wells tested contained residues, with an average value of 5 µg/L in the contaminated wells. Wells less than 30 m deep were more likely to be contaminated.

Nelson et al. (Ref. 22) studied four sites in the San Joaquin Valley with DBCP-contaminated ground water. The DBCP concentration in topsoil, subsoil, and ground water was measured. All topsoils contained µg/kg amounts of DBCP, as had earlier been noticed by Peoples et al. (Ref. 21). In subsoils between the ground surface and the water table, DBCP was found on most sites in µg/kg amounts, especially in clay and silt layers. DBCP was found in the unsaturated zone at depths as great as 15 meters (Ref. 22). These layers may sorb higher levels of DBCP, act as reservoirs, and release DBCP into downward percolating waters for years to come. DBCP in the ground water at the four sites ranged from 1.2-12 µg/L. By 1986 DBCP had been detected in 2500 irrigation, private domestic, and public wells in California and leached >120 m downward through the unsaturated zone (Ref. 23).

Other pesticides

The following are brief summaries of occurrence data for other chemicals arranged in
alphabetical order. The information for the United States is taken from two recent critical
reviews (Ref. 6 & 7) unless noted otherwise.

It should be emphasized that the validity and relevance of reports of pesticide residues in
ground water should be examined bearing in mind the following three criteria:

1. Normal pesticide use must be the most likely cause, as opposed to improper disposal and
   poor industrial practice.

2. The analytical chemistry must be reliable. In particular, for first-time occurrences,
   this requires confirmation of identity, preferably with some form of mass spectrometry.
   In situations where, for example, a laboratory is familiar with the method and is
   routinely conducting analyses, a reasonable percentage confirmation is required, e.g.
   10-20% random samples confirmed.

3. Laboratory and/or field experience with the chemical should be consistent with the
   pattern of a leachable compound, i.e., it must be mobile and persistent.
   The published literature often does not contain sufficient information to verify that
   these criteria have been met, nevertheless it reflects the present knowledge in this
   field and serves as a basis for further work.

In the discussion below and in Table 1, the term "typical positive" or "typical range" is
used. This denotes a nearly complete range, which excludes only the outliers. Statistical
tests were not used to determine the outliers; rather, this was a judgmental evaluation.

Alachlor is a chlorinated acetanilide herbicide. It has been reported in the ground water
of four U.S. states—Iowa, Maryland, Nebraska, and Pennsylvania—at concentrations that
typically range between 0.1 and 10.0 µg/L.

Aldrin is a cyclodiene insecticide. Occurrence of undetermined source was reported, where
aldrin and DDT were detected in the South Carolina ground water. Average values of 0.007
and 0.04 µg/L have been found for aldrin and DDT, respectively (Ref. 24).

Bromacil is a brominated uracil herbicide. In a test plot in Florida, a near-maximum label
rate was applied to a Lakeland sand overlying a shallow water table. Bromacil was found in
the several hundred µg/L range for the next several months.

Carbaryl is a carbamate insecticide. It was applied (Ref. 25) in rates of 25.4 kg/ha to a
sandy loam soil. The field plot contained a shallow water table (1.1 m). Carbaryl appeared
in the underlying ground water within 2 months after soil application and persisted through
the 8th month after treatment. Maximum ground water concentration, about 60 µg/L, occurred
at the end of the second month.

Carbofuran is a carbamate insecticide/nematicide. It has been found in the ground water of
three U.S. states—Maryland, New York, and Wisconsin—at concentrations that typically range
between 1 and 50 µg/L.

Cyanazine is a triazine herbicide. It has been found in the ground water of two U.S.
states—Iowa and Pennsylvania—at concentrations that typically range between 0.1 and 1.0
µg/L.

Dacthal (DCPA) is a chlorinated phthalic ester herbicide. It has been found primarily in
the form of the mono- and diacid metabolites only in the ground water of Long Island, New
York at concentrations that typically range between 50 and 700 µg/L.

DDT is a chlorinated hydrocarbon insecticide. DDE is a principal metabolite of DDT. There
are two reports of at least one of these compounds in ground water, but the sources may not
necessarily be normal agricultural practice. Sandhu et al. (Ref. 26) monitored a large
number of private wells in two rural counties for pesticides in drinking water (lindane,
heptachlor, heptachlor epoxide, aldrin, dieldrin, DDT, DDE, TDE, methoxychlor, mirex). All
water samples analyzed contained trace concentrations of these pesticides at below 1µg/L
level. DDT, the most common residue, along with TDE and DDE made up about 50% of the total
residue. DDE was detected (28 ng/L) in drinking water from city wells in Cedar Rapids, Iowa
(Ref. 15).

1,2-Dichloropropane (1,2-D) and 1,3-dichloropropene (1,3-D) are chlorinated hydrocarbon
nematicides. They have often been formulated together, although 1,3-D is the predominant
component because of its superior nematicidal properties. Both compounds are very mobile in
soil, but the former is far more persistent than the latter. This explains the fact that,
in spite of the presence of both compounds at the time of application, usually only 1,2-D
has been detected in ground water.

Mixtures of 1,3-dichloropropene and 1,2-dichloropropane have been applied to the soil for many years in certain regions of The Netherlands. In 1985, 1,2-dichloropropane was detected in 40-60 m deep drinking water wells (range <0.1-15 µg/L). Monitoring in the shallow ground water revealed concentrations up to 400 µg/L at 8-15 m depth (Ref. 27). 1,3-Dichloropropene was not found in this study.

Rexillius and Schmidt (Ref. 28) investigated the behavior of 1,3-dichloropropene in a sandy soil treated with 50 mL/m^2 (500 L/ha) Di-Trapex (a mixture of 1,3-dichloropropene and methylisothiocyanate). Soon after its application, 1,3-dichloropropene could be detected in the ground water (0.016 to 3.2 µg/L). After 140 days, this compound could still be found in shallow ground water (level 1-2 m). Methylisothiocyanate was detected only once in the ground water.

Maddy et al. (Ref. 29) studied 54 selected wells (mostly municipal) for the presence of dichloropropene and its conversion product chloroallyl alcohol. No samples of well water had detectable residues. In another, similar study in California, 1,2-D was found in well water and soil cores as much as 7.4 meters deep, whereas 1,3-D was not found in well water and only in a few shallow soil cores (Ref. 30). The 1,3-D metabolite, 1-chloroallyl alcohol, was found at 0.6 m in soil at 87 ppb. 1,2-D has also been found in the ground water of three other U.S. States—Maryland, New York, and Washington—as a result of agricultural practice. 1,3-D was not found in these studies. 1,2-D typically occurs in U.S. ground water in the range of 1-50 µg/L.

Dinoseb is a substituted dinitrophenol herbicide. In the United States, it has been found in the ground water of Long Island, New York at concentrations that typically range between 1 and 5 µg/L (Ref. 6).

Dyfonate is an organophosphate insecticide. In the United States it has been found only in the ground water of northeast Iowa. Dyfonate met the three criteria listed above only marginally. There was no question about its presence (0.1 µg/L) in the spring draining the ground water basin, or of its use in agriculture, but its persistence and mobility are such that it would be classified as a marginally leachable compound. The aquifer was composed of solution limestone and overlain by karst topography, a vulnerable environment.

EDB is a low-molecular-weight halogenated hydrocarbon nematicide/insecticide. It has been found in the ground water of eight U.S. states (Arizona, California, Connecticut, Florida, Georgia, Massachusetts, South Carolina, and Washington) at concentrations that typically range between 0.05 and 20 µg/L.

Lindane is a halogenated hydrocarbon insecticide. It was found in 5 of 19 wells investigated on the coastal aquifer of Israel. Concentrations ranged from traces to 0.015 ug/L. α-HCH was detected in one well (0.004 µg/L). These wells were between 13 m and 26 m deep; the soil above the water table was sandy. Aldrin, o,p'-DDD, p,p'-DDT, dieldrin, heptachlor, and heptachlor-epoxide were not detected (Ref. 31). Achari et al. (Ref. 24) sampled 27 wells in Georgetown County, South Carolina and found an average of 0.001 ug/L of lindane in the ground water (range: nondetectable residues to a maximum of 0.021 µg/L). The average depth of the wells was 21 m. The source of these contamination incidents was not determined and may not be normal agricultural practice.

Metolachlor is an acetanilide herbicide. It has been found in the ground water of two U.S. states—Iowa and Pennsylvania—at concentrations that typically range between 0.1 and 0.4 µg/L.

Metribuzin is an unsymmetrical triazine herbicide. It has been found in the ground water of only one U.S. state—Iowa—at concentrations that typically range between 1.0 and 4.3 µg/L.

Oxamyl is an oxime carbamate insecticide/nematicide. It has been found in the ground water of two U.S. states—New York and Rhode Island—at concentrations that typically range between 5 and 65 µg/L.

Picloram is a chlorinated picolinic acid (pyridine carboxylic acid) herbicide. It was found by Frank et al. (Ref. 32) in 2 of 159 wells investigated in Ontario. The occurrence (0.1 to 1.5 µg/L) was thought to have resulted from subterranean movement of the herbicide. Contamination of many wells with a large number of other herbicides could be ascribed to direct contamination, such as spilling, back-siphoning from spray equipment, herbicide drift during spraying, or run-off by rainwater.

Prometryne is a symmetrical triazine herbicide. It was applied to sandy loam field plots by La Fleur et al. (Ref. 33). It appeared in the underlying ground water within 2 months after soil application and persisted through the 16th month. The maximum concentration (from the 8th to the 16th month) was about 48 µg/L. The field plot had a shallow water table, about 1 m below field surface.

Simazine is a symmetrical triazine herbicide that differs from atrazine in structure by only one methyl substituent. It has been found in the ground water of three U.S. states----California, Maryland, and Pennsylvania--at concentrations that typically range between 0.2 and 3.0 µg/L.

Current projects

In light of the potential problem posed by pesticide contamination of ground water, an increasing number of ground water monitoring studies are either being carried out or are in advanced stages of planning in various countries. Since there are too many studies to describe, only the most important ones in three countries are outlined below. Some regulatory initiatives in this area are also mentioned briefly.

In the Federal Republic of Germany (FRG), several programs to monitor pesticides in ground water have been initiated by local governments and the chemical industry and will continue at least for the next 2 or 3 years. The programs will continue until the problem has been characterized, i.e., until the necessary analytical methods have been validated for the desired low detection limits and until the necessary data have been developed. In addition, the FRG has three zones of protection around public wells. Zone I is the immediate area surrounding the well, and is usually protected by a fence. Zone II covers an area which is defined by a ground water flow time of 50 days from its outer borderline to the inner center (Zone I). The diameter of Zone II amounts usually to several hundred meters. Zone III covers the area corresponding to the total area of which the ground water flow contributes to the well, and can amount to two or more kilometers. Application of pesticides are not allowed in Zone I and restricted in Zones II and III.

In The Netherlands, a network of observation wells has been set up. Monitoring is for a wide range of inorganics and organics, including several pesticides, and will continue indefinitely. In addition, drinking water reclamation areas are protected by zones of restricted pesticide usage.

In the United States, a national survey for pesticides in ground water is being designed by the Environmental Protection Agency (EPA). The design type is stratified random sampling done in three stages--(1) select counties, (2) select county segments, (3) select wells. Multi-residue methods are being developed and validated for low-level detection of over 60 different pesticides and transformation products. The goals are to characterize the extent of the problem, correlate the well results with hydrogeological and pesticide usage field conditions, and roughly estimate the human exposure. The final report is due in 1989 (Ref. 7). The EPA, the U.S. Geological Survey, and various state and local governments have cooperated and are continuing to cooperate on a number of projects to analyze ground water for individual chemicals and multiple residues. Finally, EPA has been banning and restricting the use of some pesticides due to ground water contamination, beginning with the DBCP ban in 1979.

Pesticides in ground water from improper disposal, spills and misuse, and poor handling

The principal focus of this paper is pesticide contamination of ground water as a result of normal pesticide use. There is, however, a significant potential for ground water contamination by pesticides as a result of unauthorized use. In fact, the potential for certain pesticides to leach to ground water may be increased by high concentrations of pesticides, cosolvents, and other synthetic organic materials (Ref. 34). In addition, changes in pump pressure and improper hookups to wells and water lines can cause back flow of tank mixtures into water systems, and leaching per se is not the source of contamination.

Zoeteman et al. (Ref. 35) identified pentachlorophenol as one of the compounds present in ground water in the Netherlands. The contamination resulted from waste dumps. The chlorinated hydrocarbon insecticides aldrin, isodrin, and telodrin, not normally considered to be mobile in soil, have also reached ground water following unauthorized usage. These pesticides were detected in the shallow ground water underlying a polder near Rotterdam, where contaminated mud dredged from the Rotterdam harbour has been deposited on a large surface area of polderland (Ref. 36). The original land surface was raised 7 meters. The pesticide concentrations vary with the depth, and range from <0.05 to 2.9 µg/L. Due to upward seepage, at present no leaching into the underlying aquifer occurs. Consolidation processes will take place, however, the author expect that after ca. 50 years a downward waterstream will result in contamination of the aquifer and horizontal spreading of the contaminants.

A few incidents have been confirmed, and others are suspected, where improper termite treatment with chlordane has contaminated drinking water wells (Ref. 37).

A recent study in the state of Iowa (USA) demonstrated ground water contamination as a result of poor handling by farm chemical dealers/formulators (personal communication, Hallberg, 1986).

The preceding examples of spills, disposals etc. are only illustrative and probably reflect a small fraction of such occurrences worldwide.

PROCESSES

Fate in soil (mobility and transformation)

Mobility. A portion of all pesticides used in agricultural practice reaches soils. Even
when the pesticide is applied to plant foliage, the soil is a major recipient, reservoir,
and site of potential degradation. Therefore, the fate of a pesticide in the soil has
always been a principal environmental concern. Whether a chemical that has reached the soil
surface or has penetrated into soil will remain there or will be continually redistributed
between the solid, liquid, and gaseous phases depends on the concentration of the chemical
and its equilibrium distribution coefficients between the various phases.

If the soil were a completely inert matrix, like quartz sand, then the physicochemical pa-
rameters of a compound, such as water solubility and vapour pressure, would be the primary
factors influencing all transport processes in soil. However, since soil is a complex
mixture of organic matter and inorganic components having a variable sorption potential for
organic compounds, sorption processes in combination with physicochemical parameters play a
key role in determining the mobility, and even degradability, of a substance in soil. Soil
sorption determines to what extent a compound will vaporize from the soil surface or will be
transported laterally (runoff) or vertically (leaching) by water.

Soil sorption processes have been reviewed by Bailey and White (Ref. 38 & 39), Hamaker and
Thompson (Ref. 40), Kenaga and Goring (Ref. 41) and Karickhoff and Morris (Ref. 42).
Various types of intermolecular interactions are involved in sorption, including Van der
Waals-forces, hydrogen-bonding, charge transfer, ligand exchange, ion exchange,
dipole-dipole interactions, etc. Depending on the complex nature of the soil organic matter
and the different mineralic components, the soil sorption characteristics of different soils
can vary widely.

Temperature and incubation time also seem to be essential factors influencing soil sorption
coefficients. It now seems clear that sorption does not reach equilibrium in a short peri-
od of time; apparently an immediate rapid sorption is followed by slow continued sorption
over a long period of time (Ref. 38 & 40); presumably, initial sorption is a surface
phenomenon that is followed by a slow migration of the chemical into the organic matter
matrix. This kind of sorption behavior suggests that desorption would approach equilibrium
at an even slower rate and that distribution coefficients obtained from desorption data
normally would be higher than coefficients obtained from sorption data (Ref. 43 & 44). A
corollary of the work by Karickhoff and Morris (Ref. 42) is that sorption equilibrium of
hydrophillic pesticides is likely to be much more rapid.

Despite the tremendous complexity of the sorption process in soil, a remarkably good rela-
tionship has been found between the organic matter content of soils and their capacity to
sorb most organic chemicals and, in particular, nonionic organic chemicals. Hamaker and
Thompson (Ref. 40) found that variation in sorption coefficients from various soils was much
lower when the calculation was made on the basis of the organic carbon content rather than
on a total soil basis. Rough estimates of sorption coefficients can be made on water
solubility (Ref. 45) and octanol/water partition coefficients (Ref. 46).

Much greater variability in sorption coefficients, expressed on the basis of organic carbon
content, is to be expected for ionic organic chemicals. Carboxylic acids in ionic form will
not be sorbed and may even be repelled from the soil organic matter surfaces because of
their negative charge. As the pH of the soil is lowered, the amount of unionized organic
matter and unionized compound increases. Sorption consequently increases because the com-
pound behaves more and more like a neutral molecule. Such chemicals as 2,4-dichlorophenoxy-
acetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), dalapon, dinoseb, dicamba,
chloramben, and picloram behave in this manner. These compounds also tend to be sorbed
strongly by hydrated iron and aluminum oxides, especially at low soil pH values (Ref. 38 &
40). Sorption of a phosphonic acid, such as glyphosate, appears to be related to the
phosphorus-fixing capacity of the soil rather than to the organic matter content (Ref. 47 & 48).

Sorption of cationic materials, such as the bipyridyl herbicides, chlormequat (CCC) or
nitrogen bases with high pKa's, is related to the cation exchange capacity of the soil.
Recording their soil sorption coefficients is the best current method of measuring the
comparative leachability of organic chemicals in soil. An extensive literature review on
the sorption properties of numerous organic compounds, including pesticides, is given by
Reinbold et al. (Ref. 49).

Transformation. The soil water sorption equilibrium not only governs the transport
mechanisms from the solid to the vapor and water phase, but also influences the rate of
degradation of a chemical. In most instances only the free, nonadsorbed molecule seems able
to undergo biotic transformation processes. Sorption can have differing effects on abiotic
processes as noted in the hydrolysis section below. Briggs (Ref. 50) has shown that within
the very varied group of pesticides, the correlation of increased persistence with
increasing adsorption is clear. In other words, the more mobile an organic compound is in a
soil the more easily it is degraded. Atrazine, however, is probably an exception to this theory.

Abiotic chemical reactions

Important chemical reactions are hydrolysis, oxidation, and reduction. Hydrolysis is an important reaction throughout the whole system, while photolysis is limited to the soil surface. Abiotic oxidation and reduction of organic chemicals in the subsoil may be important pathways but at this time there is lack of information in the literature.

Hydrolysis. Hydrolysis can be defined as a reaction where the bond-breaking requires the presence of water or its counterspecies hydronium ion and hydroxide ion. In less precise and less inclusive terms, it usually means breakdown of organic chemicals by water. Hydrolysis is extremely important for determining whether pesticides are likely to contaminate well water. This is because, unlike root zone degradation, volatilization, and photodegradation, hydrolysis is a mitigating process that can occur at any point in the soil, subsoil, and saturated zone environments.

This section includes discussions about mechanisms of hydrolysis, factors influencing hydrolysis and structure- reactivity relationships.

1. Mechanisms

Almost all hydrolysis reactions are unimolecular or bimolecular. (Molecularity refers to the number of ions or molecules undergoing bond breaking and/or bond making in the rate determining step.). However, most bimolecular hydrolysis reactions are experimentally pseudo-first order. That is, in normal environmental conditions, the concentrations of water and its counterions are constant and sufficiently large that the rate law only reflects the concentration of the reactant chemical.

Two examples of unimolecular reactions are solvolyses and eliminations of conjugate bases (E1CB). An example of the latter reaction is the hydrolysis of aldicarb in the pH range 5 to 8 (Ref. 51). An example of the former reaction is the conversion of ethylene dibromide to ethylene glycol in the pH range 5 to 9 (Ref. 52). Examples of bimolecular reactions are the hydrolysis of many organophosphates via either tetrahedral intermediates or the Sn2 pathway in alkaline conditions (Ref. 53), and the E2 hydrolysis of DBCP to 2-bromoallyl alcohol via 2,3-dibromopropene (Ref. 54).

2. Factors influencing hydrolysis

Several naturally occurring factors can influence hydrolysis rates--pH, temperature, sorption, and other dissolved and suspended species in water.

(a) pH

The dependence of hydrolysis rates on pH is well established. The most comprehensive, critical review of hydrolysis of organic compounds in ambient conditions, including information on pH dependence, was done by Mabey and Mill (Ref. 55). Based on this review, and other references cited in this section, the following generalizations can be made about pH dependence on hydrolysis at ambient conditions.

epoxides - neutral catalysis with some acid contribution.
esters - base catalyzed process is dominant.
organophosphates - base catalyzed and neutral catalyzed processes may be dominant, depending on the chemical.
alkyl and aryl halides - neutral catalysis dominant.
carbamates - neutral and base processes both contribute (first-order dependence on hydroxide ion).
triazines - acid catalysis important.

Some specific examples follow. These values were measured or extrapolated to pH 7 and 20°C or 25°C.

Chemical	REFERENCE	Class	Approximate half-life (weeks)	Comments
aldicarb	56, 57, 64	carbamate	50-500*	alkaline catalysis
EDB	52	halocarbon	ca. 400	no pH dependence pH 5-9
atrazine	58 & 59.	triazine	30,106	acid catalysis
methyl parathion	55	organophosphate	10	neutral catalysis
DBCP	54	halocarbon	4,000	alkaline catalysis

* Values for 15°C; total toxic residues

(b) Temperature

At ambient temperatures, hydrolysis reaction rates almost always increase with increasing temperature. The increase follows the relationship

$$lnk = -Ea/RT + lnA$$

where k = rate constant, Ea = activation energy, R = gas constant, T = temperature in K, A = Arrhenius preexponential factor. The Ea is determined by plotting lnk vs. 1/T. Obviously, temperature dependence is highly dependent on Ea, which for hydrolysis reactions usually ranges from 15-25 kcal/mole in the ambient temperature range. Thus the reader is cautioned about using the chemist's rule of thumb, k doubles for every 10°C increase. For example, the average increase in k for 21 phosphorus esters hydrolyzed at 20°C and 30°C was 3.75 (Ref. 60). It is common knowledge that shallow ground water temperatures generally equal the mean annual temperature for the particular region. For example, ground water temperatures in the northern United States are generally 5-10°C (45° N latitude). Literature rate data are usually reported at higher temperatures and are therefore higher than may be encountered in the real world.

(c) Sorption

The effect of sorption on subsurface hydrolysis rates is one area that clearly needs more research. Macalady and Wolfe (Ref. 61) recently showed that when hydrolysis reactions were studied in the presence of soil and surface water sediments "....the rate constants of pH independent ('neutral') hydrolyses are the same within experimental uncertainties as the corresponding rate constants for dissolved aqueous phase pesticides. Base-catalyzed rates, on the other hand, are substantially retarded by sorption and acid-catalyzed rates are substantially enhanced." This latter point is supported by some earlier work on atrazine, which demonstrated enhanced acid-catalyzed hydrolysis in the presence of sterile soil and also in the presence of a carboxyl resin (Ref. 62).

(d) Other Dissolved and Suspended Species

Dissolved humic material (fulvic acid) was found to retard the rate of 2,4-D ester hydrolysis (Ref. 63), similar to results cited above.

Recent studies on aldicarb have disclosed a rather surprising phenomenon. The aldicarb metabolites aldicarb sulfoxide and sulfone, as well as the parent chemical in one study, are more stable in aquifer-type environments than in laboratory systems.

Aldicarb species	Hydrolysis half-lives (weeks) at 15°C			Aldicarb species	Half-lives (weeks) at 20°C	
	pH 6.0	pH 7.0	pH 8.0			
	distilled water					
aldicarb sulfoxide	603	60	6.0		Anaerobic (pH 7.7)	Anaerobic w/limestone (pH 8.3)
aldicarb sulfone	208	20	2.1			
	well water			aldicarb	91	186
aldicarb sulfoxide	1173	117	11.7	aldicarb sulfoxide	3.7	4.1
aldicarb sulfone	347	35	3.5	aldicarb sulfone	3.7	16
(Adapted from Ref. 64).				(Adapted from Ref. 56).		

In the Miles and Delfino study (Ref. 56), water was used from the Florida (U.S.A.) Biscayne Aquifer in an abiotic, laboratory microcosm. Crushed limestone was added in one series of experiments in order to simulate more closely the limestone aquifer environment. Thus, in both studies, aldicarb species were significantly more stable to hydrolysis in the systems that most closely approximated aquifer environments. So far, there is no satisfactory explanation for this phenomenon.

Care should be exercised in interpreting hydrolysis rate studies in cases where water is not free of microorganisms and/or free enzymes.

3. <u>Structure-Reactivity Relationships</u>

The idea of structure-reactivity relationships in hydrolysis reactions is not new
(Ref. 65). Such relationships are also called Linear Free Energy Relationships
(LFERs) because they correlate free energy changes as determined by rate or
equilibrium constants between model reactions--e.g. ionization of benzoic acids--and
particular reactions of interest--e.g. hydrolysis of organophosphates. LFERs can be
powerful tools in that they provide a theoretically and experimentally valid basis
for estimating hydrolysis rates of compounds that have not been studied.
Most of the pesticide hydrolysis LFER work has been on carbamates and
organophosphates. Second order alkaline hydrolysis rate constants for four series of
carbamates have been correlated with the pKa of the leaving group alcohols. The
greater the pKa, the slower the hydrolysis rate (Ref. 66). Several series of
carbamates and oxime carbamates also have hydrolysis rates correlated with Hammett
sigma values--the greater the electron withdrawing power of the substituent, the
faster the hydrolysis rate (Ref. 67). Similar Hammett sigma relationships have been
found in two studies of the hydrolysis of organophosphate pesticides (Ref. 53).

Biological transformations

The predominant metabolic activities of microorganisms in soil must be viewed from the
aspect of energy utilization. Most organic materials can serve as the source of energy for
at least some microorganisms. The microbial conversion of pesticides is being reviewed by
the IUPAC Pesticide Chemistry Commission, and a report will appear in the near future. In
general, microbial contributions to metabolic alteration of pesticides may be classified in
several categories, as shown in the following scheme (Ref. 68).

<u>General classification of microbial metabolism of pesticides</u>

<u>Nonenzymatic</u>

      A. Participation in photochemical reactions
      B. Contribution through pH changes
      C. Through production of organic and inorganic reactants
      D. Through production of cofactors.

<u>Enzymatic</u>

      A. Incidental metabolism: Pesticides themselves cannot serve as
         energy sources

         1. Metabolism by generally available enzymes

            a. Metabolism due to generally present broad-spectrum enzymes
               (hydrolases, oxidases, etc.)

            b. Metabolism due to specific enzymes present in many microbe
               species

         2. Analogue-induced metabolism (cometabolism)

            c. Metabolism by enzymes utilizing substrates structurally
               similar to pesticides

      B. Catabolism: Pesticides serve as energy sources

            d. Pesticides or a part of the molecule are the readily avail-
               able source of energy for microbes

            e. Pesticides are not readily utilized. Some specific enzymes
               must be induced

      C. Detoxification metabolism

            f. Metabolism by resistant microbes

In the case of incidental metabolism, the pesticide molecules themselves cannot serve
primarily as energy and carbon sources for the microorganisms; they are degraded either
by broad-spectrum enzymes, such as hydrolases, reductases, and oxidases, or by specific
enzymes commonly present in many microorganisms.

Once a pesticide has been altered by general microbial activities, it then often becomes an appropriate substrate that can be used as an energy and carbon source by certain microbes in further catabolic processes. If the carbon skeleton of a chemical compound is radio-actively labeled by incorporation of ^{14}C, the rate of mineralization can easily be followed by trapping and measuring the developed $^{14}CO_2$.

The spectrum of enzymatic activities in microorganisms pertains to the following general reaction types:

<u>Hydrolysis reactions</u> represent the first step in the degradation of many compounds, such as esters, carbamates, acid amides, etc.

<u>Reductive reactions</u> probably prevail under partially anaerobic conditions. The most common types of reductive reactions are: reduction of a nitro-compound with formation of the corresponding amino-compound (Ref. 69) and dehalogenation (Ref. 70 & 71); the most well known case is the conversion of DDT to DDD.

<u>Oxidative reactions</u>

Typical examples are:

(1) Epoxidation of unsaturated hydrocarbons, such as aldrin and heptachlor, to the corresponding epoxides.

(2) Hydroxylation of aromatic ring systems (e.g., carbaryl benzanilide fungicides (Ref. 72) and bentazon (Ref. 73) and activated alkylcarbon atoms.

(3) Successive oxidation of a hydroxy-compound (alcohol) to form the corresponding carbonyl compound (aldehyde) or carboxylic acid $-CH_2OH \longrightarrow -CH = O \longrightarrow -COOH$

(4) Oxidation of thioethers to sulfoxides and sulfones.

(5) Oxidative dealkylation of alkylamines.

(6) Oxidative ring-opening processes of aromatic ring systems (e.g., chloridazon, Ref. 74 & 75).

(7) Oxidative decarboxylation.

<u>Isomerization</u> is not only a light-induced process but it can also occur as a consequence of microbial metabolic activity (e.g., formation of α-HCH from γ-HCH by certain microbes under anaerobic conditions (Ref. 76)).

<u>Synthetic metabolism.</u> Some microbial systems add certain ligands to pesticides or their metabolic intermediates. The most commonly occurring reactions are acetylation (Ref. 77) and methylation (Ref. 78).

<u>Polymerization</u> reactions may be considered a special case of synthetic metabolism. Such reactions occur mostly among halogenated anilines and phenols. From anilines, corresponding azo- and anilino-azobenzenes are formed (Ref. 79). The formation of bound residues, at least as the incorporation of pesticides or their fragments into the soil organic matter matrix is concerned, can also be regarded as a special synthetic capacity of soil microbes.

Fate in subsoil and the unsaturated zone

While conversion reactions govern the fate of organic chemicals in surface soils, not much is known about the transformation of these compounds in the subsoil environment. Scattered information obtained in recent years indicates that microbial activity, as well as chemical reactivity, occurs even at very deep layers, although the rate of these reactions has not been determined.

<u>Abiotic chemical transformation.</u> Not much is known about chemical reactions and the transformation of organic pollutants by subsoil surfaces. Qualitative and quantitative data are needed for any estimation of the role of these processes in cleaning the subsurface zone free of organic compounds. It is difficult to differentiate between abiotic and biotic transformation, especially when dealing with reactions in the subsurface environment. Some data are available on reactions that may occur with inorganic ions, such as Fe^{+2} and HS^-, with reactive groups of soil organic matter and with clay surfaces. There are some indications that biotransformations are accelerated by chemical catalysis (Ref. 80).

<u>Biotic transformations.</u> Studies on the presence and activity of microorganisms in the subsoils are scarce. Part of the problem is the difficulty in obtaining representative, undisturbed and uncontaminated subsoil samples for experimental work.

Recent measurements have shown that the physicochemical situation in water-saturated sediments in various regions in The Netherlands seems to be favorable for microorganisms, as far as pore volume, pH, salt concentration, and temperatures are concerned (Ref. 80). Sulfate-reducing bacteria in well water in Montana (Ref. 81) and nitrate-reducing bacteria down to 40 meters in the unsaturated zone of the chalk formation in England (Ref. 82), have been reported. Various other bacteria were isolated from water tables at a depth of 4 to 6 m; however, fungi were not detected in the same water table (Ref. 83 & 84). The data so far obtained indicate considerable distribution of microorganisms in the deeper subsurface zones.

In addition to their occurrence, it is important to define the activity of microorganisms in the subsoil, in a region of limited nutrients and energy sources. Microbial activity depends on the availability of nutrients and other metabolic requirements, such as oxygen or nitrates, as substrates for respiration. The limited availability of even one of these substrates, "the rate-limiting substrate," will determine activity, namely, the rate of pesticide degradation. The mathematics and modeling of this process were described recently by using a modeled biofilm kinetics approach (Ref. 3). The concept of a minimum substrate (S min) to support activity has been examined and it has been shown that below a certain concentration of a substrate a steady state cannot be supported. The minimum values for aerobic systems appear to be lower than for anaerobic systems and the biological process is quite fast, even at low substrate concentration.

Below the minimum concentration, a substrate will degrade only if it is being used as a secondary substrate. Relatively little is known of the kinetics of degradation of mixed substrates at low concentrations. In the upper layer of the water table, oxygen is being consumed by microorganisms to produce an anaerobic environment. Downward transport of organic matter, as well as deep rooting, may contribute to the presence of organic matter in ground water in some areas.

In some areas of The Netherlands, measurements of ground water at a depth of a few meters have shown differences in pH ranging from 3.5 to 8.1 (Ref. 80). Nitrate, sulfate, Fe^{+2}, and Mn^{+2} concentrations varied for the different areas from very low to high. In some areas nitrogen was detected mainly as NH_4^+, and much of the Fe and Mn ion were found in their reduced form. In many areas strong reducing conditions were measured in ground water. Thus, the differences in ground water composition may have different effects on the fate of chemicals in the subsurface.

Biodegradation studies of short-chain halogenated hydrocarbons have shown faster degradation at relatively high concentration and very slow degradation for alkyl halogens at lower concentrations when present in municipal waste water (Ref. 85). Differences in degradation were reported for different sites and different concentrations. These compounds were much more persistent in aerobic regions of the subsurface than in the anaerobic environment (Refs. 34, 86-88). The many differences in degradation have yet to be examined and understood.

The rate of conversion of aldicarb sulfoxide and aldicarb sulfone in subsoils was much faster under anaerobic incubation conditions than under aerobic conditions (Ref. 89). Similar results were obtained for two other oxime carbamate insecticides, oxamyl and methomyl (Ref. 90).

Factors influencing entry of pesticides into ground water

To assess the potential extent of the problem, it is important to understand the nature of the soil-subsoil-ground water system and the kind of physical and chemical processes that occur in the various zones. Chemicals will pass through several hydrologic zones as they migrate from the soil surface toward the water table (Fig. 1).

Structure of the soil-subsoil-groundwater system. Pesticides are applied to the surface of the soil in liquid or solid formulations. They may also be incorporated into the surface layers to a depth of about 15 cm by drilling or tilling the soil. Considerable loss of pesticide by evaporation to the atmosphere may occur on or near the soil surface. As indicated earlier, exposure to sunlight may also lead to considerable loss of certain chemicals by phototransformation. Beneath the surface of the soil many pesticides can become strongly bound to soil particles, particularly in soils with a high organic matter content; therefore, they will not easily leach toward the ground water. Within the root zone there is enormous potential for degradation of chemicals by biological and chemical processes, so that residues of many chemicals are broken down within this layer and are not detected in the subsoil.

The thickness and nature of the unsaturated zone beneath the plow layer (approximately equivalent to the root zone) is extremely variable. In areas where this zone is thick and contains a high proportion of clay and organic matter, there is little potential for ground water contamination. Conversely, where the water table is close to the surface and the unsaturated zone consists mainly of sand and gravel there is a much higher potential for

ground water contamination. In the upper layers of the unsaturated zone (the vadose zone)
the system is carbon-starved and aerobic biodegradation is a very important route for the
breakdown of many organic chemicals (Ref. 92).

Recently, an environmental index was established to rank the relative vulnerability of
different hydrogeologic settings to ground water contamination. The scheme is called
DRASTIC, an acronym which describes the seven hydrogeologic factors in DRASTIC: Ref. 91

   o Depth to ground water
   o Recharge of ground water by precipitation and irrigation
   o Aquifer media (sand & gravel, etc.)
   o Soil media (sandy loam, etc.
   o Topography (slope)
   o Impact of the vadose zone (the subsoil zone)
   o hydraulic Conductivity of the aquifer

Weighting factors on a scale of 1 to 5 have been determined for each of the parameters
above. For each environment, each of the parameters is rated on a scale of 1 to 10,
multiplied by the appropriate weight, and the sum of products of all seven parameters is the
total DRASTIC score for the particular hydrogeologic setting. in the agricultural version
of DRASTIC, depth to ground water and soil media considerations are assigned the highest
weight (5). Typical DRASTIC scores range between 100 and 200, but it is possible to have
scores 50 points lower and higher than those limits, respectively. For example, vulnerable
buried valleys in glaciated areas often have sandy loam soils, shallow depth to ground
water, and a typical DRASTIC score of 178. However, areas with glacial till over sandstone
are not as vulnerable with a typical DRASTIC score of 121. Glacial till often gives rise to
clay loam soils, and massive sandstone is not very transmissive (Ref. 91). A DRASTIC map
of the United States is shown in Fig 2.

Agricultural DRASTIC is best mapped at a scale of 1:150,000 to 1:250,000 at a level of
resolution exceeding 40 hectares.

Beneath the water table, pesticide concentrations may be further reduced by anaerobic bio-
degradation, dilution by surface water recharge, and dispersion in the moving ground water.
For certain pesticides, e.g., the carbamoyloximes, anaerobic degradation at or below the
water table may be very fast compared with aerobic degradation in soil above the water table
(Ref. 90).

DRASTIC SCORES   [   ] 50 - 101   [▨▨▨▨] 102 - 142
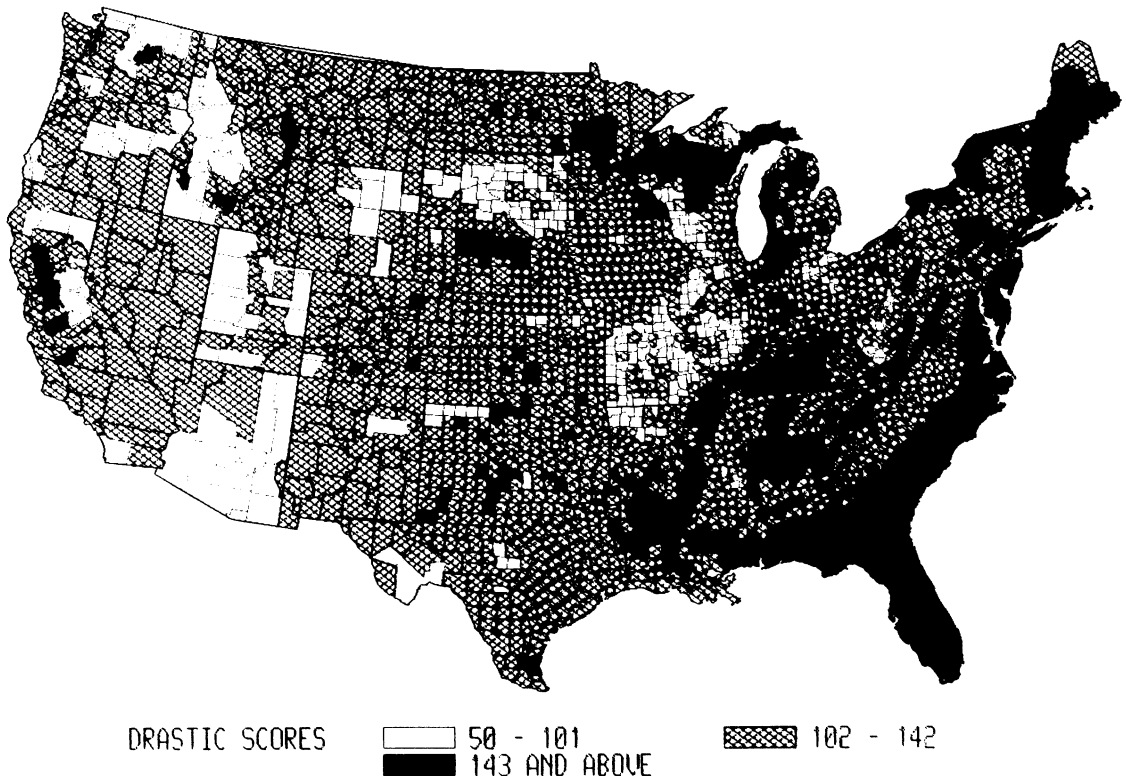   [███████] 143 AND ABOVE

Fig 2. DRASTIC map of soils in each county of the United States. The black areas are
counties very subject to leaching of pesticides, the cross-hatched areas are intermediate
and the white areas have a low leaching potential.

Chemical properties. The properties of a chemical are important in determining how it will be degraded and transported in the various zones of the soil-subsoil-ground water system. The extent to which a chemical is physically or chemically bound to soil can change with time. For example, carboxylic acids freshly applied to soil are mobile, but binding to soil (including chemical incorporation into organic matter) occurs over a period of time.

For the majority of pesticides, however, the most important characteristic is water solubility. Pesticides with low water solubility (<1 μg l^{-1}), such as DDT, dieldrin, and aldrin, have rarely been reported as contaminants of ground water; and there is experimental evidence that normal agricultural use of such pesticides is unlikely to lead to contamination of ground water. Grau and Peterle (93) applied ^{14}C-DDT in granular form to the surface of a 25 m^2 old field experimental plot at a rate of 0.45 kg ha^{-1}. Residues of DDT in air, soil, surface runoff, and ground water were determined for 12 months following the treatment. Soil was the major sink for DDT. Small amounts of ^{14}C-DDT were detected in air and runoff samples, but none was detected in ground water. In surveys of organochlorines and other organic chemicals present in Dutch waters between 1969 and 1975, Wegman and Greve (94) reported negligible contamination of five ground water samples by organochlorines. On the other hand, work by Greenberg et al. (5) indicates a statistical correlation between land-use and contamination of wells by organochlorine insecticides. This work was of a preliminary nature, however, and there were many uncertainties, e.g., imprecise definition of land-use.

Pesticides with low soil binding potential appear to present a greater potential for ground water contamination. Within this category, atrazine (water solubility 33 mg l^{-1} and aldicarb (water solubility 6.0 mg l^{-1}) have been most widely studied. Hall and Hartwig (95) studied the fate of atrazine in fine-textured, conventionally-tilled soils at application rates ranging from 1.0 to 9.0 kg ha^{-1}. Highest concentrations in leachates were correlated with highest rainfall and highest atrazine application rates. The majority of the herbicide dissipated in the plow layer. Maximum depth of penetration of atrazine in soil, as indicated by residues recovered in soil samples, was 76 cm; however, low concentrations of atrazine were detected in lysimeter leachates at 122 cm. It was concluded that application of atrazine to fine-textured, conventionally-tilled soils at rates ranging from 1.0 to 4.5 kg ha^{-1} would not seriously affect ground water supplies through contamination by internal soil drainage. In Iowa and Nebraska, transport of atrazine through the subsoil is associated with irrigation of light-textured soils in areas of high water table (Ref. 15, 96 & 97). The frequency of occurrance of atrazine and nitrates in well water were positively correlated.

The carbamoyloximes are relatively soluble in water and are only weakly adsorbed by soils. Therefore, in periods with a net downward movement of water, they may leach into deeper soil layers. In Long Island, New York, residues of aldicarb (1-50 μg l^{-1}) were detected in shallow wells in areas with sandy soils after frequent applications of aldicarb. In The Netherlands, 22 μg l^{-1} ($>90\%$ aldoxycarb) was detected in shallow, 2-m-deep, ground water in sandy soil 18 months after application of 5.3 kg of aldicarb ha^{-1} (Ref. 92).

Influence of rainfall and water management practices. Irrigation, particularly in arid areas and on sandy soils, may increase the potential for ground water contamination by pesticides. In central Nebraska it was estimated that approximately 1% of the applied atrazine migrated vertically through the vadose zone to the ground water during the 1978 irrigation season (Ref. 13). Greater vertical transport of atrazine in this area compared with soils of a similar texture in Pennsylvania was thought to be associated with differences in water management practices. The herbicide alachlor was detected in two samples of well water that also had relatively high atrazine concentrations, which suggests contamination from a pesticide formulation containing both of these herbicides. Other widely used pesticides (various organochlorines, EPTC, 2,4-D, and silvex) were not detected in any of the 14 wells found to contain atrazine (0.06-3.12 μg l^{-1}).

Tail water recovery (reuse) pits used in irrigation systems in Nebraska to control runoff may also act as storage reservoirs for both nitrates and herbicides (Ref. 98). Mean atrazine concentrations in pits serving corn fields were reported to be 13.9 and 56.2 ug l^{-1}, with a maximum of 1074 μg l^{-1}. Seepage of nitrates and atrazine from reuse pits to ground water occurs, but for most of the year the shallow, surrounding ground water probably contains higher concentrations than the pits.

In sandy soils, leaching of water-soluble chemicals has been enhanced in periods of heavy rainfall. Hebb and Wheeler (98) investigated leaching of bromacil to ground water under "extreme" conditions, i.e., a sandy, excessively drained soil, ample rainfall and a high water table (in Florida's Lakeland sand), and a persistent and mobile pesticide (water solubility 815 μg $^{-1}$) applied at a high rate (22 kg ha^{-1}). Four months after application, bromacil (1.25 μg l^{-1}) was detected in nearby ground water 4.9 m beneath the soil surface. Residues declined to <0.001 μg l^{-1} after 2 years. During this 2-year period peaks in residue concentrations were preceded by rain a week or two earlier. A direct relationship was not demonstrated, however, between rainfall and residues in ground water, presumably because of the long pathway between the soil surface and the ground water.

Runoff water containing pesticides can lead to contamination of the ground water in semiarid regions where cracks occur in the soil structure. Johnsen (99) estimated that 1.1% (3.33 kg) of picloram applied to 113 ha of a pinyon-juniper watershed left the treated area in runoff water. Most of the picloram (92%) recovered was in the surface 8 cm of the soil 1 month after treatment; however, 9 months after treatment 66% of the picloram recovered was at a depth of 90-122 cm, immediately above the impervious bedrock. Rapid penetration to this depth in surface runoff water was probably via deep soil cracks. The soils in this area contain little organic matter and crack under extreme conditions of rainfall and temperature in central Arizona.

Pesticide characteristics and field conditions. It is clear from the foregoing literature review that many variables can affect movement of chemicals to ground water. Interactions between some of these variables are important, and therefore it is difficult to make any generalized predictions concerning the influence of any one variable or set of variables in isolation from the others.

Generalizations have been made about the pesticide characteristics that give rise to potential for leaching (Ref. 6) and these are summarized below. Research also continues into the complex interactions of various field conditions which can be conducive to leaching these factors are also summarized below. The potential for ground water contamination is high when these pesticide characteristics and field conditions appear in combination.

1. **Pesticide characteristics**

    o   Water solubility -- greater than ca. 30 ppm.
    o K_d (soil/water adsorption coefficient) -- less than 5, and usually less than 1 or 2.
    o K_{oc} (K_d divided by soil organic carbon content) -- less than 300-500.
    o   Vapor pressure -- not critical for volatile liquids that are soil-injected
    o   Speciation -- if the pesticide chemical is negatively charged (either fully or partially) at ambient pH.
    o   Hydrolysis half-life (see Note a) -- greater than ca. 6 months.
    o   Photolysis half-life (see Note a) -- greater than ca. 3 days.
    o   Soil half-life (see Note a) -- greater than ca. 2-3 weeks.

2. **Field conditions**

    o   Thin soils overlying bedrock outcroppings which provide a nearly direct route for pesticides to migrate to ground water.
    o   Recharge -- total precipitation and irrigation recharge greater than ca. 25 cm/yr (Ref. 6).
    o   An agricultural DRASTIC score greater than <u>roughly</u> 150. Several years of field experience are yet needed before this number can be given with greater precision. It is also dependent, of course, on the degree of protection required, i.e. the relative toxicities of the pesticides in question.
    o   Nitrates -- high levels in ground water (several ppm over natural background) in agricultural areas are indicative of the pesticide ground water contaimination potential (Ref. 6).

PREDICTIONS

Experimental models

For chemicals showing potential for leaching, mobility in soil has to be extensively investigated, first in the lab and later under field conditions. Under the assumption that the adsorption/desorption characteristics of a certain pesticide are already known, we have to deal essentially with leaching, since water is deemed to be the main transport vehicle in soil (Ref. 100).

Diffusion of organic substances through soil by evaporation is only important in cases of high vapor pressure and low adsorption. The importance of transport via the vapor phase in the distribution of a chemical in soil can be assessed by measuring its volatility from soil surfaces. An appropriate test procedure to measure the rate of volatilization of pesticides from soil surfaces is described by Burkhard and Guth (Ref. 101). To assess to what degree a chemical will be mobile in the soil/water system, various test models are available:

Note a.   Half-life refers to the time required to effect 50% conversion to transformation products or metabolites. Note that 6% of a chemical remains after four half-lives.

1. Lab-model-tests

    (1) Soil thin-layer chromatography (Ref. 102 & 103).
    (2) Soil thick-layer chromatography (Ref. 104).
    (3) Soil column chromatography (Ref. 105-108).

All methods yield comparable and reproducible results, but column chromatography is con-
sidered to reflect the practical situation better. For the model tests, agricultural soils
are selected that are representative of the locations of intended use. The soil character-
istics of these soils, e.g., organic matter content, cation exchange capacity, pH, and
particle size distribution, should be determined.

The pesticide in these experiments is applied either in the form of the pure active ingre-
dient or as the formulated product. If the mobility/leaching of the active ingredient or
the metabolites has to be investigated, the active ingredient preferably is used in a
formulated radioactively labeled form. The top soil layer (ca. 5 cm) is substituted by a
soil in which the parent compound has been "aged" (to form metabolites) for a certain time
period (e.g., 30 days). A certain amount of water is added to the top of the column in such
a way that a continuous constant water flow is maintained throughout the experiment. The
water that has percolated through the soil column is collected and analyzed for the parent
compound and the metabolites. The residues that have remained in the soil also are
frequently determined, especially when columns have been used that can be dissected into
segments.

The column model has been criticized in that a dry sieved soil, which is poured loosely into
a column and then again saturated with water, will not correspond to the actual conditions
at the field site (Ref. 100 & 108). To overcome this disadvantage, Jarczyk Ref. 100 & 108
used specially sampled 10-cm-diameter intact soil cores that were up to 140 cm long for his
column leaching experiments. He found that leaching tendency in those columns was less than
in columns filled with dry sieved soil.

2. Lysimeter tests

Lysimeters are useful models for studying the behavior of pesticides in the biotope
soil/plant under conditions closer to the practical situation. In its simplest form,
a lysimeter is a container filled with a soil that is representative of typical agricultural
soils. A drainage system underneath allows superfluous soil water to percolate into a
receiver, where it can be sampled at appropriate intervals. Leaching experiments in this
type of lysimeter should begin only after the soil is allowed to settle (ca. 3 years).

A crop is planted in the soil and at the appropriate growth stage the product to be tested
is applied according to the recommended rate. The system permits one to follow simultane-
ously the degradation in plants and soil and leaching through the soil. If information on
the vertical movement and metabolism in soil is needed, samples should be taken from a
parallel plot, not used for leaching studies, since soil sampling would disturb the "mono-
lithic" character of the lysimeter and lead to erroneous results. To obtain information on
the metabolites formed and to obtain a material balance as complete as possible, the use of
a radioactively labeled active ingredient is advisable.

Various types of lysimeters have been described in the literature (Ref. 109-111). Soil
blocks with an undisturbed soil profile, cut out from a natural soil to a depth of 1 m and
more, have been used in lysimeter studies with good success (Ref. 108 & 112). The findings
of degradation and leaching from a lysimeter study, in combination with the recorded
meteorological data, serve as a good model for field behavior of pesticides.

3. Field studies

When a pesticide demonstrates leaching potential based on laboratory mobility and
persistence studies, and when there is some concern for possible health risks, field studies
should be conducted. Field studies for ground water concerns can be classified in three
categories, and the study objectives determine the appropriate study design. The three
categories are (ref. 7):

                    i.   large-scale retrospective studies
                    ii.   small-scale prospective studies, and
                    iii. small-scale retrospective studies.

The objective of large-scale retrospective ground water studies is to characterize the
extent of occurrence of pesticides in wells over a large area. These statistically based
surveys target wells in areas which are on the order of thousands to hundreds of thousands
of square kilometers and typically involve sampling of more than 100 wells. They are

complex and expensive surveys which typically exceed 300,000 1986 U.S. dollars, but tend toward the lower end of the range when the geographical scope is limited. One begins these surveys by stating the objectives very clearly.

One example of such objectives is the U.S. study of pesticides in drinking water wells described in the "current Projects" section above. Another example objective might be to characterize the extent of occurrence of selected herbicides in public wells in a state of the FRG, and attempt to correlate the results with depth to ground water.

The basis of large scale retrospective studies is probability sampling (7). This means that every well in the study area which meets the criteria of the study objective must have a finite probability of being sampled in a random selection process. In general, 'blind' random sampling should not be done. Rather, information on pesticide usage and potential ground-water vulnerability should be used to guide the sampling, i.e. stratify the potential sampling areas. That way, the chances of missing potential 'hot spots' would be reduced, and one could over sample the wells of interest in a statistically valid manner. This subject is discussed in more detail in reference 7.

In small-scale prospective studies, a pesticide is applied to a field along with a tracer such as chloride ion and the movement and dissipation of the pesticide is followed through soil and ground water for a period of, typically, one to two years (7). The primary objective of this study type is to characterize the subsurface fate of a particular pesticide, i.e. establish the leaching potential in a controlled study. The tracer is necessary to establish the movement of the water front relative to the pesticide in a process analogous to thin layer chromatography. This study is usually used in the registration process for new chemicals which show potential to leach below the root zone, or in cases where a chemical which has been on the market shows leaching tendencies but has an incomplete or equivocal environmental fate data base.

The final study type is a small-scale retrospective study (7). It is analogous to the previous type of study, but is mainly used for existing pesticides when concerns for potential health hazard require study results more quickly. In this case, participants enter and study a field in which a pesticide has been used at least once, and where there are accurate use records. The purposes of small-scale retrospective studies are to determine whether the pesticide in question has leached to ground water in certain fields, and to characterize the leaching pattern in the soil profile at a given point in time. Both studies require soil core sampling as well as the installation of observation wells. Both studies probably cost in the range of 200,000-400,000 U.S. dollars or greater.

In some cases subsoil has been sampled at extreme depths (12-120 meters) (Ref. 7 & 113). Special drilling devices have been developed to obtain undisturbed soil cores (Ref. 114 & 115). A simple sampling technique is the cylinder method described by Harvey (116). An alternative to taking soil samples is sampling of the soil water solution by suction tubes placed in the soil at various depths (Ref. 117).

Mathematical models

The discussion so far in this section on predictions has emphasized laboratory and field work. Once these data are generated and compiled, the goal of regulatory, industrial, and university scientists is to predict the extent and amounts of pesticides likely to leach to ground water in a qualitative or semiquantitative manner. In other words, scientists need a way to quantify their knowledge and apply it to the case of pesticide leaching. Computerized simulation models are the tools by which data on pesticides' mobility and persistence can be combined with hydrogeologic and meteorologic data for specific sites to assess the potential hazard associated with its use. In this section we discuss the use of mathematical models with particular emphasis on one-dimensional modeling in the unsaturated zone.

Presently, the literature contains a wide range of pesticide models that vary in their assumptions and complexity. King and McCarty (Ref. 118) modeled pesticide transport as a chromatographic process, while Lindstrom et al. (Ref. 119) modeled transport under saturated conditions, where adsorption was characterized with an equilibrium adsorption isotherm. Oddson et al. (Ref. 120) modeled pesticide leaching where adsorption was rate-limited and diffusion and dispersion assumed negligible. A more complex model proposed by van Genuchten and Wierenga (Ref. 121) separates pesticide transport into a mobile and an immobile region, allowing diffusion between regions. The pesticide transport model chosen for a particular situation should be commensurate with the question being asked. Van Genuchten (Ref. 122) proposed a classification scheme for various kinds of models and argues that an all-encompassing model is not suited for all tasks. Nevertheless, numerous pesticide studies have shown that the potential hazard to the environment is predicated on how the pesticide is partitioned between the adsorbed, liquid, and vapor phases (Ref. 123-125). As a result, most pesticide models are based on physiochemical processes that govern the

different pathways in which pesticide may be lost. Enfield et al. (Ref. 8) developed three simple models for evaluating the transport of organic pollutants through soil to ground water. The first calculates linear sorption/desorption and first-order degradation; the second (PESTANS) considers also dispersion; and the third considers non-linear sorption, following a Freundlich equation and first-order degradation. The models were compared with field data for the pesticides aldicarb and DDT and were found adequate to make environmental decisions, although the projected results deviated somewhat from measured field data.

A pesticide leaching model that is used by the Environmental Protective Agency is the Pesticide Root Zone Model (PRZM) (Ref. 126). PRZM is a continuous simulation model that considers interactions of pesticides in surface runoff (in water and on eroded sediment), advection in percolating water, molecular diffusion, uptake by plants, sorption to soil, and biological and chemical degradation. It is a one-dimensional, numerical model that uses daily weather records. The model was partially performance-tested for aldicarb using data from field sites in New York, Florida, and Wisconsin. The model was tested successfully with observed data at the sites using selected values for first-order degradation rate constants and sorption coefficients. It was successfully calibrated to the observed data at the New York site using selected values for first-order degradation rate constants and sorption coefficients. Calibrated parameter values were within the reported range of measured values, suggesting that the model adequately simulated relevant processes affecting the pesticide's movement.

A number of models have been developed to simulate solute transport in the saturated zone. Anderson (Ref. 127) has reviewed the availability and utility of models in this area. Also, the American Geophysical Union has compiled a list of available ground water models (Ref. 128).

Because mathematical models are tools by which we can quantify our knowledge in this area, they typically use the same basic principles and assumptions about pesticide mobility and persistence that we use in our own more intuitive assessments-e.g., first-order degradation, linear adsorption when appropriate. Otherwise, the water balance approaches used in the models described above can be used to categorize them as either deterministic or stochastic models. These two approaches to transport models are briefly described below.

Deterministic transport

In general, most pesticide transport models are physically based and are referred to as deterministic. As such, these models attempt to describe pesticide movement by combining the laws of conservation of mass with solute and water flux equations. This approach can account for pesticide movement by diffusion in the vapor and liquid phases, as well as the convection or bulk movement of pesticide with the moving soil solution. Although complex, many of these models have analytical solutions, which make them amenable for screening pesticides for use under a given set of environmental conditions. As most transport models are based on the conventional convection-dispersion equation a short formulation is presented here. Generally, the mass flux of the pesticide, J_s,

$$J_s = -D_v \frac{\partial C_v}{\partial x} - D_L \frac{\partial C_L}{\partial x} + J_w C_L \qquad [1]$$

where D_v is the soil-air diffusion coefficient (m^2/day), D_L is the soil water diffusion coefficient (m^2/day) and J_w is the water flux (m^3 water/m^2 soil/day). Large variations in the water flux J_w will result in additional mixing of the pesticide with the soil matrix. This mixing process is called hydrodynamic dispersion and is mathematically similar to diffusion. Under conditions where large variations in J_w exists equation [1] would still be valid, but D_L would be the sum of the diffusion and hydrodynamic dispersion mechanisms. Although little data is available for characterizing field-scale transport of pesticides, large variations in J_w due to large and/or frequent irrigation events suggest that the major mechanism responsible for transport may be convection, $J_w C_L$. On the other hand dry conditions associated with nonirrigated agriculture may enhance the importance of molecular diffusion.

The diffusion coefficient in the soil-air, D_v, may be estimated by utilizing the Millington and Quirk (129) tortuosity approximation

$$D_v = (a^{10/3}/\phi^2)D_{air} \qquad [2]$$

where D_{air} is the diffusion coefficient in air, and ϕ is the soil porosity (m^3 voidspace/m^3 soil) and a is the volumetric air content (m^3 air/ m^3 soil). Since the diffusion coefficient of pesticides in air does not appear to be greatly affected by temperature, it can be approximated, $D_{air} = 0.43$ m^2/day (Ref. 130).

The soil-liquid diffusion coefficient, D_L, can be estimated in a similar manner

$$D_L = (\theta^{10/3}/\phi^2)D_{water}$$ [3]

where D_{water} is the diffusion coefficient in free water and θ is the volumetric content (m^3 water/m^3 soil). Jury et al. (130) also found satisfactory results by utilizing an average, $D_{water}= 4.3 \times 10^{-5} m^2$/day.

The pesticide flux equation is then combined with the equations describing the conservation of water and pesticide. The conservation of water can be mathematically expressed as

$$\frac{\partial \theta_v}{\partial t} = - \frac{\partial J_w}{\partial x}$$ [4]

where $J_w = -K(\theta) \frac{\partial \psi}{\partial x}$ and t is the time. The hydraulic conductivity $K(\theta)$ is a function of the volumetric water content where ψ is the soil water potential. This formulation assumes that there are no plants absorbing water.

The equation describing the conservation of pesticide can be expressed as

$$\frac{\partial C_T}{\partial t} = - \frac{\partial J_s}{\partial x} - KC_T$$ [5]

which assumes a homogeneous soil with a pesticide undergoing first-order decay. The total pesticide concentration C_T (g/m^3) is made up from contributions from all three phases

$$C_T = \rho C_s + \theta C_L + aC_g$$ [6]

where ρ is the soil bulk density (kg/m^3), C_s is the adsorbed phase pesticide concentration (g/kg soil), C_L is the solution phase, pesticide concentration (g/m^3 solution), and C_v is the pesticide concentration in the vapor phase (g/m^3 air). The adsorption-liquid partitioning coefficient can be expressed as a linear isotherm, $C_s = k_d C_l$ while the liquid-vapour partitioning coefficient can be represented using Henry's law, $C_g = K_H C_L$.

The pesticide transport equation is derived by combining equations [1 -6], resulting in

$$\frac{\partial C_T}{\partial t} = D' \frac{\partial^2 C_T}{\partial x^2} - V' \frac{\partial C_T}{\partial x} - KC_T$$ [7]

where

$$D' = \frac{D_v K_H + D_L}{R}$$ [7a]

$$V' = \frac{J_w}{R}$$ [7b]

and

$$R = \theta + aK_H + \rho K_d$$ [7c]

where K_H is Henry's law constant (m^3 solution /m^3 air) for the pesticide in question.

The solution of equation [1-8c] for a pulse of duration, t_o, (days), applied to the pesticide free soil surface is included in Appendix A. The steady state deterministic model presented is simplistic and general, and as such does not attempt to account for spatial and temporarily variable field conditions. As a result, this theory does not account for rapid movement of pesticide due to preferential or macropore flow. However, the analytical solution provides a rapid inexpensive relative estimate of pesticide movement under a given set of environmental conditions. To describe field-scale movement of pesticide the model must account for the variations in the flow velocity due to preferential flow in macropores. This screening model was not designed to predict pesticide movement under field conditions.

<u>Macropore flow.</u> Recent studies indicate that preferential flow in macropores not only is responsible for the observed variations in the water flow velocity but may be the critical process governing the observance of pesticides in groundwater (131, 132). This flow process reduces pesticide transport times to groundwater by rapidly moving pesticides through large soil pores, cracks, or worm holes, thus by-passing much of the soil matrix high in organic matter. Once past the top surface horizons, pesticide mobility will increase due to a decline in organic matter. Since macropore flow is a result of relatively large water velocities, any soil process that may increase pesticide mobility would also increase the probability of pesticide observance. As a result, pesticide attachment to a fine collodial suspension or organic complexation of the pesticide molecule (131, 132) may in conjunction with macropore flow be major contributors to groundwater contamination.

A schemetic representation of the preferential flow process is shown in Fig 3. For the effect of preferential flow to be maximized, the soil pore conducting the fluid must be saturated. Such a saturated state needs to exist for only a very short period of time. Those areas of the agriculutral field most susceptible to saturated conditions are the depressed areas, which on a scale of a square meter may be numerous. Since water movement into these large pores exceeds that of the surrounding soil matrix, convergence of water flow occurs in the direction of the macropore. Consequently, a large volume of the water may be flowing through only a fraction of the porous matrix. For a soluble pesticide, such a flow process results in the pesticide by-passing many of the adsorption sites near the soil surface. As a result, pesticide transport times to the groundwater can be dramatically reduced. After convective flow in the macropore has ceased the pesticide will begin to diffuse into the soil matrix where the diffusion process will behave as a storage term; the magnitude of the diffusion coefficient being a function of the pesticide.

Since one-dimensional transport models use only a single mean value to represent each transport process, they are not capable of describing the range of water velocities occuring under field conditions, and as such cannot describe that portion of the applied pesticide that may be moving preferentially through the soil matrix (133–136). In order to simulate or predict pesticide occurrence in groundwater the model must have the ability to describe the randomness associated with the water velocity, a stochastic approach.
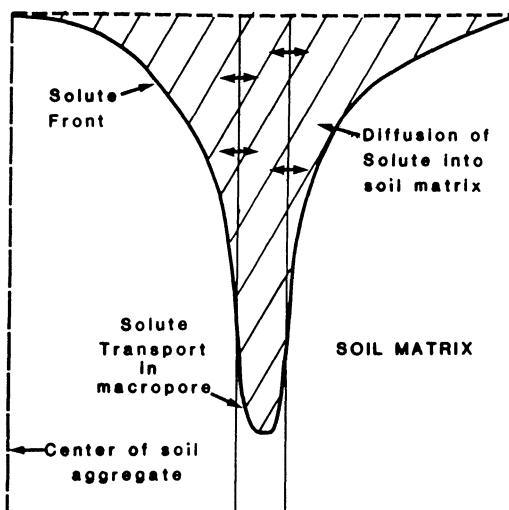

Figure 3.   Preferential Flow through Macropore

Stochastic transport

Deterministic models may be a viable tool for comparing the potential hazard associated with a particular pesticide's use. By evaluating a pesticide's physio-chemical properties, the relative mobility and volatility may be established. However, due to the randomness associated with the water velocity and other environmental processes governing transport, average values derived from purely analytical solutions may not adequately describe or predict chemical transport (Ref. 130–133).

As a result, recent model formulations have included a stochastic component (Ref. 131, 134 & 135). These models generally regard the transport region as being composed of numerous soil columns, each with perhaps different transport properties. Typically, a solution of an equation similar to the chemical transport equation, equation [6], is assumed valid for each soil column. The effect of the variable water velocity may be evaluated numerically by combining the solution of the chemical transport equation with a probabilistic representation of the water velocity. One of the major deficiencies of the stochastic models is that they require a large data set for calibration, which limits their present applicability for predictive purposes.

CONCLUSIONS AND RECOMMENDATIONS

1. From normal agricultural use, some pesticides can reach ground water. However, spillage, improper disposal, and poor industrial practices may be a significant source of pesticides in ground water.

2. The potential for a pesticide to reach ground water can often be predicted from properties (particularily mobility and persistence), use pattern of the chemical, and field conditions.

3. A tiered approach should be followed when evaluating the leaching potential of a pesticide. Substances that have proved to be highly mobile and persistent in soils in laboratory tests should be further examined (e.g., in lysimeters). For those pesticides with significant leaching potential, field studies should be conducted.

4. It is recognized that physical movement of chemicals sorbed to suspended matter (e.g. humic material) can occur. Water flow through macropores may play a significant role in transport of dissolved and sorbed pesticides.

5. Mathematical models are useful for comparing relative leaching potential of various pesticides at specific sites. In addition, they can be useful in identifying appropriate sampling sites.

6. Ground water monitoring studies are technically difficult and expensive. These studies should be designed and conducted with care to obtain meaningful data. It is essential that sample contamination is avoided and the identity of pesticide residues is confirmed.

7. When information shows the presence and range of concentrations of pesticides in ground water at specific locations, a risk assessment, based on exposure and toxicity of the chemical, should be made before action is taken.

8. Further data are needed on:

   (a) Chemical and biological transformations and sorption processes in the saturated zone.

   (b) Large scale monitoring to establish data base on the magnitude of the problem.

   (c) Intensive field studies to generate sufficient data to validate and calibrate models.

   (d) Hydrogeologic needs:

      (I) Sampling strategies that account for spatial and temporal variabilities.

      (II) Ground water vulnerability mapping to support risk assessment, best management practices and monitoring needs.

   (e) Best management practices to mitigate ground water contamination by pesticides.

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APPENDIX A

$$C_T(x,t) = \begin{cases} C_i A(x,t) + C_0 B(x,t) & o < t < t_0 \\ C_i A(x,t) + C_0 B(x,t) - C_0 B(x,t-t_0) & t > t_0 \end{cases}$$

where

$$A(x,t) = e^{(-\mu t)} \left\{ 1 - \frac{1}{2} \mathrm{erfc}\left[\frac{x-vt}{2(D't)^{1/2}}\right] - \left(\frac{v^2 t}{\pi D'}\right)^{1/2} e^{\left(\frac{(x-vt)^2}{-4D't}\right)} \right. $$
$$\left. + \frac{1}{2}\left[1 + \frac{vx + v^2 t}{D'}\right] e^{\left(\frac{vx}{D'}\right)} \mathrm{erfc}\left[\frac{x+vt}{2(D't)^{1/2}}\right] \right\}$$

$$B(x,t) = \frac{v}{v+u} e^{\left(\frac{(v-u)x}{2D'}\right)} \mathrm{erfc}\left[\frac{x - ut}{2(D't)^{1/2}}\right] + \frac{v}{v-u} e^{\left(\frac{(v+u)x}{2D'}\right)} \mathrm{erfc}\left[\frac{x - ut}{2(D't)^{1/2}}\right]$$
$$+ \frac{v^2}{2\mu D'} e^{\left(\frac{vx}{D'} - \mu t\right)} \mathrm{erfc}\left[\frac{x + vt}{2(D't)^{1/2}}\right]$$

and

$$u = \left[v^2 + 4\mu D'\right]^{1/2}$$

The pesticide concentration C_i (g/m^3) is the initial pesticide concentration present in the soil before the most recent application.