

The Impacts of Agricultural Chemicals on Ground Water Quality

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ABSTRACT: The accelerated use of agricultural chemicals over the past 20 to 30 years has profitably increased production but has also had an adverse impact on ground water quality in many of the major agricultural areas of the world. The pollution of ground water, related to nitrogen fertilizers and pesticides, from widespread, routine land application, as well as point sources has become a serious concern. Ground water contributions also impair surface water quality. Research, worldwide, has shown rates of nitrate-nitrogen ($\text{NO}_3\text{-N}$) increases in ground water typically between 0.1 to 1.9 mg/l per year for 10 to 20 years, concurrent with major increases in nitrogen fertilization. Many shallow ground water supplies now exceed the recommended $\text{NO}_3\text{-N}$ drinking water standards. While many sources contribute nitrogen into the environment, synthetic fertilizers have become the major component. There are clear economic incentives to improve management; harvested crops often account for less than 50% of the purchased fertilizer inputs. Pesticides are appearing in ground water with unanticipated frequency, typically in 0.1 to 10.0 $\mu\text{g/l}$ concentrations. While these concentrations are well below acute toxic levels (for most pesticides), many are of concern for possible chronic effects. Such widespread pollution is of real concern because of the potential for long-term and widespread exposure to the public of toxic substances through drinking water. While there are many uncertainties, agriculture must move forward toward solutions through better management.

Introduction

After many years of discussion, and often denial, the debate would seem to be ending about whether or not agriculture pollutes ground water. Recent reviews describe that the pollution of ground water, particularly with nitrates and pesticides, from routine agricultural practices is a common, and growing problem in the major agricultural regions of the world (for United States see Cast 1985; Cohen et al. 1986; Cook 1986; Fairchild 1987; Hallberg 1985; Holden 1986; Keeney 1986a,b; Olson 1986; for Europe - Aldwell and Bush 1986; Anderson and Kristiansen 1984; OECD 1986; Vrba 1983; and elsewhere - Burden 1982; Egboka 1984; Jacks and Sharma 1983). Even farm journals have begun to acknowledge the problem (e.g. DeVault 1986; Kidwell 1985; Tevis 1986; Trcka 1987). Current discussions more commonly center on how significant is this pollution, and, more constructively, what can be done about it. (The review papers, cited herein, contain extensive reference lists that are not possible to repeat here. The reader, interested in these details should refer to these publications.)

During the past 20 to 30 years we have pushed agricultural production to new levels, primarily through the use of fertilizers and pesticides. Synthetic-nitrogen is the fertilizer nutrient of primary concern for ground water quality. Most crops remove more nitrogen (N) than any other nutrient and, hence the amount of chemical-N applied, generally, far exceeds the other nutrients (e.g. Hargett and Berry 1983; OECD 1986). For Example, in the United Kingdom in 1979, total N used was about 1.5 times greater than phosphate (P) and potash (K) fertilizers combined (OECD 1986). Since 1970, P and K use has declined in many areas, but N use has typically risen.

In England and Wales, between 1938 and 1976 the total-N availability in the soil (from fertilizer, rainfall, manure, fixation, etc.) increased over 50%, and nearly 75% of the increase was in fertilizer-N (OECD 1986).

Similarly, in the United States (US) consumption of fertilizer-nitrogen (FN) has grown from a negligible amount prior to 1945 to approximately 9 million megagrams (Mg) -- or metric tons -- in 1976 (Zaporocec 1983). Of importance is how significantly the intensity of FN has

increased. Across the US average FN rates on corn increased from 72 kg/ha in 1965 to over 150 kg/ha in 1982 (Hargett and Berry 1983). Corn accounts for only 21% of US cropland, but for 43% of the US FN use. Since 1964, agricultural pesticide usage in the US has more than doubled, primarily from the increased use of herbicides. For crops such as corn and soybeans, over 90% of the total acreage are typically treated with at least herbicides. Survey data from 1982 estimated that corn and soybeans alone accounted for nearly 63% of the total mass of pesticide active ingredients used (Gianessi et al. 1986).

These major increases in the widespread land application of agricultural chemicals clearly outpaced our understanding of the movement of water and solutes through the soil and the efficiency of utilization of these chemicals.

Nitrate, Agriculture, and Ground Water

The role of agriculture and fertilizer-N in the leaching of nitrate to ground water has been debated for some time (Commoner 1970). Even a decade ago there was justifiable skepticism about the role of FN and whether or not nitrate concentrations were actually increasing in water (Tomlinson 1970; USNRC 1978). There was much discourse about all the other sources of N in the environ-

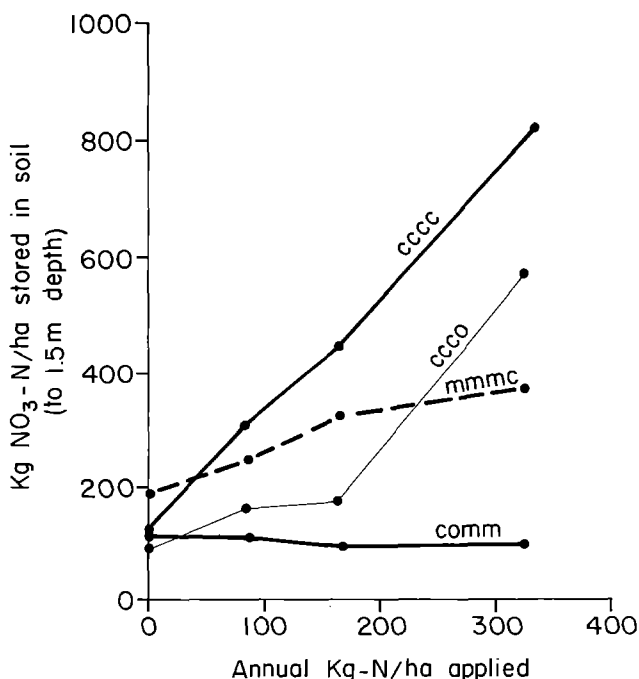
ment. Besides FN, natural soil-N, rare geologic-N deposits, manure, sewage, and other waste disposal, and even precipitation all contribute N to the soil-plant system, and likely to ground water. However, research worldwide, over this time, has clearly shown that the most extensive source of nitrate delivered to ground and surface water is agriculture (Hallberg 1986, 1987; Keeney 1982, 1986a,b; OECD 1986; Pratt 1984; Pratt et al. 1975; Singh and Sekhon 1978). In the Federal Republic of Germany, for instance, it is estimated that diffuse agricultural sources contribute over 70% of the nitrate load to water; the most affected areas are those with high fertilization rates and shallow aquifers (OECD 1986). Over 5% of the country's population now has raw water exceeding the drinking water standard (11.3 milligrams per liter (mg/l), $\text{NO}_3\text{-N}$ in the Organization for Economic Co-operation and Development (OECD) nations; 10 mg/l in the US).

Numerous studies on various scales, from controlled plot studies to basin-size inventories, have shown that nitrate concentrations in ground water (in shallow fresh water aquifers) can be directly related to agricultural land use. Many of these studies show a range from a 3- to a 60-fold increase in nitrate concentrations in ground water between forested-pasture-grassland areas (generally <2 mg/l $\text{NO}_3\text{-N}$) and nearby intensively cultivated and fertilized areas (commonly >5 mg/l, ranging to >100 mg/l $\text{NO}_3\text{-N}$). In particular, many studies show a direct relationship between nitrate leaching to ground water and nitrogen-fertilization rates and/or fertilization history.

Many standard agronomic studies can be used to illustrate these findings. Fig 1 shows the relationships among N-fertilization rate, nitrate-nitrogen ($\text{NO}_3\text{-N}$) remaining in the soil, and crop-rotation effects for 4 end members in the rotation study of Olsen et al. (1979) in Wisconsin. They found that the total amount and distribution of $\text{NO}_3\text{-N}$ in the soil profile, and the amount of $\text{NO}_3\text{-N}$ below typical corn-rooting depth was directly related to the rate of FN-application on corn, the number of years of corn in the rotation (the only crop fertilized), and to some extent, the length of time since harvest of the last corn crop. The ground water at this site was moderately deep and hence the $\text{NO}_3\text{-N}$ below the root zone had not leached to the ground water at the end of their study. However, they concluded that with the excess amounts of FN on continuous corn, there was a good probability that the ground water would be polluted -- but because of the slow rate of movement, it may not be apparent for many years.

More direct impacts on ground water are illustrated by studies of tile drainage water, which is shallow ground water (Hallberg et al. 1986). Tab 1 outlines the crop and FN histories for 1974-1978 for one such study, and Fig 2 shows the $\text{NO}_3\text{-N}$ concentration in the tile drainage water from the differentially fertilized plots. After

Fig 1 Relationships among FN rate, the amount of $\text{NO}_3\text{-N}$ stored in the soil profile, and crop rotations, Wisconsin, US, at end of 4-year rotation treatment; rotation abbreviations: c - corn, m - legume meadow, o - oats (after: Olsen et al. 1970)



several years of similar crop rotations and fertilizer treatment (prior to 1974), the plots where differentially fertilized (Tab 1). Within a few months (by July 1974) greater NO₃-N concentrations were apparent in the tile water draining from the more fertilized field (plot 1). In this area the tile lines flow only intermittently, and hence, the major differences in NO₃-N concentration was not realized until the following year. The tiles often cease flowing in mid to late summer because of limited recharge water flux through the soil (because of limited precipitation and high rates of evapotranspiration), and the water table declines below the tile lines. When recharge began again in the spring (or fall), the excess NO₃-N was leached to the ground water (the tile drainage water).

The NO₃-N losses to the ground water were proportional to the treatment. There was approximately a two-fold difference in FN applied and 1.8 times increase in NO₃-N losses over the 5 years. Plot 1 lost an average of 48 kg-N/ha/yr and plot 2 lost an average of 27 kg-N/ha/yr (Baker and Johnson 1981). This direct response between FN rate and NO₃-N losses in tile drainage is commonly noted in such studies. In a review, Baker and Laflen (1983) note: "NO₃-N losses with subsurface drainage related in nearly linear fashion to N application for rates exceeding 50 kilograms per hectare."

These and similar studies, illustrate the build up of NO₃-N in the soil from fertilization, and

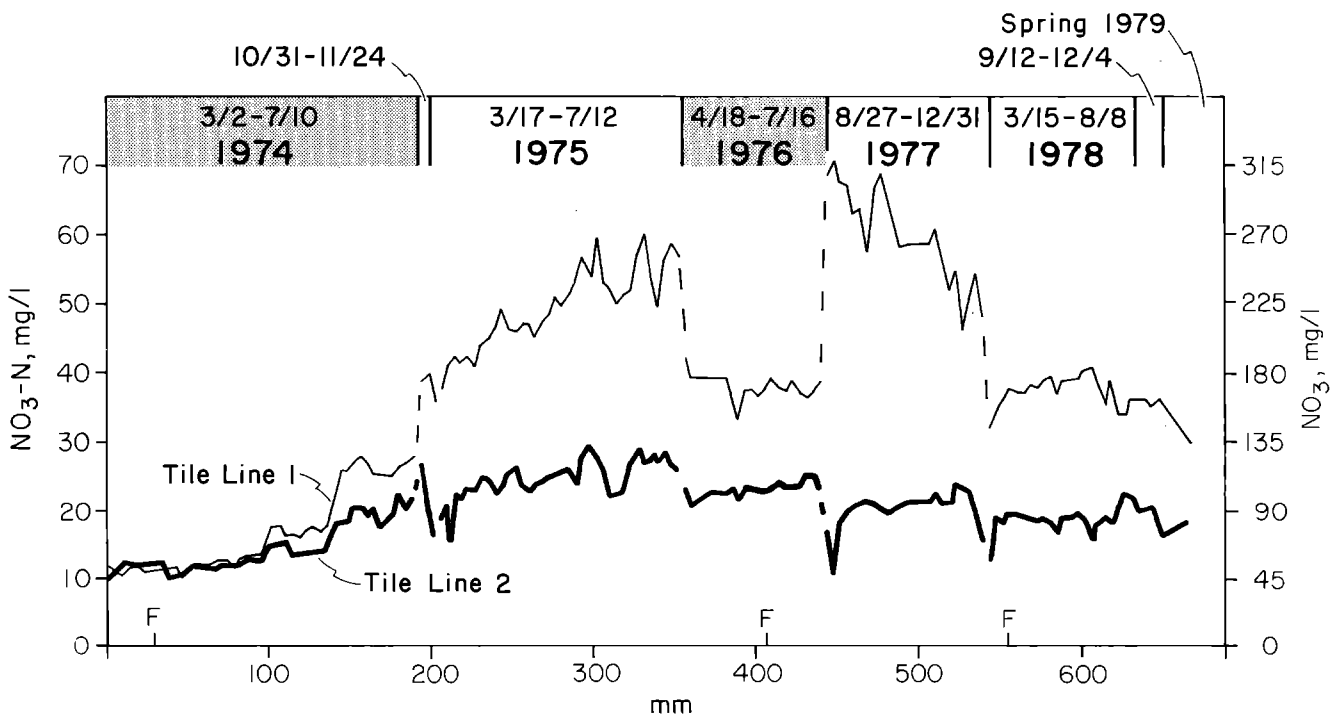
Year	Plot 1		Plot 2	
	crop	FN	crop	FN
1974	corn	250	soybeans	100
1975	soybeans	0	corn	0
1976	corn	240	oats	90
1977	oats	0	corn	0
1978	corn	90	corn	90

Note: NO₃-N concentrations in the tile-drainage water from the plots are shown on Fig 2

Tab 1 Fertilizer-N (in kg-N/ha) applied on plots 1 and 2 (tile-line 1 and 2) during 1974-1978, at Ames Experiment Station (Iowa, US); prior to 1974, the plots received similar treatment (after: Baker and Johnson 1981)

how rapidly it can be leached and lost, at least to shallow ground water. The basic reason for these losses is that, at current rates of FN use, our crop-management systems are not as efficient as once assumed. In a review, Keeney (1982) notes: "N recovery by agronomic crops is seldom more than 70%, and the average value is probably nearer to 50% ...". While the total FN uptake of many grain crops may be around 50%, the stover and roots typically remains in the field to become part of the remaining nitrogen-pool. The amount of FN actually removed in harvested grain is more typically in the range of 35% or less, particu-

Fig 2 Nitrate-nitrogen concentration for tile/plot 1 and tile/plot 2 vs. accumulated drainage (discharge) for Ames, Iowa, US studies; shading indicates years of differential N-fertilization (from: Baker and Johnson 1981)



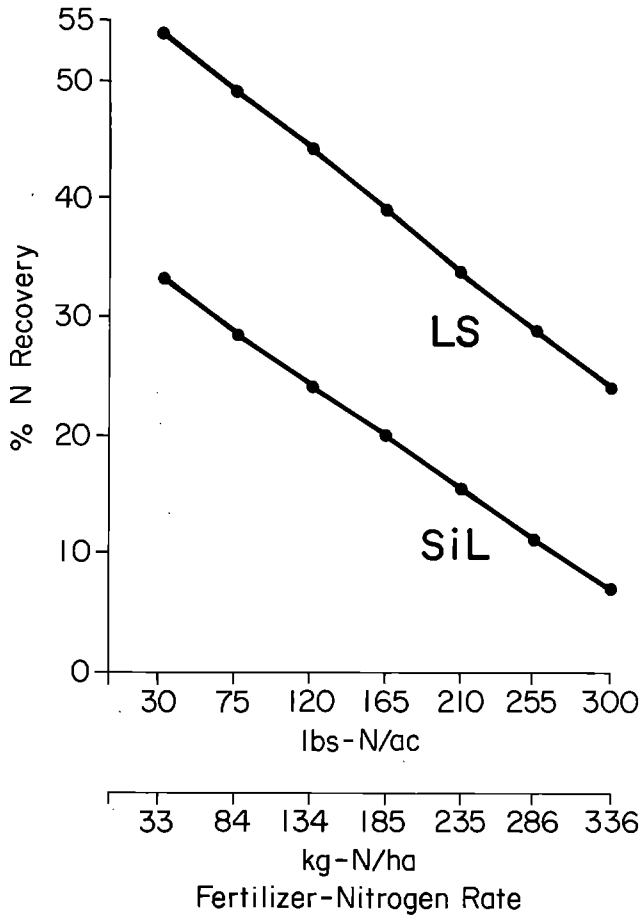


Fig 3 Percent fertilizer-nitrogen recovery by corn grain, at various fertilization rates, on irrigated silt loam and loamy sand soils in Wisconsin, US (after: Oberle et al. 1987)

larly for continuous cropping of corn or other grains (e.g., Hallberg 1986, 1987; Hill 1982; Westermann 1987).

Fig 4 Percentage of nitrogen inputs in the Big Spring basin (Iowa, US), 1958 to present (after: Hallberg 1986; 1987)

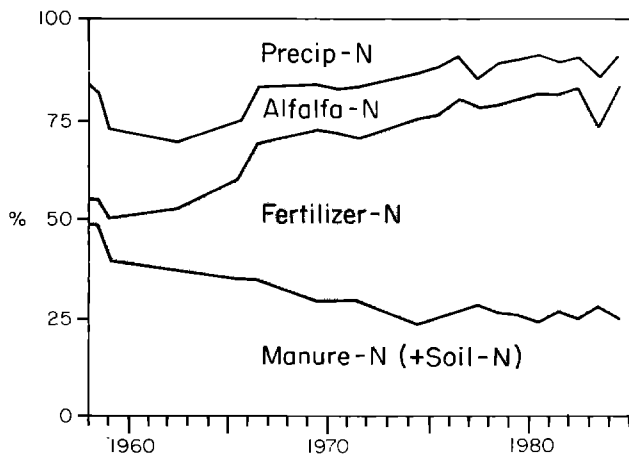


Fig 3 illustrates this point from continuous corn experiments, again from Wisconsin, US (Oberle et al. 1987). For typical fertilization rates of 150 to 200 kg/ha, the recovery of fertilizer-N in the grain is only about 20 to 40%. As inefficient as this seems, it does not mean that this was not profitable for the producer. Unfortunately this leaves substantial amounts of mobile nitrogen in the soil, potentially to be leached to ground water, particularly after many years of such practices.

Many variables affect the resultant concentrations of nitrate that reach ground water, but most studies indicate that, over the long term, there are several primary controlling factors: the amount of N-source available, the amount of infiltrating or percolating water, conductivity of the material, depth to the water table, and the potential for nitrate reduction and/or denitrification.

As summarized by Keeney (1986b), the greatest problems arise with the heavy fertilization in the intensive row-cropping practices in rain-fed grain production (such as corn), in intensively irrigated grain agriculture, in the irrigation and fertilization of shallow-rooted vegetable crops (e.g., potatoes) on sandy soils, and locally in intensive animal feeding and handling operations. Nitrate leaching in relation to fertilization/nutrient management has been well documented for citrus crops, vegetable, and other specialty crops as well (Embleton et al. 1986; Hill 1982; Keeney 1986b).

Ground Water Studies

While the examples above illustrate why nitrate leaching occurs, ground water case studies illustrate how pervasive the problem has become. Illustrative are data from the Big Spring ground water basin in NE Iowa. The hydrogeology of the area has been intensively studied, and quantity and quality of both surface and ground water are measured. The basin is 270 km² in size and is wholly agricultural. Land treatment, farming practices, and agricultural-chemical use are inventoried annually and various historic records have been compiled.

In the 1930s, nitrate concentrations in the Big Spring basin aquifer were <1 mg/l NO₃-N. During the 1950s and '60s the nitrate concentration in the ground water averaged about 3 mg/l NO₃-N. By the 1980s the NO₃ had increased three times, to an annual average of 9 mg/l NO₃-N in water-year 1982 and to 10.1 mg/l NO₃-N in 1983.

Fig 4 shows the percentage of various nitrogen inputs to the basin from 1958 to the present. The two primary sources of N in this basin are manure and fertilizer. Fertilizer-N increased during the last 25 years from a relatively minor source to the major nitrogen input, while the contribution of manure-N decreased from 50 to 25%. The actual mass of manure-N increased 0.3 times, while

fertilizer-N applied increased 2.5-3 times, as a function of increasing rate of application and the increase in corn acreage. The increase in nitrate in ground water directly paralleled the increase in the amount of fertilizer-N applied in the basin (Fig 5). The estimates of N removed with harvested grain (Fig 5) amplify the prior relationships noted; from the late 1960s to the present, as the difference between the amount of FN applied and the amount of N removed by crops increased, the nitrate concentration in the ground water increased, too. Since 1982, the amount of NO₃-N lost to water from the Big Spring basin has ranged from 816,000 to 1,315,000 kg/year, an annual loss of 50 to 80 kg-N/ha of cropped land area. These losses were equivalent to about 33% to 55% of the average amount of fertilizer-N applied (Libra et al. 1986, 1987). Other large-scale studies have shown similar losses (Carey and Lloyd 1985; Davis et al. 1969; Hallberg 1986; Pratt 1984). These losses, and the parallel linear increase in NO₃-N in ground water and fertilizer-N applied are directly comparable with the small-scale agronomic studies previously outlined.

This relationship is not unique. In Merrick County, Nebraska, Spalding et al. (1978) noted the average nitrate concentration in ground water increased from 2.8 mg/l NO₃-N in 1947-1951, to 12.1 mg/l in 1974, with the major source being N-fertilizers. In 1976-1977 they found that over 70% of the wells sampled exceeded 10 mg/l NO₃-N. In Holt County, Nebraska, Exner and Spalding (1974) noted that nitrate concentrations were increasing at about 1.1 mg/l per year beneath N-fertilized and irrigated areas.

For the last 10 to 20 years in many agricultural areas in England, rates of nitrate increases in ground water ranging from 0.2 to about 1.0 mg/l per year have been noted, and these rates are projected to increase over the next 40 years, because of the slow transit time into some aquifers (Carey and Lloyd 1985; Howard 1985). In Denmark FN inputs increased 6.5 times from 1950 to 1980, but total N inputs only rose 2-fold. Over this time frame, however, NO₃-N in surface water increased nearly 2-fold in 20 years and average NO₃-N concentrations in ground water tripled (Schroder 1985). In central Europe, nitrate in ground water increased from about 1 mg/l to 15 mg/l NO₃-N over a 10 year period, related to high rates of N-fertilization (Csaki and Endredi 1981).

In France, Probst (1985) described that NO₃-N losses in water are related to fertilizer inputs and in wet years losses can equal 40 to 50% of fertilizer applied. An OECD (1986) review notes that in the Paris basin, nearly 50% of ground water sources now exceed 5 mg/l NO₃-N and concentrations are "rapidly rising" (p.89). In the Yonne area about 300 water sources have been monitored. In 1965 all had less than 5 mg/l NO₃-N, but by 1977, 60% exceeded 5 mg/l, and nearly 15% were over 10 mg/l. In the Brie agricultural zone,

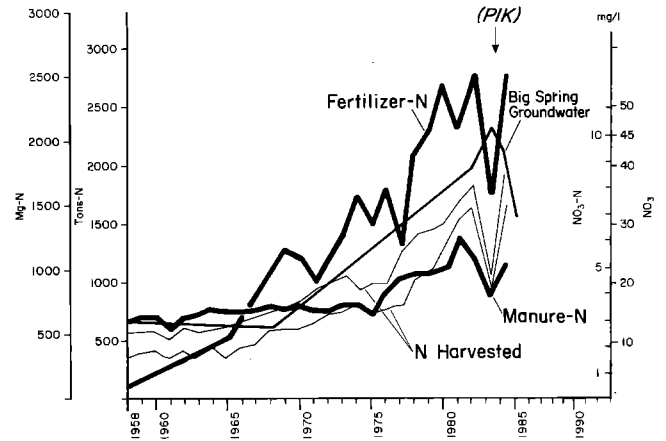
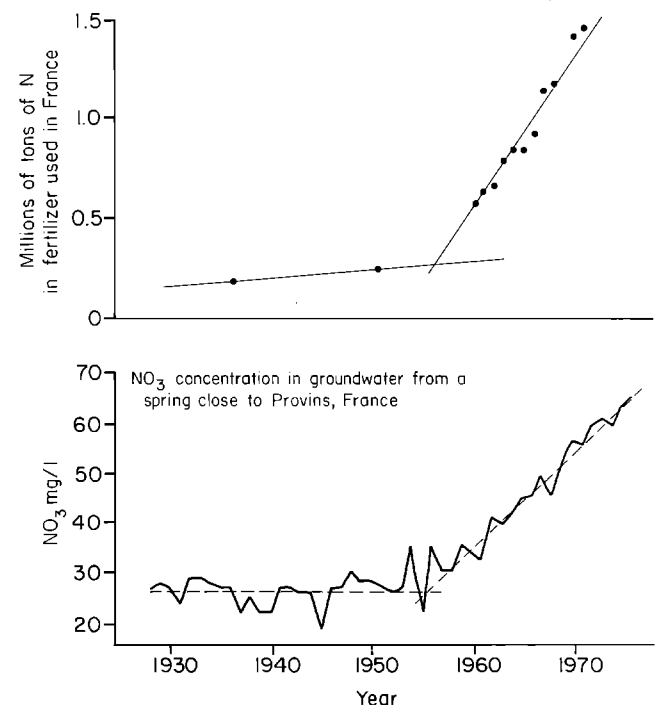


Fig 5 Mass of fertilizer-N and manure-N applied in the Big Spring basin (Iowa, US) and annual average nitrate concentration in ground water at Big Spring (line labeled Big Spring ground water) and mass of N harvested in corn grain; the scales on left show the amount of applied nitrogen in metric tons: Mg-N and short tons: Tons-N (from: Hallberg 1986, 1987; Hallbert et al. 1984)

nitrate concentrations in ground water were relatively constant from 1928 to 1955 (Fig 6). Since then NO₃-N has increased over 250%, averaging about 0.4 mg/l/yr, and now averages about 15 mg/l NO₃-N (68 mg/l as NO₃; Fig 6). The parallelism between increasing fertilizer-N use and NO₃-N in the ground water is again striking, similar to Fig 5. The amount of NO₃-N lost to

Fig 6 Metric tons of N-fertilizer used and nitrate concentration (as NO₃; multiply by 0.22 to convert to NO₃-N) in a carbonate spring in the Brie agricultural area, France (after: OECD 1986; Pierre 1983)



ground water increased from 6.5kg/ha in 1950-51, to 28 kg/ha in 1976/77. By contrast in the Champagne area little increase in nitrate in ground water has been recorded. However, as in other studies (Carey and Lloyd 1985; Hallberg 1986), research showed that this is because of slow travel time, and the ground water will likely become polluted in the next decade (OECD 1986).

In the USSR, in a monitored agricultural basin, similar findings were reported as well (Kudeyarov and Bashkin 1980). Over a 10-year period (1967 to 1977), the fertilizer-N input increased 5 times and manure-N increased 1.5 times. This resulted in increased NO₃-N leaching and an 8-time increase in NO₃-N in ground water; average concentrations rose from 0.8 to 6.5 mg/l.

Even in New Zealand, where many NO₃-N problems are related to concentrated livestock and manure usage, increasing NO₃-N concentrations in ground water are often related to fertilizer-N usage, particularly where coupled with irrigation. NO₃-N in many areas is increasing by 0.3 to 0.6 mg/l per year, with the increase in "nitrogen fertilization (sic) and irrigation of horticultural and crop land" (Burden 1982).

These examples point out an important facet of the leaching of nitrate to ground water: the magnitude of nitrogen losses should clearly be an economic, as well as an environmental concern. Clearly, there is room for improved efficiency and economic gains. Many sources of N contribute to the nitrate being delivered to ground water. The nitrate, from whatever source, is leached to ground water because the N inputs are in excess of N uptake. However, on the broad scale as efforts

are targeted to resolve these problems, fertilizer-N must be the focus of attention because it has become the greatest input to the system in many circumstances, it is the most controllable N input, and -- perhaps most important -- it is the input we pay for.

Pesticides in Ground Water

Nonpoint Sources

It has often been easy to be skeptical, and discount agriculture's role in nitrate pollution, because of all the other sources of N in the environment. Such is not the case with many pesticides. Compared to nitrate, however, there are not many studies that have dealt with pesticides in ground water. While details are not readily available, pesticide residues, from routine agricultural use, have been found in ground water in various European countries. Problems with methyl bromide and phenoxyalkanoic acid herbicides (e.g., 2,4-D) have been reported as well as concern with toxic-impurities (dioxins and TCDD for instance) either in formulations or as "inert" or carrier ingredients (OECD 1986). In the US, problems associated with aldicarb in ground water in Florida, Long Island (New York), and Wisconsin have been widely noted as have been problems with EDB and DBCP in Florida, Georgia, and Hawaii (Cohen et al. 1984, 1986; Holden 1986; Zaki et al. 1982). A variety of research has been done in Iowa and Nebraska, dealing with atrazine and other pesticides in ground water (e.g., Hallberg 1986; Kelley et al. 1986; Wehtje et al. 1983).

Common Name Active Ingredient	Typical Concentration µg/l	Number of States
Herbicides		
alachlor	0.10 - 10.0	4
atrazine	0.3 - 3.0	5
bromacil	300	1
cyanasine	0.1 - 1.0	2
DCPA (and acid products)	50.0 - 700.0	1
dinoseb	1.0 - 5.0	1
metolachlor	0.1 - 0.4	2
metribuzin	1.0 - 4.0	1
simazine	0.2 - 3.0	3
Insecticides and Nematicides		
aldicarb (sulfoxide and sulfone)	1.0 - 50.0	15
carbofuran	1.0 - 50.0	3
DBCP	0.2 - 20.0	5
1,2-DCP	1.0 - 50.0	4
dyfonate	0.1	1
EDB	0.05 - 20.0	8
oxamyl	5.0 - 65.0	2
1,2,3-trichloropropane (impurity)	0.1 - 5.0	2

Tab 2
Typical positive results of pesticide ground water monitoring in the US; the 17 pesticides have been detected in a total of 23 different states (after: Cohen et al. 1986)

With the concerns that have developed about pesticide exposure and pesticide occurrence in drinking water supplies, this situation is rapidly changing. In a 1984 review, Cohen et al. (1984) summarized studies noting the occurrence of 12 pesticides in ground water (from routine use) in 18 different states in the US. In a 1986 review, Cohen et al. (1986) noted that "at least" 17 pesticides have been found in ground water in 23 states, as a result of routine agricultural practices (Tab 2). They note that the largest number of pesticide species in ground water have been detected in California, Iowa, and New York. This is primarily a function of the intensity of monitoring in these states. They use the term "at least" because many new studies have been initiated, and several additional pesticides and states can be added to the list (e.g., Hallberg 1986).

This is apparent comparing Tab 2 and 3. Tab 3 summarizes recent monitoring data from the mid-western US "corn-belt" states of Iowa and Minnesota. The data from Minnesota, and more recent Iowa data are not included on Tab 2. It is not known if all of these detections in Tab 3 result from routine use, but obvious point-source data are not included. These are some of the more extensive data sets available, resulting from sampling of more than 700 wells in Iowa and more than 500 wells in Minnesota. Even though a portion of this extent of pesticide sampling was targeted to potential problem areas, the extent of pesticide pollution was much greater than expected; pesticide residues were found in 33 to 38% of wells (across all geologic conditions). In more

susceptible settings and private rural well monitoring, between 40 and 90% of wells sampled showed detectable residues. In all these studies, typically 20 to 25% of all analyses showed the presence of two or more pesticides, as well.

As indicated on Tab 2, typical concentrations for most pesticides in ground water are in the 0.1-1.0 micrograms per liter (µg/l) range. Some of the more mobile pesticide products and soil-fumigant nematicides do range much higher even from routine use.

These, and other studies (see Hallberg 1986) suggest that many of the most commonly used pesticides, particularly herbicides, are leaching into ground water in a variety of environments. Many of the pesticides have been detected in winter and spring water samples, prior to new application. These findings indicate that several of the herbicides are persisting in ground water year-round. In particular, atrazine is routinely found in shallow ground water samples now, albeit in low concentrations. This suggests that herbicides are persisting in the subsoil and then can be leached by water flux through the soil during winter or spring recharge. To date, most studies have only been for parent compounds, and it is not known if metabolites, or breakdown products, of these or other pesticides are present. In some cases the metabolites may be as, or even more toxic than parent products.

It was generally thought that pesticides would not leach to ground water, except under rare circumstances, and, hence, there are few historic data. From a review of available data, and "surrogate" surface water baseflow data, there are sug-

Tab 3
Pesticides detected in ground water supplies in Iowa and Minnesota, US (from: Hallberg 1986; Kelley et al. 1986; Klaseus 1987)

Common Name Active Ingredient	Maximum Concentration µg/l Iowa/Minnesota	Percent of Detections % Iowa/Minnesota
Herbicides		
alachlor	16.6/9.8	15/11
atrasine	21.1/42.4	72/72
chloramben	1.7/ND	<1/0
cyanasine	13.0/0.10	12/1
dicamba	2.3/2.1	2/2
metolochlor	12.2/2.1	10/2
metribuzin	6.8/0.78	9/2
picloram	ND/0.13	0/1
propachlor	1.7/0.62	1/3
simasine	ND/2.6	0/<1
trifluralin	0.2/ND	1/0
2,4-D	0.2/4.2	<1/2
2,4,5-TP	ND/0.26	0/1
Insecticides and Nematicides		
aldicarb	ND/50.6	0/<1
carbofuran	0.8/ND	2/0
chlorpyrifos	0.07/0.21	<1/2
fonofos	0.90/ND	1/0
phorate	0.10/ND	<1/0
terbufos	12.0/0.63	2/<1

gestions that pesticide residues in ground water may be increasing (Hallberg 1986).

Compared to nitrogen, pesticide losses in ground water and surface water are quite low, usually less than 5% (Baker and Johnson 1983; Hallberg 1986; Wauchope 1978). Hence, there is not the clear economic incentive to reduce inputs. (These figures are based on parent product losses; added losses based on breakdown products are not well known.) However, these amounts lost approximate the same amount of active ingredient that actually reaches their target pest (Pimental and Levitan 1986). This again emphasizes the relative inefficiencies of current production methods. Given the health concerns with pesticide exposure, improvement is clearly warranted.

Quasi Point Sources

Besides the low concentrations of pesticides in ground water resulting from routine agricultural use, there are local situations that are much more serious and have caused the closing of public and private water supply wells in several states (Hallberg 1986; Holden 1986). These are the point source problems in the vicinity of local agricultural supply-mixing and/or rinsing facilities (Hallberg 1986; OECD 1986). Tab 4 summarizes data from case studies in Iowa. Many of these cases turned up inadvertently, from monitoring of public

water supplies, for example. Most of these were not cases where anyone was clearly suspected of negligence or improper handling of chemicals or rinse water, at least not by past standards.

In these problem areas the concentrations in the local ground water or in drinking water may be increased 10- to 20-fold for nitrate, and 100 times or more for pesticides, above the background concentrations. Also because of the localized high concentrations, chemicals that have not typically been detected elsewhere are leaching to ground water, for example, chemicals related to fumigants such as carbon-tetrachloride. As mentioned above, between 15 to 30 pesticides have been detected in ground water, likely from routine use. When the quasi point source situations are included, an additional 50 to 60 pesticide compounds have been noted (Holden 1986).

Though such pollution may be very localized, it can be very serious. The subheading refers to these sites as "quasi" point sources because, even though these are discrete sites, there are so many such facilities in intensive agricultural areas, for example, that their potential impact may be widespread.

Surface Water - Ground Water Interaction

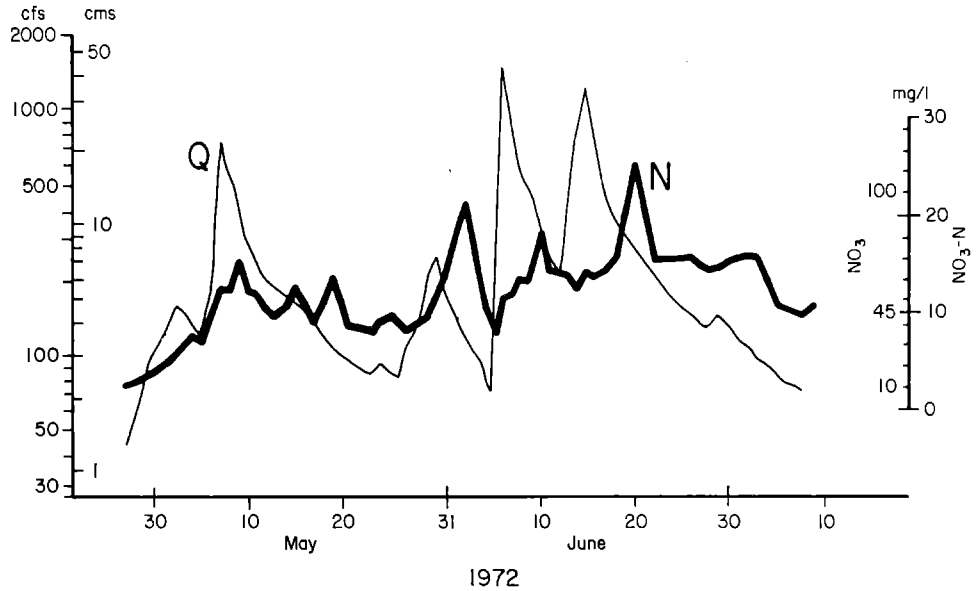
Another expressed concern which is sometimes overlooked, is the interaction, or interconnection

Chemical	Maximum Concentrations Detected	
	Affected Ground Water	Local Background Ground Water
Herbicides (in µg/l)		
alachlor	580.0	ND - 1.30
atrazine	600.0	ND - 1.60
cyazifluthrin	38.0	ND - 0.30
metolachlor	250.0	ND - 0.30
metribusin	28.0	ND - 0.20
trifluralin	0.2	ND
Insecticides (in µg/l)		
carbofuran	0.2	ND
fonofos	1.3	ND - 0.3
Fumigants (in µg/l)		
EDB	1.0	ND
1,2-DCE	2.0	ND
Carbon Tet	66.0	ND
Chloroform	4.0	<1.0
Nutrients (in mg/l)		
Nitrate-N	20-117	4-9
Ammonia-N	290	<1.0
Potassium (K)	510	1.5

Tab 4
Selected pesticide and nitrate concentrations from case studies in Iowa where ground water has been polluted in the vicinity of farm-chemical supply dealerships (after: Hallberg 1987)

ND = not detected

Fig 7
Discharge (Q) and NO₃-N (N)
concentration for the Skunk
River near Ames, Iowa, US
(after: Johnson and Baker 1973)



of ground and surface water (Hallberg 1985, 1986, 1987; OECD 1986). There are two general considerations: 1) the contribution of pollutants from ground water to streamflow and 2) the delivery of pollutants in surface water into ground water in karst areas.

Ground Water Flux to Streamflow

In humid environments, ground water discharges into major streams, providing perennial flow. This is why streams continue to flow even after many weeks with no runoff-producing events. This interconnection also affects surface water or stream water quality. The pollution of surface water is also of concern for its use as drinking water and for recreation, and also because of other potential ecological effects.

Over the past years a great deal of energy has gone into resolving some of our surface water quality problems by developing sewage treatment facilities and by working with industry to control point source discharges into streams and lakes. Yet even where waste treatment effects have been minimized, high nitrate loads have continued or increased in many streams.

In the United Kingdom, records of 25 rivers were analyzed, some extending back to 1928. Nitrate increased at all sites (averaging 0.15 mg/l/yr), with the major increases registered after 1960; approximately doubling over the past 20 years (OECD 1986). In the Garonne Basin (France), Probst (1985) described that phosphorus exportation in streams is quite low, but the main contribution is from point sources of sewage effluent. However, nitrogen loading is quite high and related directly to the magnitude of fertilizer-N used, and most is delivered by various components of ground water flow.

This is where the interconnection between ground water and surface water again plays a role. The high nitrate concentrations that appear in many streams are related to periods of high recharge from shallow ground water. The nitrate is mobilized by water infiltrating through soil, recharging shallow ground water, which then discharges into the stream.

This is illustrated in Fig 7, which shows the discharge of the Skunk River and the NO₃-N concentration in the water over time. Note that as the discharge rises, the NO₃-N concentration is either stable or actually decreases. That is because the overland water that forms these discharge peaks is actually quite low in NO₃-N. Nitrate forms in the soil and hence is picked up by the water moving through the soil (i.e., ground water), not by water moving over it (i.e., runoff, or surface water). On Fig 7, note that the peaks of NO₃-N occur as the river discharge is receding. The recession of discharge events are periods of enhanced ground water flux into the streams (from tile lines and other shallow ground water movement). Thus, after the runoff water peak has rapidly moved by, the slower moving ground water, added by the rain that generated the event (and bank storage, etc.), moves through the soil, mobilizing nitrate, and discharges into the stream producing the increases in NO₃-N concentration. The timing of NO₃-N fluctuations is related to seasonal recharge, not necessarily to the timing of seasonal agricultural practices.

Pesticide residues in streamflow are also of concern, but the mechanisms may be different than for nitrate. While runoff water tends to have very low nitrate concentrations it also tends to have greater pesticide concentrations than infiltrating water, because of the lower solubilities and surface application of many pesticides (Baker 1985b; Wauchope 1978). Fig 8 and 9 show discharge and

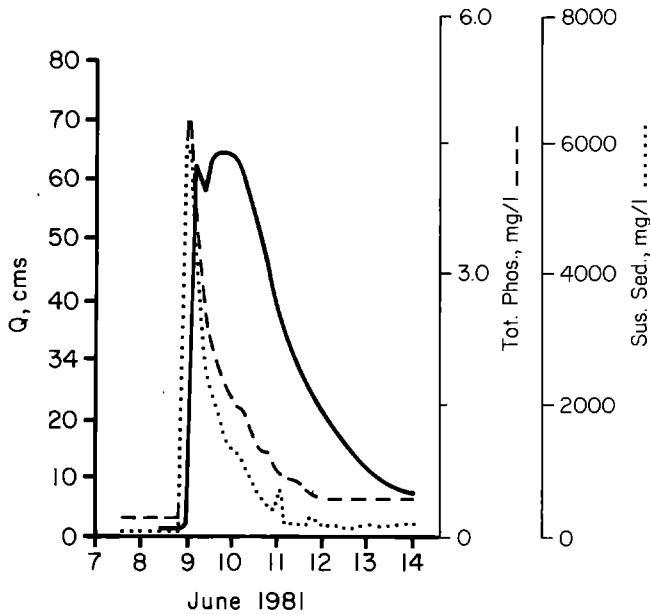
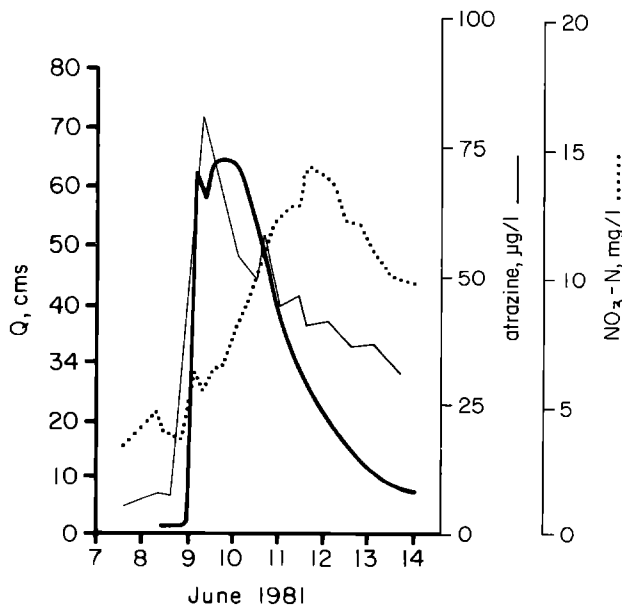


Fig 8 Discharge (cms = m^3/sec), suspended sediment, and total phosphorus concentration from a runoff event in a northern Ohio stream (after: Baker, D. 1985)

water-quality data for a runoff event on a stream in northern Ohio, US (Baker, D. 1985). Fig 8 shows the rapid rise and decline of suspended sediment associated with the rising stage and runoff component of the hydrograph. Phosphorus compounds have a very low solubility, and hence are transported almost exclusively in the runoff and parallel the sediment. The NO_3-N shows the same relationship noted in Fig 7, rising in concentration during the hydrograph recession, when ground water flux increases.

Fig 9 Discharge and NO_3-N and atrazine concentration, as in Fig 8 (after: Baker, D. 1985)



The primary point is the intermediate behaviour of atrazine, shown on Fig 9. The peak concentration occurs with the runoff phase, typically slightly later than the suspended sediment and phosphorus. The atrazine concentration does not rapidly decline like the other runoff components, however. Rather it declines slowly, during hydrograph recession. This implies that atrazine is also mobilized by the increased ground water flux, particularly the shallow interflow, or 'subsurface' runoff, ground water component. Typically, atrazine would continue to recede back to the baseflow concentrations it exhibited before the event.

Such behaviour might be expected for many of the more common herbicides. Many such compounds are of moderate solubility and most of the losses, even in runoff, are in the water phase (Baker and Johnson 1983; Baker 1985a, b). Generalizations, however, must be tempered because there are many physical-chemical properties that affect pesticide movement (Baker 1985b). It is possible that desorption from sediments also plays a role in the recession of atrazine. This would not seem to be a major factor, however, because the same phenomena can be seen in tile-line discharge (Hallberg 1986; Hallberg et al. 1986) and equilibration between the sediment and water phases takes place very rapidly, relative to the duration of a runoff event (Wauchope and Meyers 1985). This can cause short episodes of high pesticide concentrations in drinking water supplied by surface water sources (Baker, D.B. 1985). Most current treatment practices have little effect on such pollution (Baker, D.B. 1985; Butler and Arruda 1985; Kelley 1987).

Karst Areas

In karst terrains surface water containing various pollutants can directly enter the ground water system through sinkholes and related features. This can result, for example, in higher concentrations of pesticides being delivered into the ground water system than typically would occur through infiltration recharge. The ground water quality for particular wells may be seriously affected, particularly where localized flow systems occur, as shown in Tab 5.

The direct entry of surface water into the ground water system can deliver a variety of other unusual contaminants, such as less soluble chemicals, suspended sediment and organics, and pathogenic microbes (Hallberg 1985; Hallberg et al. 1984). The special concerns with karst-carbonate aquifers are becoming widely noted (Astruc et al. 1986; OECD 1986; Quinlan and Alexander 1987; Quinlan and Ewers 1985). Unfortunately, karst settings are often viewed as unique. However, karst-carbonate aquifers underlie extensive agricultural areas throughout Europe and the US, and the complex problems of these areas must be recognized.

Conclusion - Commentary

The occurrence of potentially toxic or hazardous chemicals in ground water, even in low concentrations, is of real concern because of the potential for long-term and widespread exposure to the public. At the present time, only relatively shallow aquifers are affected. However, this may simply be a function of time. Over time, if such chemicals persist in ground water, they may be transmitted to deeper aquifers (e.g., Hallberg 1986).

With our current state of knowledge about agricultural chemicals (or any toxic or hazardous substances) in ground water or drinking water, we are presented with many questions for which we have few wholly satisfactory answers. The pesticide concentrations, which are being routinely detected, are far below acute toxic (poisonous) levels. There are, however, many uncertainties about the potential long-term chronic health effects (e.g., cancer, immune system disorders) from the ingestion of pesticides in drinking water. Pesticide concentrations included in Tab 2 and 3 exceed some proposed health standards, based on chronic concerns for carcinogenicity or mutagenicity (Anderson et al. 1986). These concerns are amplified by the presence of multiple pesticide residues and likely their metabolites, in relation to other environmental factors. As mentioned in section on pesticides in ground water, 20 to 25% of wells in which pesticide residues were detected had not one but two or more pesticides present. In addition, pesticides in ground water typically are found together with high concentrations of nitrate. The implications of the coexistence of these chemicals in drinking water with microbial pathogens (in untreated rural water supplies) and with other man-made organic compounds or metals are unknown. The potential widespread, but unforeseen, exposure to the public through drinking water (in combination with other routes) and the possible synergistic interactions necessitate a careful and critical assessment.

It is difficult to measure, let alone prove, the long-term health impacts of such environmental exposure. Various epidemiological studies suggest cause for concern and point to the clear need for more intensive study (Blair et al. 1987; Dorsch et al. 1984; EEC 1980; Fiore 1987; Hardell and Sandstrom 1979; Hoar et al. 1986; Isacson et al. 1985; WHO 1978). Unfortunately, epidemiological 'proof' often takes a generation of exposure and may never satisfactorily answer such questions.

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Pesticide	Concentration (µg/l)	
	Typical	Maximum
alachlor	ND	250.0
atrazine	0.3	13.0
cyanazine	ND	1.0
metolachlor	ND	14.0

Tab 5 Pesticide concentrations from a private water supply well in a local karst flow system in Iowa, US (from: Hallberg et al. 1987)

Our technical shortcomings have also played a role. Our past lack of understanding of the preferential flow of water and solutes through the soil is one reason such widespread leaching of chemicals was not foreseen. Undoubtedly, this is a very important mechanism in the potential rapid leaching of agricultural chemicals (and all land applied chemicals). Past models (conceptual or analytical) based on Darcy's concept of water and solute transport suggested this would not occur. At this point in time, the importance of preferential flow cannot be over emphasized (Beven and Germann 1982; Hallberg 1986; Hallberg et al. 1986; Thomas and Phillips 1979; White 1985).

Various work, briefly reviewed here, is providing a definition of the problem between land application of agricultural chemicals and water, particularly ground water, quality. Now we must work toward solutions. The debate has begun on the development of new legislative, regulatory, and enforcement programs to deal with agricultural pollution. Amidst this debate critics must realize that as long as chemicals are applied on land, within the vagueries of climatic conditions, that losses into the environment cannot be eliminated but they clearly can be minimized. The farm sector must also realize that most other industries have undergone and continue to undergo such scrutiny.

These water quality problems can only be resolved through a more complete approach to agricultural management. We must couple our standard concerns for efficient crop production, soil conservation, and surface water quality with the need to protect ground water, as well. Better chemical and nutrient management must play a part. In this sense we must broaden the scope of our agronomic research beyond yield studies to look at the whole of the agroecosystem.

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