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Cover Photograph

Groundwater issuing from Falling Spring in the bluffs along the Turkey River in northeastern Iowa. The water flows out of an underground cavity in the carbonate rocks, below the water table in the land, but high above the level of the river. Photograph courtesy of George R. Hallberg, Iowa Geological Survey.

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Foreword

In response to requests received from persons concerned about the effects of modern agriculture on groundwater quality, a committee was established to evaluate the issue. The committee reported at the meeting of the CAST Board of Directors in July 1983. The report was discussed at length by the Board without reaching a consensus because of the complexity of the subject matter and the lack of a plan of attack to do justice to the numerous agriculture-related practices and substances that might affect groundwater quality. Eventually, the suggestion was made that the subject might be reduced to manageable dimensions by emphasizing the principles rather than the individual substances. The Board accepted this idea, and a motion to develop a task force report was passed. The report eventually was organized according to classes of substances, but the treatment of the various subjects emphasized the principles, as visualized by the Board.

The task force developed to produce the report included expertise in agricultural engineering, agronomy, animal science, aquatic plant management, crop science, dairy science, entomology, food science, geology, horticulture, meat science, nematology, plant growth regulation, plant pathology, poultry science, range management, rural sociology, soil science, soil testing and plant analysis, veterinary toxicology, and weed science. The numerous disciplines involved provide an indication of the extensive ramifications of agricultural practices in terms of groundwater quality.

The task force first developed an outline of the subject matter. Certain members of the task force then prepared drafts of their assigned topics and eventually met in Kansas City in May 1984 to review and revise the existing contributions and to complete the others. The task force chairman assembled these into a first draft, which was sent to task force members for review and comment in June 1984. The task force's third draft, prepared by the chairman, was sent to task force members and the CAST Editorial Review Committee for comment. The draft was sent also to Ralston J. Graham of Lincoln, Nebraska, for editing. The comments received were worked into the edited version prepared by Mr. Graham, and this new draft and another prepared subsequently were submitted to task force members. Comments received on the second edited draft were taken into account in preparing the galley proof, which was sent for review and final approval to members of the task force, the CAST Editorial Review Committee, and the CAST Executive Committee in January 1985. Final corrections then were inserted, and the copy was prepared for the printer.

On behalf of CAST, I thank members of the task force and all the others who gave of their time and talents to prepare this report as a contribution of the scientific community to public understanding. I thank also the employers of task force members, who made the time of their employees available at no cost to CAST. The members of CAST deserve special recognition because the unrestricted contributions they have made in support of the work of CAST have financed the preparation, publication, and distribution of this report.

The report is being distributed to certain members of Congress, the Environmental Protection Agency, and the U.S. Department of Agriculture; to institutional members of CAST; and to an additional selected list of persons, including members of the news media who have asked to receive CAST publications. Individual members may receive a copy upon request.

The report may be republished or reproduced in its entirety without permission. If republished, credit to the authors and CAST would be appreciated.

Charles A. Black
Executive Vice President
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Contents

Summary 1
Overview 3
  Groundwater 3
  Salinity 3
  Fertilizers 3
  Inorganic soil amendments 4
  Organic residues 4
  Pesticides 4
Introduction 7
Nature of groundwater and groundwater recharge 7
  Groundwater glossary 7
  Groundwater recharge and the hydrologic cycle 9
  Nature of groundwater flow 9
  Unique concerns for groundwater contamination 10
  Special considerations 11
  Transport through the unsaturated zone 12
  Transport processes 13
  Effect of adsorption on transport 13
  Effect of water movement 14
  Degradation of chemicals in soil 14
  Measuring the downward movement of chemicals 14
Salinity 15
  Extent of irrigated agriculture 16
  Salinity of irrigation and drainage water 16
  Health effects in drinking water 18
Fertilizers 18
  Movement of fertilizer constituents to groundwater 19
  Nitrogen 19
    General behavior 19
    Nitrogen relations in the Corn Belt 22
    Nitrogen relations in the East and Southeast 22
    Nitrogen relations in the Great Plains 23
    Nitrogen relations under irrigation 23
    Nitrogen relations of shallow-rooted crops 25
    Nitrate management 25
    Nitrogen fertilizer management 26
    Irrigation 28
    Tillage 28
    Cropping system 28
  Health effects of nitrate in drinking water 29

Inorganic amendments 30
Liming materials 30
Gypsum 31
Sulfur 31
Other amendments 32
Effects on pesticides 32
Organic residues 33
Nitrate 33
Bacteria 37
Pesticides 38
Volatilization 39
Decomposition 40
Sunlight 40
Water 42
Microorganisms 42
Retention by soil 44
Transport by water 44
Occurrence in groundwater 45
Health effects in drinking water 46
Information needs 48
Literature cited 49
Appendix 54
A. Chemical groups of pesticides classified by uses 54
Herbicides 54
Insecticides 54
Fungicides 55
Nematicides 55
B. Chemical structure of pesticides and rate of microbial decomposition in soils 55
C. Retention of organic pesticides by soils 55
D. Appendix tables 57

Summary

Agricultural production systems in the United States involve the use of fertilizers to supply plant nutrients; inorganic and organic amendments to improve soil quality; and pesticides to control weeds, insects, and other pests. Irrigation water is used in many areas where water is deficient.

These practices are very important in agricultural production. One of their possible side effects, however, is the transport of chemicals to groundwater. Most of the chemicals used in agriculture do not accumulate in groundwater in important quantities except in unusual situations, but a few are of legitimate concern. Groundwater is the source of drinking water for half of the U.S. population. Accordingly, the focus of this report is on the effects of agriculture on groundwater quality.

In humid regions, the precipitation flushes dissolved salts from soils at intervals, and the salinity of the groundwater remains low because the precipitation is almost pure water, and there is a great deal of it relative to the amounts of salts present. In dry regions, the precipitation is supplemented by irrigation water, which always contains dissolved salts. When the water evaporates, the salts remain behind, and they increase the salt content of the soils. To keep the soils productive, the excess salts must be flushed out periodically, and they can eventually reach the groundwater. Excessive salinity of groundwater is undesirable in agriculture because some of the groundwater may be pumped directly for irrigation while some reappears as surface water in streams and may be used again downstream for irrigation. Excessive salinity in groundwater used for drinking is undesirable because of objectionable tastes and the laxative effect of the sulfate.

Fertilizers add small amounts of salts to groundwater, but the principal concern is for the possible health implications of ingesting nitrate. When nitrate is ingested in excess, the resulting nitrite produces methemoglobinemia, a condition that can lead to death from asphyxiation. A number of infants died from methemoglobinemia until the cause and cure were discovered about 40 years ago. Where water supplies are high in nitrate, bottled water now is recommended for infants in their first year. Adults tolerate far higher concentrations than do infants. Several other possible health effects of excess nitrate have been suggested. Nitrate loss to groundwater may be reduced by modifying various agricultural practices. To date, however, the ease of adjusting to the health hazard of nitrate in drinking water from wells in rural areas has meant that practical considerations related to the economics of agricultural production have been of prime concern in nitrate management.

Other chemicals added to soils in agriculture are classed as inorganic soil amendments. These include liming materials that raise the pH value of acid soils, acidifying materials that lower soil pH, and gypsum, which is used to increase the rate of entry of surface water into certain soils. To date, the magnitudes of the possible effects of these chemicals on groundwater have not been great enough to be of concern.

Organic residues, including crop residues, food processing wastes, animal manures, and sewage sludges, are valuable in agriculture as soil conditioners and fertilizers. The principal concern about the possible effects of these residues on groundwater quality is for nitrate associated with animal feeding operations in out-of-door feedlots. Bacterial contamination also is of some concern. Both excess nitrate and bacterial contamination generally can be avoided by drilling farm wells deeper and properly casing them at upper levels to avoid entry of the contaminated water.

The pesticides used at present are mostly synthetic organic compounds. As a result of loss from the soil by volatilization and decomposition, or retention by the soil (mostly by the organic matter or, for some pesticides, the ion-exchange properties of the soil), relatively few pesticides have been found in groundwater.

EPA has estimated that as many as 50 of the more than 1,000 registered pesticides possess the potential for appearance in groundwater under conditions conducive to downward movement. According to a 1984 listing, 12 have been detected in drinking water wells under certain conditions. Typical concentrations exceeded the health-advisory concentrations for several of these pesticides.

To date, no verified adverse health effects appear to be on record as a result of pesticide residues in groundwater used for drinking. For a pesticide for which the common safety factor of 100 has been used, a 22-pound child would have to drink 26 gallons of water with the health-advisory concentration per day every day to ingest an amount of the pesticide equivalent to the maximum daily intake that produced no observed detrimental effect in the lifetime feeding test with animals used as a basis for calculating the health-advisory concentration.

If a significant concentration of a pesticide is found in groundwater as a result of use in agricultural production, further increases in the concentration may be limited by discontinuing the use of this pesticide in the affected area. Integrated pest management (IPM) may suggest ways to control the target pest using lower amounts of the chemical without loss in efficiency of pest control. Environmental warnings on pesticide

labels should always be heeded. Techniques to reduce the concentrations of pesticides in drinking water include substituting alternative water sources, distilling the water, using ultraviolet light to decompose the pesticide residues, and passing the water through an activated carbon filter to remove the residues.

Overview

Groundwater

Much of the drinking water used by humans and domestic animals is derived from groundwater, and this is the primary reason for the concern about the influence of agriculture on its quality. This report summarizes the available information on quality of groundwater as related to agriculture.

Groundwater is the water that occurs in the earth below the depth to which water will rise in a well. Below this depth, the pore spaces between the solid particles are all filled or saturated with water. The soil and other unconsolidated materials above this depth contain water, but the larger pore spaces are not filled with water. These materials collectively make up the unsaturated zone. Water must move down through the unsaturated zone before it reaches the saturated zone, where it becomes groundwater.

In some places, particularly in areas in humid regions where the land is relatively level, the saturated zone may be only a few feet below the surface of the soil. In others, particularly in arid regions, the saturated zone may lie several hundred feet below the surface of the soil. Water carrying dissolved materials moves downward from the surface of the soil through the unsaturated zone to the saturated zone. The time in transit may be only a few days in humid regions where the satuated zone is close to the surface, the soil is readily permeable to water, and the precipitation is excessive, but it may be measured in centuries in arid regions. Irrigation may greatly hasten the downward movement.

Salinity

Water often is termed the "universal solvent." The water in streams, lakes, oceans, and soils naturally contains a variety of dissolved substances. In humid regions, the precipitation continually flushes the soluble substances from soils and moves them to the groundwater. Neither the soils nor the groundwater are saline because of the small amounts of salts relative to the amounts of almost pure water received in the precipitation.

For crop production in dry regions, the precipitation is supplemented by additions of irrigation water from streams, lakes, and groundwater, and the dissolved substances from these sources thus are added to the soils. When the water evaporates from plant surfaces or directly from soils, it leaves the soluble salts behind, and this increases their concentration in the remaining water. If so little water is added that all of it evaporates without drainage, all the salts remain in the soil. If the content of dissolved salts in the irrigation water is great enough, repetition of this process over a period of only a few years may make the soil too salty or saline to support plants. On the other hand, if enough irrigation water is added to flush the excess salts out of the soil, the salinity of the groundwater is increased. This dilemma cannot be resolved by any known technology. The addition of salts to groundwater from irrigated lands can be reduced by careful water management, but the principal practical limitation of this kind of management is the cost of installing, maintaining, and operating the irrigation system required.

Excessive salinity of groundwater is undesirable in agriculture because some of the groundwater may be pumped for irrigation, and some of it reappears as surface water in streams and may be used again downstream for irrigation. Excessive salinity in groundwater used for drinking is undesirable because of objectionable tastes and the laxative effect associated with sulfate. The Environmental Protection Agency has recommended that concentrations of chloride or sulfate should not exceed 250 parts per million in domestic water supplies. The National Academy of Sciences suggested that water having a total salt content or salinity of 3,000 parts per million or less should be satisfactory for livestock. Waters having total salinity of 3,000 to 5,000 parts per million were reported to be satisfactory for most farm animals, but not for poultry. The salinity of groundwater in some areas is in excess of these values.

Fertilizers

Among the dissolved inorganic substances occurring naturally in surface water and groundwater are the nutrients plants require for growth. Originally, agriculture depended almost entirely upon nutrients from the soil and from organic residues derived from agriculture. This system resulted in impoverished soils of low productivity. Eventually agriculture was improved by introducing legumes as an integral part of cropping systems. The legumes added available nitrogen as a result of fixation of atmospheric nitrogen by the bacteria that live in nodules on their roots. Now chemical fertilizers are used to supplement the natural supplies of nitrogen and other inorganic nutrients in soils that are required for plant growth, and agricultural productivity is consequently much increased.

Plants absorb only part of each of the nutrients present in soluble forms in the soil. As the concentration in the soil water increases (generally leading to greater uptake by plants and greater yields), the percentage of the total amount absorbed decreases, and greater residues are left in the soil. Most of the chemical ions added in fertilizers are retained by soils as a result

of chemical interactions, but a few are not. Of those not retained, only nitrate is of concern in groundwater used for drinking. Although loss of nitrate from soils to groundwater is a natural process, the potential for loss to groundwater is increased in local areas by high concentrations of livestock and in much of the cropland by nitrogen fertilizers.

Accumulation of nitrate in groundwater has been suggested as the cause of several human health problems, including birth defects, cancer, nervous system impairment, and methemoglobinemia. Only the last of these is well verified. Methemoglobinemia is caused by alteration of some of the nitrate to nitrite in the digestive tract, absorption of nitrite into the bloodstream, and interaction of the nitrite with the hemoglobin in the blood to produce methemoglobin, a form that does not carry oxygen to the body cells. A number of infant deaths from methemoglobinemia occurred until the cause was discovered about 40 years ago. Now the cause of and cure for methemoglobinemia are well known among medical doctors. Where water supplies are high in nitrate, bottled water is recommended for infants in their first year. Adults tolerate far higher concentrations of nitrate than do infants.

Various agricultural practices may be used to reduce the loss of nitrate to groundwater. These include (1) reducing the amounts of nitrogen fertilizers applied in current cropping systems, (2) adjusting nitrogen fertilizer applications on the basis of soil or plant-tissue tests, (3) applying nitrogen fertilizer in small amounts as needed during the growing season, (4) using slow-release fertilizers, (5) using chemical inhibitors to delay the formation of nitrate from the ammonium and other forms in which much of the fertilizer nitrogen is applied, (6) avoiding fall applications of nitrogen fertilizers for crops to be planted in the following spring, (7) spraying plants with solutions of urea in place of supplying nitrogen fertilizer to the soil, and (8) changing to cropping systems that derive their supplemental nitrogen from legumes and can be used with little or no nitrogen fertilizer. The effectiveness of the last practice is understood to be a consequence of a smaller addition of nitrogen and the slow release of the legume nitrogen. In the end, the legume nitrogen is changed to nitrate.

To date, the adoption or nonadoption of alternative agricultural practices that would reduce nitrate loss from soils to groundwater has been based upon economics and convenience. There has been no special incentive to override these practical considerations with health concerns for private wells because the use of bottled water for drinking by infants has made it possible to adjust to the hazard of nitrate occurrence in groundwater at little cost and inconvenience. Some municipalities, however, have incurred considerable expense in efforts to develop alternative sources of water so the water supply will conform to the public health standard for nitrate.

Inorganic Soil Amendments

Another group of chemicals added to soils in modern agriculture is classed as inorganic amendments. These include limestone and other materials that neutralize soil acidity, sulfur and other materials that acidify soils, and gypsum, which is used to increase the rate of entry of surface water into certain soils. Both the neutralizing materials and the acidifying materials may influence to some degree the reactions pesticides undergo in soils and the potential for transfer of these substances to groundwater. The acidifying materials and gypsum have the potential for increasing the soluble salt content of groundwater. To date, however, the magnitudes of the possible effects on groundwater have not been considered great enough to be of concern.

Organic Residues

Organic materials added to soils include crop residues, food processing wastes, animal manures, and sewage sludges. These materials, which are valuable in agriculture for their properties as soil conditioners and fertilizers, have the potential for contaminating groundwater with nitrate and bacteria. Nitrate contributes to the hazard of methemoglobinemia and bacteria to the hazard of diarrhea and other diseases.

The principal concern is for nitrate associated with animal feeding operations in out-of-door feedlots. The reason is the deposition of great quantities of nitrogen in the excreta on small areas of land. In the presence of free oxygen, the nitrogen is transformed gradually to nitrate. Nitrate from animal manures and other organic sources behaves like that from fertilizers.

Bacterial contamination also is of some concern. Some shallow farm wells located near livestock quarters are contaminated with fecal coliform bacteria. There is evidence that infant diarrhea associated with consumption of bacterially contaminated water from such wells greatly enhances the risk of methemoglobinemia from the nitrate also present in the water. Both excess nitrate and bacterial contamination generally can be avoided by drilling shallow wells deeper and casing them properly at upper levels to avoid entry of contaminated water.

Pesticides

The pesticides used at present are mostly synthetic organic compounds. The principal processes that influence their potential for loss from soil to groundwater are volatilization (and subsequent diffusion), decomposition, retention by the soil, and transport by water.

Substances used as fumigants must be relatively volatile so they will vaporize and move in effective concentrations as gases throughout the soil. Pesticides that have a marked tendency to volatilize and a low solubility in water tend to be lost from the soil to the atmosphere; their residues are unlikely to reach the groundwater. Ethylene dibromide (EDB), a volatile liquid used for nematode control, is relatively soluble in water. This solubility in water, together with the typically large quantities applied and the low retention by soil solids, help to explain why EDB has been found in groundwater under conditions favorable for downward movement.

Synthetic organic pesticides may be decomposed in different ways. Those applied to plant foliage or the soil surface may be broken down rapidly by sunlight. Decomposition by sunlight may be one reason for the fact that most of the pesticides that have been detected in groundwater are applied to soils.

Some pesticides react with water in soil to form new compounds. The fungicide captan, for example, reacts rapidly with water to form an innocuous product, so that downward movement of the parent fungicide to groundwater is not a matter for concern. The nematicide DBCP also reacts with water to produce a new compound that lacks the pesticidal properties of the parent compound, but the rate at which this reaction occurs under the usual environmental conditions in soils is inconsequential. For this and other reasons, DBCP has been detected in groundwater.

Breakdown of organic pesticides in soils beyond that involving reaction with water is attributed to microorganisms and catalytic effects of soils. Pesticides such as dalapon, barban, 2,4-D, malathion, and parathion that break down rapidly (50% decomposition in 2 weeks or less under favorable conditions) are not likely to be detected in groundwater. Some organic pesticides, such as chlordane, DDT, and dieldrin, decompose very slowly and may persist for years. These pesticides, however, are not of concern as groundwater contaminants from agricultural use because they are relatively insoluble in water and are retained strongly by soils.

The soil constituent of greatest importance in retaining pesticides is the organic matter. Binding to the organic matter decreases the potential for downward movements of many pesticides in soils. The capacity of the soil to hold positively charged ions in exchangeable form is important in retaining paraquat and other pesticides that are positively charged.

The principal mechanism by which pesticides are transported from soil to groundwater is downward percolation of water containing dissolved pesticides. The relative potentials for movement of different pesticides to groundwater in different soils may be estimated by applying known quantities of the pesticides to the soils, adding equal quantities of water, and measuring the content of the various pesticides in the drainage water or the distance to which the pesticides move in the soil. The potentials found in this way depend mostly upon the retention of the pesticides by the soil. They exceed the "worst case" situations for comparable thicknesses of soil in the field because they do not allow for the full effects of loss by volatilization and decomposition by microorganisms.

An Environmental Protection Agency official has estimated that as many as 50 of the more than 1,000 registered pesticides possess the potential for detection in groundwater under conditions conducive to downward movement. According to a 1984 listing, 12 have been detected in drinking water wells under certain conditions from the limited monitoring that has been done. Typical concentrations exceeded the health-advisory concentrations for four pesticides (bromacil, DBCP, D-D, and EDB), were less than the health-advisory concentrations for seven pesticides (alachlor, atrazine, carbofuran, DCPA, dinoseb, oxamyl, and simazine), and approximately equaled the health-advisory concentration for one pesticide (aldicarb).

Despite the existence of residues of certain pesticides in some groundwaters in excess of the health-advisory concentrations, no verified adverse health effects appear to be on record as a result of pesticide residues in groundwaters used for drinking. One reason may be the safety factors involved in the health-advisory concentrations. To derive the health-advisory concentration for a pesticide, each of two animal species is treated with a range of doses of the pesticide in lifetime studies. The maximum dosage that produces no observable detrimental effect in the more sensitive of the two species then is divided by a safety factor, commonly 100. For a substance for which a safety factor of 100 has been used, a 22-pound child would have to drink 26 gallons of water with the health advisory concentration per day every day to ingest an amount of the pesticide equivalent to the maximum daily intake that produced no observable detrimental effect in the test animal.

If a significant concentration of a pesticide is found in groundwater as a result of agricultural usage, further increases in the concentration may be limited by discontinuing the use of this pesticide in the affected area. Integrated pest management (IPM) may suggest ways to control the target pest using lower amounts of the chemical without loss in efficiency of pest control. Environmental warnings on pesticide labels should be heeded. Techniques to reduce the concentrations of pesticides in potable water include substituting alternative water sources, distilling the water, using ultraviolet light to decompose the pesticide residues, and passing the water through an activated carbon filter to remove the residues.

Summary of Prominent Facts About the Constituents of Principal Concern in Groundwater Underlying Cropland

Constituent	Sources	Soil Processes Affecting the Amount Lost to Groundwater	Tendency to Move Downward Through Soils in Percolating Water	Comments
Soluble salts	Irrigation water Organic materials Fertilizers Weathering of soil minerals Rainfall	Precipitation and dissolution of carbonates and sulfates Weathering of soil minerals	High	Must be leached from most irrigated soils to maintain crop production
Nitrate	Nitrogen fertilizers Organic materials Atmospheric nitrogen fixed by legumes Rainfall	Production and removal by microorganisms Removal by plants	High	Loss to groundwater is incidental to water movement and is a loss to crop production potential
Pesticides	Commercial products	Retention by soil Decomposition Volatilization Removal by plants	Varies widely among pesticides and soils	Principal occurrences in groundwater result from pesticides that remain in solution in the soil, are not decomposed rapidly, and are applied to sandy soils with groundwater near the surface and with much water movement through the soil to groundwater

Introduction

Groundwater is an important resource. It is used as a source of drinking water by about 50% of the total U.S. population and by about 85% of the rural population. About 86% of the total water resource in the United States is in groundwater aquifers. Aquifers furnish about 24% of the nation's fresh water supply. Of the total groundwater use, 68% is used for irrigation of cropland. Contamination of groundwater with substances that will make it unsuitable for human use in drinking and food production thus is a matter for concern.

Groundwater always has contained a variety of chemical substances, and the current capability for detecting many substances in concentrations of parts per billion or parts per trillion has multiplied the number of substances that can be identified. Agriculture is an important source of certain chemicals found in groundwater.

Agriculture is a chemical process. Starting with a few inorganic nutrients and water from the soil, carbon dioxide from the air, and energy from the sun, plants synthesize many organic chemicals. Plant chemicals are consumed by humans and animals that synthesize many other chemicals. Humans use animal products also, some for food and some for other purposes.

The quantity and quality of life have been improved by three major scientific and technological advances in agriculture: (1) Learning enough about nature's chemistry to find what chemicals are used in plant growth and then supplying these chemicals as supplements to make up natural deficiencies and increase crop productivity. (2) Processing certain chemicals that have been produced by plants and synthesizing other new chemicals to protect crops and animals against pests that compete with humans for the products of agriculture. (3) Learning enough about the chemistry of inheritance to develop new varieties of plants and breeds of animals that are more productive for human purposes than those evolved by nature.

Because accomplishing the production and protection objectives requires the use of the chemicals in the environment, an inescapable by-product is the presence of these chemicals in the environment. When chemicals used in agricultural production are found in places such as groundwater in which they have the potential for unfavorable effects on humans, there is naturally concern about whether they are now or might in the future be having such effects.

This report addresses the concerns about possible health effects of agriculture-related chemicals in groundwater. There is little evidence for unfavorable health effects, however. In this age of industrial chemicals, people are living longer and are generally in better health than in preindustrial days. Realistically, the issues of major concern are the indirect effects of decreases in product availability and increases in price associated with the unfavorable impacts of agriculture on groundwater and of groundwater on agriculture. The principal emphasis in this report thus is on providing a basis for understanding through a review of the scientific background related to the processes and chemicals involved. With continuing monitoring and study, effects of agriculture on groundwater that have a significant direct unfavorable influence on human health hopefully can be avoided or kept to a minimum.

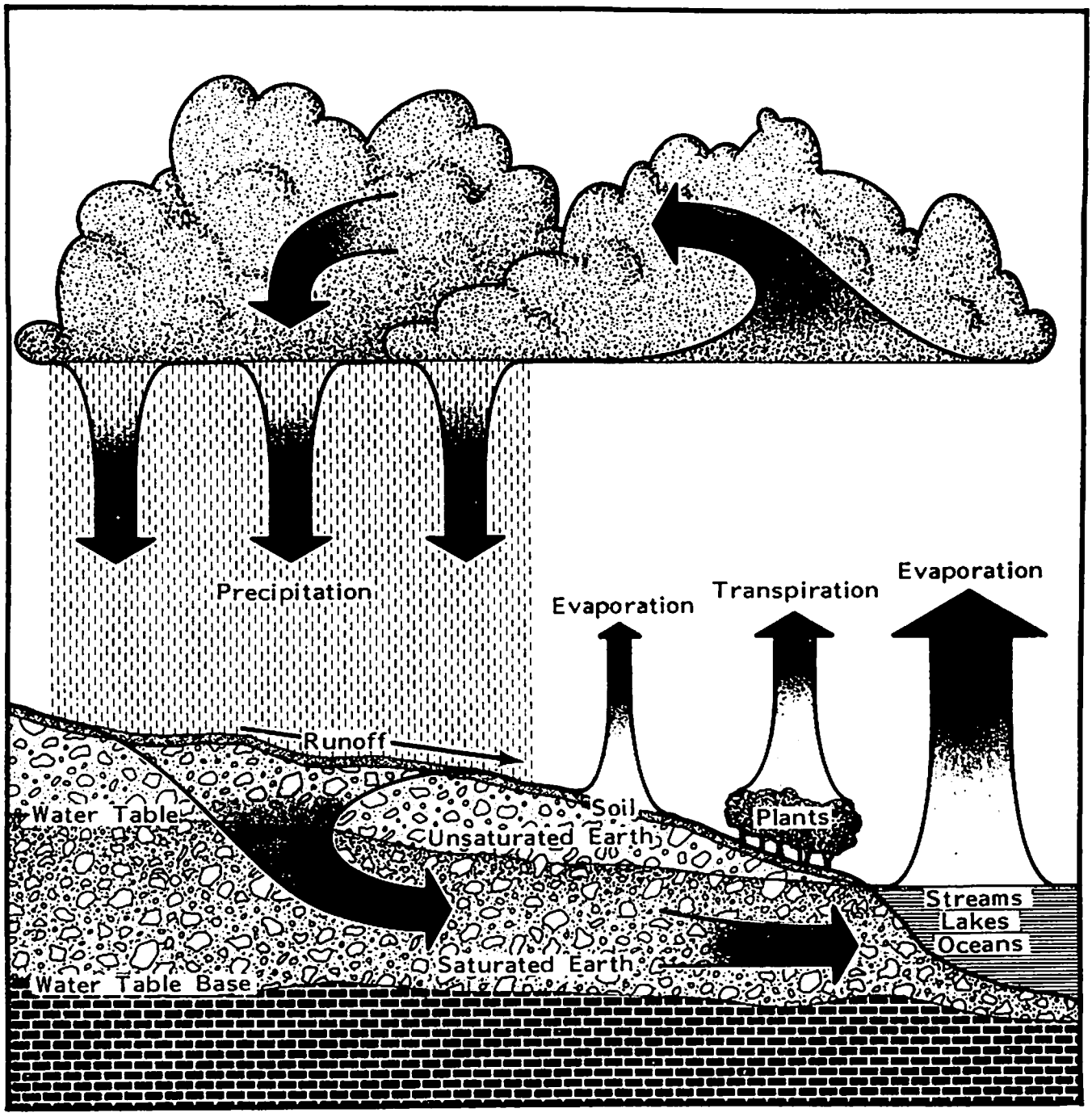
Nature of Groundwater and Groundwater Recharge

Water often is termed the "universal solvent." Thus, groundwater naturally contains a variety of dissolved inorganic salts, gases, and even small amounts of some organic materials. Historically, groundwater has been valued as a safe source of drinking water because it is generally free of the bacterial and viral contaminants that often occur in surface water. By the time surface water has percolated through soils and rock formations to become groundwater, most pathogenic organisms have disappeared. Many natural and manmade chemical compounds, however, are transported to and in groundwater.

Groundwater Glossary

Groundwater may be considered to be any water in the ground, but generally it is referred to as the water below the level at which the pore spaces in the soil or rock materials are fully filled or saturated with water. The top of the *saturated zone* is the *water table* — the level to which water will rise at atmospheric pressure in a hole dug or bored into the earth. Above the water table, some of the pore spaces are not filled with water, and this gives rise to the term *unsaturated zone.*

In most settings, groundwater moves slowly through



The hydrologic cycle. [Drawing by Rex Heer, Iowa State University.]

the small pores and cracks among the particles. The most rapid movement can occur in coarse-grained sediments (*sands and gravels*) with relatively large pores. Fine-grained sediments (*clays and silts*) permit slower movement. The property that describes the tendency of the water to move under standard conditions is called the ***hydraulic conductivity***. Soil and rock formations that have a great enough hydraulic conductivity to allow water to be pumped out through wells at practical rates to provide water for drinking, irrigation, and industrial uses are termed ***aquifers***.

Aquifers may be overlain and separated by ***aquitards*** (confining layers), which are soil and rock formations of low hydraulic conductivity, such as shale. Although these materials are saturated with groundwater if they are below the water table, the water moves through them slowly, and they do not provide a significant amount of water to wells. They may also have

significant effects on the flow and quality of groundwater because they separate aquifers from one another.

In many humid areas, ***perched water tables*** (temporary water tables) occur above the true water table in early spring. These may be caused by layers of materials at shallow depths that restrict downward movement of water. Although some wells may obtain water from these temporary water tables, most wells are supplied from deeper, more permanent aquifers.

Groundwater Recharge and the Hydrologic Cycle

Water is circulated continually among the oceans, the atmosphere, and the land in what is referred to as the ***hydrologic cycle.*** On land, water is supplied to the hydrologic system as precipitation. During and following precipitation (or snowmelt), a portion of the precipitated water enters the soil, and some is intercepted directly by plants. The water that does not enter the soil may run off the land surface as overland flow into streams, lakes, or the ocean. The major portion of the water that enters the soil is returned to the atmosphere by ***evapotranspiration***, a combination of evaporation directly from the soil and transpiration of water taken from the soil by plants. Of the remaining water, some may flow underground at a shallow depth, reappearing as flow in streams, and some may move on downward to recharge deep aquifers.

Because the processes are complex (Freeze and Cherry, 1979; Pettyjohn, 1982; Thomas and Phillips, 1979), the amounts of water and dissolved materials that enter the soil and eventually recharge the groundwater vary both seasonally and regionally. During wet and/or cool seasons, recharge may occur readily, causing the water table to rise. During dry and/or hot seasons, particularly with active plant growth, shallow water tables may be lowered by evapotranspiration. The application of agricultural chemicals, their uptake by plants, and their degradation are also seasonal. Thus, the potential for movement of these chemicals or their residues into groundwater varies with the times of application as well as the times and amounts of water entry into the overlying soils.

Regionally, the amount of recharge, the depth to the water table, and the fluctuations of depth to the water table vary with climate, soils, topography, and near-surface geologic materials. The climate, of course, affects the amounts of precipitation and evapotranspiration. The properties of the soils affect the rate of water entry, and the properties of near-surface geologic materials affect the rate of groundwater movement. The topography affects the time precipitation may have to move into the soil. For example, water may stand in a shallow layer on the surface of level land until it soaks in, whereas on steep slopes it may run off almost immediately. In the humid Midwest, broad areas of relatively level land occur, and the soils are predominantly fine in texture with moderate to low hydraulic conductivities. As a result, the water table is commonly 5 to 30 feet below the surface. Groundwater recharge occurs almost every year. In the semiarid and arid regions of the West, on the other hand, the precipitation is low, the potential for evaporation is high, and groundwater recharge is limited. In most years, there is none. Here the water tables are commonly 50 to 150 feet deep. With all these variations, groundwater recharge varies from negligible amounts up to 40 or 50% of precipitation.

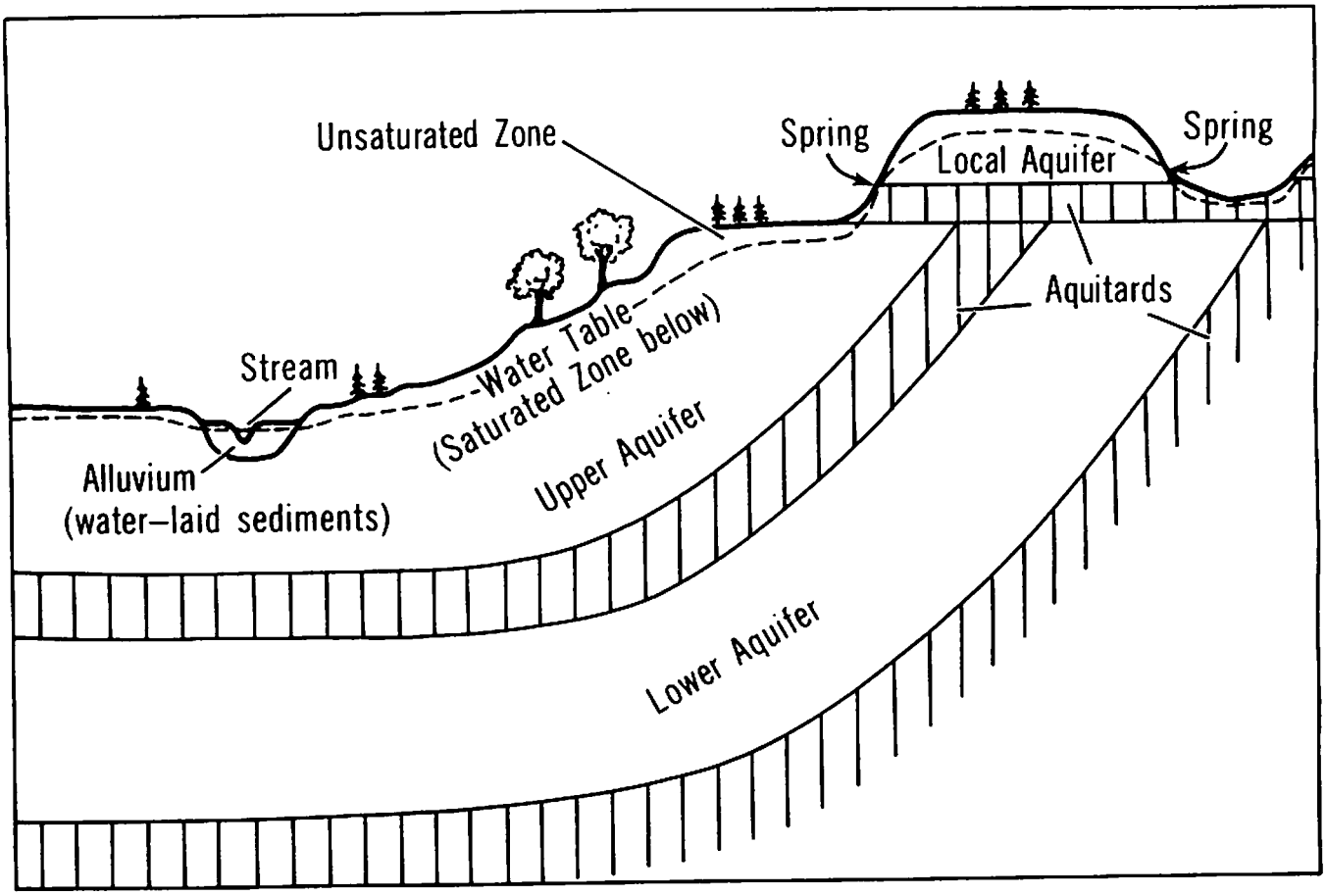
Nature of Groundwater Flow

The driving mechanism behind groundwater flow is ***gravitational pressure.*** Groundwater flows from areas of high pressure toward areas of lower pressure. The rates and directions of flow between two points are related to the pressure difference and distance between the points, and to the thickness and hydraulic conductivity of the intervening materials. The flow may be in any direction, even upward. For example, some of the water that enters a well in porous material below the water table comes up through the bottom of the well because the pressure of the water in the well is less than that in the water in the porous material immediately below the well. In real field situations, the detailed flow patterns may be difficult to document because of the complexities of interbedded aquifers and aquitards, the generally slow rate of water movement, and the many subsurface measurements that must be made.

The accompanying figures illustrate the general principles of groundwater flow for a simple system. The upper aquifer extends to the land surface and is recharged by direct movement of water through the unsaturated zone to the water table. The groundwater moves from recharge areas higher in the landscape to those lower in the landscape. The water discharges to springs (flow paths A to B), streams (C and G to D), or lakes. Such groundwater flow may provide a year-around discharge to springs, perennial streams, and lakes.

In contrast to the situation illustrated in the figures, many of the water tables in arid regions are lower than the streams and lakes. Here, the surface waters in streams and lakes recharge the groundwater. In some areas, large ponds are constructed to retain stream flows and increase groundwater recharge.

In the local aquifer shown at the upper right in the accompanying figures, the downward flow of groundwater is impeded by the lower hydraulic conductivity of the underlying aquitard. As a result, much of the groundwater moves laterally (A to B). Nonetheless, some groundwater "leaks" through the aquitard to recharge the upper and lower aquifers (from A to E and A to F).



Schematic landscape cross section showing the relationships among the water table and various aquifers and aquitards.

Groundwater flow in the lower aquifer is also from areas of high pressure to areas of low pressure. Because it is confined, much of the flow is lateral, along the length of the aquifer. As shown at H and I, however, the lower aquifer also has vertical components of flow that slowly discharge groundwater either upward through the aquitard into the upper aquifer or downward, as pressure gradients dictate. In most groundwater systems, flow is very slow.

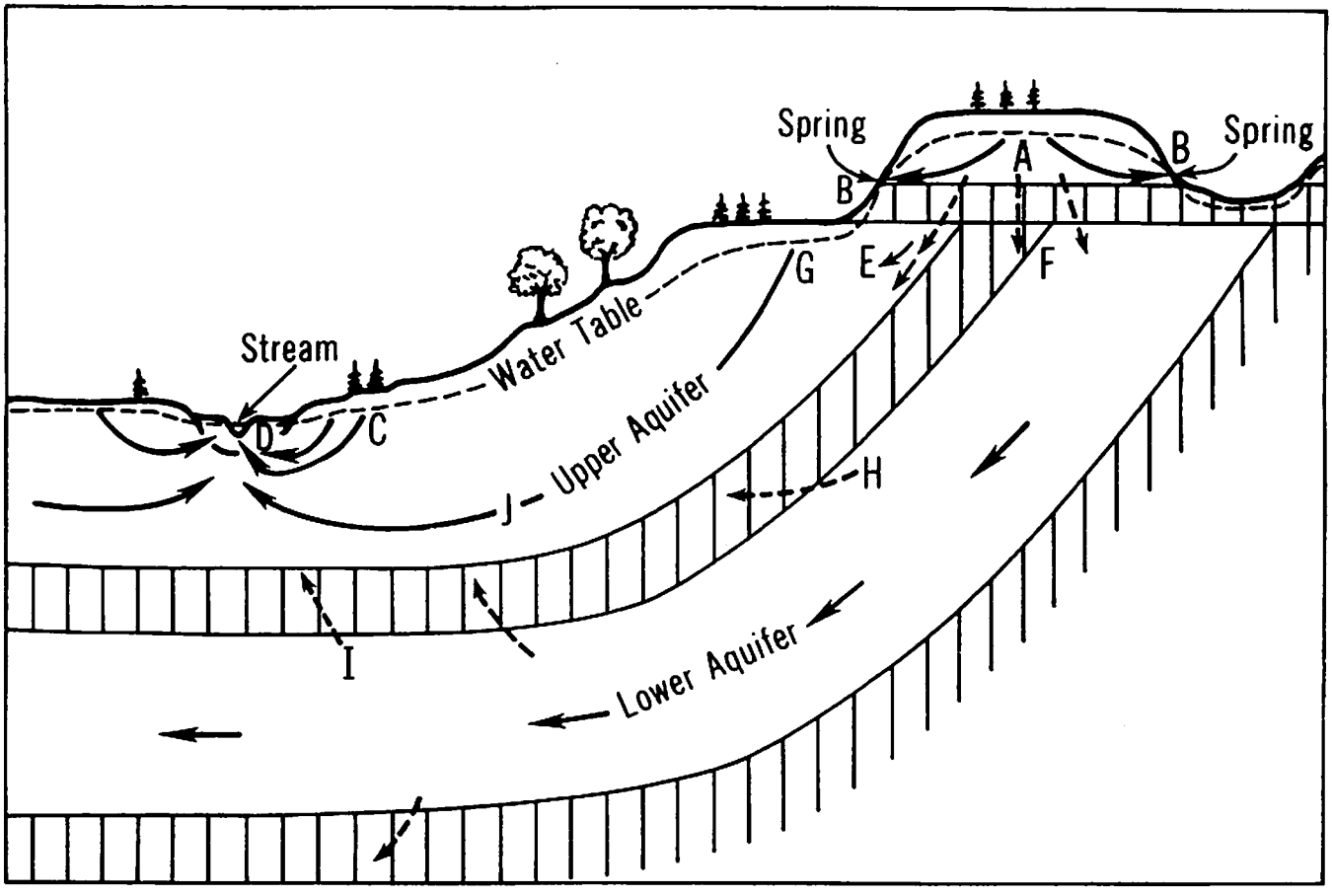
Given all the complexities discussed, it is not surprising that the ***residence time*** of groundwater is variable. In small, local, water-table flow systems, and in fractured aquifers (discussed later), the residence time may be only days or weeks. In many major regional aquifers, however, groundwater flow from recharge to discharge areas may be measured in hundred to even thousands of years (Perry et al., 1982; Desaulniers et al., 1982; Gilkeson and Cowart, 1982).

Unique Concerns for Groundwater Contamination

The potential for groundwater contamination by human activities is of concern in part because of its unknown element. Groundwater is "out-of-sight," and groundwater systems are complex. Thus, contamination often is not readily apparent, and its extent and importance are often uncertain. A second reason for concern is that by the time contamination is discovered, it already may have moved through an aquifer extensively enough that very little can be done about it. Expensive treatment may be required to make contaminated groundwater acceptable for some uses.

The contamination of groundwater by chemicals applied on the land surface has been of primary concern in situations corresponding to the upper aquifer in the accompanying figures. In most studies, the degradation of groundwater quality from agricultural chemicals has been noted only in upper aquifers. The depth of contamination varies, but it may be as great as 300 feet below the water table (Freeze and Cherry, 1979, pp. 442-444; Hallberg and Hoyer, 1982; Hallberg et al., 1983). In many areas, the poor quality of water supplied by shallow aquifers has necessitated drilling deeper wells. Where these are properly cased to prevent entry of the shallow water, they often supply water of satisfactory quality.

The shallow distribution of agriculture-related contaminants observed currently is to some extent a consequence of the slowness of movement and the relatively short time agricultural chemicals have been used exten-



Schematic cross section from the preceding figure, with lines and arrows showing the direction of groundwater flow discussed in the text.

sively. Deep aquifers may become contaminated eventually. Even now there are a few known examples. In California, wells as deep as 1000 feet have been affected by surface contaminants over the past several decades (Freeze and Cherry, 1979, pp. 443-444; Broadbent, 1971).

Of particular concern with agriculture is the fact that agricultural chemicals are applied to vast areas of land. Thus, if there is contamination, it may be regional in nature and impractical to treat. In contrast, waste-disposal sites or industrial plants may deliver much greater concentrations of contaminants into groundwater, but the areas involved are relatively small, so that the problems are more amenable to remedial action.

Special Considerations

There are many unique situations in the realm of groundwater. In relation to agriculture, the effects of two are worthy of note — "fractured" aquifers and irrigation.

Where large underground openings exist, as in large tubes in lava flows or caves in carbonate rocks, groundwater flow in these large openings is analogous to flow through a pipe. If such openings are at or near the land surface, water may enter the groundwater system rapidly, and the dissolved chemicals may travel long distances in a short time with little dilution.

Of particular interest are ***karst regions***, which have irregular topography with "sinkholes" on the surface and caverns or conduits underground resulting from dissolution of the underlying limestone or carbonate rocks. At the surface, sinkholes form closed depressions and collect surface drainage, sometimes swallowing entire stream systems (Thornbury, 1969). The sinkholes provide a direct conduit for unfiltered surface waters to run into underground cavities in the limestone (Hallberg and Hoyer, 1982; Hallberg et al., 1983). As a consequence, karst-carbonate aquifers are highly susceptible to contamination by surface runoff. Potential contaminants in this water include sediment from soil erosion, sediment-attached chemicals and other chemicals of high and low solubility, various organic materials, and microorganisms that normally would not be carried in drainage water (Hallberg et al., 1983). Karst-carbonate aquifers exist under extensive, important agricultural areas in the United States,

Carbonate rocks may dissolve over periods of geologic time, leading to underground cavities, such as the one on the left, or to sinkholes, such as the one on the right. Groundwater may move through these openings far faster than it moves through soil material. Photographs courtesy of George R. Hallberg, Iowa Geological Survey. The photograph on the left was taken by Timothy J. Kemmis of the Iowa Geological Survey.

including Minnesota, Iowa, Indiana, Kentucky, Texas, New Mexico, Florida, Puerto Rico, Pennsylvania, and New York (LeGrand and Stringfield, 1973).

Irrigation has two important impacts on groundwater in the dry western states. First, groundwater is being used for irrigation in widespread areas where the rate of recharge is very slow. As a result, the supply of groundwater is being depleted (Fischer, 1977; Hallberg, 1977). In a few areas, irrigation already has ceased because of the increased cost of pumping from the lowered water tables. Second, irrigation water adds to soils the salts in the water, and irrigation increases the amount of salts moved downward through soils to groundwater.

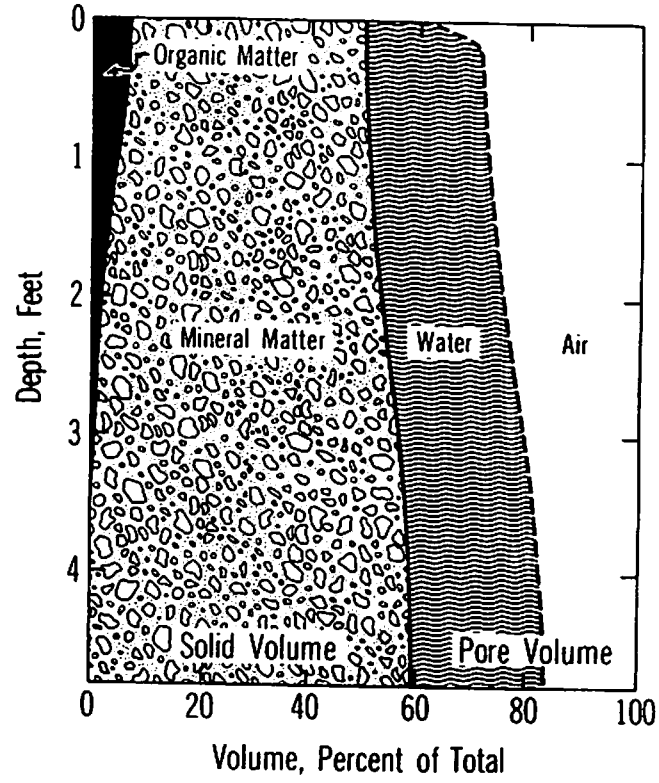
Transport Through the Unsaturated Zone

The unsaturated zone includes the soil at the surface and the underlying materials down to the water table. The soil is characterized by the presence of organic matter, the content of which typically decreases with depth. The proportion of the volume occupied by solids commonly is about 50% and tends to increase somewhat with depth in soils with medium and vertically uniform texture.

Conversely, the proportion of the soil volume occupied by pore space commonly is greatest near the surface and decreases somewhat with increasing depth. Except for tillage effects at the surface, the total volume of pore space remains about the same with time. The proportion of water tends to increase and the proportion of air to decrease as the water table is approached, but the proportions vary greatly with time in the upper few feet of soil, depending upon additions and losses of water. Sometimes the pores at the surface are essentially filled with water while those beneath contain considerable air. This variability is the reason for using a broken line to portray the boundary between air and water in the accompanying figure.

Agricultural chemicals applied to soil may potentially occur in the soil air or the soil water, on the surface of the soil solids, or as discrete undissolved particles.

Surface views of fresh sinkholes that opened in cornfields in northeastern Iowa between passes of a cornpicker. Sinkholes, which form in limestones and other soluble rocks, may "swallow" surface runoff water and the contaminants it may carry, allowing the water to enter directly into the groundwater system. Photographs courtesy of George R. Hallberg, Iowa Geological Survey. The upper photograph was taken by E. A. Bettis, III, and the lower by Greg Ludvigson.



Vertical distribution of the volumes of solids, water, and air in a hypothetical soil. The relative volumes of water and air vary greatly with time and depth.

Under normal circumstances, chemicals are transported to groundwater in solution and not as gases or as components of solid particles. Therefore, the remainder of this section will focus on the movement of dissolved chemicals between the land surface and the groundwater.

Transport Processes

Dissolved chemicals move through soil by two mechanisms: (1) movement of the water in which they are dissolved (known also as *mass flow*), and (2) *diffusion*, resulting from the random motion of the molecules and ions of the dissolved chemicals (Gardner, 1965). In practice, both mechanisms occur simultaneously, and movement of the water occurs at different rates through pores and channels of different sizes, so that the incoming water mixes to some extent with the existing water while displacement of the latter is occurring. The overall process is known as *hydrodynamic dispersion* (Bear, 1971; Biggar and Nielsen, 1976). Only movement of water containing dissolved chemicals is effective in transport over distances such as those implied in the accompanying figures.

Effect of Adsorption on Transport

Certain chemicals in the soil water are attracted to the surfaces of clay minerals, organic matter, or both. These attractive interactions, which remove chemicals from solution and attach them to solid surfaces, are called *adsorption*. Adsorption decreases the rate of transport of chemicals because it reduces the amount in solution (van Genuchten and Wierenga, 1976).

Positively charged ions (*cations*), such as calcium, magnesium, potassium, ammonium, and sodium, are adsorbed by both clay minerals and organic matter. Clay and organic matter have the capacity to hold positively charged ions in forms that will exchange with other positively charged ions. Because of the chemical equivalence of the exchange, the positively charged ions added to soil may be adsorbed by the soil in exchangeable form, but other positively charged ions will emerge in the drainage water in chemically equivalent amounts.

Among the negatively charged ions (*anions*), nitrate and chloride are not adsorbed appreciably. The sulfate anion is adsorbed readily by clay particles in acid soils.

The phosphate anion is either adsorbed or precipitated from solution under nearly all conditions, and thus does not move freely (Ryden and Pratt, 1980).

Neutral nonionic organic compounds, such as many pesticides, are adsorbed primarily by soil organic matter (Green, 1974; Weed and Weber, 1974). As a consequence, the transport of many pesticides to groundwater is restricted in soils having a high content of organic matter.

Effect of Water Movement

Since transport by moving water is the principal mechanism by which dissolved chemicals are moved through the distances required to reach the groundwater, the amount of water movement through the unsaturated zone to the groundwater is an important determinant of the extent of groundwater contamination by the agricultural chemicals applied. Under otherwise equal conditions, the amount of downward movement increases with the amount of water applied by precipitation or irrigation.

The distance dissolved chemicals can be transported by a given amount of water moving downward depends in part upon the capacity of the soil to hold water. For example, application of 1 inch of water at the surface may result in 5 to 10 inches of downward transport in a sand with a low capacity to retain water, but by only 2 to 3 inches in a clay with a much higher capacity to retain water.

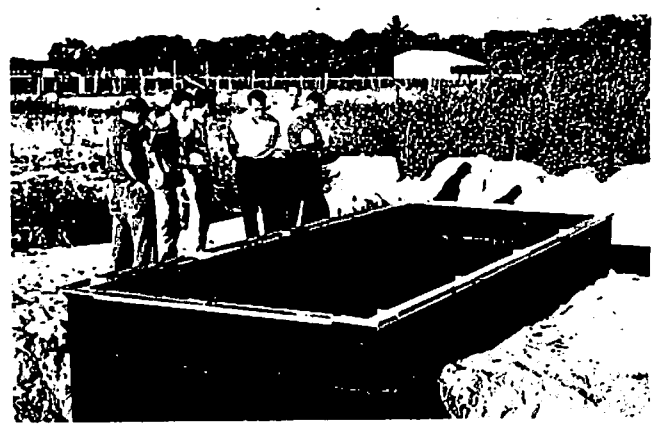
Preferential flow paths, such as cracks, old root channels, animal burrows, and, on a grand scale, the large channels in limestone in karst areas, may promote rapid downward transport (Thomas and Phillips, 1979; Beven and Germann, 1982; Hallberg and Hoyer, 1982; Hallberg et al., 1983). Preferential flow paths permit rapid and deep movement of a small part of the total amount of dissolved chemicals (Kissel et al., 1973).

Degradation of Chemicals in Soil

Dissolved organic chemicals, including pesticides, are broken down at different rates, and the breakdown reduces the downward transport of the original substances through the unsaturated zone to the groundwater. An index sometimes used to represent the rate at which this breakdown takes place is the time for 50% of the added chemical to decompose. Chemicals that decompose to the extent of 50% within a few weeks or less usually disappear before reaching groundwater.

Measuring the Downward Movement of Chemicals

The downward movement of a chemical in the field generally is measured by applying a known amount of the chemical at the surface and then measuring at one or more later times the increase in the amount of the chemical found at different depths in all or part of the unsaturated zone. Alternatively, the downward movement may be represented more simply by the increase in the amount of the chemical below some arbitrary depth, such as the root zone. Because of the variability from one site to another, measurements at many locations are needed to obtain a good estimate of the downward movement in an area such as a field (Biggar and Nielsen, 1976; Van de Pol et al., 1977; Jury et al., 1982).



The lysimeter is a standard device for studying the loss of soluble substances from soils. Lysimeters are of various sizes, shapes, and depths, but all permit the collection and analysis of the drainage water. Pictured here is the installation of a large lysimeter at the Hancock Experiment Station in Wisconsin. At this location, two lysimeters are placed side by side, and the drainage is collected in containers in an adjacent cellar that can be entered. Photograph courtesy of Dennis R. Keeney, University of Wisconsin.

In humid climates, water tables generally are close to the land surface, and freely moving dissolved chemicals, such as nitrate salts, may move from the point of application to groundwater in a year or less (Saffigna and Keeney, 1977). Conversely, in arid climates, groundwater tables are frequently tens or even hundreds of feet below the surface, and the residence time of agricultural chemicals in the unsaturated zone can be very long. Pratt et al. (1972) took deep soil cores below a number of commercial citrus groves and concluded that from 19 to 49 years were required for nitrate to move from the surface to the 100-foot depth. These extremely long travel times are probably typical for irrigated fields in low rainfall areas when irrigation management provides water applications that are sufficient for plant and evaporation demands, but when little water passes through the root zone.

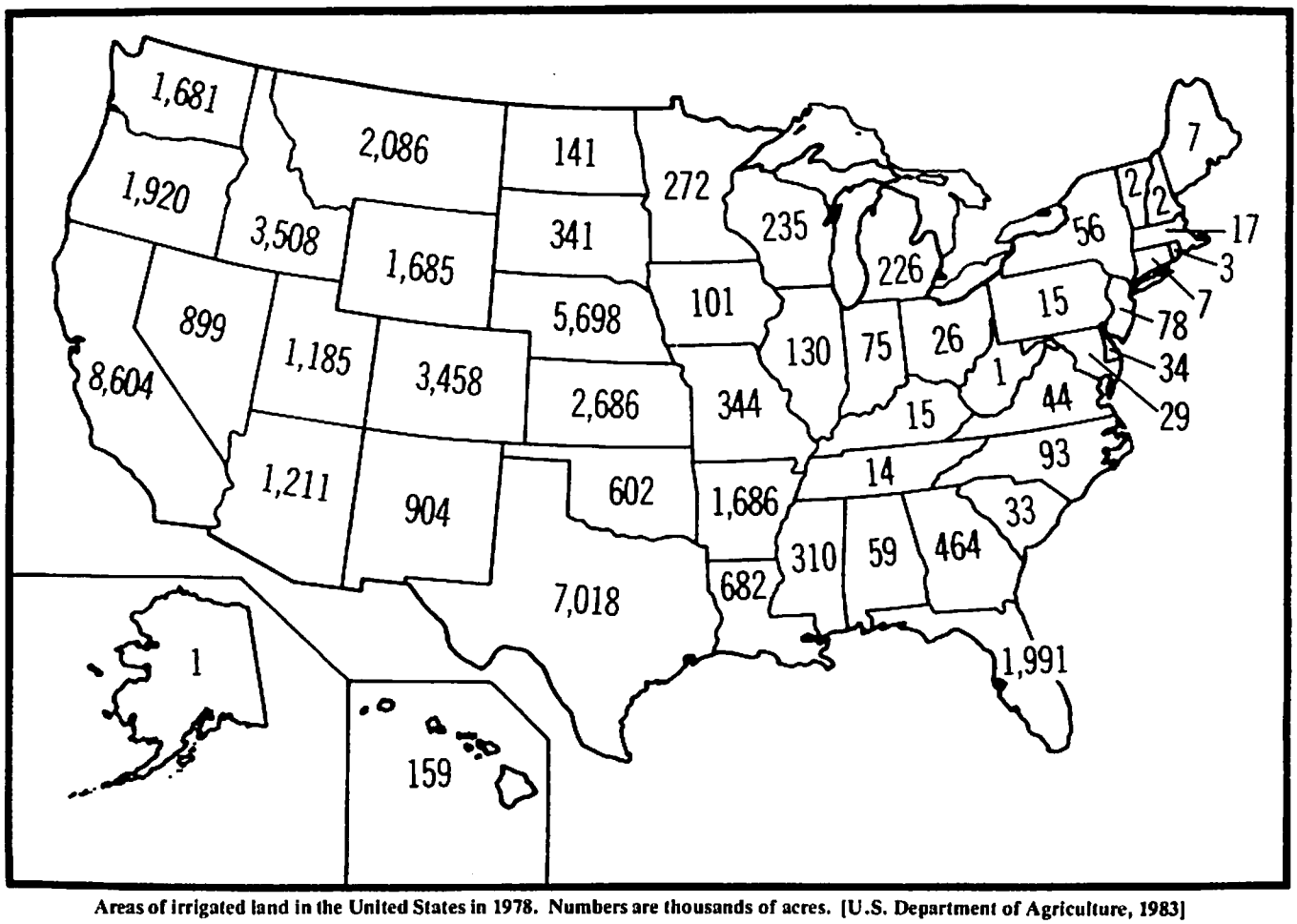
Salinity

Salinity refers to the concentrations of the calcium, magnesium, sodium, and potassium salts of chloride, sulfate, nitrate, and bicarbonate. These are the major salts in surface waters and groundwaters. Trace amounts of other inorganic ions and of dissolved organic compounds are usually not considered. The main sources of salinity are soil weathering, inorganic fertilizers, organic amendments, and the cycling of nutrients through plant roots, stems, and leaves (crop residues).

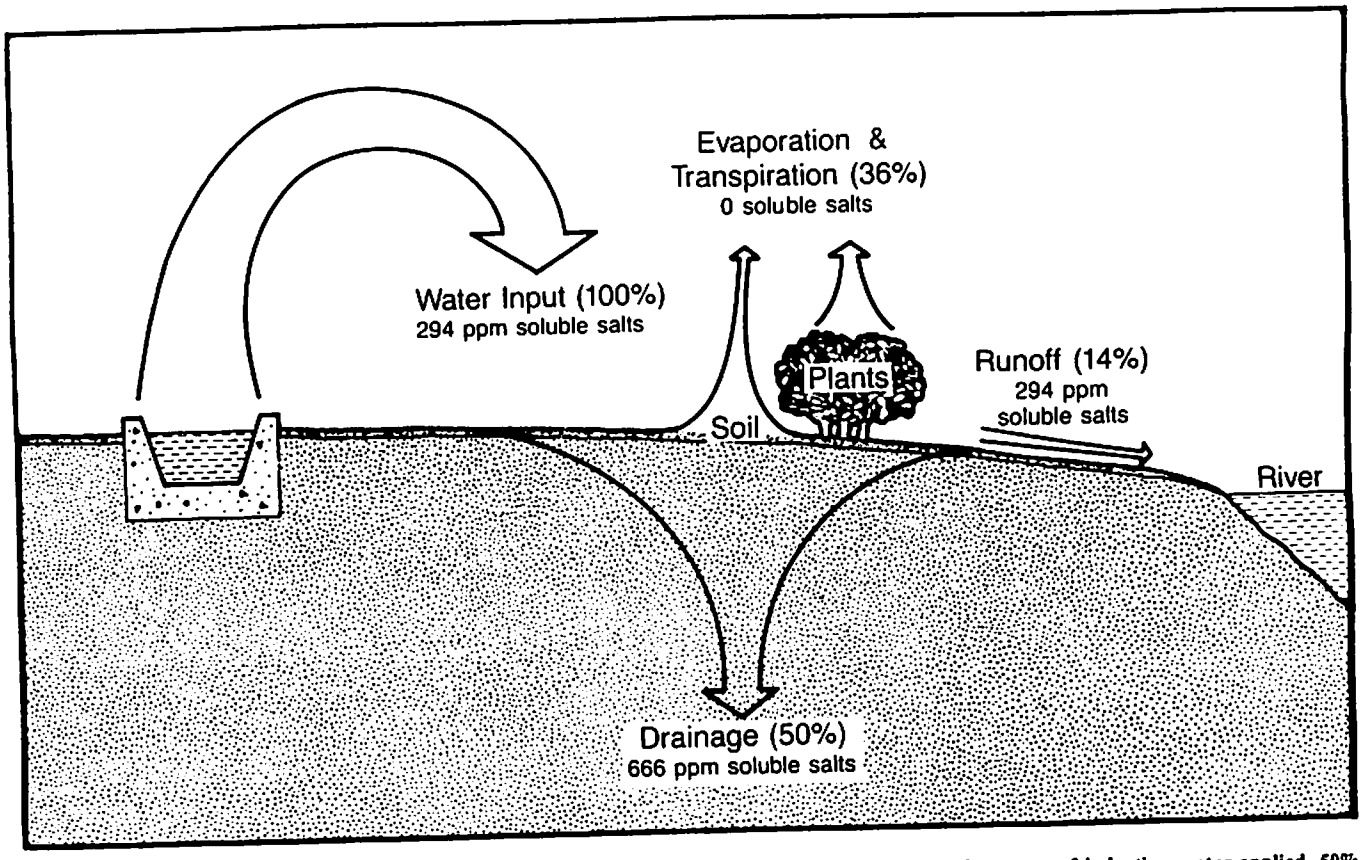
Water moving through soils always contains dissolved salts. In humid regions, however, the salt concentrations usually are low, and the contribution of agriculture to the salinity of water leaving the root zone and entering the groundwater is small. The major salinity problem is encountered in irrigated lands, where the predominant source of salts is the irrigation water.

Irrigation is used to provide water for crop production on lands that otherwise would produce no crops, small yields of desired crops, or crops of relatively low value. The plants take up some of the salts from the soil and the irrigation water, but the water that evaporates from their surfaces contains no salts. The salts remain behind in the soil and the plants. Therefore, crop irrigation is a salt-concentrating process. If water is not added in sufficient quantities to move through the soil and leach the accumulated salt out of the root zone, the increasing salinity will reduce root growth and crop yields. These downward-moving waters have higher concentrations of salts than the irrigation waters used, and they contribute to the total salinity of groundwater. Thus, soil salinity is an agricultural problem. The solution is to leach the salts below the root zone, moving them to subsurface drainage systems or groundwater. Low volumes of percolating water favor the precipitation of some of the less soluble salts (calcium and magnesium carbonates and calcium sulfate) within the soil, but there is no known technology for preventing the more soluble salts from eventually moving into subsurface drains or groundwater.

Salinity in groundwater is of concern when groundwater is used for irrigation or for drinking by people and farm animals. The occurrence of boron in groundwater may be a problem for crop production. This element is toxic to some plants at concentrations as low



Areas of irrigated land in the United States in 1978. Numbers are thousands of acres. [U.S. Department of Agriculture, 1983]



Disposition of water and soluble salts in 203,000 acres of irrigated land in southern Idaho. Of the total amount of irrigation water applied, 50% appeared as groundwater, 36% was lost by evaporation and transpiration, and 14% was lost as runoff. Because the water lost by evaporation and transpiration carried no salts with it and because there was little rainfall, the water lost by drainage had a higher salt concentration than the irrigation water added. Additional salts in the drainage water were derived from fertilizers and the soils. [Carter et al., 1971; Carter, 1972]

as 0.5 part per million (ppm) in the soil water. Boron, however, does not represent a problem in drinking water for animals or humans.

In some instances, salinity results from geological deposits or from seawater intrusion into aquifers as a result of heavy pumping of fresh water supplies from coastal aquifers. These conditions are important in some local areas, but they are not discussed in detail here. Emphasis here is upon the major problem, which is salinity resulting from irrigation.

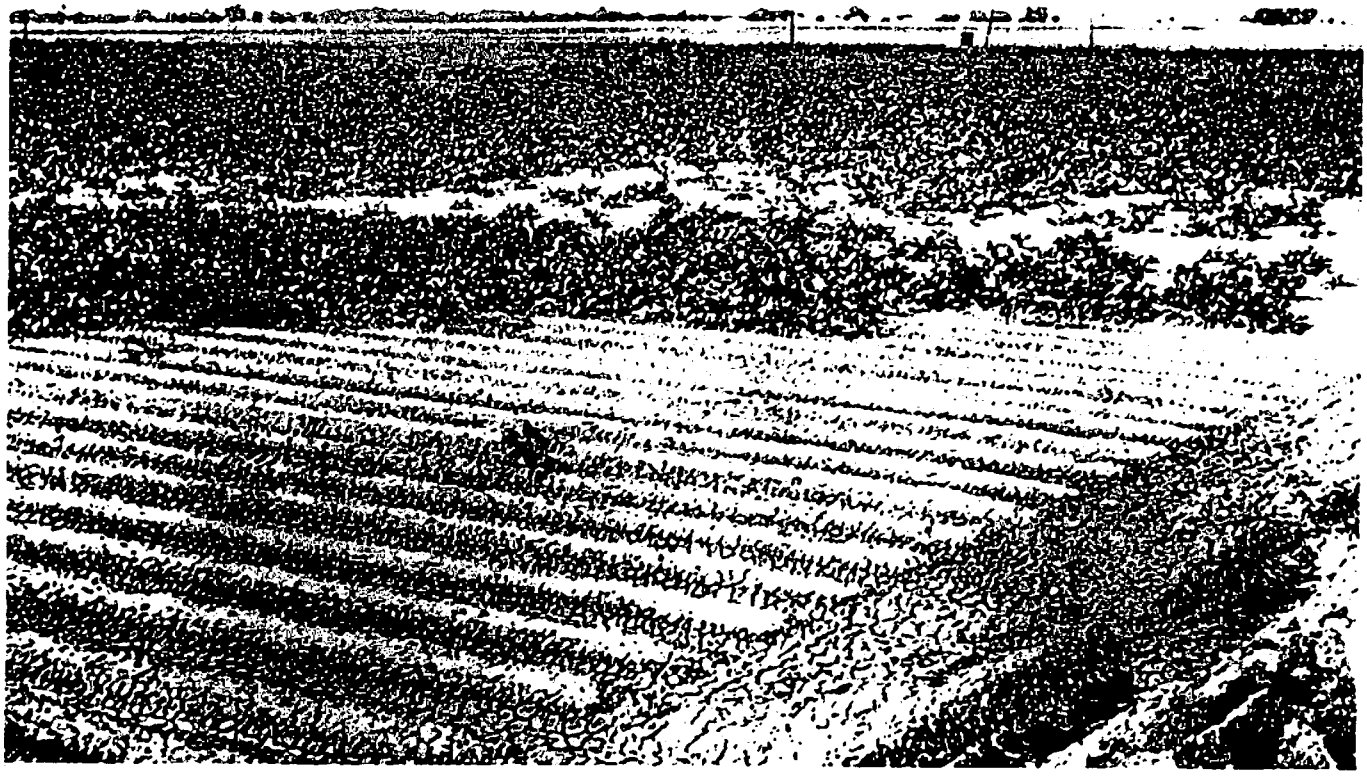
Extent of Irrigated Agriculture

Irrigation is practiced throughout the United States, but some states have only a few hundred acres. Most of the irrigated land is found in the arid, semiarid, and subhumid regions of the western United States. The total amount of irrigated land in the United States has steadily increased over the past few decades. The U.S. Bureau of the Census (1982) listed 29.6 million acres of irrigated land for 1954 and 50.8 million for 1978. The major reason for this increase in irrigated land is profitability. The same census reported that the market value of products sold from farms in 1978 was $108.1 billion. Of this amount, products from irrigated farms accounted for $31.2 billion or 28.9% of the total. This production from irrigated farms came from only 12.2% of the total farms and 13.1% of the total cropland. One factor in the high value of products from irrigated land is that large proportions of the fruits and vegetables marketed in the United States are grown under irrigation (Tucker and Hauck, 1978).

Salinity of Irrigation and Drainage Water

The salinity in irrigation water expressed in total dissolved solids ranges from a few tens of ppm in the case of runoff from mountain snows to several thousand ppm in some highly salinized rivers, groundwaters, and waste waters. The salinity of eight river waters that have salt contents typical of river waters in the western United States may be estimated from the work of Rhoades et al. (1973) to range from approximately 64 to 2000 ppm. The salt content of most groundwater shows a similar range.

The main factors that control the salt concentrations in water that drains from irrigated lands are (1) the salt concentration of the irrigation water, (2) the *leaching fraction* (LF, defined as the fraction of the irrigation water entering the soil that appears as drainage water), and (3) the loss of salts from the water to the soil or the gain from the soil. Small LF values can be obtained by



A "salted out" field of irrigated sugarbeets in California. The salts appear as the white caps on the ridges, left there when the irrigation water evaporated. Irrigation waters contain dissolved salts, and these remain behind when the water evaporates from the soil and from plant surfaces. To prevent the development of the condition found in this field, it is necessary to apply enough water to carry excess salts below the root zone. Sooner or later, this salty water becomes a part of the groundwater. This photograph by W. E. Wildman appeared in the October 1984 issue of *California Agriculture* and was supplied by Richard V. Venne, University of California, Berkeley.

careful irrigation to apply water uniformly and efficiently. Most successful irrigation projects have LFs of 0.25 to 0.50 or higher because there are practical limitations to reducing LFs, such as variations in rate of water intake by soils, variations in plant response caused by soil heterogeneity, and the high costs of applying water uniformly. In general, the salt concentration of the water leaching below the root zone is approximately two to four times greater than that of the irrigation water. If the LF is greater than 0.5, the salt concentration in the drainage water will be less than twice that of the irrigation water. In less arid regions and in humid regions where supplemental irrigation is practiced, rainfall can produce high LFs, and the salt concentration in the drainage water can be much less than twice that of the irrigation water used.

Data published by Carter et al. (1971) and Carter (1972) illustrate the practical situation in an area of 203,000 acres of irrigated land in southern Idaho. Fifty percent of the water applied in irrigation and precipitation appeared as subsurface flow (groundwater), 14% appeared as surface return flow, and the remaining 36% presumably was lost by evaporation from the soil and the plants. In this instance, the average ratio of salt concentration in the effluent water to that in the added water was 2.26.

In an experiment in a citrus orchard in southwestern Arizona (Hoffman et al., 1984), a drip-irrigation system gave an LF value of 0.2, and a flooding system gave an LF of 0.47. The drip-irrigation system used less water than the flood-irrigation system, and it added less total salt to the drainage water, but it added this salt in a relatively concentrated solution.

The dilemma of keeping excess salts out of waters that move downward beyond the root zone of crop plants or continuing to flush them out of the root zone to maintain a reasonably salt-free growth medium cannot be resolved by any known technology (Haise and Viets, 1972). The severity of effects of irrigation on the salinity of groundwater ranges from no deleterious effects to severe degradation, depending upon many local conditions, such as the initial salinity of the groundwater, the salinity of the irrigation water, the LF, the amount of water used, and the rainfall.

The addition of salt to groundwater from irrigated lands can be reduced by careful water management to reduce the LF and precipitate more of the salts in the soil and/or reduce the dissolution of salts from the soil. The principal practical limitation of this approach is the cost of installing, maintaining, and operating the irrigation system required (Jensen, 1977).

Salinity of groundwater has no direct effect on the crops grown on the land above it as long as the groundwater remains in place, but it can have an important

Salt that has accumulated from irrigation waters in the Imperial Valley of California is flushed out of the soil as needed by ponding an excess of water on the surface. The water is held on the fields by dikes. This photograph by C. A. Beasley appeared in the October 1984 issue of *California Agriculture* and was supplied by Richard V. Venne, University of California, Berkeley.

effect if it is pumped for use in irrigation. And the portion of the groundwater that reappears in streams as surface water may have an effect on crop production downstream if it is used again for irrigation.

Health Effects in Drinking Water

Excessive salinity in drinking water is undesirable because of objectionable tastes and the laxative effect associated with sulfate. The U.S. Environmental Protection Agency (1976) recommended that concentrations of chloride or sulfate should not exceed 250 ppm in domestic water supplies.

The National Academy of Sciences (1974) suggested that water having a total salinity of 3,000 ppm or less should be satisfactory for livestock. Waters having total salinity of 3,000 to 5,000 ppm were said to be satisfactory for livestock but not for poultry, especially turkeys. Dyer et al. (1974) noted that for livestock it is important to distinguish between the value of 3,000 ppm set on a physiological basis by the National Academy of Sciences and a higher value that corresponds to a practical or economic limit. They stated that livestock tolerate drinking water with total salinity at least as great as 10,000 ppm, generally with no more apparent effects than mild diarrhea. They pointed out that if the maximum permissible limit were to be set below 10,000 ppm, some areas where livestock are now raised would be closed to this enterprise.

Fertilizers

Historically, agricultural productivity depended almost entirely upon nutrients from soils and from wastes and crop residues. This system resulted in impoverished soils of low productivity and in human migrations to more fertile areas. As a result of the development of modern scientific concepts of plant nutrition and soil science, starting in the nineteenth century, modern agriculture depends upon chemical fertilizers to supplement the natural supplies of nutrients.

Farm output in the United States more than doubled from 1935 to 1974 (Barlowe and Barrows, 1980).

According to a review by the International Fertilizer Development Center (1979), increased fertilizer use was credited by various authors with 25 to 55% of the increases in production of one or more crops during various intervals partly or wholly within the 1935 to 1974 period. Other factors that have contributed to increased agricultural output include greatly improved crop varieties, pesticides, irrigation, and overall improved management.

The relatively high yields of today's crops remove more phosphorus, potassium, and particularly nitrogen than can be supplied by many soils without fertilizers. Some soils require additions of sulfur and other nutrients needed by plants in smaller quantities to maintain the crop yields. The quantities of major plant nutrients found in various crops, widely used fertilizer materials, fertilizer use in the United States, use of fertilizer nutrients in different U.S. regions, and quantities of nutrients applied to major crops are shown in Appendix D, Tables 1 through 5, respectively.

Movement of Fertilizer Constituents to Groundwater

Fertilizers supplement the natural supplies of the inorganic salt constituents in soils that are required for plant growth. In most instances, the chemical forms added in fertilizers are the same as those naturally present in soils and absorbed by plants, but in some instances the forms added are transformed after addition to the forms naturally present in soils.

Plants absorb only part of each of the nutrients present in soluble forms in soils. As the concentration of the nutrients in the soil water increases, generally leading to greater total nutrient absorption and greater crop yields, the percentage of the total amount absorbed by the plants decreases. Thus, when fertilizers are added to supplement the supplies of particular nutrients that are deficient in soils, one result is greater residues of the nutrients in the soils. Part of the excess may be lost to the groundwater if it remains in solution.

Most of the chemical ions added in fertilizers are retained to some degree by soils as a result of chemical interactions, and this reduces their potential for loss to groundwater. Phosphorus is an extreme example. Two ions, however, nitrate and chloride, undergo virtually no chemical attachments to soils and are highly mobile in water. The contribution of nitrogen fertilizers to nitrate in groundwater is of concern for possible specific health effects to be discussed in the next section, but not on account of the increase in the salt content of the water. Fertilizers are not regarded as making an important contribution to the salinity of groundwater. For example, 200 to 1,000 pounds of fertilizer might be added per acre in a year, but 2 feet of irrigation water containing salts at a concentration of 1,000 ppm (a typical addition) would add 5,400 pounds of salts per acre.

Nitrogen

General Behavior

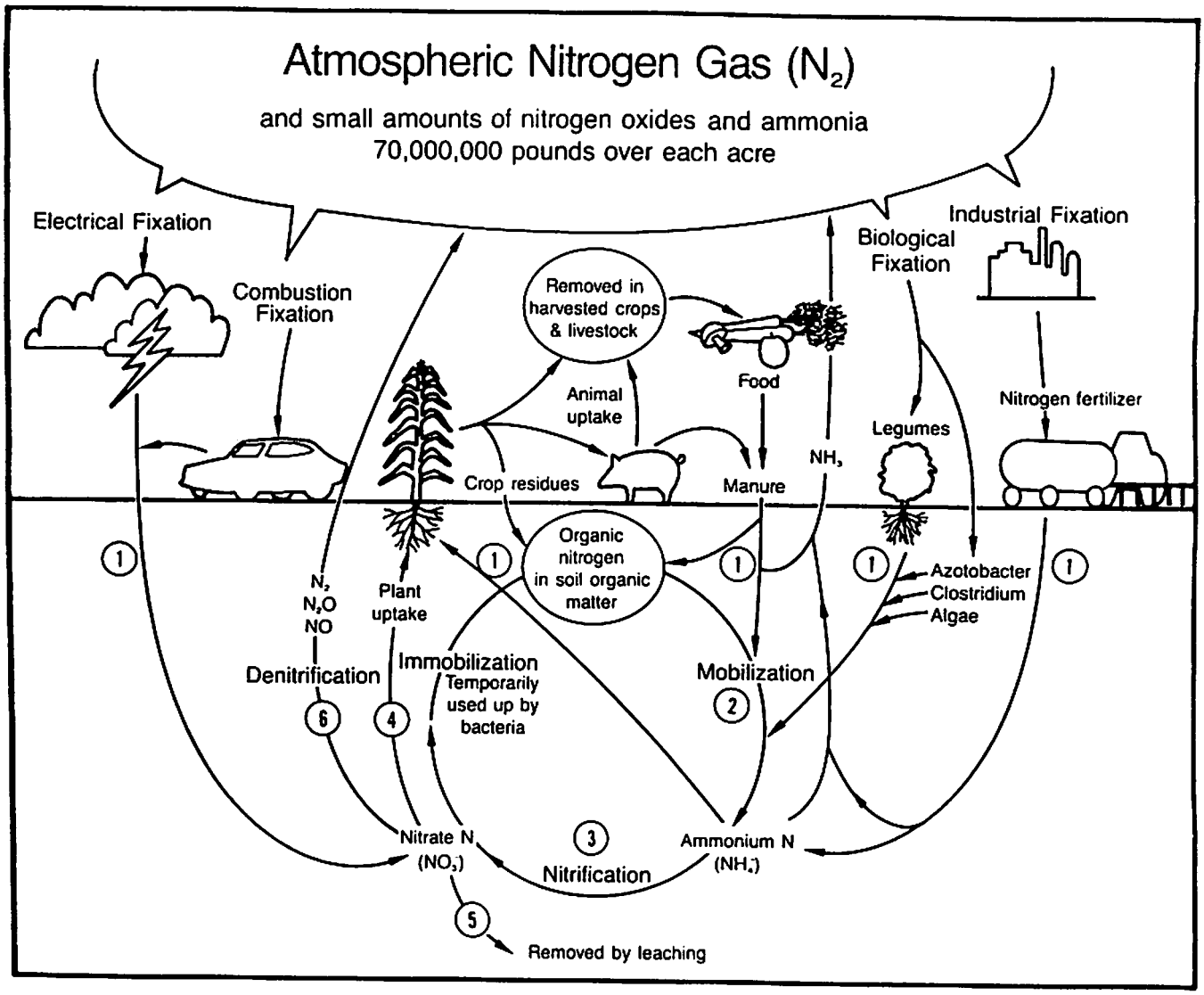
The nitrogen crops derive from soils is taken almost exclusively from inorganic forms. For nonleguminous crops, these are principally nitrate and ammonium. Legumes take up the same forms, but in addition the bacteria in the root nodules on these crops can utilize gaseous nitrogen from the soil air.

Most crops remove more nitrogen than any other fertilizer element (Appendix D, Table 1), and the total amount of nitrogen applied in fertilizers far exceeds the amounts of other nutrients. But the amounts used and their possible effect in increasing the salt content of the groundwater are not the reason for concern about nitrogen. Rather, the principal reason for concern is the potential impact of nitrate on human health when groundwater high in nitrate is used for drinking by human infants.

The behavior of nitrogen in the environment is complex. It occurs in great quantities in the atmosphere. It occurs in plants, animals, and humans. It occurs in soils, surface waters, groundwaters, and minerals. There are many chemical forms of nitrogen — some inorganic and some organic, some gaseous and others not, some soluble and others not. Nitrogen is cycled among these forms and sites by many reactions and processes.

Usually, most of the nitrogen in soils and organic residues is present in organic forms that are mostly insoluble and unavailable to plants. Transformation of the organic nitrogen to inorganic forms, including nitrate, is accomplished by microorganisms. The transformation is a long-term process. Much of the nitrogen of crop residues may be released in inorganic forms in the first year or two, but many years are required to release the balance. Net release of inorganic forms of nitrogen from the organic forms in soil organic matter may take place at a rate of only 1 or 2% per year in temperate regions.

The large populations of microorganisms that develop on the decomposing organic materials require nitrogen as an essential component of their tissues. They tie up ammonium and nitrate as organic nitrogen if the nitrogen content of the decomposing organic material is low. They release nitrogen in inorganic forms only when the nitrogen available to the population of microorganisms exceeds the need, as where the original material contains an excess of nitrogen or where enough of the readily decomposable organic matter has been decomposed to produce an excess of nitrogen. After this stage is reached, net release continues as decomposition proceeds. Delayed release occurs most often with certain low-nitrogen plant residues, such as straws. With manures and sewage sludges, the nitrogen content is generally high enough and the decomposition is sufficiently advanced that continued decomposition



The nitrogen cycle (modified from Aldrich, 1980). In step 1, nitrogen in plant and animal residues and nitrogen derived from the atmosphere through electrical, combustion, biological, and industrial fixation processes (processes by which molecular nitrogen, N_2, is combined with hydrogen or oxygen) is added to the soil. In step 2, nitrogen in the residues is mobilized as ammonium, NH_4^+, by soil organisms as an end-product of residue decomposition. Plant roots adsorb a portion of the ammonium. In step 3, much of the ammonium is converted to nitrate, NO_3^-, by nitrifying bacteria in a process called nitrification. In step 4, nitrate is taken up by plant roots and (along with the ammonium absorbed) is used to produce the protein in crops that are eaten by humans or fed to livestock. In step 5, some nitrate is lost to groundwater or drainage systems as a result of downward movement through the soil in percolating water. In step 6, some nitrate is converted by denitrifying bacteria into molecular nitrogen and nitrogen oxides (N_2O and NO) that escape into the atmosphere, completing the cycle.

brings only net release of nitrogen in inorganic forms.

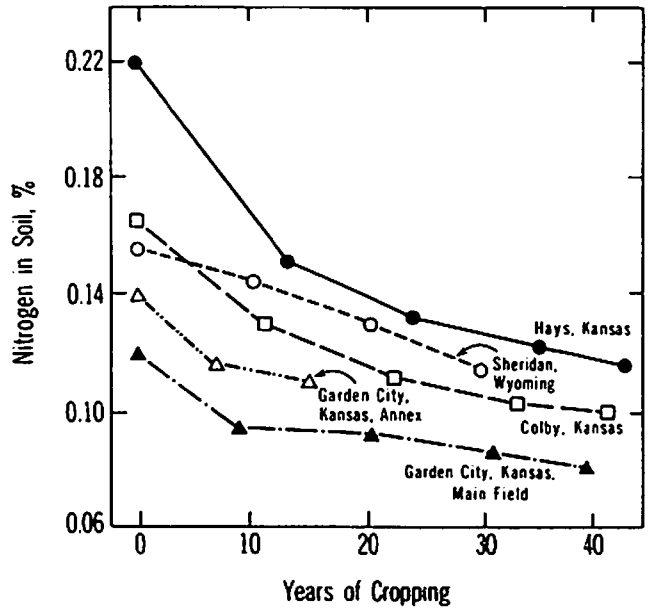
The first inorganic form of nitrogen released from organic materials by microorganisms is ammonium (NH_4^+). Nitrate (NO_3^-) is produced from ammonium in a separate microbiological process. Ammonium is produced in either the presence or absence of free oxygen from the atmosphere, but nitrate production requires oxygen. When nitrate is present but free oxygen disappears, some microorganisms are capable of using the oxygen from nitrate as a substitute for atmospheric oxygen to carry on their own metabolism. The nitrogen of the nitrate then is lost as gaseous forms, including nitrogen gas (N_2) and nitrous oxide (N_2O). Ammonium is not lost in this way, but it may be volatilized as ammonia (NH_3) gas if the pH of the decomposing material is high and the material is not covered by soil (Hoff et al., 1981; Loehr et al., 1983).

The cycling of nitrogen and the accompanying loss of nitrate to groundwater were occurring long before agriculture began, as indicated by the occurrence of low concentrations of nitrate in very old groundwaters and by the occurrence of fossil deposits of nitrate. High concentrations of nitrate have been found deep in the deposits of wind-blown soil materials in southwestern and central Nebraska (Boyce et al., 1976) and in the water-laid deposits beneath the soils of the west side of

the San Joaquin Valley in California (Strathouse et al., 1980). Although this nitrate is not a result of human activity, it could enrich the groundwater when these areas are irrigated. For example, Boyce et al. (1976) found that most of the fossil nitrate had disappeared beneath older irrigation sites.

When currently cultivated soils were first tilled, the organic matter started to decompose more rapidly, the nitrogen in the decomposed portion was released, and most of it was transformed to nitrate, which is the principal source of nitrogen for nonleguminous crops. Directly or indirectly, decomposition of native soil organic matter was no doubt the major source of nitrate moved to groundwaters in the early days of agriculture before the advent of commercial nitrogen fertilizers. In some areas with low rainfall and deep water tables, the nitrate derived from the initial rapid decomposition of the organic matter is still in transit to the water table.

Initially, many soils supplied more nitrogen in the form of nitrate than was needed by crops, but as time went on, the supply from the soil diminished, and it was necessary to supplement the soil supply with nitrogen fixed from the atmosphere by leguminous crops. Even-



Decline in nitrogen content of soil at different locations in the Great Plains with years of cropping (Haas et al., 1957).

A storage tank holding anhydrous ammonia for use as fertilizer. Anhydrous ammonia is the most economical of the commercial nitrogen fertilizers, and large amounts of it are used. The potential for contaminating groundwater with nitrate, an end-product of microbiological transformation of ammonia and other nitrogen compounds in soils, is greater with nitrogen fertilizers than with animal or human wastes because greater quantities of nitrogen are applied in fertilizers. Photograph courtesy of Dennis R. Keeney, University of Wisconsin.

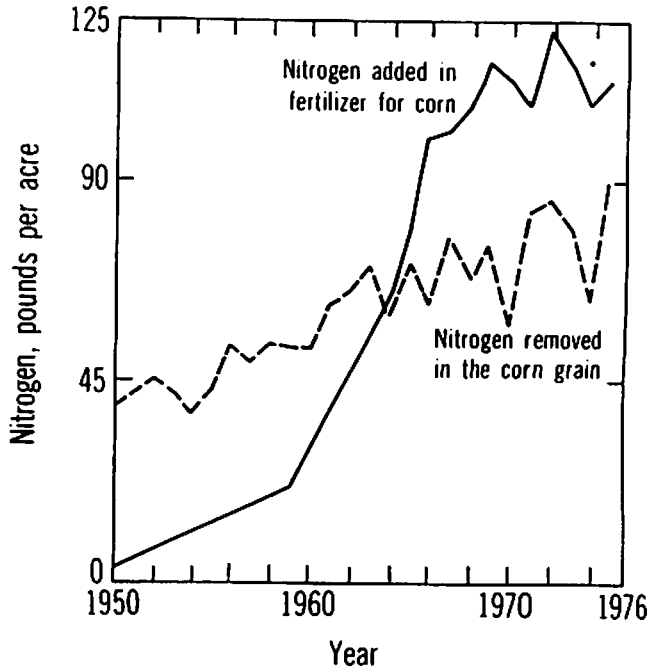
tually, much of the nitrogen from leguminous crops was displaced by fertilizer nitrogen (most of which is produced by combining nitrogen from the atmosphere with hydrogen to produce ammonia—NH_3) for economic reasons. The potential for loss of nitrate to groundwater then was increased when relatively large amounts of nitrogen fertilizers were added.

Nitrogen Relations in the Corn Belt

Concern about the contribution of nitrogen fertilizers to the nitrate content of streams was sparked by Commoner (1970) and the ensuing media coverage. His most important evidence was an increase in nitrate content in the Kaskaskia River in Illinois between 1945-1950 and 1956-1968, a time when the usage of nitrogen fertilizer was increasing rapidly. Although this specific evidence was criticized (see Aldrich, 1980), there is no doubt that nitrogen fertilizers do contribute to nitrate in groundwater. The question has been (and remains) how much. Possible sources of nitrate in surface and ground waters include nitrogen fertilizers, soil organic nitrogen, sewage, animal manures, and precipitation. Some of the nitrate that appears in the waters may have been derived originally from fertilizers but cycled one or more times through crops and livestock before being lost as nitrate.

The five major corn-producing states (Iowa, Illinois, Indiana, Minnesota, and Ohio) have 57% of the total U.S. harvested corn area and use 26% of the fertilizer nitrogen (Hargett and Berry, 1983). Average applications of fertilizer nitrogen for corn in the Corn Belt have increased from about 65 pounds per acre in 1965 to 137 pounds per acre currently. Since about 1965, more fertilizer nitrogen has been added for corn production in Illinois than has been removed in the corn grain.

Fertilizer nitrogen not removed by crops is stored in the soil in organic or inorganic forms or lost from the soil by drainage, by runoff of surface waters or by reactions that result in loss of nitrogen back to the atmosphere. An accompanying figure summarizes results of four experiments in Cornbelt states in which measurements were made of losses of nitrate in the water draining from tile lines located several feet below the surface of the soil. Losses occurred in all experiments, all of which were continued for 3 years or longer. Concentrations of nitrate-nitrogen in the tile drainage water ranged from a minimum approximating the public health standard of 10 ppm to a maximum of 81 ppm. The maximum concentration was reported in the third and final year of the experiment in Minnesota for the treatment with 400 pounds of fertilizer nitrogen per acre annually. This application is about three times the average for commercial fields.

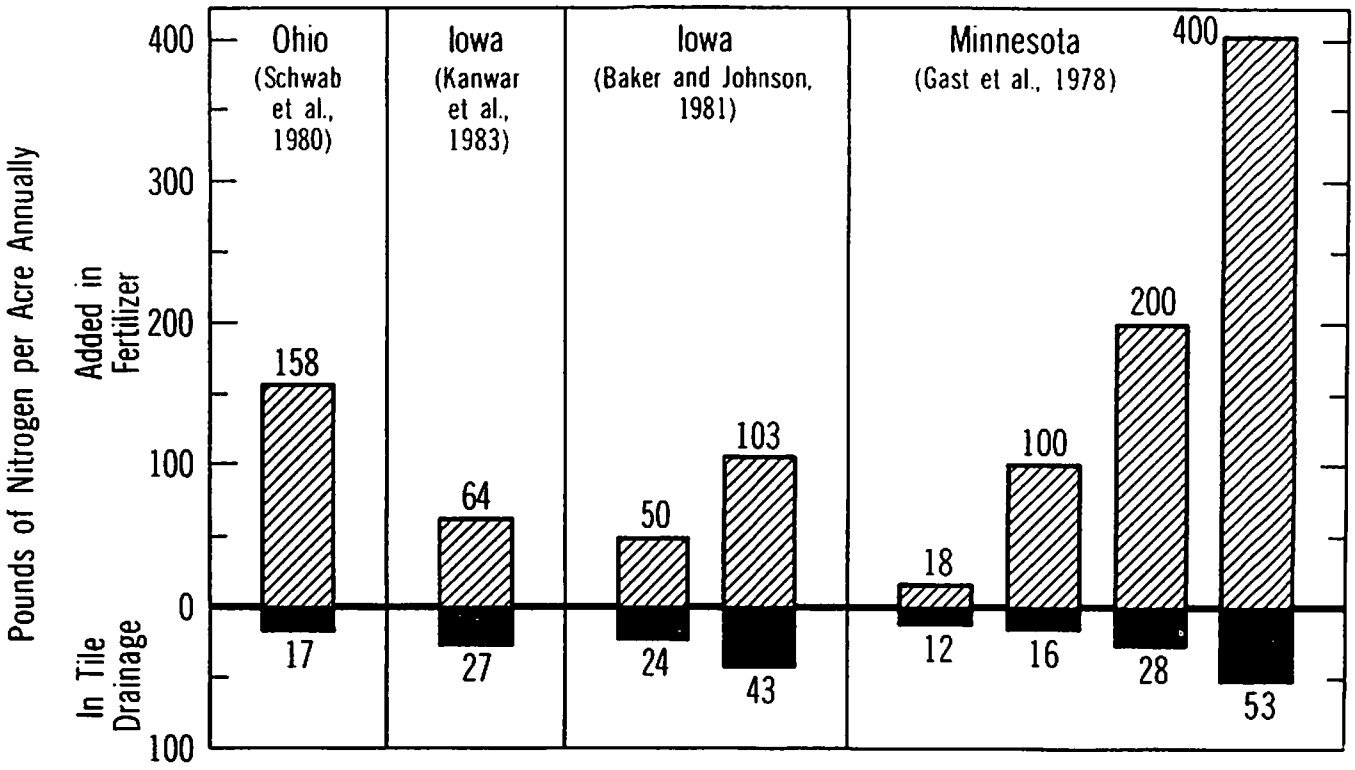


Average annual additions of fertilizer nitrogen for corn production in Illinois, and removal of nitrogen in the corn grain. (National Research Council, 1978; reproduced with permission of the National Academy of Sciences, Washington, D.C.).

Nitrogen Relations in the East and Southeast

There is less documentation of groundwater contamination by nitrate in the eastern United States than in the Corn Belt. High leaching rates, especially in summer, would be expected in the Northeast because of relatively high rainfall and low evapotranspiration (Thomas, 1970). High-nitrate groundwaters exist in Long Island, New York, likely resulting from home sewage disposal systems and excessive use of nitrogen fertilizer (Meisinger, 1976; Aldrich, 1980). In this area, where the rainfall is high, the soils are sandy, and the water tables are close to the surface, nitrate concentrations in the upper groundwater decrease within 1 year after the quantities of nitrogen fertilizer are decreased. Johnson et al. (1976) monitored nitrate in streamflow from a large rural watershed in central New York and concluded that nitrate levels in drinking water would remain low even if agricultural land use expanded.

In the Southeast, most of the drainage from soils takes place during the winter. High evapotranspiration during the summer months limits the drainage from the soils (Thomas, 1970). In the North Carolina Coastal Plain, nitrate accumulates in the shallow groundwater in response to agricultural activities, but because of underlying zones lacking free oxygen (Gilliam et al., 1974; Daniels et al., 1975), the nitrate is transformed microbiologically with loss of nitrogen in gaseous forms to the atmosphere. Consequently, the nitrate does not



Nitrogen added in fertilizer and lost as nitrate in tile drainage water in experiments in Ohio, Iowa, and Minnesota.

reach deep aquifers.

Florida also has large areas of poorly drained sandy soils with high water tables under intensive crop production (particularly citrus). Large losses of nitrate from these soils may occur, especially during heavy rains (Calvert et al., 1981). Decomposition of organic matter in drained, cultivated organic soils can also be a major source of nitrate (Hortenstine and Forbes, 1972). A study by Messer and Brezonik (1983) indicated that peninsular Florida is not currently experiencing widespread contamination of groundwater with nitrate. Presumably the nitrate moved to the groundwater is diluted with enough water from the relatively high rainfall to keep the concentration low.

Nitrogen Relations in the Great Plains

In nonirrigated portions of the Great Plains, nitrate movement to groundwater would not be expected often because of the low annual precipitation and the high evaporation and transpiration. For example, Sommerfeldt and Smith (1973) found that with good management, including addition of fertilizer in relation to crop needs, fertilizer nitrogen applied to grasslands did not contribute to groundwater pollution in semiarid southern Alberta, Canada. Similar findings were made by Olson and Swallow (1984) for winter wheat in Kansas and by Smith et al. (1982) for sorghum-sudangrass in Oklahoma.

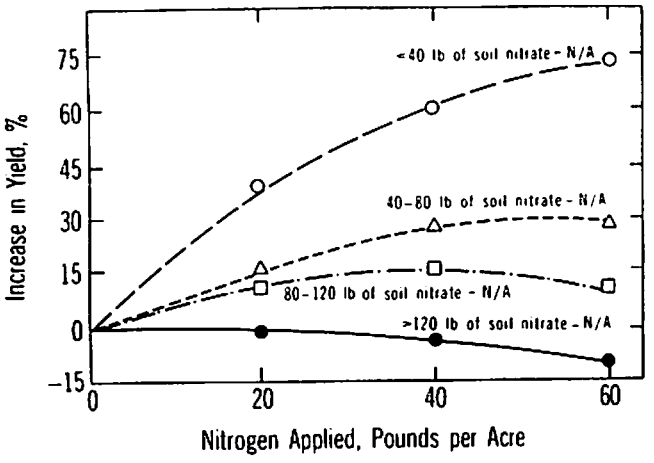
As Thomas (1970) pointed out, however, heavy summer rains can result in movement of nitrate deep into the soil. Olson (1982) found that about 45 pounds of fertilizer nitrogen per acre were moved below the 5-foot depth during an especially wet winter in Kansas, and Campbell et al. (1983) noted that a considerable amount of nitrate was leached from wheat fields in southwestern Saskatchewan in years of above-average precipitation or during heavy spring rains.

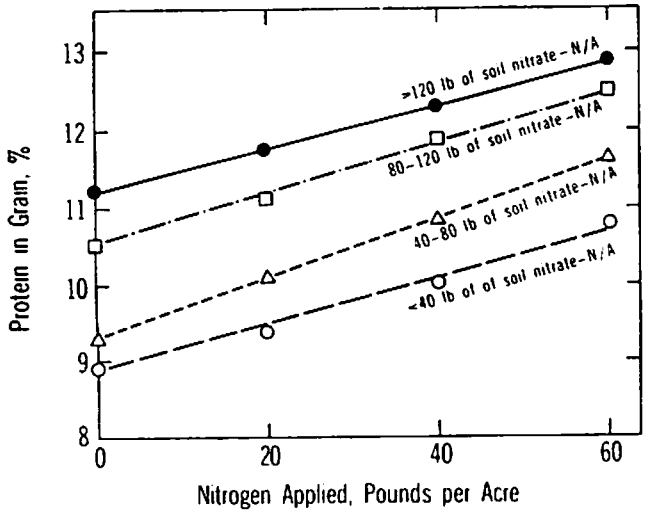
Nitrogen Relations Under Irrigation

Downward movement of nitrate in many soils under irrigation is a potentially serious problem (Keeney, 1982). Heavy applications of nitrogen fertilizer (because of good economic returns for most irrigated crops), rapid production of nitrate by the microbial population, and rapid downward movement of water are considered to be important contributing factors.

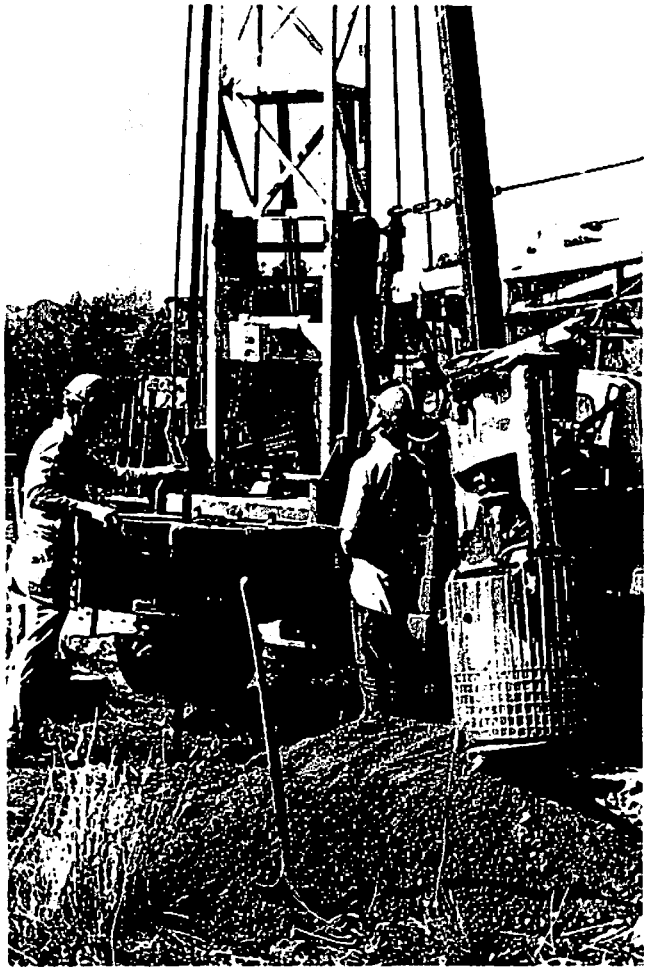
Development of sprinkler irrigation in Coastal Plain areas of Georgia has increased the potential for contaminating the groundwater with nitrate, especially where the subsoils are permeable. Hubbard et al. (1984) found that the nitrate-nitrogen concentration in shallow groundwater under sprinkler-irrigated land averaged 20 ppm, whereas under a forest it was less than 1 ppm.

The impacts of irrigated agriculture on nitrate concentrations in surface water and groundwater have been





The upper graph shows the effect of nitrogen fertilizer on the yield of wheat grown in the wheat-fallow cropping system in 74 experiments in Nebraska, classified according to the nitrate content of the soil at the time of planting. Note that the lower the nitrate content of the soil, the greater was the increase in yield from fertilization. Even where no increase in yield resulted, the wheat took up some of the nitrogen supplied by the fertilizer, and the protein content of the grain was increased, as shown in the lower graph. There were 10 experiments with less than 40 pounds of nitrate-nitrogen per acre to a depth of 6 feet in the soil at the time of planting, 27 with 40 to 80 pounds, 19 with 80 to 120 pounds, and 18 with more than 120 pounds (Olson et al., 1976). In the drier parts of the Great Plains, water usually limits crop yields, and nitrogen supply also is important. In the past, wheat generally was grown in alternate years without nitrogen fertilizer. The intervening year was devoted to fallow, ostensibly to accumulate enough water in the soil to produce a profitable crop of wheat the following year. At the same time, however, nitrate accumulated in the soil, and this also increased the yield of wheat in many instances. Now some nitrogen fertilizer is applied to supplement the soil nitrate. In areas where the wheat-fallow cropping system is used, fallowing does increase the supply of soil moisture for the crop. In the process, it results in deeper moisture penetration into the soil and to loss of nitrate below the root zone in some years. Where the precipitation is sufficient to produce a crop each year, a crop is grown each year for economic reasons; this keeps the water content of the soil low and limits the loss of nitrate below the root zone in most years (Muir et al., 1976).



A truck-mounted rig taking samples in a study of the downward movement of nitrate through the unsaturated zone to deep water tables in southern California. The results indicated that from 19 to 49 years were required for nitrate to move from the surface to a depth of 100 feet under irrigated citrus groves. The unsaturated zone contained little nitrate under unfertilized areas without irrigation. Photograph courtesy of Parker F. Pratt, University of California, Riverside.

evaluated most extensively in California (Pratt, 1978). Branson et al. (1975) reported that for an area *having a* large concentration of dairy cows, the average concentrations of nitrate-nitrogen in the soil water at a depth of 10 to 20 feet were 405, 326, and 290 ppm under corral, pasture, and cropland, respectively. At the top of the water table, the respective nitrate-nitrogen concentrations were 251, 326, and 198 ppm. Both pasture and cropland had received dairy manures in unknown quantities. Adriano et al. (1972) found that nitrate-nitrogen concentrations at 10- to 50-foot depths below nine row-crop sites in an area east of Los Angeles ranged from 36 to 122 ppm in the extracts of the saturated soils. They estimated that from 10 to 50 years would be required before current fertilization practices would affect the nitrate concentration of the ground-

water because of the slow downward movement of water. Current fertilization practices for vegetables supply about 120 pounds more nitrogen per acre per year than is removed by the crops.

In contrast, several monitoring studies of irrigation drainage have indicated little or no increase in nitrate related to agricultural activities. These include the Imperial Valley (Meek et al., 1969) and Coachella Valley (Bower et al., 1969) in California, and the upper Rio Grande River system of New Mexico and Texas (Bower and Wilcox, 1969). Ideal conditions for loss of nitrate-nitrogen from the soils to the atmosphere are probably largely responsible for the low nitrate concentrations in the drainage waters in these valleys.

The California findings (Pratt, 1978) indicate that the nitrate-nitrogen concentrations in groundwater under irrigated croplands are 25 to 30 ppm, and only when the quantities applied exceed those efficiently utilized by the crop does the loss of nitrate in drainage water become excessive. In fact, for many crops, with good agronomic practices and profitable production, nitrate-nitrogen concentrations of about 20 ppm in drainage effluents may be the lowest achievable with current technology.

In irrigated croplands in Colorado, Ludwick et al. (1976) found about 130 to 160 pounds of nitrate-nitrogen per acre in the upper 3-foot depth of soil after cropping. A gradual accumulation of nitrate occurred over time, apparently because of overfertilization. Even larger amounts were found in the surface 6 feet of irrigated loess-derived soils with excessive fertilization in Nebraska (Herron et al., 1968).

Nitrogen Relations of Shallow-Rooted Crops

Management of both nitrogen fertilizer and water tends to be difficult when shallow-rooted crops, such as Irish potatoes, are grown on soils of coarse texture because the capacities of the soils to hold available nitrogen and water in the root zone are so limited. Potatoes have a high nitrogen requirement (Saffigna et al., 1977), and to prevent tuber malformations they must not be subjected to water stress, even for short periods. Therefore, irrigation and nitrogen fertilization are usually essential.

A monitoring study (Saffigna and Keeney, 1977) in the sand plain region of central Wisconsin, where about 20% of the area is under sprinkler irrigation (25% of this area in potatoes), showed that the nitrate-nitrogen concentrations of groundwater in cropped areas were significantly above those of uncropped areas and ranged from 4 to 23 ppm. Field research suggested that much of the nitrogen was derived from fertilizers.

For potato fields on Long Island, New York, Meisinger (1976) calculated that with an average recharge of 50% of the annual precipitation of 43 inches,

A potato field under irrigation in the sand plain region in Wisconsin. Tuber malformations occur if potato plants are deficient in water for even a short time. The plants have a shallow root system, which increases the hazard of water deficiency, particularly with sandy soils because of their low water-holding capacity. Potatoes also have a high nitrogen requirement and receive considerable fertilizer nitrogen. This combination of factors increases the probability that water containing nitrate will percolate down through the soil below the root zone and will enrich the groundwater with nitrate. Photograph courtesy of Dennis R. Keeney, University of Wisconsin.

application of 50 pounds of fertilizer nitrogen per acre in excess of the nitrogen uptake by the crop would result in 10 ppm of nitrate-nitrogen in the recharge water. According to his analysis, a maximum of about 150 pounds of fertilizer nitrogen per acre would result in environmentally acceptable nitrate-nitrogen levels in the water without seriously decreasing the yields under average weather and management conditions. The present applications of fertilizer nitrogen in this area are about 200 pounds per acre.

Nitrate Management

Reducing the loss of nitrate to groundwater would be beneficial from the standpoint of human health hazards and would be of economic benefit to farmers. The cost of nitrogen fertilizer, however, has been low in relation to the increases in crop value that result from its use. Thus, the economic incentive for conservation has not been great, and generous applications have been the rule. There are also some costs in reducing the loss of nitrate. Moreover, a practice that may be desirable from the standpoint of reducing nitrate loss to the groundwater may be undesirable from some other standpoint. In general, reduction of the movement of nitrate to groundwater has not been considered important enough to modify agricultural systems in the direction of reduced profitability to achieve it.

The rate at which nitrate is lost from the soil as a result of downward movement of water depends upon the volume of water that moves downward and the concentration of nitrate in the water. Practices to

reduce nitrate loss in the drainage water thus must decrease the amount of drainage, the concentration of nitrate in the water, or both.

Precise quantitative predictions of the effects of management practices cannot be made, but the effects of a number of practices on nitrate loss have been investigated, and the principles involved provide a guide to ways of reducing the loss. The more important practices are reviewed in following paragraphs.

Nitrogen Fertilizer Management

The most effective way to reduce the loss of fertilizer-derived nitrate to groundwater is to reduce the quantity of nitrogen fertilizer applied. When the quantity of nitrogen applied in the fertilizer exceeds the quantity absorbed by the crop, as often is the case, considerable nitrate may be moved to the groundwater (Kurtz, 1980; Keeney, 1982). With decreasing applications of nitrogen in fertilizer, the nitrate remaining in the soil decreases, and the potential for loss to the groundwater decreases. And generally the crop yield decreases, slowly at first if the application of fertilizer has been generous, but more rapidly as the application decreases. Small amounts of nitrate can be lost from soils to groundwater even when no nitrogen fertilizer is applied and crop yields are low as a result of nitrogen deficiency.

With present prices of nitrogen fertilizers, the maximum profitability of nitrogen fertilization is often obtained with relatively heavy applications, in many instances exceeding the amounts of nitrogen removed in the harvested crops. Even with applications of smaller amounts, the recovery of the added nitrogen by crops is seldom more than 70%, and the average value is probably nearer to 50%. Most of the unabsorbed nitrogen has the potential for adding to the nitrate content of groundwater.

When properly done, soil tests, including measurements of the amounts of nitrate present in soils in the spring (Keeney, 1982), can be a useful guide as a basis for avoiding excessive or deficient applications of nitrogen fertilizer, although the limitations of soil tests for nitrogen are well known (Stanford, 1982). Suitable tests made on tissues of growing plants are useful for perennial crops but are less useful than soil tests for annual crops because the proper time for the most effective treatment may have passed before the results of the tests are known.

Supplying the nitrogen as it is needed by the crop (Olson and Kurtz, 1982) holds the potential for increasing the efficiency of recovery of fertilizer nitrogen by crops and decreasing the potential loss of nitrate to groundwater. One technique for doing this would be to employ fertilizers that would release the nitrogen for crop use as it is needed. Slow-release fertilizers are available, but they are now too expensive for use except on turf and ornamentals.

A second technique is to apply the nitrogen fertilizer in small amounts through the growing season. This technique works best with crops irrigated by sprinkler or drip irrigation because the nitrogen fertilizer can be supplied in the irrigation water in concentrations to fit the circumstances (Smika and Watts, 1978). Small doses of nitrogen fertilizers can be applied efficiently where this operation can be combined with another, such as cultivation, but more than two applications are seldom used. Each application increases the production costs, and the use of field equipment is usually limited to the early part of the growing season, when the crop is too small to sustain much damage.

A third technique is to use with the fertilizer a substance that inhibits the microbiological transformation of nitrogen in the soil from the ammonium form to nitrate. Ammonium is held in the soil against downward movement with drainage water, and in the presence of an effective inhibitor it can persist for crop use longer than ammonium that is immediately subject to transformation to nitrate. Recent work in Minnesota (Malzer and Graff, 1983) has shown that inhibitors are effective in prolonging the retention of fertilizer nitrogen in sandy soils in Minnesota and increasing the yields of corn, especially in years with heavy rainfall in May and June. Numerous inhibitors are known, but only one (nitrapyrin or N-Serve®) has been approved for sale in the United States. The effectiveness of inhibitors decreases with time after application.

If transformation of ammonium or ammonium-producing forms of nitrogen in the fertilizer could be delayed through use of slow-release forms or chemical inhibitors, the acceptability of fall fertilization would be increased. Use of nitrapyrin with fall-applied nitrogen fertilizer has conserved nitrogen in several experimental situations (Kurtz, 1980; Nelson and Huber, 1980), but most research to date has been related to decreasing the conversion of nitrogen from nitrate to gaseous forms of nitrogen rather than to decreasing the loss of nitrate in the drainage water.

Ammonium and urea (a simple organic compound of nitrogen used as a fertilizer) are effectively absorbed by plant leaves. The proportion of the fertilizer nitrogen recovered in plants from applications to the leaves is greater, and the potential for loss to the groundwater is less, than with nitrogen applied broadcast on the surface of the soil. Sprays containing urea have been used for many years on high-value truck crops, citrus, and deciduous orchards to supplement the soil nitrogen supply. Applying urea to the foliage is most convenient and economical with crops that are irrigated by sprinkler systems or that require frequent spray treatments with micronutrients or pesticides. Primarily because of the cost of application and the possibility of

Nitrogen fertilizer is important in crop production in the United States. Most of the fertilizer nitrogen is applied as ammonia or other forms that release the nitrogen as ammonium in the soil. Soil microorganisms then change the ammonium to nitrate, which may be lost in drainage water. The use of certain chemical substances in the ammonia to inhibit the microbiological transformation may reduce the loss of nitrate. Delaying the application of nitrogen fertilizer until the crop roots have extended through most or all of the area between the rows, as has been done in this field, also reduces the potential loss of nitrate below the root zone because the roots take up ammonium and nitrate rapidly. Photograph courtesy of the U.S. Department of Agriculture.

damage to the plants, urea-containing sprays have not been widely adopted for field crops, such as corn, cotton, and wheat.

Application of fertilizer nitrogen in the fall in cool climates for the next growing season has long been a controversial subject (Beauchamp, 1977). Fall application has the advantages to the farmer and fertilizer industry of spreading out the labor and equipment demand, and soil conditions often are more favorable for machine traffic in the fall than in the spring. Field experiments comparing the relative efficiency (usually expressed as yield response) of fall- and spring-applied fertilizer nitrogen have given results ranging from no difference to large yield advantages with spring application (Keeney, 1982). This divergence of findings is likely due principally to climatic differences between regions and year-to-year differences in weather within regions, but also to other factors that may vary from one location to another.

The usual recommendations are that ammonium and ammonium-producing forms of fertilizer not be applied in the fall until the soil temperature is lower than 50°F, that fall fertilization not be practiced on soils with coarse texture or poor drainage, and that perhaps 10 to 20% more fertilizer nitrogen be used in fall than in spring applications. Transformation of ammonium to nitrate continues at reduced rates at temperatures between freezing and 50° F, however, and the rate of transformation will increase as the temperature increases above 50° F in the spring. Hence, a warm, wet spring could result in extensive leaching of fertilizer nitrogen. Thus, fall fertilization is often discouraged as

an environmentally and economically unsound practice (Keeney, 1982).

Irrigation

To assure that crops have an adequate supply of water, the amount of water added in irrigation is commonly well in excess of the minimum required to avoid the development of salinity in the soil from the soluble salts (including nitrates) left behind when the irrigation water evaporates. By increasing the efficiency of water use, it may be possible to reduce substantially the amount of nitrate lost in the drainage water (Keeney, 1982), although the concentration of nitrate in the smaller volume of effluent may increase (Devitt et al., 1976).

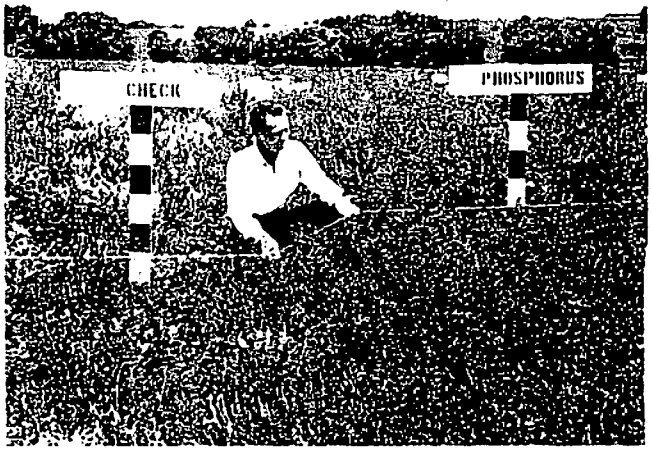
Drip irrigation and other new irrigation methods are now available (Hiller and Howell, 1983) that consume less water than the commonly used flood, sprinkler, and furrow systems (Taylor and Ashcroft, 1972). The new methods can reduce the amount of nitrate lost from soils to groundwater, but they require more intensive management than the commonly used systems. The extent to which they are adopted is expected to be contingent primarily upon the economics of water use. The economic feasibility of the intensive management required has not been evaluated for most situations. The effect of the new techniques on nitrate movement to groundwater may be expected to be a by-product of the economics of water use, not a primary deciding factor.

Tillage

Conventional tillage, also called clean tillage, involves plowing under the residues of the preceding crop and disking the plowed soil (generally twice) to prepare a seed bed. It enhances the release of nitrate from the soil organic matter and speeds the decomposition of the crop residues, with eventual release of nitrate. It also promotes soil erosion.

Conservation tillage, also called reduced tillage, embraces a variety of practices in which the amount of tillage and tillage costs are reduced, and some portion of the residues of the preceding crop is left on the surface of the soil, reducing soil erosion. Less nitrate is released from the soil organic matter, the rate of decomposition of the crop residues is decreased, and the proportion of the precipitation that enters the soil is often increased. The overall result may be somewhat greater loss of nitrate to the groundwater than occurs with conventional tillage (Tyler and Thomas, 1977), but under some circumstances the amount of nitrate-nitrogen lost by conversion to gaseous forms may be enhanced.

Conventional tillage thus appears to be preferred over conservation tillage from the standpoint of nitrate loss to groundwater, but not from the standpoint of soil erosion control and costs of production. Further research is needed on this subject.



Alfalfa is a favorite legume in crop rotations dependent upon fixation of atmospheric nitrogen as a source of nitrogen beyond that supplied by the soil. Fertilization of alfalfa with phosphorus often benefits the succeeding nonleguminous crops indirectly by increasing their supply of both phosphorus and nitrogen. Fertilizer phosphorus is retained by soils and is not of concern for groundwater quality, but atmospheric nitrogen fixed by legumes may be transformed subsequently to nitrate, which may move to groundwater. Crop rotations supplied with extra nitrogen by alfalfa or other leguminous crops are not considered important sources of nitrate in groundwater because the nitrate is released gradually, and normally the ratio of nonlegumes to legumes is high enough to deplete the available nitrogen in the soil. Photograph courtesy of Robert A. Olson, University of Nebraska.

Cropping System

The old crop rotation systems built around the growth of forage legumes (such as clover) to supply nitrogen for the associated nonlegumes resulted in little loss of nitrate to groundwater because, for economic reasons, they generally were adjusted so as to maximize the number of years in which the land was devoted to profitable nonleguminous crops that would keep the soil nitrate low. In drier areas, the need to conserve soil moisture for other crops was a prominent economic factor limiting the use of alfalfa and some other legumes because these crops deplete the supply of soil moisture, and time is required for replenishment.

As a result of the change from horse power to tractor power and the availability of nitrogen fertilizers and effective pesticides at prices low enough to encourage extensive use, the old crop rotations have given way to increased acreages of more profitable nonleguminous crops, such as corn and cotton, in continuous culture. This practice promotes the loss of nitrate to groundwater because of the increased use of nitrogen fertilizers to obtain more profitable yields. Generally the nitrogen is added in a single heavy dose early in the season when the crop is not able to use it rapidly.

Loss of nitrate can be reduced by alternating the nonlegume with soybeans, which utilize nitrate from the soil and do not require nitrogen fertilization (Johnson et al., 1974). The soybean crop provides a relatively good economic return and diversifies the farming operation. Although the soybean crop fixes atmospheric nitrogen, some of which eventually is transformed to nitrate, it has a self-regulating mechanism that reduces the amount of atmospheric nitrogen fixed in proportion to the amount of nitrogen the plants derive from the soil.

A somewhat similar alternative may be to grow corn continuously by a no-tillage or reduced-tillage method in a solid continuous stand of crownvetch, a legume. Crownvetch is adapted from Minnesota and Iowa eastward to the Atlantic Ocean. The crownvetch must be treated with a herbicide to control it while the corn is growing.

Cropping systems using nonleguminous grass or grain crops, such as sudangrass or sorghum, as well as those using two crops grown concurrently (intercropping) or consecutively in the same year (double cropping) may be effective in reducing nitrate loss from the soil (Nelson et al., 1977) if they receive little or no nitrogen fertilizer. Profitability is the first requirement in crop production, however, and nitrogen fertilizer is a key factor in this. An effective means of reducing the residual nitrate in the soil without compromising the profitability in some circumstances is to grow a "cover crop" after the principal crop has been harvested. Cover crops may be legumes in some parts of the country, and they generally are grown primarily for erosion control, not for profit. Some of the nitrogen absorbed by the cover crop during the fall (and early spring if it lives through the winter) may be released in available form for the principal crop in the following growing season. Establishing a cover crop may be difficult in dry regions or in wet fall seasons in the Northeast.

Health Effects of Nitrate in Drinking Water

The potential adverse health effects that have been suggested for nitrate in drinking water include birth defects, cancer, nervous system impairment, and methemoglobinemia. Only the last of these is well verified. Nitrate was linked to birth defects in a study in Australia (Dorsch et al. 1984). The evidence on cancer is contradictory (Fraser and Chilvers, 1981). The most recent epidemiological study (Forman et al., 1985) indicated that high nitrate intake was associated with a low incidence of gastric cancer. The nervous sytem impairment has been represented as a subclinical form of methemoglobinemia. The potential adverse effects of nitrate on humans and animals have been reviewed by Shuval and Gruener (1972), Ridder and Oehme (1974), National Research Council (1977, 1978), Lechowich et al. (1978), Fraser and Chilvers (1981), Newberne (1982), and Black (1983).

Nitrate is a normal body constituent. According to White (1975), the average daily ingestion of nitrate-nitrogen per capita in the United States is 22.5 milligrams (an amount equivalent to the nitrate that would be ingested in 2.4 quarts of drinking water containing nitrate-nitrogen at the public health standard of 10 ppm. Of this total, 86% is derived from vegetables and only 1% from water on the average. The proportion and absolute amount derived from the water supply may of course be much greater among the relatively small numbers of individuals who consume water high in nitrate.

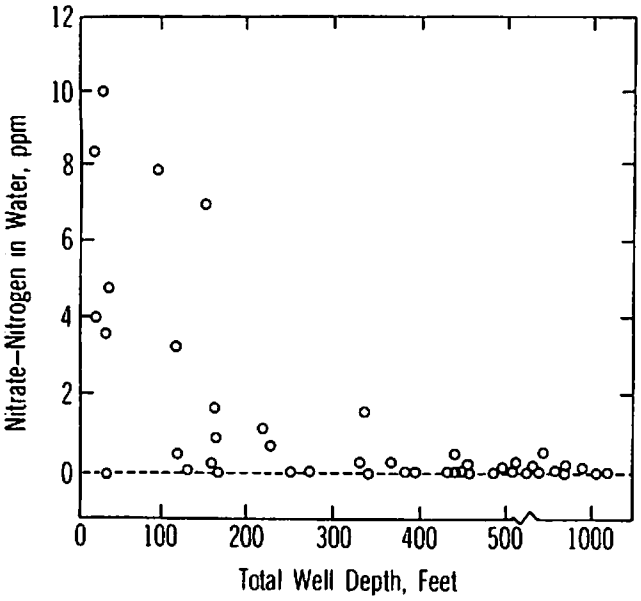
In the human body, nitrate is absorbed rapidly into the bloodstream from the stomach and upper intestines and is excreted in the urine. A small amount is recycled in the saliva and is reduced to nitrite in the mouth, from whence it is swallowed into the stomach. Additionally, nitrate and nitrite are formed in the intestines from other nitrogenous compounds, and nitrate may be formed elsewhere in the body. Normally, most of the nitrite to which the body is exposed appears to be produced in the intestines.

When ingested in excess, nitrate produces methemoglobinemia, a condition that can lead to death from asphyxiation. The cause is reduction of some of the nitrate to nitrite in the digestive tract. The nitrite is absorbed into the bloodstream, where it interacts with the hemoglobin to produce methemoglobin, a form that does not carry oxygen to the body cells. Small amounts of methemoglobin are normal in blood, but large amounts can be fatal.

Methemoglobinemia in humans from excess nitrate in drinking water is a problem only with infants, particularly those affected by diarrhea. High nitrate concentrations and contamination with bacteria are common in water from shallow farm wells located near livestock quarters.[1] A number of infant deaths from methemoglobinemia occurred until the cause and cure became generally known among medical doctors.

Infant deaths from methemoglobinemia now are very rare because doctors recommend the use of bottled water in instances in which the content of nitrate-nitrogen in the water exceeds the public health standard of 10 ppm. In Iowa, for example, where the cause of the disease was discovered in 1945, no infant deaths from methemoglobinemia have been reported since 1948. The hazard remains, and cases occasionally

[1] The concentration of nitrate in groundwater tends to be greatest near the source of the nitrate. Where high concentrations of nitrate are found in shallow wells, these often can be avoided by drilling wells deeper and protecting them against contamination from water derived from shallow depths. The figure on page 30 shows a plot of nitrate concentrations versus depths of wells sampled in northeastern Iowa. A survey of nitrate concentrations in waters from 8,844 wells in Illinois (Aldrich, 1980) yielded similar results. Wells used for municipal water supplies generally are deep and low in nitrate.



Concentration of nitrate-nitrogen in water from wells differing in depth in Clayton County, Iowa [Hallberg and Hoyer, 1982].

occur, but with adequate knowledge methemoglobinemia can be avoided or successfully treated. (The use of bottled water for drinking by expectant mothers in high-nitrate areas would be effective also in eliminating birth defects from nitrate in drinking water, should this be verified as a cause.)

The explanation favored for the sensitivity of human infants is that in newborn infants the stomach and upper part of the intestinal tract are not strongly acid, and as a result these organs act as bacterial fermentation chambers in which the nitrate is changed to nitrite. As infants develop gastric acidity, their sensitivity to nitrate declines. In older infants and adults, whose stomachs and upper intestines are acid, growth of bacteria is inhibited, and nitrate is absorbed into the bloodstream as nitrate (and is excreted in the urine in that form) before the contents of the digestive tract reach the lower intestines, which are not strongly acid and which support the growth of bacteria that produce nitrite from nitrate.

The public health standard of 10 parts of nitrate-nitrogen per million (45 parts of nitrate per million) of drinking water was set many years ago as the concentration below which no cases of infant methemoglobinemia had been identified. Now there is evidence (Cornblath and Hartman, 1984; Hegesh and Shiloah, 1982) that infants will tolerate considerably higher values if diarrhea is not a problem. Diarrhea may increase the pH of the stomach and intestines of infants enough to permit the growth of bacteria that can reduce the nitrate to nitrite.

In livestock, nitrate poisoning is primarily a problem of ruminants, especially cattle. The sensitivity of ruminants to nitrate derives from the fact that the first stage of digestion is a bacterial fermentation (in the rumen) in which nitrate reduction to nitrite can occur, as in human infants. The National Academy of Sciences (1974) noted that water used for livestock could contain nitrate-nitrogen in concentrations up to 100 ppm with no adverse effect. This observation was supported by a study of the effects of high-nitrate water on dairy cows (Crowley et al., 1974) in which it was concluded that water containing nitrate-nitrogen at concentrations up to 90 ppm had no significant effect on incidence of stillborn calves, abortions, retained placentas, cystic ovaries, milk production, milk fat production, or the general health of the cows.

Inorganic Amendments

Inorganic amendments are chemicals added to agricultural lands primarily to improve the chemical, physical, or microbiological properties of soils for crop growth. The principal inorganic amendments are liming materials, including limestone and the crude hydroxides and oxides of calcium and magnesium; gypsum (calcium sulfate); and sulfur (see Appendix D, Table 6).

Liming Materials

Liming materials are used on acid soils. They neutralize soil acidity, decrease the toxicity of aluminum and manganese to plants, increase the availability of certain nutrients to plants, supply calcium and magnesium as nutrients in acid soils that are deficient in these nutrients, and increase the fixation of atmospheric nitrogen by the association between leguminous plants and the bacteria that inhabit the nodules on their roots (Coleman et al., 1958; Pearson and Adams, 1967). Initial applications to strongly acid soils range from less than 1 ton per acre to as much as 10 tons per acre, with subsequent applications in smaller amounts at intervals of a few years.

Pulverized limestone, the predominant form used, has only slight solubility and remains in the soil in that form if it does not react with the soil. Reaction with the soil increases the amounts of calcium and magnesium held by the soil particles in adsorbed or exchangeable form, but does not increase the soluble salt content appreciably. Hence, it does not lead to rapid downward movement of calcium and magnesium in the soil (Brown et al., 1956) or to any substantial increase in the salts available for movement to groundwaters (MacIntire, 1926; Coleman et al., 1958).

Applying ground limestone to acid soil in New York. The limestone contains calcium carbonate, which is decomposed by acid soil. The calcium is held by the soil. The carbonic acid formed in the reaction breaks down to water and carbon dioxide gas. Thus, the groundwater is not enriched with salts as a result of liming. Photograph courtesy of the U.S. Department of Agriculture.

Gypsum

Gypsum is used to increase the rate of entry of surface water into certain soils with low salt content (Oster, 1982) and into soils containing an excess of exchangeable sodium (Fitts et al., 1944; Kelley, 1951; Bower et al., 1951; Padhi et al., 1965). Associated with the increased rate of water intake in high-sodium soils are improved physical, chemical, and biological conditions for plant growth. Initial applications of gypsum for the latter purpose range from 2 to 20 tons per acre. Quantities used for maintenance applications in connection with irrigation waters that have high ratios of sodium to calcium plus magnesium are much smaller (Oster, 1984).

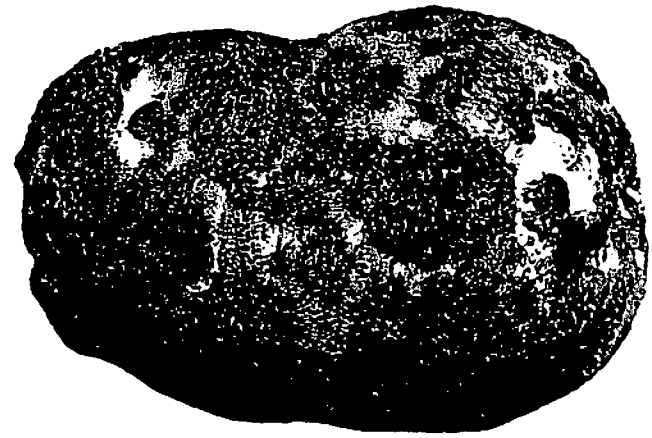
Although empirical information on the effect of gypsum on the quality of groundwater is limited, theoretical understanding of the interaction of gypsum with soils indicates that much of the sulfate added has the potential for increasing the salt content of groundwaters under conditions where oxygen is not deficient. If, however, the sodium sulfate that moves downward in solution from the layer at the surface of high-sodium soils passes through soil materials having largely calcium ions in adsorbed or exchangeable form, the sodium can replace calcium, with subsequent precipitation of calcium sulfate (Jury et al., 1978), thus decreasing the potential effect on the salinity of the groundwaters.

If the soils treated with gypsum are saturated with water and have enough decomposable organic matter to cause the microorganisms to use the sulfate ($SO_4^{=}$) as a source of oxygen (as may occur in production of rice under flooded conditions), the sulfate may be converted to sulfide ($S^{=}$). The sulfide is immobilized in the soil as iron sulfide, a substance with very low solubility. The calcium then will remain in the soil as exchangeable calcium or calcium carbonate until oxygen returns, whereupon the sulfide will be converted back to sulfate, and calcium sulfate will be regenerated.

Sulfur

One use of sulfur is to acidify soils. Under the influence of certain soil microorganisms, sulfur interacts with oxygen and water to produce sulfuric acid, which increases the soil acidity. The sulfuric acid reacts with the soil to produce sulfate salts that can

Azaleas, rhododendrons, gardenias, and some other plants may make poor growth because of iron deficiency if they are not grown on acid soils. For use with potted plants, such as the azalea shown here, iron sulfate (or aluminum sulfate) is often used as an amendment to acidify the soil. Part of the sulfate may be lost in the drainage water, but the iron and aluminum change to insoluble forms that remain in the soil. Photograph courtesy of the U.S. Department of Agriculture.



A potato tuber severely affected by scab caused by *Streptomyces scabies*. This disease of potatoes, common in slightly acid to alkaline soils, is usually controlled by acidifying the soils with sulfur. The sulfur is oxidized by certain soil microorganisms to sulfuric acid, which reacts with the soil and eventually increases the content of sulfate salts in the drainage water. Although quantities of 400 to 2,000 pounds of sulfur may be added per acre to acidify soils, only small quantities are needed subsequently for maintenance applications. Consequently, the contribution to the sulfate content of groundwater on an annual basis is relatively small. Photograph courtesy of the U.S. Department of Agriculture.

contribute to the salinity of the water draining from the soil and entering the groundwater.

Soils sometimes are acidified to create a more favorable nutritional environment for some plants, including certain ornamentals and berries, that thrive on acid soils. Sulfur may be used also to acidify soils to control potato scab, a disease caused by certain microorganisms whose growth is inhibited at low soil pH values. Pratt (1961) reported sulfur requirements of from 400 to 2,000 pounds per acre to control potato scab in soils of coarse texture in California.

The reaction of sulfuric acid with calcium carbonate to produce calcium sulfate makes sulfur useful for reclaiming high-sodium soils that contain calcium carbonate. In such soils, sodium sulfate will be an important component of the soluble salts available for downward movement in the drainage water. As with additions of gypsum, however, the additions of salts to the groundwaters over a period of decades will be small in relation to the amount of salts added in many irrigation waters. In most instances, maintenance of the soil in an acid condition requires only small amounts of sulfur after the initial addition.

Other Amendments

Other amendments occasionally are used to acidify soils. These include sulfuric acid, iron sulfate, aluminum sulfate, and ammonium fertilizers, particularly ammonium sulfate.

In moderately acid to alkaline soils, iron and aluminum sulfates produce sulfuric acid and insoluble hydrous oxides of iron and aluminum. The sulfate salts of iron and aluminum are favored for use with ornamental plants grown in containers. They are not of significance in field operations. Sulfur is favored for field treatments.

Ammonium-bearing fertilizers undergo microbiological change in soil to produce nitric acid. Ammonium sulfate, $(NH_4)_2SO_4$, is especially effective because each molecule produces two molecules of nitric acid and one of sulfuric acid. Ammonium fertilizers may have an important acidifying effect over a period of years, but they usually are used in relatively small quantities as sources of nitrogen rather than as amendments to acidify soils.

Effects on Pesticides

Little has been published on the effects of soil amendments on pesticide behavior, but the effects probably are most significant with amendments used to alter soil pH values. Soil pH influences (1) the rate of interaction of some pesticides with water to form new and

often nonpesticidal compounds (or in some instances to produce the active forms of pesticides from inactive forms added), (2) the activities of the populations of soil microorganisms that are of principal importance in decomposing most pesticides, and (3) the adsorption or retention of some pesticides by soil. All these effects of soil pH modify the potential of pesticides for downward movement to groundwater.

Organic Residues

Vast amounts of organic residues are produced in crop production, livestock and poultry enterprises, food processing industries, and sewage plants. For example, the nine leading crops in the United States produce about 400 million tons of dry residues per year (Larson, 1985). More than 100 million tons of dry livestock and poultry manures are produced annually in the United States (Appendix D, Table 7), translating to more than 1 billion tons of manure on a wet basis. And 24 billion gallons of domestic sewage are discharged every day (Freshman, 1977).

Organic residues traditionally have been applied to soil. They are well recognized for their value as both soil conditioners and fertilizers.

As soil conditioners, organic residues improve soil physical properties and increase biological activity. Examples of their influence are increased water-holding capacity and nutrient-holding capacity, increased rate of intake of surface water, improved soil workability and aeration, and reduced loss of soil by erosion.

As fertilizers, organic residues have the advantage of containing at least low concentrations of all the nutrients required to grow the plants from which the residues are derived. In total, the value of the plant nutrients is great. For example, at 1984 prices for nutrients in chemical fertilizers, the value of the nitrogen, phosphorus, and potassium in the 46% of the livestock and poultry manure estimated to be collectible (Appendix D, Table 7) is about $1.5 billion per year. The nitrogen, phosphorus, and potassium in sewage sludge would cost about $880 million annually if purchased in chemical fertilizers.

On the other hand, organic residues have several disadvantages as fertilizers: (1) They are dilute sources of nutrients in comparison with chemical fertilizers (see Appendix D, Tables 8, 9, and 10). (2) They are variable in composition (see Appendix D, Tables 8, 9, and 10). (3) Their fertilizer value with regard to nitrogen, phosphorus, and sulfur depends in part upon the rate of release of these nutrients in inorganic forms from the organic compounds in which a share of each of these nutrients exists in the residues. (4) Some sewage sludges contain cadmium, zinc, copper, nickel, and certain other elements, derived mostly from industrial discharges, in quantities that may become toxic to plants with cumulative applications of contaminated sludges on a given site. There is further concern for the possible toxicity to animals and humans of cadmium absorbed by plants from sludge applied to soil. (5) Applications of animal manures to land near living sites may be objectionable because of odors and flies.

Animal feeding, food processing, and sewage operations tend to concentrate relatively large quantities of organic residues in small areas because it is profitable to transport the original foods, feeds, or other products some distance for use. The residues, however, are of lower value and because of their bulk cannot profitably be transported far. As a consequence, the residues generally are applied to soils near at hand, and the amounts of nitrogen added per acre may far exceed the amounts removed by crops. Aside from odors, the potential effect of principal concern about this concentration process is an increase in the nitrate content of groundwater. Of secondary concern is bacterial contamination of the groundwater.

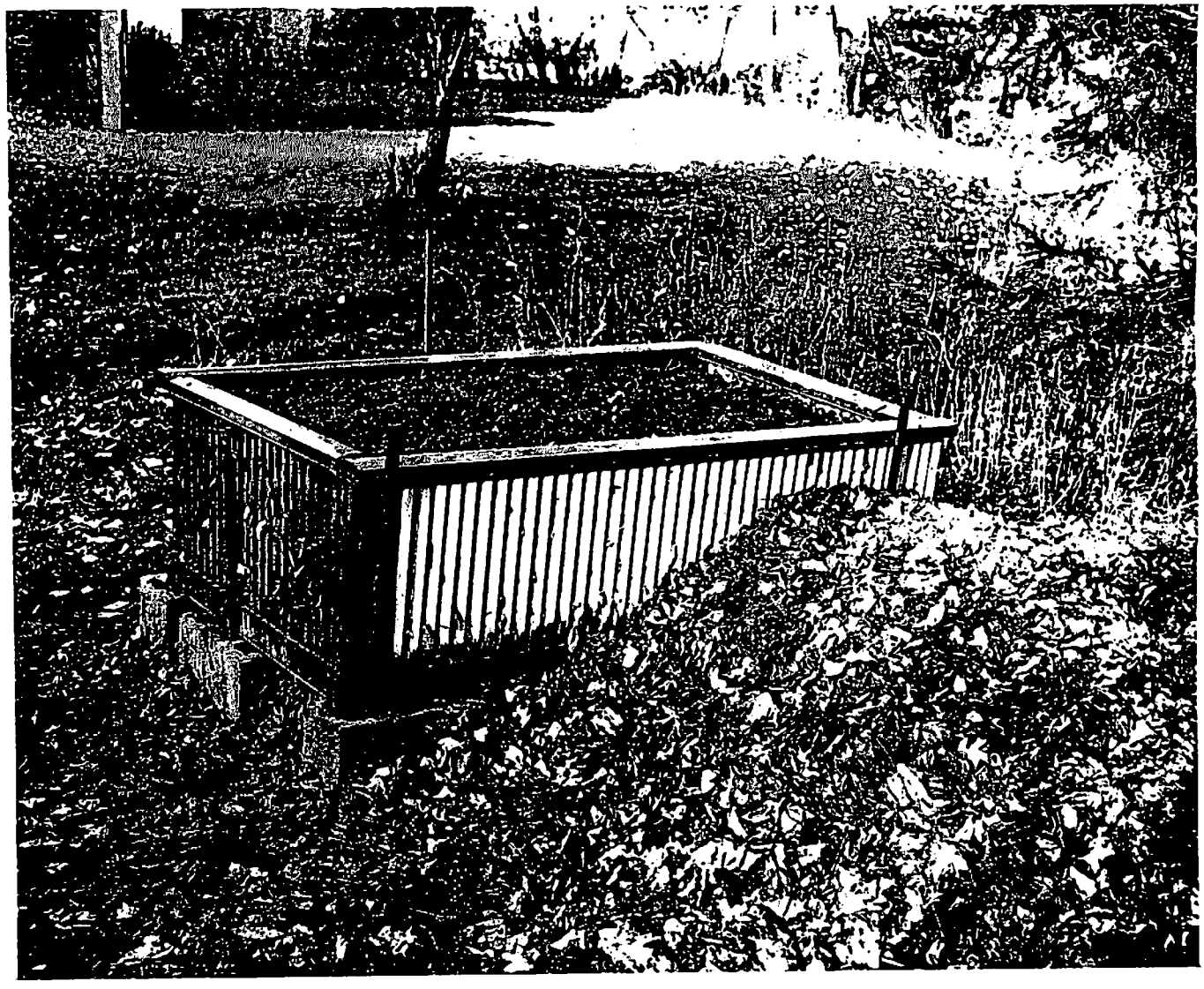
Nitrate

The general principles of nitrate movement with water in soils apply for nitrate derived from the nitrogen in organic residues as well as for nitrate derived from fertilizers or other sources. The presence of the organic matter and the management processes, however, introduce some complications.

The residues of crops left in the field after harvest are not normally a significant source of nitrate in drainage water. Low concentrations of nitrate may be present in drainage water from cropped soils treated with normal applications of a few tons of manure per acre, but higher concentrations may be present when heavy applications of manure are made for disposal purposes (Haghiri et al., 1978; Amoozegar-Fard et al., 1980; Walker and Kroeker, 1982; Westerman et al., 1983; and Pratt, 1984). When large amounts of manure are produced in feedlots or other small areas, adequate land for disposal purposes is needed nearby.

Also of concern in arid regions is the salt content of manure from beef cattle (Stewart, 1974). Beef cattle in feedlots are fed rations high in salt, which adds to the potential for increasing groundwater salinity. Extra irrigation water is needed to move the excess salt below the root zone, and the additional water itself adds more salt.

Cattle feedlots may be major nitrate sources in some areas. Feedlots are localized sites where large quantities of nitrogen are concentrated from crops grown in other



Organic residues are valuable as soil conditioners and as sources of nutrients for plants. Here, hardwood leaves are being composted in a bin, and a pile of freshly raked leaves has been collected alongside to refill the bin as soon as the existing compost is transferred to the home garden. Fertilizers may increase the content of plant nutrients in tree leaves, lawn clippings, and crop residues, and these nutrients are released in the soil as the residues decay. The nutrients are absorbed in part by succeeding generations of plants, but some portion may be lost to the groundwater. Fertilizers thus may contribute directly to the content of soluble salts in groundwater when nutrients supplied by fertilizers are carried below the root zone by percolating water without being absorbed by plants, and they may contribute indirectly when fertilizer-derived nutrients that have been cycled through plants are lost to groundwater. Photograph courtesy of the U.S. Department of Agriculture.

areas. Viets (1971) estimated that in a 1-acre cattle feedlot of average density (360 animals) used for an entire year, the animals would consume about 2,800 tons of feed and would excrete about 25 tons of nitrogen. In an experiment by Gilbertson et al. (1970) in eastern Nebraska, the manure removed from experimental feedlots by cleaning and hauling contained an average of 51% of the nitrogen excreted. The remaining portion of the 25 tons of nitrogen, on the basis of Viets' average values, would be about 12.25 tons of nitrogen, an amount 383 times greater than the average application of nitrogen in commercial nitrogen fertilizers to cropland of the United States in 1980—equivalent to 9,000 parts of nitrate-nitrogen per million in one surface foot of water.

The potential concentration is not realized because of a combination of factors. These include (1) incomplete decomposition of the organic matter, (2) loss of ammonia by volatilization, (3) inhibition of biological formation of nitrate because of the high pH values associated with ammonium and sodium accumulation, (4) loss of nitrate by change to gaseous forms of nitrogen in the portion of the manure and soil lacking free oxygen, and (5) the virtual exclusion of water from the soil by a surface seal caused by compaction of the soil by the cattle hoofs and plugging of the pores by clay and organic materials.

Most of the formation of nitrate in the soil occurs

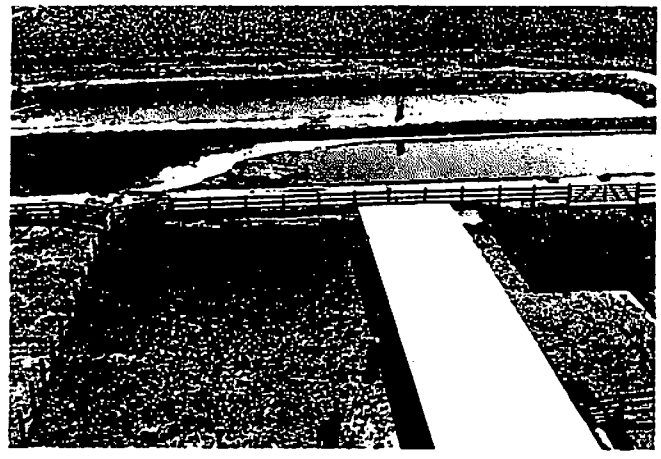
when feedlots stand unused. Then the surface seal breaks down, oxygen from the atmosphere enters the soil, the soil pH decreases, and nitrate production from the accumulated ammonium occurs (Ellis et al., 1975). Measurements by Mielke and Ellis (1976) on abandoned cattle feedlots in eastern Nebraska showed that the average concentration of nitrate-nitrogen in the upper part of the groundwater was 40 ppm. Measurements on soils under corn from other areas showed an average concentration of 6 parts of nitrate-nitrogen per million in the upper part of the groundwater.

Cattle feedlots thus may be significant sources of nitrate in the groundwater beneath them. The total area of such feedlots in the United States, however, was estimated by Ellis et al. (1975) to be less than 130,000 acres or 203 square miles, an area much less than that in a county of average size. Cattle feedlots are of greatest concern because most are located outdoors on bare soil. Hogs, chickens, and turkeys generally are produced indoors, where the accumulated manure is collected and applied as fertilizer to land of considerably greater area. Sheep are raised mainly on rangeland.

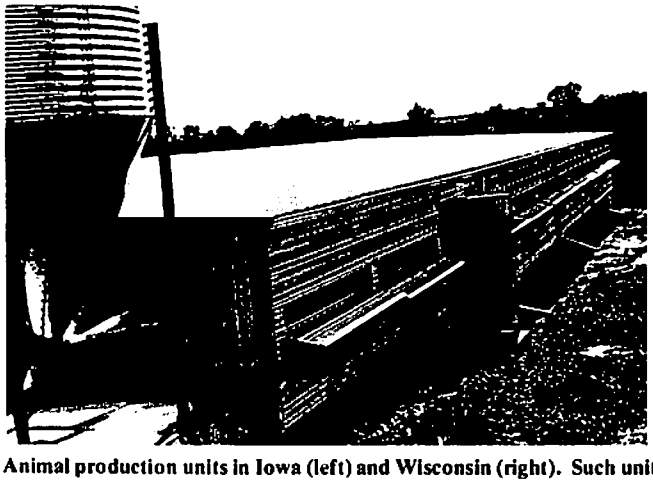
Overall, the potential for accumulation of nitrate in groundwater from animal wastes is less than that from fertilizers. Pratt et al. (1975) estimated the total nitrogen applied annually in commercial chemical fertilizers to be 2.6 times greater than the total amount of nitrogen in all livestock and poultry manure produced each year.

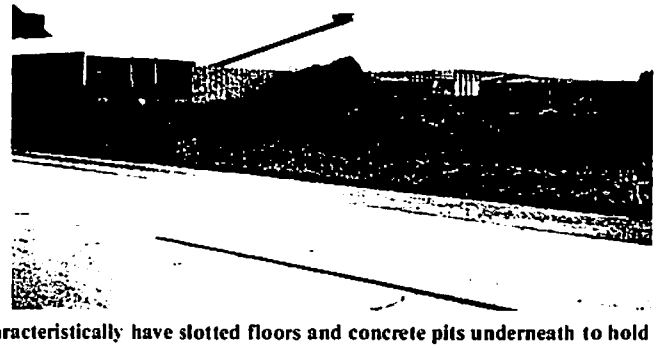
At present, considerable use is made of shallow ponds and deeper pits to store wastes from livestock and food processing operations, and the potential of these structures for groundwater pollution has been of concern (Sewell, 1977). Experiments have shown that some leaching may occur in the first 2 to 4 months when a structure is first put into operation (Davis et al., 1973; Oliver et al., 1974). In time, however, the soil is sealed by organic matter, and the movement of water through the seal is insufficient to have a significant effect on groundwater quality (Oliver et al., 1974; Ritter et al., 1980). Culley and Phillips (1982) found less than 1 part of nitrate-nitrogen per million of drainage water. Sowden and Hore (1976) found no evidence of groundwater contamination by excess nitrogen from concrete-base and gravel-base solid manure storage areas used for 30 years in Canada.

Disposal of sewage sludge on land has been more controversial. The principal concern voiced has been the contamination of certain sludges with cadmium and other metallic ions that could become toxic with con-

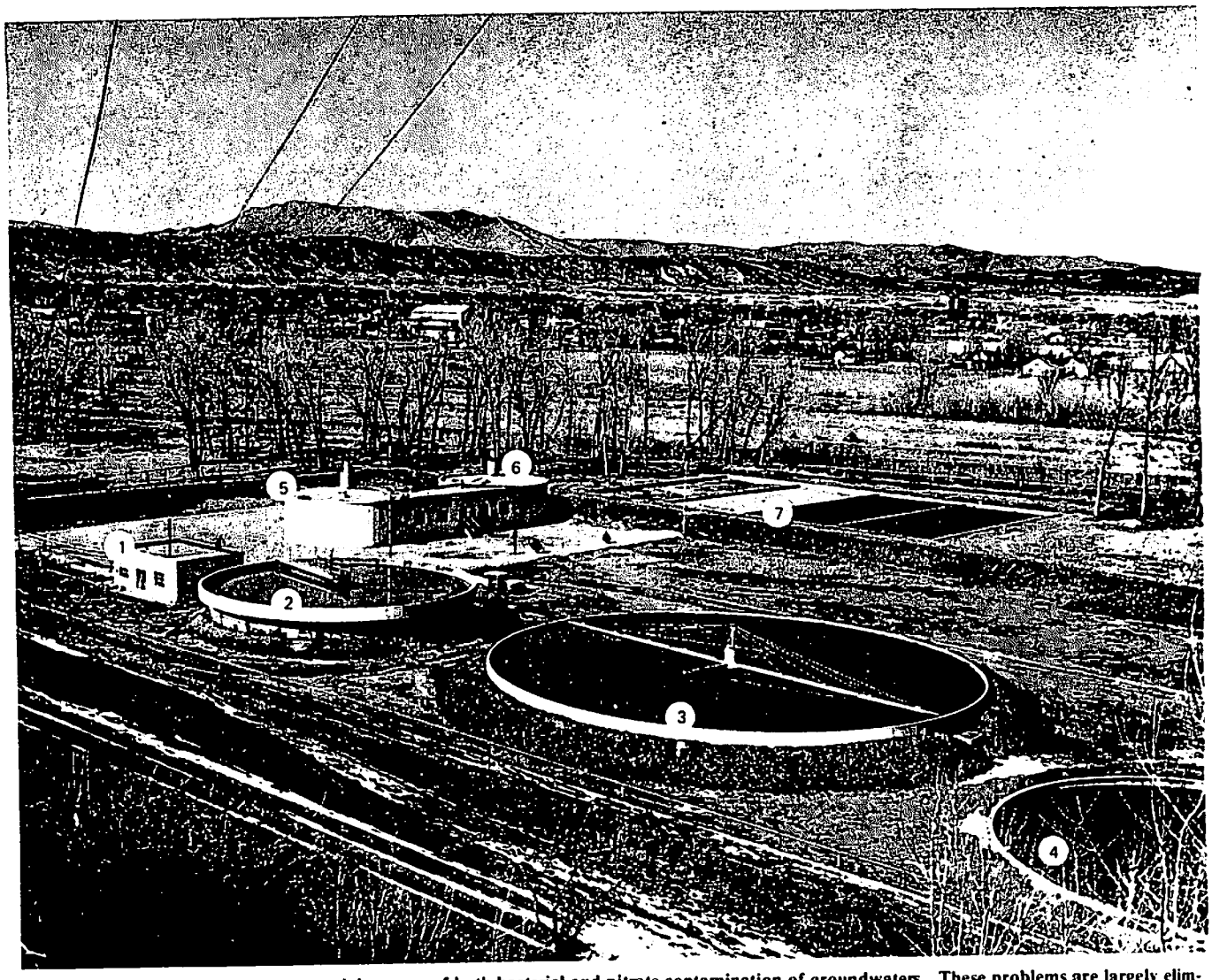


A concrete cattle feedlot with a two-stage runoff control system in Indiana. The runoff first enters the adjacent debris basin. The solids settle out and remain in the basin. The liquid is carried off through a pipe leading to the second liquid-holding basin. Periodically, the contents of the two basins are spread on pasture or cropland. Little loss of nitrate to groundwater occurs in such a system. Photograph courtesy of Alan L. Sutton, Purdue University.





Animal production units in Iowa (left) and Wisconsin (right). Such units characteristically have slotted floors and concrete pits underneath to hold the wastes. The wastes are pumped out periodically and applied directly to cropland or pasture, or they may be discharged in a pile near the building (as at the right) for subsequent distribution. The latter practice may permit considerable loss of dissolved material if the wastes are located on soil. Such losses can be prevented if the wastes are located on a walled concrete slab. Adequate amounts of land must be available for disposal to avoid excessive loss of nitrate in the drainage water. Photographs courtesy of Dennis R. Keeney, University of Wisconsin.



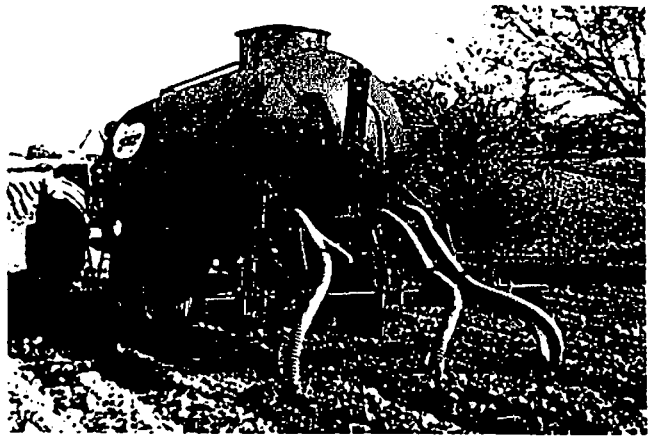
Organic wastes from humans are potential sources of both bacterial and nitrate contamination of groundwaters. These problems are largely eliminated by municipal sewage disposal systems in which part of the nitrogen is retained in the form of sludge, part is evolved in gaseous forms to the atmosphere, and part is discharged into streams. In the plant shown here, (1) is the screen, which removes rags and sand, (2) is the primary clarifier, in which suspended solids are settled out, (3) is the trickling filter, in which soluble and colloidal organic substances are decomposed by microorganisms as the liquid trickles through a bed of solids, and (4) is the final clarifier, in which the suspended microorganisms settle out. The liquid effluent from (4) is discharged into a stream. The solids from (2) and (4) are combined and pumped into (5), the primary digester, where the readily decomposable organic substances are converted to methane and carbon dioxide, then into (6), the secondary digester, in which further decomposition occurs, and the sludge is thickened by removal of water to a consistency of about 8 to 10% solids, and finally into (7), the drying beds. The drying beds are used in succession. The beds contain sand with drainage pipes at the bottom to remove the liquid. After a layer of about 8 inches of sludge is added to a bed, the bed is allowed to stand. Water gradually is lost by evaporation and drainage, and a final consistency of 25 to 28% solids is attained. Only the liquid from the final clarifier is discharged into a receiving stream. Liquids from other stages are recycled. In older plants, such as the one shown, the total nitrogen content of the water discharged is commonly 25 to 30 ppm. Much of this nitrogen may be transformed to nitrate in the stream. Except in dry areas where the water table is below the level of the stream, however, there is little contamination of groundwater because groundwater is moving into the stream from the surrounding land. Photograph courtesy of the U.S. Department of Agriculture.

tinuing applications. These substances remain in the soil and do not move downward to groundwater. Concern for the contamination of groundwater with sludge-derived nitrate has been secondary. On an area basis, the potential problem with nitrate is minor. Sommers (1977) estimated that in most states less than 1% of the agricultural land would be required for application of sewage sludge in quantities that would supply 89 pounds of available nitrogen per acre, a modest application by today's standards.

Pratt (1979) noted that for organic residues in general, the maximum amounts of different residues that can be applied to land without posing the hazard of an undue increase in the nitrate content of groundwater need to be determined on a regional or local basis. The reason is the great variation that exists in climatic

conditions, residue properties, soil properties, and management practices.

Burning organic residues effectively eliminates their potential for contributing to high concentrations of nitrate in groundwater because the nitrogen then is lost as a gas to the atmosphere. Nitrogen is a valuable resource, however, and so is the organic matter that is lost with it during burning. An additional problem with burning is that manure and sewage sludge usually must be dried artificially before they will burn, and this is expensive. As is true with fertilizers, the question of applying organic residues to soils has been decided on the basis of criteria other than the hazard of nitrate accumulation in groundwater.



Applying sewage sludge to cropland. Use of this resource on crops is productive if the sludge is not contaminated by excessive amounts of heavy metals or other substances from industrial discharges that might become toxic to crops, animals, and humans. Sewage sludge is a source of nitrate. Photograph courtesy of Dennis R. Keeney, University of Wisconsin.

Bacteria

Organic residues added to soils contain a vast array of microorganisms, some of which have the potential for causing human and animal disease. Reviews of the scientific literature by Ellis and McCalla (1976) and Reddy et al. (1981) indicate that, although microorganisms pathogenic to humans and animals do not survive well outside their hosts when in competition with naturally occurring mixed populations of microorganisms, the length of the period of survival may vary considerably with the pathogen and the circumstances.

As an indication of the microbiological quality of water for drinking, attention is focused upon the content of fecal coliform bacteria. The numbers of these bacteria present are used as an index of the contamination of the water with human or animal wastes. Most studies indicate that microorganisms present in water entering soil are effectively filtered out as the water moves through the soil. An investigation by Sopper and Kerr (1981), however, showed that coliform bacteria can move to groundwater through soil. They noted that the occurrence of large pores in soil is an important consideration in the use of soil as a microbial purification system. When soil is saturated with water, the water moves relatively fast through wormholes, old root channels, and other large pores. Bacterial contamination can be particularly evident in "fractured aquifers," such as those in karst areas, where shallow seepage water and surface water can move directly into the groundwater system, sometimes contaminating an aquifer to substantial depth. Such settings may require that the water be chlorinated or treated in some other way to make it suitable for drinking.

In a nationwide study of rural drinking water supplies, including those in the open country and in places of less than 2,500 population, Francis et al. (1982) found that 29% of all households were served by water containing more than one coliform bacterium per 100 milliliters (one-fifth pint). Fecal coliform bacteria were found in the drinking water supplies of 12% of all rural households. "Households served by dug and bored wells, wells in which the water leaves the casing above ground level, wells with inadequate covers, inadequately maintained wells, and shallow wells all tended to have high coliform levels more commonly than those served by wells without those characteristics."

The diarrhea that promotes methemoglobinemia in human infants whose formulas are made with well water contaminated with nitrate and bacteria may arise from infection with pathogenic bacteria contained in the water. In the survey by Francis et al. (1982), fecal coliform bacteria were found in the water supply of only 4.5% of rural households using community water systems. In the absence of bacterial contamination, infants can tolerate relatively high concentrations of nitrate in their drinking water (Cornblath and Hartmann, 1984; Hegesh and Shiloah, 1982).

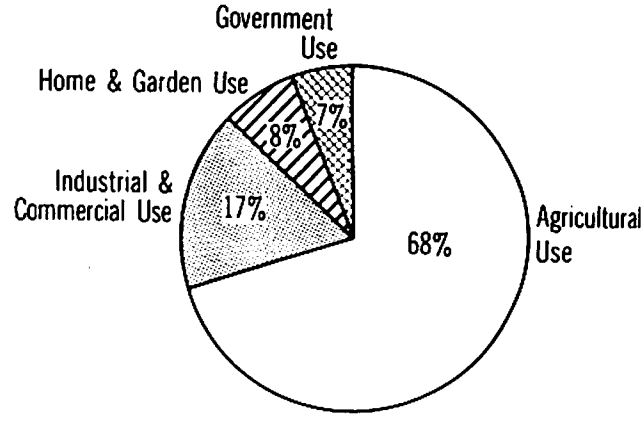
Pesticides

Chemicals have been used to combat pests since ancient times. The first account described the use of sulfur by early Greek physicians to treat human scabies (Fitzwater, 1972). Early pesticides were inorganic substances or extracts of organic substances from plants (for example, nicotine from tobacco). The pesticides developed within the last 50 years are synthetic organic compounds (Crosby et al., 1983). This report uses the common names of pesticides, but for the reader's convenience the trade names and use classes for a number of pesticides are given in Appendix D, Table 11.

The Economic Research Service (1983) estimated that 550 million pounds of active pesticidal ingredients were applied to 13 major field crops in 33 states in 1982 and that 82% of the total amount was herbicides, 13% was insecticides, 1% was fungicides, and 4% was miscellaneous pesticides. (This survey did not include California, where large amounts of pesticides are used.) According to U.S. Tariff Commission reports, the sale of synthetic insecticides, fungicides, and herbicides[2] more than doubled between 1961 and 1980. The greatest increase was in herbicides. Insecticide use dropped between 1976 and 1982 (U.S. Department of Agriculture, 1983), largely because of the introduction of new types of insecticides that are used at relatively low dosages, many at 0.1 pound or less per acre. There was little change in fungicide use.

Appendix D, Table 12, gives the domestic usage of certain pesticides, and Tables 13 and 14 (also in Appendix D) give the usage of insecticides and herbicides on certain crops. Total pesticide sales in 1983 were 1.1 billion pounds (Storck, 1984). Of the total, 68% went for agricultural use, 17% for industrial and commercial use, 8% for home and garden use, and 7% for government use.

Of principal concern in this report is the downward movement of pesticides in water through soils, and the occurrence and significance of pesticide residues in groundwater. The potential for loss of pesticides to groundwater exists wherever pesticides are used, but the extent varies with the chemical nature of the pesticide and the soil as well as with other circumstances. First to be considered will be the factors affecting the potential loss of pesticides from soil to groundwater (the properties of the principal chemical groups of herbicides, insecticides, fungicides, and nematicides as they relate to their potential for downward movement in soils are discussed briefly in Appendix A). The potential effect on humans from the occurrence of pesticide residues in groundwater used for drinking, another quite distinct matter, is then discussed.



Use of pesticides in the United States (Storck, 1984).

The potential for loss of pesticides from soil to groundwater is determined by innumerable factors and conditions, which for convenience are classified here according to their influence on four processes: volatilization (with subsequent loss to the atmosphere), decomposition, retention by the soil, and transport by water. The first two processes reduce the total amounts of pesticides available for downward movement, the third decreases the availability of the existing amounts for downward movement, and the fourth has to do with the adequacy of the processes capable of causing movement. In addition, small quantities of pesticides are removed from the land in agricultural products.

Table 1 summarizes the behavior of pesticides in terms of these four processes in five zones of the environment, namely, the atmosphere, the above-ground crop zone, the soil surface, the root zone, the unsaturated zone below root depth, and the saturated zone (groundwater). Shown in parallel with the behavior of pesticides in these zones is the behavior of water, in which most of the movement of pesticides occurs in soils and underlying materials. The individual processes are discussed in some detail in following paragraphs.

The amount applied, an important factor for water-soluble pesticides that are relatively mobile, is not considered here because normally only small quantities are applied per acre. With relatively mobile water-soluble pesticides, the potential for movement to groundwater may be much increased where large amounts have entered the soil, as in areas used for fill stations, tank

[2]Although insecticides, fungicides, and herbicides are substances used to kill insects, fungi, and higher plants, respectively, the Tariff Commission reports follow the terminology in the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), in which the following arbitrary definitions are used: (1) Insecticide — for use against insects and other invertebrate pests. (2) Fungicide — for use against plant diseases caused by fungi, bacteria, viruses, or protozoa. (3) Herbicide — for use against weeds.

Table 1. Behavior of Water and Pesticides in the Atmospheric and Soil Environments*

Environment Zone	Water Behavior	Pesticide Behavior
Atmosphere	*Addition* by evaporation from land and water surfaces, transport by air movement, and sprinkler irrigation *Loss* by precipitation, transport by air movement, condensation, and sprinkler irrigation	*Addition* by application, volatilization from plants and soils, and transport by air movement (drift) *Loss* by deposition on plants and soils, transport by air movement, and decomposition by sunlight
Above-ground crop zone	*Addition* by precipitation, sprinkler irrigation, and condensation *Loss* by throughfall, evaporation, and transpiration	*Addition* by application to foliage and by transport by air movement *Loss* by volatilization, throughfall, wash-off, and decomposition by sunlight and plant metabolism
Soil surface	*Addition* by precipitation, lateral movement on the surface, irrigation, condensation, and upward movement from the zones beneath *Loss* by evaporation, lateral movement on the surface (runoff), and movement into the zones beneath	*Addition* by application to the soil, transport by air movement, throughfall and wash-off from plants, lateral transport on the surface, and upward transport from the zones beneath *Loss* by volatilization, lateral transport on the surface (runoff), transport into the zones beneath, and decomposition by chemical and biological means *Retention* by the soil
Root zone (unsaturated soil)	*Addition* by movement from the soil surface and zones beneath *Loss* by uptake by roots and movement to the soil surface and the zones beneath	*Addition* by subsurface application and by transport from the soil surface and zones beneath *Loss* by decomposition by chemical and biological means, by uptake by roots, and by transport to the soil surface and the zones beneath *Retention* by the soil
Unsaturated zone below root depth	*Addition* by movement from the zones above and beneath *Loss* by movement into the zones above and beneath	*Addition* by transport from the zones above and beneath *Loss* by decomposition by chemical and biological means and by transport into the zones above and beneath *Retention* by the soil
Saturated zone (groundwater)	*Addition* by movement from the zones above and by lateral and vertical movement within the saturated zone *Loss* by movement into the zones above and by lateral and vertical movement within the saturated zone	*Addition* by transport from the zones above and by lateral and vertical transport in groundwater *Loss* by transport into the zones above, by lateral and vertical transport within the saturated zone, by discharge to bodies of surface water, and by decomposition by chemical and biological means *Retention* by the soil

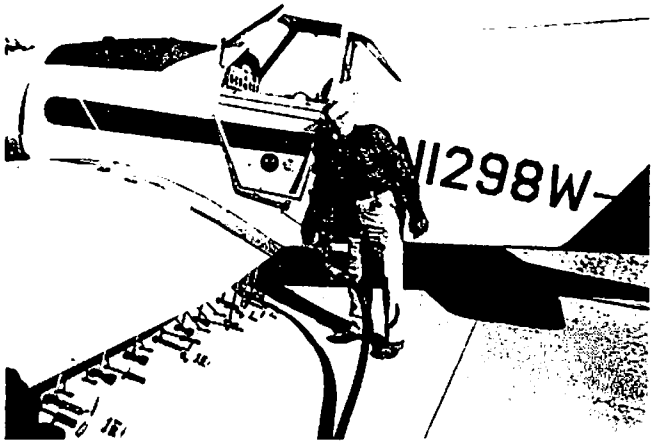
*This table is a modified version of one prepared by R. E. Green and N. P. Kefford, University of Hawaii.

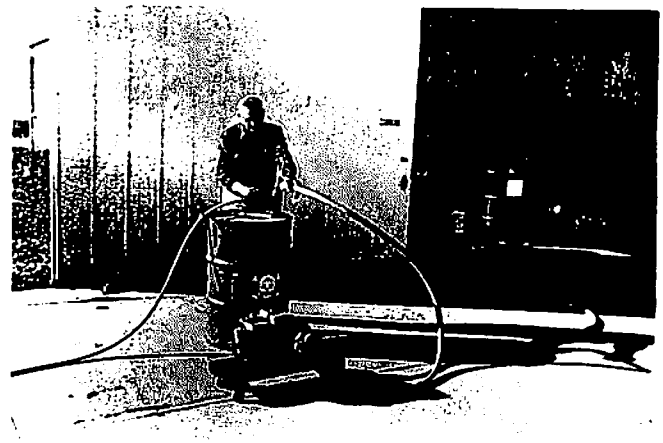
rinsing, and equipment washing. In most states, these practices must be carried out on concrete pads, and the liquid must be collected for proper disposal.

Volatilization

Substances used as fumigants must be relatively volatile so they will move in effective concentrations as gases throughout the material to be fumigated. Ethylene dibromide and dichloropropene have been used as soil fumigants by injecting them into the soil to a depth of about 6 inches to limit the rate of loss to the atmosphere. They vaporize to some extent and move in the soil as gases and also in the soil water. More volatile substances (such as methyl bromide) may be injected into the soil or, for seed beds, may be added to trays placed on the soil surface. In either case, the soil is covered by plastic sheeting for a day or more to permit the fumigant to diffuse throughout the soil and to prevent unduly rapid loss to the atmosphere. When the sheeting is removed, the residual chemical that has not been decomposed or retained by the soil is gradually lost to the atmosphere, where it is more susceptible to decomposition by sunlight. The total amount of a pesticide that has the potential for reaching groundwater obviously is reduced by the amount lost to the atmosphere.

Pesticides that are volatile and have low solubility in water tend to be lost from the soil to the atmosphere and are unlikely to be transported extensively into soil, although under exceptional circumstances small quanti-





Filling and emptying pesticide tanks on planes nowadays is usually a mechanized operation. On the left, a pilot is attaching a hose to his plane to fill the tank for another trip. On the right, he is operating a filling mechanism that transfers the pesticide to the tank in a closed-system operation. This technique is most useful for highly toxic pesticides. For less toxic materials, the pesticide concentrate may be diluted with water in an open mixing tank and then pumped into the plane. After spraying, pilots try to return to the hangar with empty tanks. If some diluted spray is left over, it may be transferred to a holding tank and used subsequently for diluting the next batch of the same kind of pesticide. To rinse the tank and nozzles, the usual procedure is to add water to the tank and to spray the very dilute solution on a field that has been sprayed recently with the same pesticide. These techniques help to limit the heavy local deposits of pesticides that might otherwise contribute to groundwater contamination at fill locations. Photographs courtesy of Edward F. Vitzthum, University of Nebraska.

ties still may reach groundwater. An example of such a pesticide is butylate, a thiocarbamate herbicide with a vapor pressure of 0.00002 atmosphere at 77° F and solubility of 45 ppm in water. Although this vapor pressure is far lower than that of water (0.031 atmosphere at 77° F), it is high for pesticides.

Ethylene dibromide (EDB) and 1,2-dibromo-3-chloropropane (DBCP) are both volatile liquids used for nematode control, and both are relatively soluble in water (4,300 and 700 ppm, respectively). The solubility in water, together with the typically large quantities applied and the low retention by soil solids, help to explain why these substances have been found in groundwater under conditions favorable for downward movement despite their volatility. All soil uses of these substances have been canceled by the Environmental Protection Agency.

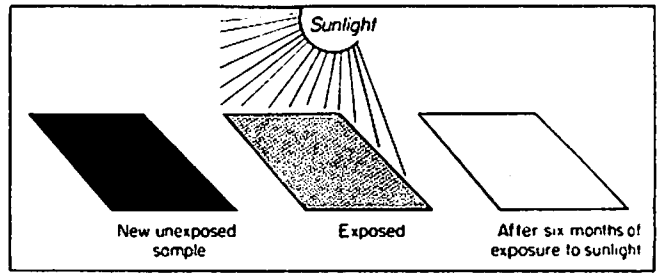
Even pesticides such as the herbicide trifluralin, which has a moderate vapor pressure for pesticides (0.0000001 atmosphere at 77° F), can undergo substantial volatilization from plant or soil surfaces. Trifluralin is a member of the major class of herbicides known as dinitroanilines. Short-range vapor movement is important for effective action of many of these compounds, and they usually are incorporated into the soil promptly to avoid excessive loss by volatilization.

Decomposition

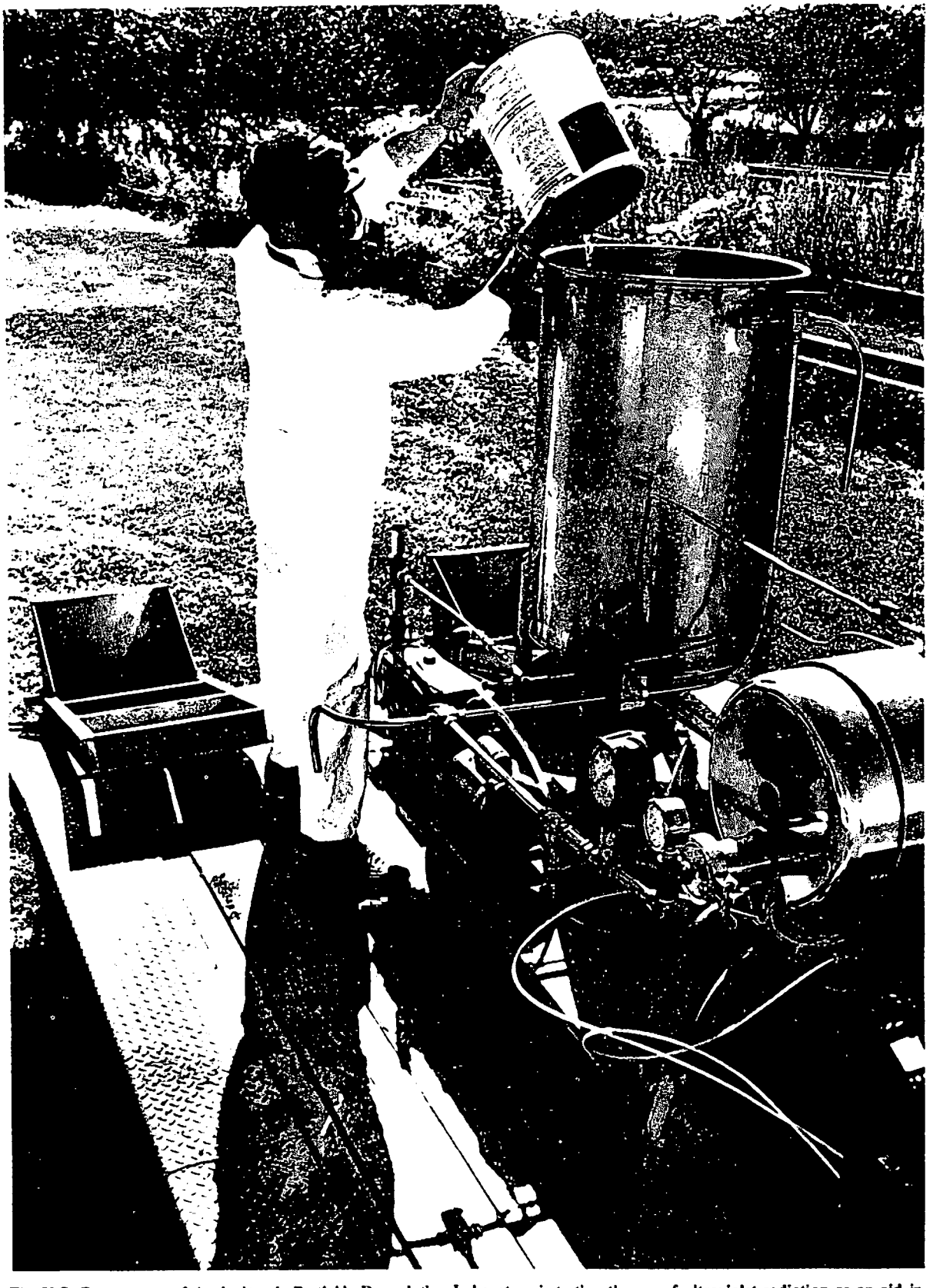
Sunlight

In addition to causing sunburn and killing bacteria, sunlight breaks down organic molecules (a process known as photodecomposition). Thus, organic pesticides that are sprayed on plants or the surface of the soil may lose effectiveness owing to photodecomposition, whereas those incorporated into the soil are protected.

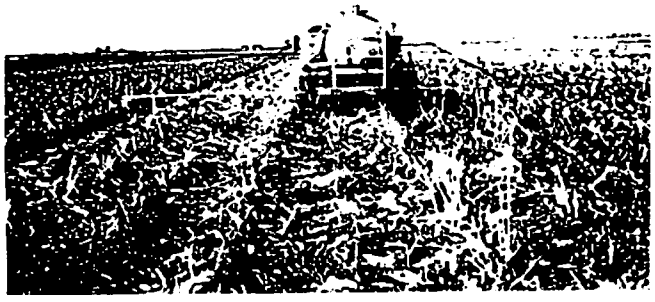
According to a review by Helling et al. (1971), studies have shown that a number of herbicides, insecticides, and fungicides are decomposed at measurable rates by the sun's energy. Organic pesticides that are not broken down by sunlight appear to be in the minority. Crosby and Li (1969) expressed the opinion that conditions can be found under which probably all present-day herbicides and plant-growth regulators will be decomposed by sunlight. Some herbicides that have been shown to be effectively degraded by the sun's energy include 2,4-D, MCPA, 2,4,5-T, silvex, and bromoxynil (Crosby and Tutass, 1965); simazine (Jordan et al., 1964a); and monuron and diuron (Jordan et al., 1964b). Wolfe et al. (1977) found that the insecticide methoxychlor is



Like the organic chemicals used to dye fabrics, organic pesticides are decomposed by exposure to sunlight. When incorporated into the soil, the pesticides are protected from light, but then are subject to decomposition by soil microorganisms. Courtesy of Terry L. Lavy, University of Arkansas.



The U.S. Department of Agriculture's Pesticide Degradation Laboratory is testing the use of ultraviolet radiation as an aid in decomposing the residues of pesticides left over from spraying operations. Here a scientist is pouring pesticide waste into a holding tank on portable apparatus that subjects the pesticide solutions to high-energy ultraviolet radiation. The partially decomposed residues are more susceptible to decomposition by microorganisms than are the original pesticides. In the next step of the process, the irradiated solutions are transferred into a disposal tank of soil and gravel for further breakdown by soil microorganisms. Photograph courtesy of the U.S. Department of Agriculture.



Applying a preemergence herbicide in preparation for the new crop. Other things equal, pesticides that are applied to soils are more likely to find their way to groundwater than are pesticides sprayed on plant foliage. Photograph courtesy of Dennis R. Keeney, University of Wisconsin.

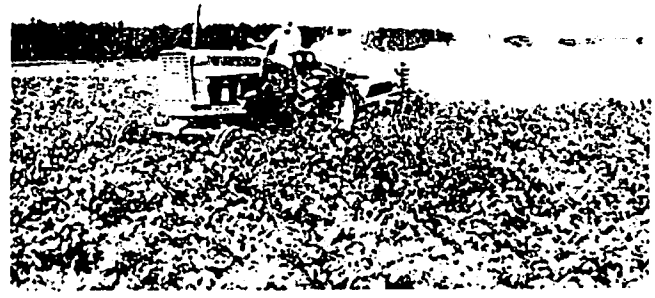
rapidly decomposed by sunlight in aquatic systems. It appears that similar breakdown products are produced by sunlight, microorganisms, and plant metabolism.

Water

Some pesticides react with water in soil to form new compounds. With a number of these pesticides, the rate of the reaction varies with the soil pH. From the standpoint of potential groundwater contamination, the products of such reactions may be placed in two classes, depending upon the pesticidal properties of the products.

The first class includes pesticides that react with water to produce new compounds that lack the pesticidal properties of the original compounds and are usually less toxic. Captan is an example. Captan reacts rapidly with water (Wolfe et al., 1976) to form an innocuous product, so that downward movement of the parent fungicide to groundwater is not a matter for concern. A second example is the nematicide DBCP. This pesticide reacts with water to produce a new compound that lacks the pesticidal properties of the parent compound and is relatively innocuous, but the rate at which this chemical reaction occurs under the usual environmental conditions in soils is inconsequential.

Pesticides of the less common second class behave in a manner opposite to that of the first. That is, reaction with water produces the parent pesticide from the compound applied in the formulation. The "decomposition" reaction thus may be described as activation. An example is sesone, a phenoxy-type herbicide that is not active until it reacts with water and forms 2,4-D in the soil. When such pesticides are used, the rate of reaction is rapid. The initial formulation may be a matter of chemical convenience, or it may have some other useful property, such as reducing the volatility to avoid undesired loss of pesticides sprayed on plants.



Potatoes often are sprayed at weekly intervals to control late blight, a fungal disease. To control this disease, the plants must be sprayed before the disease appears because the fungus reproduces rapidly, and the disease is so devastating that available fungicides are not capable of arresting it, once infection has occurred. Although in some situations fungicides may be applied frequently, members of this class of pesticides have not been implicated in groundwater contamination, perhaps in part because their solubility in water is usually low. Additionally, fungicides that are applied to plant foliage may be decomposed by sunlight. Photograph courtesy of Dennis R. Keeney, University of Wisconsin.

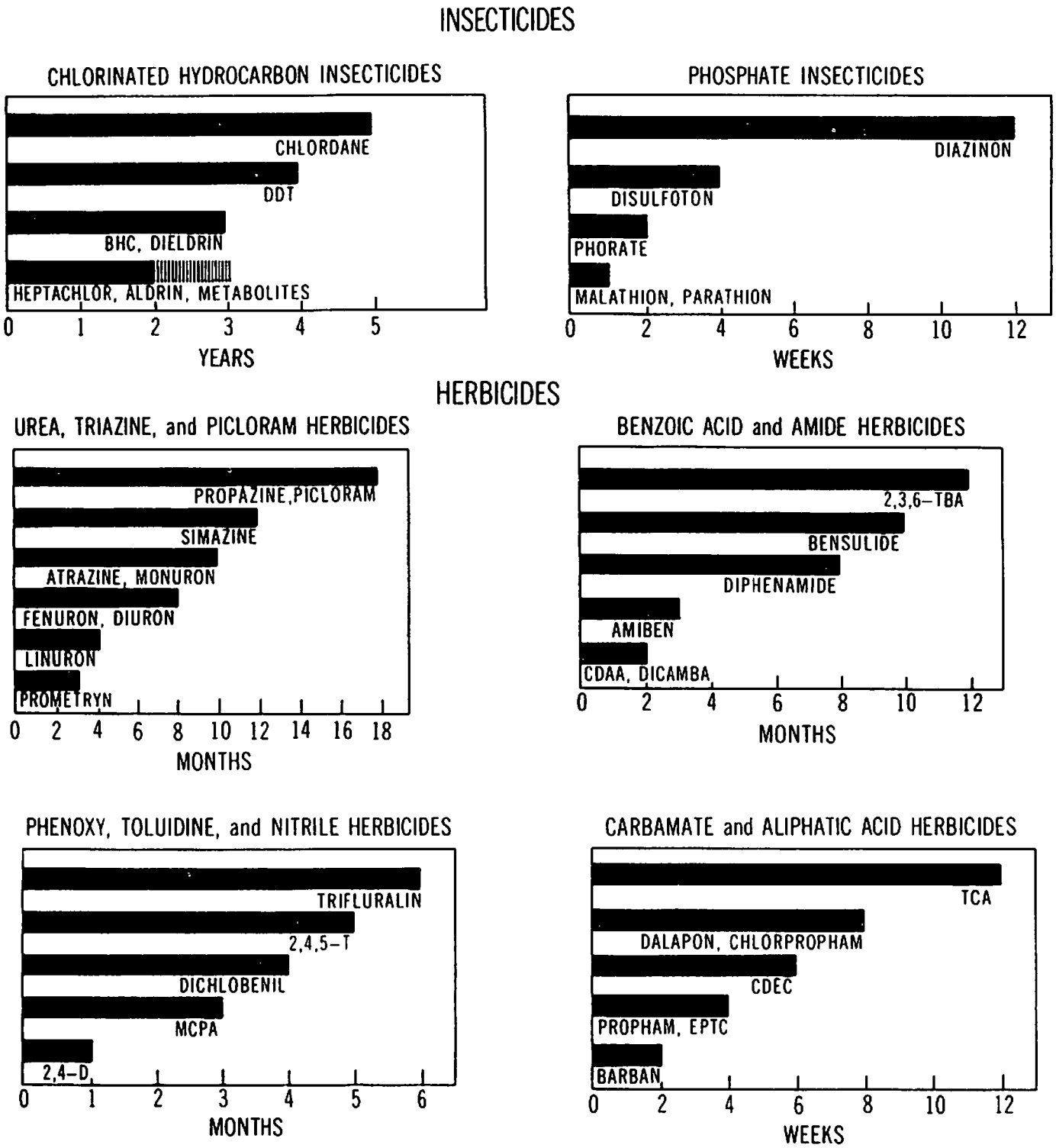
Microorganisms

Reaction of pesticides with water is a chemical process that may or may not be hastened by the associated microbial activity in soils. The predominant means of pesticide breakdown in soils is biochemical processes carried out for the most part by microorganisms and to a smaller extent by plants (pesticides taken up by plants may be broken down by plant enzymes). Fertile soils contain millions of microorganisms per ounce of surface soil. Organic pesticides may serve as sources of nutrients and energy for microorganisms.

The rate of microbiological breakdown of pesticides varies with their chemical structure. See Appendix B for a brief discussion.

How rapidly a given pesticide is broken down by soil microorganisms will depend upon how much of it is present and upon various other factors. These include the presence or absence of free oxygen, the temperature, water content, pH, prior use of pesticides, and supply of nutrients and energy, as well as the plant cover.

The persistence of pesticides in soils under a given set of conditions is often expressed in terms of the length of time required for 50% of the pesticide to decompose to products other than the pesticidal substance as added or as formed in an activation reaction after addition. If the 50% decomposition time is short, e.g., 1 to 2 weeks, no appreciable movement of the pesticide to groundwater should occur in most instances despite an otherwise high potential for downward movement. The reduction in the total amounts of easily decomposable pesticides in soils is probably the major reason that certain pesticides



Persistence of certain pesticides in soils. The lengths of the bars represent the time required for loss of 75 to 100% of the biological activity under agricultural conditions with normal rates of application. The values were derived from a review of approximately 80 sources concerned with pesticide persistence in soils. (Kearney et al., 1969)

of moderate to high mobility have not been detected in groundwater.

In a summary of 12 studies, Tinsley (1979) noted that the 50% decomposition times for certain pesticides increased in the order malathion, 2,4-D, diazinon, atrazine, diuron, DDT. Wide differences in the absolute values were found, depending upon the experimental conditions. For example, the 50% decomposition time for DDT was 240 days in a tropical environment, 3840 days in a temperate environment, and 33 days in a laboratory test done in the absence of free oxygen. The 50% decomposition times were greater

when measured in subsoil samples than in surface soil samples, presumably because of lesser microbiological activity in the subsoil samples. The accompanying figure shows the relative persistence in soils of a number of pesticides grouped according to chemical classes. These results represent a summary of tests on various soils under agricultural conditions.

Retention by Soil

Retention of organic pesticides by soil is generally referred to as ***adsorption***. Adsorption decreases the concentration of pesticides in solution and thus decreases their availability for downward movement in drainage water. It also increases the length of time during which they are subject to decomposition by microorganisms in the more active surface soil, although the rate of decomposition may be decreased.

Pesticides are retained by soils to different degrees, depending upon the properties of the pesticides, the soils, and their interaction. Pesticide-related properties are reviewed briefly in Appendix C. The soil property of greatest importance for most pesticides is the organic matter content. The greater the organic matter content, the greater is the adsorption. The capacity of the soil to hold positively charged ions in an exchangeable form is important with paraquat and other pesticides that are positively charged. Soil pH also is of some importance. Adsorption increases with decreasing soil pH for ionizable pesticides, including 2,4-D, 2,4,5-T, picloram, and atrazine.

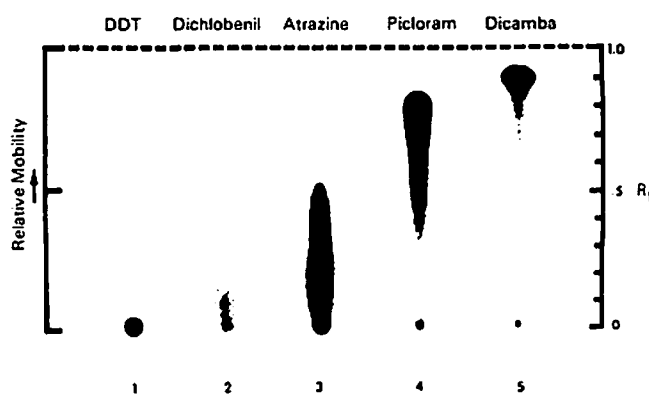
Transport by Water

For highly volatile pesticides, such as EDB, diffusion through soil as a gas can be rapid as long as enough of the pesticide remains to produce high concentrations of the gaseous form in the soil air. Below these concentrations, and for most pesticides, which have little tendency to vaporize, the diffusion that occurs in the soil water is too limited to be of importance as a mechanism for transporting pesticides to groundwater. Of principal importance in transport is movement of dissolved pesticides in the water as it percolates downward through the soil.

To compare the tendency of different pesticides to move down through soils to groundwater and to evaluate the differences among soils, the best results are obtained from suitable tests under uniform conditions in the laboratory or in the field (Helling and Dragun, 1981; Weber and Whitacre, 1982).

Table 2 groups a large number of pesticides into five mobility classes on the basis of many experiments by different scientists in which the relative movement of various pesticides through soils with moving water was determined. The results of these empirical measurements are in good agreement with the values for pesticide adsorption in Appendix C. As indicators of the relative potentials for movement of the various pesticides to groundwater, values such as those summarized in Table 2 have the disadvantage of resulting from short-term measurements that do not take into full account the losses of pesticides from soils by volatilization and decomposition that may take place over time and reduce the potential for groundwater contamination.

There are many possible combinations of conditions ranging from (1) pesticides that are persistent and mobile applied to soils that have little adsorption capacity with water tables that are shallow and precipitation that causes much movement of water to the groundwater every year to (2) pesticides that are rapidly decomposed or strongly adsorbed, applied to soils that have considerable adsorption capacity with water tables that are deep, and precipitation so limited that the amount of water reaching the water table is negligible. An Environmental Protection Agency official has estimated (Pesticide and Toxic Chemical News, 1983) that as many as 50 of the approximately 1450 registered active pesticidal ingredients (of which 435 have established tolerances permitting use on food crops) possess the



Relative mobilities of different pesticides in Hagerstown silty clay loam soil. DDT is essentially immobile, and dicamba is very mobile. The numbers below the individual pesticides refer to the five classes of mobility in Table 2. The figure was obtained by placing a small amount of each pesticide (synthesized in radioactive form) along the R_f = 0 line on a thin layer of soil that had been dried on a glass plate. The bottom of the plate then was immersed in water in a closed chamber to inhibit evaporation, and the water was allowed to move upward by capillarity. When the water reached the height indicated by R_f = 1.0, the plate was removed from the chamber and dried. Sensitive photographic film then was placed against the soil, and the blackened zones that resulted upon development of the film after a few days of exposure to the radiation showed the locations of the pesticides. As a result of the relatively high solubility of dicamba and its slight adsorption by soil, this pesticide moved almost as far as the water, whereas DDT remained at its original location. High mobilities of pesticides by this technique indicate high susceptibility to downward movement in percolating water. The limited blackening of the film by dichlobenil is a consequence of loss of part of this pesticide by volatilization. Autoradiograph courtesy of Charles S. Helling, U.S. Department of Agriculture. The autoradiograph was published in an article by Helling (1971).

Table 2. Relative Mobility of Pesticides in Soils[a] (Helling et al., 1971)

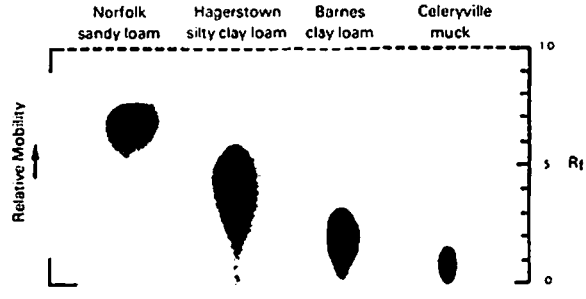
Very Mobile	Moderately Mobile	Slightly Mobile	Nearly Immobile	Immobile
TCA	Picloram	Propachlor[c]	Siduron	Neburon
Dalapon	Fenac	Fenuron	Bensulide	Chloroxuron
2,3,6-TBA[b]	Pyrichlor	Prometone	Prometryn	DCPA
Tricamba[c]	MCPA	Naptalam	Terbutryn	Lindane
Dicamba	Amitrole	2,4,5-T	Propanil	Phorate
Chloramben	2,4-D	Terbacil	Diuron	Parathion
	Dinoseb	Propham	Linuron	Disulfoton
	Bromacil	Fluometuron	Pyrazon	Diquat
		Norea	Molinate	Chlordimeform
		Diphenamid	EPTC	Dichlormate[c]
		Thionazin[c]	Chlorthiamid	Ethion
		Endothall	Dichlobenil	Zineb
		Monuron	Vemolate	Nitralin
		Atratone	Pebulate	Fluorodifen
		Cyanazine	Chlorpropham	ACNQ[c]
		Atrazine	Azinphosmethyl	Morestan
		Simazine	Diazinon	Isodrin[b]
		Ipazine		Benomyl
		Alachlor		Dieldrin[b]
		Ametryn		Chloroneb
		Propazine		Paraquat
		Trietazine		Trifluralin
				Benefin
				Heptachlor[b]
				Endrin[b]
				Aldrin[b]
				Chlordane
				Toxaphene[b]
				DDT[b]

[a]Ranked according to estimated order of decreasing mobility within each class.
[b]Most or all uses canceled by the Environmental Protection Agency as of November 1984.
[c]Not used at present in the United States.

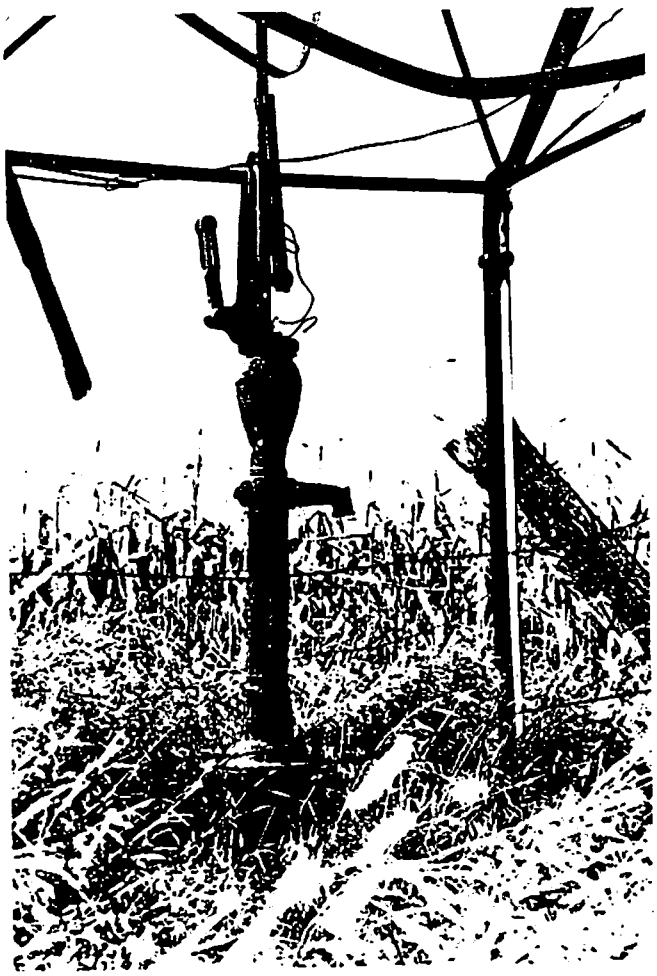
potential for detection in groundwater under certain conditions. The potential of these 50 pesticides for occurrence in groundwater is greatest when the prevailing conditions of soil and environment are those enumerated in (1).

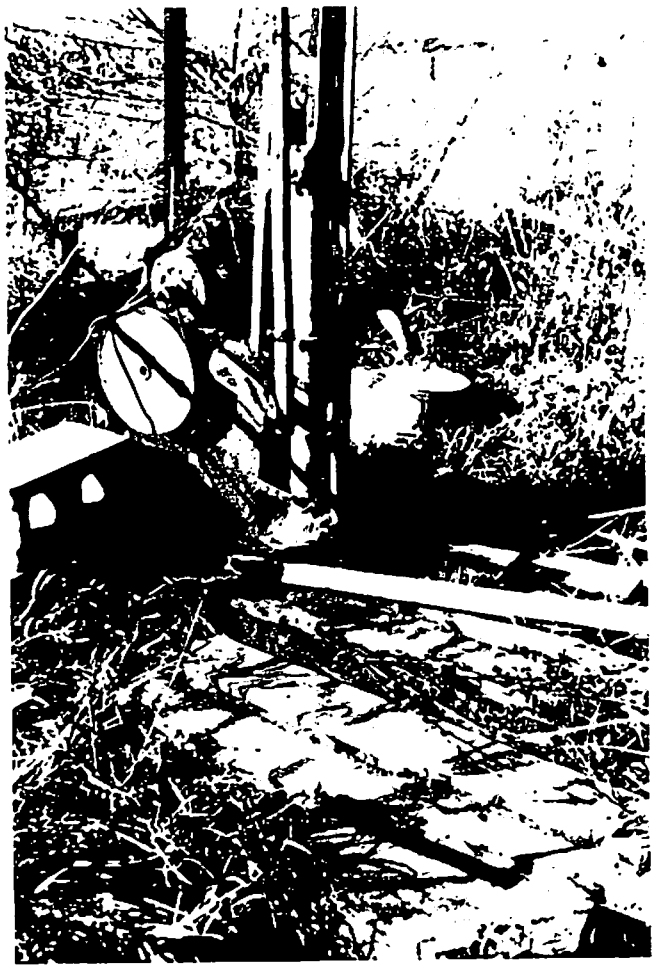
Occurrence in Groundwater

The detection of a number of pesticides in groundwater in recent years has been made possible by the development of analytical methods capable of measuring concentrations in the parts per billion (ppb) range (1000 ppb = 1 ppm) or even lower. For the most part, the locations for analysis have been selected because of relatively heavy usage of pesticides and conditions favorable for movement of the pesticides to groundwater. An example is the detection of EDB in groundwater in Florida (Florida Department of Health and Rehabilitative Services, 1984), where four to five times the normal application had been used over a 20-year period and where the soils have a very low capacity to retain pesticides against downward movement under the influence of the relatively heavy rainfall. These heavy applications were made in buffer strips around nematode-infested citrus groves and portions of groves, not only to kill the nematodes, but also to kill the citrus roots and prevent spread of the infestation to new areas. The nematodes move along the roots, but otherwise are essentially immobile.



Relative mobilities of propham herbicide in five soils. The range is from almost no mobility in Celeryville muck soil to moderate mobility in Norfolk sandy loam soil. The organic matter content of the soils increases from left to right, and the mobility decreases in the same order. Organic matter is usually the most important soil constituent in retaining organic pesticides against movement with percolating water. The locations of the herbicide after movement with water from the original placements along the $R_f = 0$ line were determined by its radioactivity. The procedure was analogous to that described for different pesticides on the preceding page. Autoradiographs courtesy of Charles S. Helling, U.S. Department of Agriculture.





Two old, unused "first generation" wells. The pumps were operated by windmills, the one on the right being updated later with an electric motor. Such wells are generally shallow and inadequately protected from surface contamination. Photographs courtesy of Thomas D. Glanville, Iowa State University.

Where pesticides have been detected in wells used for drinking water, the affected localities almost always have been in heavily treated agricultural areas where rural homes are dependent upon groundwater from private wells sited in or directly adjacent to repeatedly treated fields and drilled only to shallow water-table aquifers.

The Environmental Protection Agency (Cohen et al., 1984) has listed 12 pesticides that have been detected in drinking water wells under certain conditions from the limited monitoring that has been done. Table 3 gives typical positive results noted for these pesticides found in groundwater from agricultural uses. Most of the pesticides listed are applied to the soil surface or are incorporated into the soil, as opposed to being sprayed onto growing crops. (Exceptions include the uses of carbofuran and oxamyl above ground as insecticides and the uses of atrazine and dinoseb as herbicides applied to growing weeds.)

Health Effects in Drinking Water

Evaluating the potential health effects of residues of pesticides in drinking water, food, and other possible sources is a continuing goal of regulatory and public health agencies. The no-observable-effect level (NOEL) of intake is a key concept in this process. The NOEL for each pesticide is determined by dosing laboratory animals with different amounts of the pesticide in question over a lifetime. The responses then are plotted against the doses and, by interpolation, the maximum dose at which no observable detrimental effect can be observed is determined. The value thus found for the NOEL in the more sensitive of two species tested is divided by an arbitrary safety factor to obtain the acceptable daily intake (ADI). The "standard" value for the safety factor is 100, which means that if humans have the same sensitivity as the test species the intake could be 100 times greater than the ADI before any observable detrimental effect could be observed. In practice, the safety factor may be less than 100 in instances in which there is considerable evidence from human studies, and it may also be greater than 100 — often as great as 1,000. The ADI is expressed in milligrams of the pesticide per kilogram of body weight (parts of pesticide per million of body weight) per day.

Table 3. Typical Positive Results for Pesticides Found in Drinking Water Wells From Agricultural Uses and Suggested Health-Advisory Concentrations for These Pesticides in Drinking Water (Adapted From Cohen et al., 1984)

Pesticide	Chemical Class	States in Which Identified	Typical Positive Value, ppb[a]	Suggested Health-Advisory Concentration, ppb
Alachlor	Acetanilide	NE	0.4	700[b]
Aldicarb (sulfoxide & sulfone)	Oxime carbamate	NY, WI, FL, MO, AZ, ME, VA CA, NC, NJ, OR, TX, WA	1 - 50	10 - 50
Atrazine	Triazine	NE, WI, IA	0.3 - 3	150[b]
Bromacil	Uracil	FL	300	7.5[b]
Carbofuran	Carbamate	NY, WI	1 - 5	50[c]
DCPA (& metabolites)	Phthalate	NY	50 - 700	5000[c]
DBCP (1,2-dibromo-3-chloropropane)	Chlorinated hydrocarbon	CA, AZ, HI SC, MD	0.02 - 20	0.05
D-D[f] (1,2-dichloropropane and related hydrocarbons)	Chlorinated hydrocarbon	MD, NY, CA	1 - 50	5 - 10
EDB (1,2-dibromoethane)	Chlorinated hydrocarbon	GA, HI, FL, CA	0.05 - 20	0[d]
Dinoseb	Dinitrophenol	NY	1 - 5	12.5[e]
Oxamyl	Oxime carbamate	NY	5 - 65	250[e]
Simazine	Triazine	CA	1 - 2	1500[b]

[a]These results represent findings by adequate analytical methods and consistent with expectations based on chemical properties and use patterns.
[b]From National Research Council (1977).
[c]Unofficial.
[d]Detection limit = 0.02 to 0.1 ppb.
[e]Calculated from the U.S. Environmental Protection Agency's ADI value on the basis of EPA's convention that a 22-pound child will consume 1.06 quarts of water per day.
[f]The most active ingredient in D-D is 1,3-dichloropropene. This compound, which has not been detected in groundwater, is marketed currently under other names and without 1,2-dichloropropane.

On the basis of the daily intake of 1.06 quarts of water by a 22-pound child or 2.12 quarts by a 154-pound adult, the concentration of the pesticide in the water required to provide an ADI equivalent then is calculated, and this concentration is used as a suggested "health-advisory level." Suggested health-advisory concentrations for pesticides found in drinking water are given in Table 3. Several of the pesticides listed in this table are discussed briefly in the following paragraphs.

The product D-D is a mixture of 1,2-dichloropropane, 1,3-dichloropropene, and related hydrocarbons that has been used at 7 to 60 gallons per acre since the late 1940s as a preplant fumigant to control nematodes on certain vegetable and field crops. It is lost from the soil by volatilization and is decomposed in the soil, primarily by microbial action. Low temperatures and high rainfall extend its residual life. Mainly because of its relatively high solubility in water, 1,2-dichloropropane has been detected in groundwater. The maximum concentrations found have exceeded the suggested health-advisory concentration. D-D has been withdrawn from the market for economic reasons.

Aldicarb and its decomposition products are soluble in water and are not adsorbed by mineral soils, although they may be held by soils of high organic matter content (Chesters et al., 1982). In susceptible areas, residues have been detected in groundwater at concentrations above the Environmental Protection Agency's suggested health-advisory concentration of 10 ppb (Baier and Robbins, 1982; Rothschild et al., 1982; Zaki et al., 1982). Steps to prevent recurrence of such incidents have been taken in several states (Florida Department of Agriculture and Consumer Services, 1983; Jackson and Weberdorfer, 1983; Maine Department of Agriculture, Food and Rural Resources, 1983; Wisconsin Department of Agriculture, Trade & Consumer Protection, 1983; Zaki et al., 1982).

When ingested by humans, aldicarb depresses the activity of cholinesterase, an enzyme involved in transmission of nerve impulses. But the effect is temporary and reversible, and there are no known long-lasting effects (Wilkinson et al., 1984). A NOEL of 0.125 mg/kg/day is generally accepted, and safety factors of

25 to 125 have been applied to obtain an ADI of 0.001 to 0.005 mg/kg/day. From this, suggested health advisory concentrations of 10 to 50 ppb for drinking water may be derived (Food and Agriculture Organization of the United Nations, 1983; Johnson, 1981; National Research Council, 1977). New York uses 7 ppb.

Oxamyl is a general-purpose insecticide and nematicide. Although this pesticide is highly soluble in water and is not adsorbed by soil, its uptake by plants and breakdown in soil are so rapid that little residue is available for transport to groundwater even with heavy rainfall (Harvey and Han, 1978). In the sandy soils on Long Island, fewer than 100 of 6,000 wells tested contained concentrations of oxamyl above the 1 ppb limit for analytical detection. The concentrations found in well water are far below the suggested health advisory concentration of 875 ppb that may be derived by EPA's conventions.[3] Oxamyl is acutely toxic in excess, but it has no known long-lasting or delayed effects.

Atrazine is a herbicide commonly used to control weeds in corn. Low concentrations of atrazine have been reported in shallow groundwater in several states (Junk et al., 1980; Spalding et al., 1980; Wehtje et al., 1983; Richard et al., 1975; Hallberg et al., 1983; Libra et al., 1984). The NOEL value for atrazine in the dog is 3.75 mg/kg/day, from which an ADI of 0.0375 mg/kg/day is derived, using a 100-fold safety factor. A health-advisory concentration of 150 ppb in drinking water has been suggested by the National Research Council (1977). The values commonly found are far below the suggested health-advisory concentration. The highest value found, 174 ppb, was reported by Schwab et al., (1973) in the water from tile drains in Ohio. Tile effluents usually are not classified as groundwater, but they are derived from some distance below the soil surface.

Although suggested health-advisory concentrations have been developed for several pesticides (National Research Council, 1977), these concentrations are not available for many others. Recently the Environmental Protection Agency has shown increased interest in establishing ADIs and health-advisory concentrations for pesticides detected in groundwater as well as interest in developing procedures for monitoring the pesticide content of groundwater.

When there is concern for the possibility that unfavorable health effects may develop from pesticide accumulation in groundwater, test measurements can be made in the field to determine the presence and concentrations of pesticides at different locations from the surface of the soil downward. These observations must be correlated with other measurements to obtain an indication of the potential.

If the concentration of a pesticide in groundwater used for drinking approaches the health-advisory concentration, further increases in the concentration may be limited by discontinuing the use of this pesticide in the affected area. Integrated pest management (IPM) may suggest ways to control the target pest using lower amounts of the chemical without loss in efficiency of pest control. Environmental warnings on pesticide labels should always be heeded. Despite the existence of residues of certain pesticides in some groundwaters in concentrations exceeding the health-advisory concentrations, no verified adverse health effects appear to be on record as a result of pesticide residues in groundwater used for drinking. One reason may be the safety factors involved in the health-advisory concentrations. For a substance for which the safety factor of 100 has been used, a 22-pound child would have to drink 26 gallons of water with the health-advisory concentration per day every day to ingest an amount of the pesticide equivalent to the maximum daily intake that produced no observable detrimental effect in the test animal. A 154-pound adult would have to drink 53 gallons per day.

To reduce the concentrations of pesticides in drinking water, one may substitute alternative water sources, pass the water through an activated carbon filter to remove the pesticide residues, distill the water, or use ultraviolet light to decompose the pesticide residues. Wells may be tested at intervals to determine when corrective measures may be discontinued.

[3]A NOEL of 50 ppm in the diet of rats is the basis for EPA's ADI value of 0.025 mg/kg/day. Fifty ppm in the diet of rats is approximately 2.5 mg/kg/day. Divided by a safety factor of 100, this yields 0.025 mg/kg/day. A 10-kg (22 pound) child consuming 1 liter (1.06 quarts) of water per day would ingest this amount of the pesticide if the water contained 10 x 0.025 = 0.25 mg per liter (ppm) or 250 ppb.

Information Needs

Perhaps the major need is for official health-advisory concentrations for individual pesticides. Analytical techniques are capable of detecting pesticides at concentrations far below those of biological significance. When no official guidelines are established, however, members of the public are not inclined to accept any concentration as safe, no matter how low it may be, because they have no basis for judgment. The basic information on the no-observable-effect level must be available before a pesticide is registered, and the Environmental Protection Agency publishes this value and the acceptable daily intake in the *Federal Register* when

it establishes tolerances for pesticide residues in raw agricultural commodities. For pesticides approved since these information requirements were established, therefore, all that is lacking is an official designation by the Environmental Protection Agency of the health-advisory concentrations for these pesticides in drinking water.

From the physical standpoint, there are additional information needs. These have to do with the behavior of agricultural chemicals in the environment. Much is known about these chemicals and their potential for moving to groundwater, but it is evident from the coverage of the subject in this report that the knowledge is mostly qualitative. The interactions of the various processes and factors are not well understood. Quantitative predictions for specific circumstances are of limited accuracy. The value of the capability for quantitative predictions is that when the appropriate measurements are made, one can predict what would happen under specific circumstances of interest without resorting to experimentation or trial and error. One can then avoid use of the chemicals under conditions that in the end would turn out to be inappropriate. Information needs considered important for improving quantitative predictions in the future include the following:

1. Improved concepts are needed to clarify the movement of agricultural chemicals through soil and the unsaturated zone below, and in groundwater.

2. More information is needed on the fate of agricultural chemicals applied to soils to answer questions such as the following: Does a particular chemical break down to harmless products in the soil, how long does the decomposition process require, what causes the decomposition, and what environmental conditions affect the decomposition? Does a particular chemical move through the soil to reach groundwater, in what concentration does it move, and how long does it persist in groundwater?

3. As a follow-up on item 2, information is needed on the conditions favorable for breakdown of chemicals by soil microorganisms, including the importance of microbial activity at lower depths in soils and possible ways to manipulate the soil microbial population to decompose pesticide residues in soils and waters.

4. Information on management techniques to reduce the potential for downward movement of agricultural chemicals is needed. Answers are needed to questions about the effects of irrigation scheduling, methods of applying chemicals (including application in the irrigation water), and the significance of different chemical formulations.

5. Improved methods are needed to assess hydrogeologic and environmental variability.

6. Mathematical models suitable for making accurate computerized projections of long-term movement of chemicals in the environment under different circumstances are needed.

7. More complete information is needed on the potential health effects of some agricultural chemicals.

8. Improved communication of research findings to the public is needed to provide for better understanding and decision making.

Research on these points is underway for many chemicals. Results are generally reassuring, but work must be continued to confirm that residues detected are not a valid cause for public concern with regard to use of water for drinking.

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low water solubility and strong tendency to adsorb to soil have virtually precluded their appearance as groundwater contaminants as a result of agricultural applications.

Organophosphorus insecticides present a wide spectrum of both physicochemical properties and agricultural uses. They are generally less persistent than organochlorines and have been used to replace some organochlorine insecticides no longer permitted in the United States. Breakdown in soil typically begins with reaction with water by natural and microbial hydrolysis. Examples of organophosphorus compounds include mevinphos, malathion, and methyl parathion, listed in order of increasing stability. This class of insecticides has not been linked with groundwater problems.

Three important members of the carbamate group are carbaryl, carbofuran, and aldicarb. These are listed in order of increasing water solubility, susceptibility to hydrolysis, and mammalian toxicity. Aldicarb (used also as a nematicide) is readily oxidized in soil. Aldicarb, its metabolites, and carbofuran, have all been detected in some groundwaters.

Pyrethroids include both natural products and the newer family of synthetic derivatives, e.g., permethrin, cypermethrin, and fenvalerate. They are usually degraded quickly in soil and have presented no leaching threat.

Fungicides

This group of pesticides has not been implicated in groundwater pollution problems, perhaps in part because water solubility is usually low. The dithiocarbamates, such as maneb, are relatively unstable in soil or water, as is the benzimidazole benomyl, which readily hydrolyzes to a fungitoxic product. Binapacryl, a dinitrophenol ester, probably hydrolyzes to form the free phenol, identical in structure to the herbicide dinoseb. Only after such a transformation might there be some potential for leaching. A few other chemical groups include phthalimides, organotins, quinones, pyrimidines, and various other aromatic and nonaromatic fungicides.

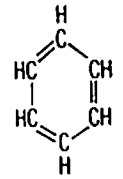
Nematicides

Of the relatively small number of nematicides, at least four have, under certain circumstances, leached to groundwater. They include the carbamates aldicarb (discussed earlier as an insecticide) and oxamyl; and the halogenated aliphatics EDB and DBCP. These two aliphatics are both volatile liquids, relatively persistent in soil, and soluble in water (4300 and 700 ppm, respectively). These factors, coupled with the apparently low soil adsorption and typically high application rates, help to explain why extensive migration of these pesticides might occur.

B. Chemical Structure of Pesticides and Rate of Microbial Decomposition in Soils

The rate of microbiological breakdown of pesticides in soils varies with the chemical structure of the pesticides. A rough rule is that the rate of breakdown decreases as halogen (chlorine, bromine, fluorine) atoms substitute increasingly for hydrogen atoms. For example, methane (CH_4, the principal constituent of natural gas) is readily transformed to carbon dioxide and water by microorganisms in the presence of free oxygen. When a bromine atom is substituted for one of the hydrogen atoms to produce the fumigant methyl bromide (CH_3Br), the rate of breakdown of the compound by microorganisms is decreased. In one test, 20 days were required for half of the amount of the compound to be broken down in soil (Mabey and Mill, 1978). When all four of the hydrogen atoms are substituted by chlorine atoms to produce carbon tetrachloride (CCl_4), the compound becomes almost unassailable. In the same test with methyl bromide, the rate of breakdown of carbon tetrachloride was so slow that an estimated 7,000 years would have been required for decomposition of half of the amount added.

For the many pesticides that are chemical derivatives of benzene (C_6H_6), a compound in which one hydrogen



Benzene

atom is attached to each of six carbon atoms joined in a ring structure, splitting of the ring by microbial action occurs where two of the hydrogens have been substituted by -OH groups and where the substitution occurs on adjacent carbon atoms or on carbon atoms separated by two other carbon atoms. Generally, ring cleavage occurs only after other reactions, such as splitting off of the acetic acid sidechain in the herbicide 2,4-D.

C. Retention of Organic Pesticides by Soils

Retention of organic pesticides by soils, generally referred to as **adsorption**, decreases their concentration in solution. Chemical characteristics of pesticides generally associated with greater adsorption include (1) high molecular weight, (2) a tendency to form positively charged pesticidal ions (cations) in water, and (3) the presence of chemical groups that increase the affinity of the pesticide molecules for soil surfaces.

Cations may be formed as a result of affinity of one or more parts of a pesticide molecule for hydrogen of

water to form, for example, $R\text{-}NH_2\text{-}H^+ + OH^-$, where R refers to the carbon-containing portion of the pesticide molecule. Pesticidal cations are retained in exchangeable form by the clay and organic matter in soils (as are the inorganic cations, including calcium, magnesium, potassium, and sodium) and do not move downward in drainage water as readily as do their neutral counterparts. The tendency of pesticides to undergo the reaction described to become positively charged ions increases with the acidity of the soil. The chemical groups referred to in (3) include hydroxyl (-OH) and carbonyl ($\geq C=O$) groups and molecular structures in which two double bonds between carbon atoms are separated by a single bond (e.g., -CH = CH-CH = CH-.

In addition to the structural properties of pesticide molecules that are related to their adsorption by soils, relationships have been found with certain physicochemical properties. One of these is the solubility. Within series of chemically similar compounds, the greater the solubility in water, the lower is the adsorption or retention of the pesticide by the soil.

An index of the tendency of pesticides to be adsorbed by the organic matter in soil is provided by the octanol: water partition coefficient (Karickhoff et al., 1979). Octanol is an alcohol that does not mix with water. When these two liquids are shaken up together and allowed to separate, the ratio of the concentration of a pesticide in the octanol to that in the water will vary with the pesticide. Within groups of chemically similar pesticides, the higher is the ratio of the concentration in octanol to that in water, the greater is the tendency of the pesticide to be adsorbed by soil organic matter. For example, the ratios for malathion and parathion are 790 and 6,300, respectively (Verschuren, 1983). The relative values for these pesticides show the same trend as the relative adsorption of the pesticides by soils. DDT, which has a dissimilar structure and is far more strongly adsorbed by soils, has an octanol:water partition coefficient of 1,600,000.

Some pesticides have a tendency to release a hydrogen ion (H^+) and to become a negatively charged pesticidal ion (anion) in water. The adsorption of pesticidal anions by soils is relatively weak. Thus, pesticides that form anions tend to have higher potential for downward movement in water than do those that form cations. The tendency of pesticides to release a hydrogen ion and form a pesticidal anion is a matter of degree and is affected by the pH of the soil. For example, at pH 4.6, 98% of the herbicide 2,4-D in solution exists as a pesticidal anion, but only 50% of the dinoseb in solution exists as an anion. As the pH increases, the proportion of the dissolved ionic pesticides found in negative pesticidal ions increases. Thus, at pH 7 the proportion of the dissolved 2,4-D that exists as a pesticidal anion will be 99.99%, and the proportion of the dissolved dinoseb that exists as a pesticidal anion will be 99.6%. These figures are based upon data obtained by Cessna and Grover (1978).

Although the foregoing characteristics are of value in suggesting the comparative adsorption of different pesticides by soils, it is generally more satisfactory to make direct measurements. A common procedure is to allow aqueous solutions of individual pesticides in different concentrations to interact with a given soil and to calculate from the measured values of adsorption a "Freundlich adsorption coefficient" or K.

The content of organic matter or organic carbon is most often the soil characteristic that correlates best with pesticide adsorption evaluated by the Freundlich adsorption coefficient, which implies that the organic matter is the soil constituent primarily responsible for pesticide adsorption. Most of the differences in K values among soils are attributable to differences in content of organic matter. As a consequence, dividing the K values by the corresponding values for organic matter or organic carbon yields numbers for different soils that are relatively concordant and more characteristic of the pesticides than are the original K values. Table C1 provides a comparison of different pesticides in these terms. Such data suggest that lindane, trifluralin, parathion, and DDT would be strongly adsorbed by soil organic matter and that they would not be subject to downward movement in drainage water to any significant degree. And dicamba, *cis*-1,3-dichloropropene, and EDB, at the other end of the spectrum, would be lost relatively readily. Fortunately, other factors, especially decomposition, intervene to reduce the potential loss of these weakly adsorbed pesticides to groundwater. Excessive migration of dicamba, for example, has led to injury to deep-rooted plants, but dicamba does not seem to have been found in groundwater.

The significance of the retention of pesticides by soils as a factor influencing the downward movement of pesticides through soils in percolating water may be inferred from a comparison of Table C2 with Table 2 shown in the text on page 45. Table C2 shows mathematically derived estimates of the relative mobility of various pesticides based on a predictive equation including a term for pesticide adsorption by soil and a term for the tendency of pesticides to be lost from soil to the atmosphere. The latter term is the ratio of the vapor pressure or volatility of a pesticide to its solubility in water. In general, the qualitative rankings of pesticide mobility shown in Table C2 agree fairly well with the corresponding ratings in Table 2, which were derived from experimental measurements of relative mobility.

Table C1. Relative Adsorption of Different Pesticides by Soils (McCall et al., 1981)

Pesticide	Relative Adsorption[a]
Dicamba	0
cis-1,3-Dichloropropene	26
EDB	32
Monuron	83
DBCP	130
Atrazine	170
EPTC	280
Lindane	1,300
Trifluralin	3,900
Parathion	10,000
DDT	240,000

[a]As estimated by the quotient of the Freundlich adsorption coefficient K and the content of organic carbon in percent in the soils tested.

Table C2. Relative Mobility of Various Pesticides in Soils as Inferred From a Mathematical Prediction Equation[a] (Jury et al., 1984)

Very Mobile	Moderately Mobile	Slightly Mobile	Nearly Immobile	Immobile
2,4-D	Bromacil	Atrazine	Phorate	Triallate
Methyl bromide	Ethoprofos	Monuron	Diazinon	Methyl parathion
Carbofuran	Simazine	EPTC	Lindane	Trifluralin
EDB		Napropamide		Parathion
		Diuron		Dieldrin
		Prometryn		DDT

[a]Ranked according to estimated order of decreasing mobility within each class.

D. Appendix Tables

Table 1. Total Amounts of Major and Secondary Essential Nutrients Contained in Various Crops, With Yields Indicated (International Minerals and Chemical Corporation, undated)

Crop	Crop Yield per Acre[a]	Nutrients Contained in Crop, Pounds per Acre					
		Nitrogen (N)	Phosphorus (P_2O_5)	Potassium (K_2O)	Calcium (Ca)	Magnesium (Mg)	Sulfur (S)
Alfalfa	5 tons	250[b]	60	225	160	25	23
Corn	150 bu	220	80	195	58	50	33
Cotton	1.5 bales	95	50	60	28	8	4
Coastal bermudagrass	6 tons	150	60	180	33	22	40
Soybeans	40 bu	145[b]	40	75	7	9	7
Rice	6,500 lb	135	51	18	20	15	18
Tobacco	2,800 lb	95	25	190	105	24	21
Wheat	60 bu	125	50	110	16	18	16
Oats	100 bu	100	40	120	14	20	20
Potatoes	400 bu	200	55	310	50	15	18
Peanuts	3,000 lb	220[b]	45	120	105	28	25
Sorghum grain	8,000 lb	260	110	220	45	36	38

[a]Pounds per bushel of wheat, 60; corn, 56; soybeans, 60; oats, 32; sorghum, 56; potatoes, 60; rice, 45.
[b]Considerable nitrogen is obtained from the atmosphere by symbiotic fixation.

Table 2. Widely Used Nitrogen, Phosphorus, and Potassium Fertilizer Materials

Fertilizer	Grade[a]
	(1) (2) (3)
Anhydrous ammonia	82- 0- 0
Urea	46- 0- 0
Ammonium nitrate	33.5- 0- 0
Ammonium sulfate	21- 0- 0
Urea-ammonium nitrate (liquid)	28- 0- 0
Concentrated superphosphate	0- 45- 0
Diammonium phosphate	18- 46- 0
Monoammonium phosphate	11- 55- 0
Potassium chloride	0- 0- 60

[a]The fertilizer grade lists, in order, (1) the total nitrogen content, (2) the available phosphorus, determined as the phosphorus soluble in ammonium citrate solution and calculated as P_2O_5 ($P_2O_5 \times 0.44 = P$), and (3) the water-soluble potassium, calculated as K_2O ($K_2O \times 0.83 = K$). All values are in percent by weight.

Table 3. Nitrogen, Phosphorus, and Potassium Fertilizer Use in the United States in Different Years (Hargett and Berry, 1983)

	Millions of Tons Used in Indicated Year[a]			
Nutrient	1955	1970	1980	1982
Nitrogen (N)	2.0	7.5	11.4	11.1
Phosphorus as P_2O_5	2.3	4.6	5.4	4.8
Potassium as K_2O	1.9	4.0	6.2	5.6

[a]In English units (1 ton = 2,000 pounds).

Table 4. Percentage of Nitrogen, Phosphorus, and Potassium Fertilizer Use by Region in 1982 (Hargett and Berry, 1983)

	Percentage of Total Use of Indicated Nutrient		
Region	N	P_2O_5	K_2O
New England	0.1	0.6	0.7
Atlantic	11.0	14.2	19.4
North Central	55.9	56.7	63.2
South Central	17.7	17.1	13.3
Mountain	6.1	5.4	0.6
Pacific	8.6	5.6	2.2

Table 5. Quantities of Nitrogen, Phosphorus, and Potassium Applied to Four Major U.S. Crops in Different Years (Hargett and Berry, 1983)

		Quantities Applied in Indicated Year, Pounds per Acre				
Crop	Nutrient[a]	1965	1970	1975	1980	1982
Corn	N	65	106	99	124	126
	P	17	27	22	25	23
	K	30	51	42	58	54
Cotton	N	63	56	50	51	58
	P	14	12	9	10	8
	K	21	18	14	12	13
Wheat	N	15	24	29	39	40
	P	5	7	6	7	7
	K	4	4	6	7	5
Soybean	N	1	3	3	4	3
	P	2	4	4	6	5
	K	5	12	12	21	17

[a]To convert P to P_2O_5, multiply by 2.29. To convert K to K_2O, multiply by 1.20.

Table 6. Amounts of Inorganic Soil Amendments Used in the United States in Three Years

	Thousands of Short Tons[a] Used in Indicated Year		
Amendment	1979	1980	1981
Quicklime[b]	10	25	32
Hydrated lime[b]	61	54	42
Pulverized limestone[b]	32,875	33,262	29,028
Calcareous marl[b]	326	391	448
Gypsum[c]	1,700	1,658	1,525
Sulfur[d]	299	308	383

[a]2000-pound tons.
[b]Data from U.S. Department of Agriculture (1982).
[c]About 45% is byproduct gypsum. Data from Pressler (1984).
[d]Total used in agriculture for all purposes (Morse, 1984).

Table 7. Estimated Livestock and Poultry Waste Production in the United States in 1974 (Van Dyne and Gilbertson, 1978)

Class of Animal	Millions of Tons of Dry Matter Produced[a]	
	Total	Collectible
Beef cattle (range)	52.1	1.9
Feeder cattle	10.4	10.4
Dairy cattle	25.2	20.4
Hogs	13.4	5.5
Sheep	3.8	1.7
Laying hens	3.4	3.3
Turkeys	1.2	1.0
Broilers	2.1	2.1
Total	111.6	46.3

[a]ton = 2,000 pounds.

Table 8. Composition of Undecomposed Fresh Animal Manure (Sommers and Sutton, 1980)

Source		Solids %	Content of Indicated Element on a Dry-Matter Basis								
			Nitrogen, %	Phosphorus, %	Potassium, %	Sodium, %	Calcium, %	Magnesium, %	Sulfur, %	Copper, ppm	Zinc, ppm
Cattle:											
Beef	Range	12-27	2-8	0.5-1.6	2-4	0.1-2.8	0.6-1.4	0.4-0.7	0.4-0.6	23-33	68-100
	Mean	16	4.2	0.9	2.6	0.8	0.8	0.5	0.5	28	84
Dairy	Range	10-16	3-4	0.4-0.7	2-3	0.1-1.3	1.3-1.7	0.3-0.7	0.2-0.5	28-33	83-133
	Mean	14	3.5	0.6	2.4	0.5	1.5	0.5	0.3	30	108
Swine	Range	6-28	2-10	0.6-2.5	1-6	0.6-2.9	0.3-3.2	0.3-0.5	0.5-0.8	18-163	215-805
	Mean	13	5.2	1.5	3.2	1.5	2.0	0.4	0.6	90	546
Sheep	Range	24-29	4-6	0.4-0.9	2-4	—	0.8-2.5	0.3-0.8	0.3-0.4	—	—
	Mean	26	4.4	0.6	3.0	0.8	1.7	0.5	0.3	16	81
Poultry:											
Layers	Range	24-29	3-6	0.9-2.3	1-2	0.5-0.9	3.4-6.4	0.5-1.1	—	18-71	120-330
	Mean	26	4.8	1.8	1.8	0.7	5.5	0.7	0.5	40	225
Broilers	Range	—	3-6	1.1-2.1	1-2	0.5-0.9	1.4-2.1	0.4-1.1	—	18-105	125-253
	Mean	25	4.4	1.7	1.9	0.7	1.9	0.7	0.4	46	168
Turkeys	Range	22-27	5-6	0.6-2.0	1-3	—	—	—	—	—	—
	Mean	25	5.4	1.2	1.9	0.5	2.8	0.6	—	70	520
Horses	Range	21-40	2-3	0.3-0.5	1-2	—	0.7-2.9	0.3-0.4	0.2-0.3	—	—
	Mean	30	2.4	0.4	1.5	—	1.9	0.3	0.2	19	56

Table 9. Composition of Sewage Sludges Produced by Municipal Waste Water Treatment Plants (Sommers and Sutton, 1980)

Type of Digestion	Component	No. of Sludges	Content of Indicated Element in the Dry Matter, Percent			
			Minimum	Maximum	Median	Mean
Anaerobic	Nitrogen, %	85	0.5	17.6	4.2	5.0
	Phosphorus, %	86	0.5	14.3	3.0	3.3
	Potassium, %	86	0.02	2.6	0.3	0.5
	Zinc, ppm	108	108	27,800	1,860	3,370
	Copper, ppm	108	85	10,100	1,000	1,420
	Nickel, ppm	85	2	3,520	85	400
	Cadmium, ppm	98	3	3,400	16	106
Aerobic	Nitrogen, %	16	3.5	7.6	5.4	5.5
	Phosphorus, %	16	1.8	5.5	3.8	3.6
	Potassium, %	15	0.3	1.1	0.7	0.7
	Zinc, ppm	19	730	14,900	1,130	2,100
	Copper, ppm	19	280	2,600	960	970
	Nickel, ppm	10	2	390	8	47
	Cadmium, ppm	19	6	2,170	11	125
Activated	Nitrogen, %	21	0.5	7.5	4.5	4.6
	Phosphorus, %	21	1.1	3.8	2.4	2.4
	Potassium, %	21	0.08	0.5	0.3	0.3
	Zinc, ppm	33	108	5,500	1,800	2,100
	Copper, ppm	33	85	2,900	975	920
	Nickel, ppm	30	10	1,700	46	172
	Cadmium, ppm	32	5	435	130	160
All[a]	Nitrogen, %	191	0.1	17.6	3.3	3.9
	Phosphorus, %	189	0.1	14.3	2.3	2.5
	Potassium, %	192	0.02	2.6	0.3	0.4
	Zinc, ppm	208	100	27,800	1,740	2,790
	Copper, ppm	205	84	10,400	850	1,210
	Nickel, ppm	165	2	3,520	80	320
	Cadmium, ppm	189	3	3,410	16	110

[a]Includes the sludges in the three preceding groups and others.

Table 10. Content of Solids, Nitrogen, and Phosphorus in Waste Waters From Selected Vegetable, Fruit, and Meat Processing Plants (Soderquist, 1975; Witherow, 1973)

Material Processed	Total Solids, ppm	Total Nitrogen, ppm	Total Phosphorus, ppm
Greenbean-A	4,830	112	22
Greenbean-B	9,450	217	36
Cherries-A	13,600	82	19
Cherries-B	18,600	74	35
Pears	28,450	131	24
Corn	22,850	318	91
Blackberries	2,480	19	4
Meat (raw water)	3,405	99	11
Meat (after anaerobic digestion)	1,950	97	13

Table 11. Common Names, Trade Names, and Use Classes for Some of the Pesticides Mentioned in the Text

Common Name	Trade Name(s)[a]	Use Class[b]
alachlor	Lasso®	H
aldicarb	Temik®	I, N
atrazine	AAtrex®	H
benomyl	Benlate®	F
bromacil	Hyvar®-X	H
butylate	Sutan®	H
carbaryl	Sevin ®	I
carbofuran	Furadan®	I, N
chloramben	Amiben®	H
cypermethrin	Ammo®, Cymbush®	I
2,4-D	(numerous)	H
DBCP	Fumazone®, Nemagon®	N
DCPA	Dacthal®	H
diazinon	Spectracide®	I
dicamba	Banvel II®, Banvel D®	H
dinoseb	Premerge®3	H
disulfoton	Di-Syston®	I
diuron	Karmex®	H
EDB	Bromofume®, Soilbrom®40	I, N
EPTC	Eptam®, Eradicane®	H
fenvalerate	Pydrin®	I
lindane (γ-BHC)	Gammexane®, Kwell®	I
linuron	Lorox®	H
metolachlor	Dual®	H
oxamyl	Vydate®	I, N
paraquat	Gramoxone®, Dextrone®, Ortho Paraquat CL®	H
permethrin	Pounce®, Ambush®	I
picloram	Tordon®	H
propachlor	Ramrod®	H
propanil	Stam® M-4, Stampede® 3E, Rogue®	H
propazine	Milogard®	H
simazine	Princep®, Primatol®	H
2,4,5-T	Weedar® 2,4,5-T, Esteron® 245 BE	H
trifluralin	Treflan®	H
vernolate	Vernam®	H

[a]Most pesticides have additional trade names. Different trade names commonly are given to different formulations of a given pesticide and to formulations including two or more pesticides.
[b]F = fungicide, H = herbicide, I = insecticide, and N = nematicide.

Table 12. Use of Major Herbicides, Desiccants and Defoliants, and Plant Growth Regulators in the United States in 1971, 1976, and 1982 (U.S. Department of Agriculture, 1983)

Use Class of Compounds	Active Ingredients Used in Indicated Year, Millions of Pounds			Percentage of Total Herbicide Used in Indicated Year		
	1971	1976	1982	1971	1976	1982
Herbicides						
Alachlor	14.0	88.5	84.6	6.8	23.7	18.7
Atrazine	53.9	90.3	76.0	26.0	24.1	16.8
Butylate	5.6	24.4	54.9	2.7	6.5	12.2
EPTC	3.4	8.6	8.3	1.6	2.3	1.8
Linuron	1.7	8.4	6.4	0.8	2.2	1.4
Metolachlor	—	—	37.0	—	—	8.2
Propachlor	22.3	11.0	7.8	10.8	2.9	1.7
2,4-D	30.3	38.4	23.3	14.6	10.3	5.2
Trifluralin	10.3	28.3	36.1	5.0	7.6	8.0
Others	65.7	56.0	116.9	31.7	20.4	26.0
Total	207.2	373.9	451.3	100.0	100.0	100.0
Desiccants and defoliants	17.4	8.6	9.4	—	—	—
Growth regulators	5.0	6.3	6.0	—	—	—

Table 13. Insecticide Use on Certain Crops in 1971, 1976, and 1982 (U.S. Department of Agriculture, 1983)

Crop	Active Ingredients Used in Indicated Year, Millions of Pounds			Percentage of Acres Treated in Indicated Year		
	1971	1976	1982	1971	1976	1982
Row crops:						
Corn	25.5	32.0	30.1	35	38	37
Soybeans	5.6	7.9	10.9	8	7	12
Cotton	73.4	64.1	16.9	61	60	36
Grain sorghum	5.7	4.6	2.5	39	27	26
Peanuts	6.0	2.4	1.0	87	55	48
Tobacco	4.0	3.3	3.5	77	76	85
Total	120.2	114.3	64.9	31	29	26
Small grain crops:						
Rice	0.9	0.5	0.6	35	11	16
Wheat	1.7	7.2	2.4	7	14	3
Other[c]	0.8	1.8	0.2	3	5	1
Total	3.4	9.5	3.2	6	12	3
Forage crops:						
Alfalfa	2.5	6.4	2.5	8	13	7
Other hay	d	d	0.1	d	d	b
Pasture and range	0.2	0.1	a	0	b	b
Total	2.7	6.5	2.6	b	1	b
Total	126.3	130.3	70.7	6	9	8

[a]Less than 50,000 pounds of active ingredient.
[b]Less than 1%.
[c]Includes barley, oats, and rye in 1971 and 1976 and barley and oats in 1982.
[d]Included in the figures for alfalfa.

Table 14. Herbicide Use on Certain Crops in 1971, 1976, and 1982 (U.S. Department of Agriculture, 1983)

Crop	Active Ingredients Used in Indicated Year, Millions of Pounds			Percentage of Acres Treated in Indicated Year		
	1971	1976	1982	1971	1976	1982
Row crops:						
Corn	101.1	207.1	243.4	79	90	95
Soybeans	36.5	81.1	125.2	68	88	93
Cotton	19.6	18.3	17.3	82	84	97
Grain sorghum	11.5	15.7	15.3	46	51	59
Peanuts	4.4	3.4	4.9	92	93	93
Tobacco	0.2	1.2	1.5	7	55	71
Total	173.3	326.8	407.6	71	84	91
Small grain crops:						
Rice	8.0	8.5	13.9	95	83	98
Wheat	11.6	21.9	18.0	41	38	42
Other[a]	5.4	5.5	5.9	31	35	45
Total	25.0	35.9	37.8	38	38	44
Forage crops:						
Alfalfa	0.6	1.6	0.3	1	3	1
Other hay	b	b	0.7	b	b	3
Pasture and range	8.3	9.6	5.0	1	1	1
Total	8.9	11.2	6.0	1	1	1
Total	207.2	373.9	451.4	17	22	33

[a]Includes barley, oats, and rye in 1971 and 1976 and barley and oats in 1982.
[b]Included in the figure for alfalfa.