# PROGRAM OVERVIEW AND SELECTED PAPERS FROM THE TOXIC-WASTE PROGRAM TECHNICAL MEETING: TUCSON, ARIZONA, MARCH 20-22, 1984

By Stephen E. Ragone and Dennis J. Sulam, editors

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## CONVERSION FACTORS AND ABBREVIATIONS

The following factors may be used to convert the International System (SI) units of measure used in this report to inch-pound units:

| Multiply | By | To obtain |
|---|---|---|
| nanometer (nm) | $3.937 \times 10^{-8}$ | inch |
| micrometer (μm) | 0.00003937 | inch |
| centimeter (cm) | 0.394 | inch |
| millimeter (mm) | 0.03937 | inch |
| meter (m) | 3.281 | foot (ft) |
| kilometer (km) | 0.621 | mile (mi) |
| hectometer (hm) | 100.0 | meter (m) |
| centimeter per second (cm/s) | 0.0328 | foot per second (ft/s) |
| square centimeter ($cm^2$) | 0.1550 | square inch ($in^2$) |
| square meter ($m^2$) | 10.765 | square foot ($ft^2$) |
| square hectometer ($hm^2$) | 2.471 | acre |
| milligram (mg) | 0.0000353 | ounce (oz) |
| gram (g) | 0.035 | ounce (oz) |
| kilogram (kg) | 2.205 | pound (lb) |
| nanogram per gram (ng/g) | $1.0000 \times 10^{-9}$ | ounce per ounce (oz/oz) |
| nanogram per milliliter (ng/mL) | $133.497 \times 10^{-9}$ | ounce per gallon (oz/gal) |
| microgram per milliliter (μg/mL) | $133.497 \times 10^{-6}$ | ounce per gallon (oz/gal) |
| microgram per liter (μg/L) | 0.00005841 | grain per gallon (gr/gal) |
| microgram per gram (μg/g) | $1.0000 \times 10^{-6}$ | ounce per ounce (oz/oz) |
| milligram per liter (mg/L) | 1.0 | part per million (ppm) |
|  | 0.05841 | grain per gallon (gr/gal) |
| milligram per kilogram (mg/kg) | $1.0000 \times 10^{-6}$ | ounce per ounce (oz/oz) |
| gram per cubic centimeter ($g/cm^3$) | 62.43 | pound per cubic foot ($lb/ft^3$) |
| gram per liter (g/L) | 0.06243 | pound per cubic foot ($lb/ft^3$) |
| milliliter (mL) | 0.0338 | ounce, fluid (oz) |
| liter (L) | 1.0567 | quart (qt) |
|  | 0.2642 | gallon (gal) |
| milliliter per gram (mL/g) | 0.007491 | gallon per ounce (gal/oz) |
| degrees Celsius (°C) | (1.8 x °C) + 32 | degrees Fahrenheit |

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# PREFACE

In March 1984, a meeting was held in Tucson, Arizona, to review the technical progress of the U.S. Geological Survey's program on Toxic Waste--Ground-Water Contamination. This report, one of a series published as a result of the meeting, provides a brief description of the major components of the Toxic Waste--Ground-Water Contamination Program and includes selected overview and research papers presented at the March meeting.

S. R.
D. S.

# CONTENTS

Page

Chapter D--Capacities and mechanisms of sorption of organic compounds by water-saturated and unsaturated soils, by Cary T. Chiou, Lakewood, Colorado.

Chapter E--Use of detrended correspondence analysis to identify factors that affect the structure of aquatic communities, by Harry V. Leland and James L. Carter, Menlo Park, California.

Chapter F--Modeling sorptive processes in laboratory columns, by David B. Grove, Lakewood, Colorado.

CHAPTER G--Microbial populations and nutrient concentrations in a jet-fuel-contaminated shallow aquifer at Tustin, California, by Garry G. Ehrlich, Menlo Park, California; Roy A. Schroeder and Peter Martin, San Diego, California.

Chapter H--Adsorption and desorption of hexavalent chromium in an alluvial aquifer near Telluride, Colorado, by Kenneth G. Stollenwerk, Lakewood, Colorado.

## ILLUSTRATIONS

Figure

C-4 through C-6. Maps showing:

## TABLES

# PROGRAM OVERVIEW AND SELECTED PAPERS FROM THE TOXIC-WASTE PROGRAM TECHNICAL MEETING: TUCSON, ARIZONA, MARCH 20-22, 1984

By Stephen E. Ragone and Dennis J. Sulam, editors

## INTRODUCTION

The U.S. Geological Survey's Program on Toxic Waste--Ground-Water Contamination, hereafter referred to as the Toxic-Waste Program, was begun in fiscal year 1982[1] to coordinate and support Geological Survey projects and research relating to toxic-waste contamination of aquifers (Ragone, 1984). The program supports several types of studies which range from basic research to applied field studies. The basic-research component addresses the chemical, physical, and microbiological processes that affect contaminant occurrence and transport in the subsurface. Field studies consist of regional nonpoint source contamination research and interdisciplinary research of point-source contamination. An additional component of the Toxic-Waste Program is the development of scientific guidelines for siting hazardous-waste-disposal facilities.

Information obtained through these studies has wide application in local and regional efforts to protect the Nation's ground-water resources. For example, new improvements in sampling and analytical methods will help to ensure that water samples collected for analysis are representative of the source from which they were obtained and that the results are reliable. Research findings that help to explain and predict the occurrence and movement of chemical contaminants within an aquifer system will be useful in the prevention or mitigation of ground-water contamination problems.

Although many of these studies are conducted independently by Geological Survey scientists, it is the intent of the Toxic-Waste Program to enable researchers in the Geological Survey and in other Federal agencies and universities, to share the information. One approach is to encourage collaboration at the field sites. This collaboration brings new perspectives and techniques to the field and promotes the application of basic research findings to real-world problems.

A second way in which the Toxic-Waste Program makes the information from these studies accessible to the technical community is through the publication of reports. This volume describes the Toxic-Waste Program and presents 10 of the papers that were given at the 1984 meeting in Tucson, Ariz. It is the fourth volume to be issued in this series. Other reports describing results of studies supported by the Toxic-Waste Program are mentioned in the following pages and are referenced at the end of this section (p. 7). For convenience, an abstract of each paper given herein is included. (See p. 5.)

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[1] Fiscal year extends from October 1 through September 30.

## THE TOXIC-WASTE PROGRAM

The Geological Survey's Toxic-Waste Program, established in fiscal year 1982, consists of four components: (1) basic research; (2) interdisciplinary point-source contamination research; (3) regional nonpoint source contamination research; and (4) development of guidelines for siting hazardous-waste-disposal facilities (fig. 1). Each of these components is briefly described below.

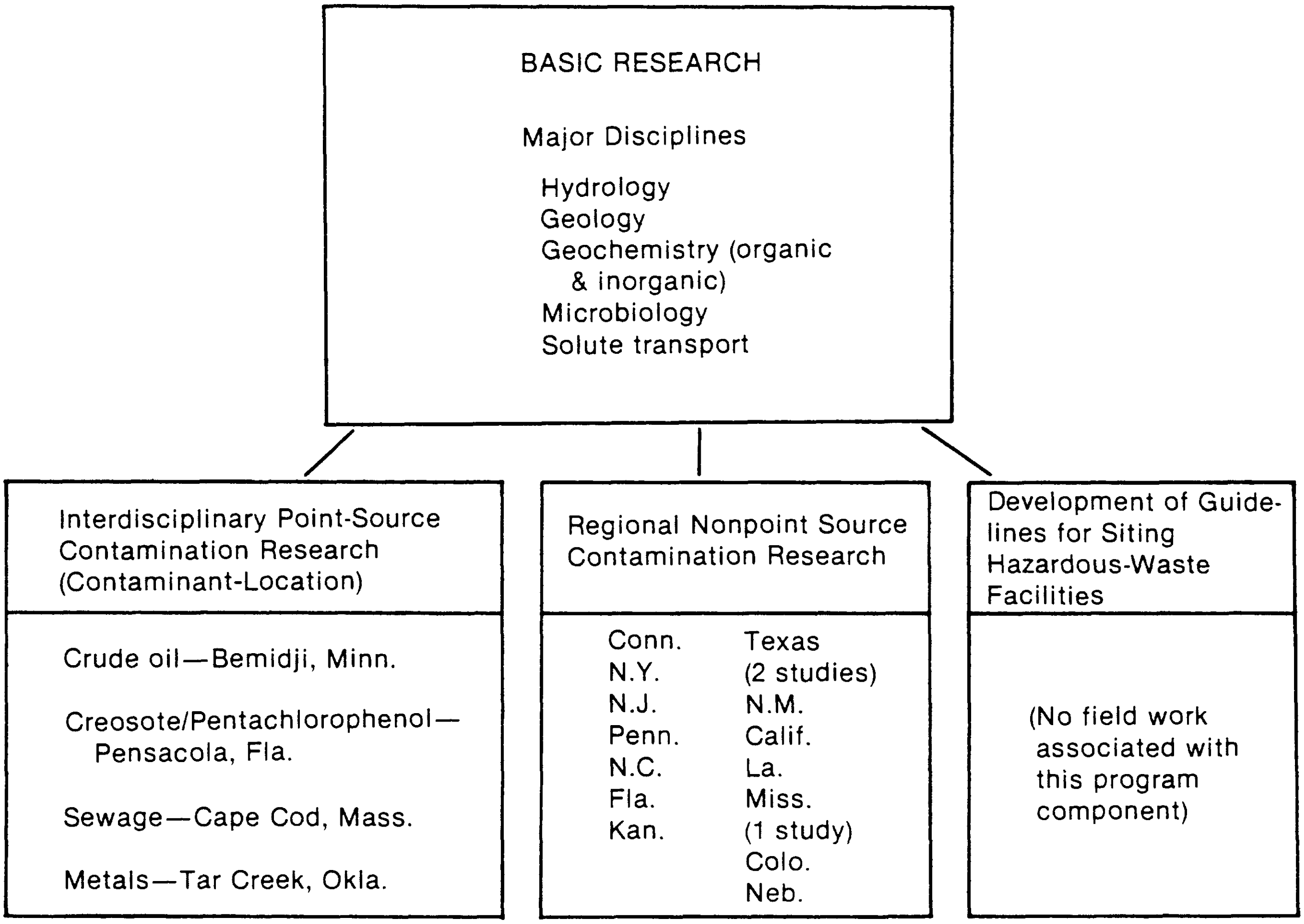

Figure 1.--Components of the U.S. Geological Survey's Program on Toxic Waste--Ground-Water Contamination, fiscal year 1984.

### Basic Research

Efforts to solve the Nation's hazardous-waste and ground-water contamination problems requires knowledge of the physical, chemical, and microbiological processes that determine the subsurface movement and fate of contaminants. Studies conducted since the early 1970's throughout the Nation have helped to explain these basic processes but, at the same time, have demonstrated that natural ground-water systems can be extremely complex and difficult to study. The objective of the basic research component of the Toxic-Waste Program is to increase current understanding of the physical, chemical, and microbiological processes in the subsurface in order to better describe the transport and fate of ground-water contaminants. Some studies also are addressing processes that occur within the unsaturated zone and within surface waters to evaluate their effect on ground water and the movement of contaminants. Basic research provides earth-sciences knowledge in support of the other components of the Toxic-Waste Program described next.

## Interdisciplinary Point-Source Contamination Research

To evaluate the extent to which present hydrologic knowledge can be used to quantitatively describe ground-water conditions, scientists from the U.S. Geological Survey and universities representing the major earth-science disciplines began studies in fiscal year 1983 at four ground-water-contamination sites. The sites represent contamination resulting from: (1) a crude-oil pipeline break near Bemidji, Minn., (2) the infiltration of creosote and pentachlorophenol from waste-disposal pits near Pensacola, Fla., (3) the infiltration of treated sewage on Cape Cod, Mass., and (4) the migration of zinc, lead, and cadmium from abandoned mining operations near Tar Creek, Okla. The contaminants at these sites are commonly associated with ground-water contamination elsewhere within the Nation. Thus, the field studies not only have helped to develop an understanding of the processes that affect contaminant transport at each site, but the knowledge gained through these studies has transfer value to sites in similar hydrogeologic and climatic settings at which similar contamination has occurred.

Even though the studies at these four sites are predominantly ground water oriented, they include some study of the unsaturated zone and of surface water as possible sinks or sources of organic or inorganic constituents.

The site investigations began with the development of a work plan to aid in the exchange of information and ideas among the individual researchers and to ensure that all major processes that affect contaminant transport were being considered. Papers presented at the meeting in Tucson in 1984 which summarized the first year of research at the Bemidji, Pensacola, and Cape Cod sites have been published as separate volumes (Hult, 1984; Mattraw and Franks, 1986; and LeBlanc, 1984). Work at these sites and the Tar Creek site is continuing. Studies of ground-water contamination by gasoline and chlorinated hydrocarbons in the Yakima River Valley, Wash., and Picatinny Arsenal, N.J., began in 1985.

## Regional Nonpoint Source Contamination Research

About half of the population of the Nation relies on ground water as a source of drinking water. In some places, for example, Florida, New Mexico, and Long Island, N.Y., ground water supplies more than 90 percent of the population. Although only a small percentage of ground water is presumed to be affected by point-sources of contaminants (Lehr, 1982), the billions of gallons of wastes infiltrating the ground annually from a variety of industrial and domestic point sources (Miller, 1980), indicates a high potential for widespread ground-water contamination. In addition, nonpoint (diffuse) sources, of contamination from differing land uses may also affect ground-water quality. Pesticides, for instance, have been found in ground waters in many States as a result of their widespread agricultural use (Cohen and others, 1984), and sewage disposal has affected the quality of ground water in many areas that use domestic inground water-disposal systems (Katz and Ragone, 1980).

Although evidence suggests that every State has ground water that has been and continues to become contaminated, our knowledge of these occurrences has come after the fact and unsystematically. This is for several reasons: (1) our ground-water resources are vast, inaccessibile, and can be within extremely complex systems; (2) we are unable to collect samples in sufficient quantity to form a representative sampling; and (3) many of the sampling and analytical methods are relatively new and untested.

In an attempt to evaluate ground-water-quality conditions throughout the Nation, the Toxic-Waste Program began 14 reconnaissance-phase ground-water-quality assessments in fiscal year 1984. A detailed description of the objectives and approach to be used in the assessment is given in Helsel and Ragone (1984). Briefly, the objective of the assessments is to develop a systematic approach to collection of hydrogeologic, land-use, and water-quality data to: (1) provide information on aquifer chemistry, with emphasis on organic substances and trace metals, and (2) identify the effects of hydrologic conditions and human activities, and other natural and anthropogenic processes that may affect ground-water quality in similar areas elsewhere.

The study areas selected for this part of the program range in size from a few tens to a few thousand square miles. Each area has relatively uniform climatic and geohydrologic conditions. Also the hydrology and ground-water flow system within each area are relatively well understood, and available data on land uses and inorganic chemical quality of ground water are adequate.

The results of the reconnaissance studies will be used as a basis for modification of the sampling networks and data-collection schedules to improve results and cost effectiveness. Additional sampling and analyses will be scheduled as needed to determine long-term changes and trends. The frequency of future samplings will depend on such factors as hydrogeologic setting and land uses.

### Development of Guidelines for Siting Hazardous-Waste Facilities

About 90 percent of the solid waste produced in the United States is disposed of in landfills (National Research Council, 1983). Secured landfills (those designed to isolate hazardous wastes from the environment), are the newest form of land-based disposal. However, the long-term integrity of these sites is not yet established. A potential problem in maintaining the integrity of landfills is that many of the sites may not have the necessary geologic, hydrologic, or geochemical characteristics necessary to maintain waste isolation if engineering measures fail. Earth-science considerations, along with the economic, engineering, and social criteria are essential in deciding on the suitability of a site for disposal of hazardous wastes.

The geologic, hydrologic, and geochemical characteristics of the site need to be identified in order to define the effect of the particular type and form of waste on the environment. For example, nondegradable wastes that present a hazard to the environment require permanent isolation from the biosphere. Burial or injection in a geologic environment, if it is to provide adequate safety with a minimum of continuing operational or maintenance efforts, must take advantage of geologic, hydrologic, and geochemical barriers that prevent migration of the wastes to the hydrosphere. Criteria used to site storage systems of this type include site stability, ground-water velocities and flow paths, locations of discharge areas, the potential for chemical retardation of waste movement, conditions favorable for chemical or biochemical degradation of waste, and, for some wastes, conditions suitable for deep burial.

Earth-science considerations for long-term containment of hazardous wastes is the topic of Chapter C herein, which also presents a scientific approach to the development of guidelines for the disposal and storage of hazardous wastes.

## ABSTRACTS

This section presents abstracts of 10 of the papers given at the March 1984 meeting in Tucson; the papers are given in their entirety further on. The first three are overviews of pertinent literature on several topics relevant to the Toxic-Waste Program; the last seven are research summaries that describe the application of information from earth-science disciplines to problems in toxic-waste contamination of ground water.

The role of geochemical processes in hazardous-waste studies; by Francis H. Chapelle. Predicting the mobility of waste derivatives in hazardous-waste studies requires an understanding of the geochemical processes that affect waste materials. This paper describes how geochemical techniques such as mass-balance, chemical-equilibria, and chemical-kinetic calculations, can be applied to waste-mobility problems. The paper demonstrates the difficulties in quantitatively treating geochemical processes and discusses the application of solute transport and geochemical principles to the study of specific problems. To this end it presents several examples of how geochemical principles can be applied.

An overview of organic compounds in ground water; by Anne C. Sigleo. The transport and fate of organic pollutants in ground water are influenced by the processes of dispersion, chemical hydrolysis, sorption/desorption, and biological degradation. This paper describes the hydrologic, geochemical, and microbiological processes that influence the fate of both biological and synthetic organic compounds.

The role of earth-science criteria in the selection of hazardous-waste disposal sites; by Albert M. La Sala, Jr. The selection of suitable sites for disposal systems of hazardous-waste material should involve the use of

earth-science information in combination with engineering, economic, social, and environmental-impact considerations. This paper describes a stepwise process that can lead to identification of sites potentially suitable for waste-disposal. Factors of geology, hydrology, and geochemistry pertinent to the long-term safety of disposal sites need to be investigated to develop a rational, objective basis for siting disposal facilities for hazardous waste.

Capacities and mechanisms of sorption of organic compounds by water-saturated and unsaturated soils; by Cary T. Chiou. Mobility of a chemical in hydrologic and geologic environments is determined to a large extent by its sorptive interaction with soil constituents. This research paper discusses characteristics of soil sorption of nonionic organic compounds that vary with respect to soil composition, moisture content, and solvent medium from which the solutes are sorbed. In aqueous systems, the controlling sorptive mechanism is considered to be solute partition into the soil-humic phase. When soils are fully hydrated, adsorption of the organic solutes by soil minerals becomes relatively insignificant. By contrast, the soil uptake of these compounds on dry soils is effected mainly through mineral adsorption.

Use of detrended correspondence analysis to identify factors that affect the structure of aquatic communities; by Harry V. Leland and James L. Carter. Detrended correspondence analysis is shown in this paper to be an effective method for analyzing biological-monitoring data and displaying major factors that control the spatial distribution of periphyton and benthic macroinvertebrates. The method proved highly sensitive to differences among samples and consistently provided ecologically meaningful species ordination.

Modeling sorptive processes in laboratory columns; by David B. Grove. A common type of chemical reaction that occurs during the movement of solutes in porous media is sorption of the solute onto the solid surface through a physical attraction or an exchange process. This paper describes sorption isotherms, discusses the shapes and significance of different slopes, and describes equations used to evaluate the slopes of isotherms. Computer codes can be used to compute concentrations of the effluent from a laboratory column and the concentration profile within the column.

Microbial populations and nutrient concentrations in a jet-fuel-contaminated shallow aquifer at Tustin, California; by Garry G. Ehrlich, Roy A. Schroeder, and Peter Martin. Jet-fuel leakage from unlined earthen pits has contaminated a shallow aquifer of low permeability; hence, conventional cleanup operations are relatively ineffective. This paper discusses a remedial strategy for cleanup that involves use of indigenous hydrocarbon-degrading bacteria, which are shown to be present in the aquifer. Laboratory studies found that nutrient enrichment of jet-fuel and ground-water mixtures stimulated growth of hydrocarbon-degrading bacteria and resulted in the production of hydrocarbon emulsifiers that might promote dispersion of pockets of trapped fuel in the aquifer. Injection of inorganic nitrogen, phosphrous, and oxygen, in conjunction with operation of a conventional depression-pump and oil-scavenger recovery system, could enhance restoration of the site.

Adsorption and desorption of hexavalent chromium in an alluvial aquifer near Telluride, Colorado; by Kenneth G. Stollenwerk. An evaluation of reactions between alluvium and hexavalent chromium Cr(VI) was conducted to determine the mechanisms responsible for these reactions. This paper discusses results of a laboratory investigation. One significant result indicates that desorption of Cr(VI) from alluvium occurs after the contaminated plume has passed. Initial desorption of Cr(VI) is rapid; followed by a steady decrease. Adsorption, it was found, of Cr(VI) is by specific and nonspecific mechanisms. Cr(VI) absorbed by nonspecific processes is desorbed by chromium-free ground water. Stronger bonds formed between Cr(VI) and alluvium during specific adsorption result in slow release of this fraction; thus, adsorbed Cr(VI) will serve as a secondary source of contamination long after the original plume has passed.

Effects of pentachlorophenol on the methanogenic fermentation of phenol; by Edward M. Godsy, Donald F. Goerlitz, and Garry G. Ehrlich. Pentachlorophenol (PCP) and creosote, two widely used pesticides, contribute potential contaminants to ground-water resources. This paper describes a study to investigate the interactions of PCP and phenol compounds on creosote in anaerobic laboratory digestors. PCP was found to be inhibitory to the methanogenic fermentation of phenol. The inhibition could be relieved when the PCP concentration was low enough to undergo biodegradation.

The role of complexation and adsorption processes in toxic metal transport; by James A. Davis and Christopher C. Fuller. The transport of toxic metals in ground-water systems has become an important water-quality issue. This research paper describes a detailed laboratory study of cadmium uptake into a calcareous, sandy aquifer material. A strong complexing agent (EDTA) was used to increase mobility of cadmium (II) while being present at very low concentrations.

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## CHAPTER A

# THE ROLE OF GEOCHEMICAL PROCESSES IN HAZARDOUS-WASTE STUDIES

By Francis H. Chapelle, Columbia, S.C.

## ABSTRACT

An important aspect of hazardous-waste studies is evaluating the mobility of waste derivatives in the hydrosphere. Several kinds of geochemical techniques are currently available that may aid such evaluations. These include mass-balance, chemical-equilibria, and chemical-kinetic calculations. Depending on the type of problem and on the kinds of information available, evaluations of waste mobility may range from quantitative to qualitative. In all cases, however, such evaluations require an explicit understanding of the geochemical processes that affect the waste materials.

This paper presents a series of idealized examples to illustrate how geochemical techniques may be applied to waste-mobility problems. These examples include:

1. A formulation of reactive solute transport in terms of a boundary value problem.
2. A demonstration of how equilibrium speciation calculations can be applied to complex-forming metals.
3. An evaluation of the solubility of metal-oxide compounds in aqueous solution.

## INTRODUCTION

Subsurface containment is commonly a technically and economically feasible alternative for the disposal of hazardous wastes. In designing subsurface containment structures, the ultimate goal is isolation of hazardous material from the surrounding environment. Experience has shown, however, that perfect isolation is difficult, if not impossible, to achieve. It is therefore important to evaluate the mobility of wastes or waste derivatives in the hydrosphere.

Waste materials in subsurface repositories are acted on by physical, biological, and geochemical processes. Distinguishing between these three types of processes may be difficult because of their mutual interaction. Geochemical processes, for example, usually occur within the framework of a physical ground-water flow system, and many geochemical processes are biologically mediated. While recognizing these complexities, this paper concentrates specifically on geochemical processes and their role in chemical interactions between waste materials and the environment.

It is generally recognized that any quantitative evaluation of geochemical processes is complex. The approach taken in this paper is to look at specific geochemical processes with the goal of better understanding the sources of this complexity. Several examples of how geochemical principles can be used to evaluate mobilities of chemical species are presented to illustrate how a knowledge, or at least an appreciation, of geochemical processes may be useful in hazardous-waste studies.

## HISTORICAL DEVELOPMENT OF GROUND-WATER GEOCHEMISTRY

The systematic study of rock and water interactions in the subsurface is a relatively young discipline. Geochemical work in the early 20th century was pioneered by F. W. Clark in the United States and V. M. Goldschmidt in Norway, and centered on describing the composition of the Earth's crust. These workers studied the physical-chemical processes that influence and (or) control the fractionation, migration, and deposition of chemical elements in geologic materials.

By the middle of the 20th century, it was recognized that the chemical action of subsurface water controlled the occurrence of some types of economic mineralization, such as roll-type uranium deposits (Krauskopf, 1967, p. 526-531). This realization led to an increased interest in ground-water geochemistry.

In the 1960's, fundamental principles of chemical equilibria were applied to ground-water systems by Garrels and Christ (1965), Garrels and Mackenzie (1967), and Bricker and others (1968). In addition, Garrels and Mackenzie demonstrated the use of mass-balance calculations for identifying important geochemical processes. During the 1970's and 1980's, computer technology was increasingly used to perform complex geochemical calculations. Truesdall and Jones (1974) developed the program WATEQ (WATer EQuilibrium) to perform chemical-speciation and equilibrium calculations. Many such programs are now available, and several of them have been compared by Nordstrom and others (1979). Parkhurst and others (1982) developed a program called BALANCE, which performs mass-balance calculations. Parkhurst and others (1980) developed a program called PHREEQE (pH REdox EQuilibria) to couple chemical equilibria and mass-balance calculations. This program is particularly useful in evaluating the reaction paths of chemical processes.

The overall philosophy of developing reaction models for ground-water systems has been summarized by Plummer and others (1983). The mathematics of coupling chemical processes with ground-water diffusion and dispersion processes has recently been summarized by Rubin (1983). An application of this approach has been given by Valocchi and others (1981). Application of similar techniques to surface-water systems has been documented by Bencala and Walters (1983).

This brief history of ground-water geochemistry emphasizes that many of the available theoretical tools are relatively new. Also, many of the techniques (such as mass balance, chemical equilibria) were developed specifically for natural (unaffected by human activities) rock and water systems.

During the 1970's and 1980's, increasing attention was given to the application of geochemical principles to hazardous-waste problems. This has resulted in a significant, but generally unappreciated, change in the philosophy of ground-water-geochemistry studies. Where once it had been sufficient to understand the chemical processes in a natural system, it was now necessary to understand the <u>change</u> in that system produced by human-induced hydrologic or chemical stresses. Keeping in mind the fact that natural systems commonly are not well understood, evaluating changes in these systems is much more difficult.

## SOLUTE TRANSPORT OF REACTING CHEMICAL SPECIES

### Quantitative Evaluation and Problem Formulation

In dealing with some hazardous-waste problems, it is desirable to predict the migration of dissolved chemical species in space and time. In some well-defined cases, this migration can be described quantitatively in terms of a boundary-value problem. Commonly, these problems involve the transport of a particular chemical by ground water under conditions of saturated flow. For this case, the mobility of a particular chemical species is governed by: (1) diffusion gradients, (2) dispersion by flowing ground water, and (3) chemical reactions; for one-dimensional transport this is described by the equation:

$$\underbrace{\theta \frac{\partial c}{\partial t}}_{\text{Total change in mass of solute species}} = \underbrace{D \frac{\partial^2 c}{\partial x^2} - Q \frac{\partial c}{\partial x}}_{\text{Change in mass due to hydrodynamic processes}} + \underbrace{\text{CHEM}}_{\text{Change in mass due to chemical reactions}} \qquad (1)$$

where: $\theta$ = effective porosity;
$c$ = concentration of chemical species;
$D$ = coefficient of hydrodynamic dispersion;
$t$ = time;
$Q$ = average flow velocity;
$x$ = distance; and
CHEM = term defined by nature of chemical reactions.

Equation 1 is subject to particular boundary and initial conditions and is based on the principle of conservation of mass; it is a general description of solute transport in saturated porous media.

The physics of diffusion and dispersion are, for practical purposes, similar for all problems. However, the physics of solute transport due to chemical reactions depends specifically on the nature of the chemical reactions. For some simple chemical reactions, the CHEM term can be evaluated directly; for example, if a linear adsorption isotherm governs partition between the adsorbed and aqueous phases (Konikow, 1981), then

$$\text{CHEM} = -\rho \frac{\partial \bar{c}}{\partial t}$$

where: $\bar{c}$ = concentration of adsorbed solute; and
$\rho$ = bulk density of the solid.

For more complex chemical reactions, however, the CHEM term cannot be evaluated directly, and more sophisticated mathematical formulations are necessary.

Rubin (1983) presents an elegant description of the relationship between the nature of chemical processes and the mathematical formulation of solute-transport problems. Rubin's approach is based on a three-level classification scheme of chemical processes (reproduced in fig. A-1). The first level of classification (level A in fig. A-1) distinguishes between kinetically fast reactions (sufficiently fast and reversible) and kinetically slow reactions (insufficiently fast and (or) irreversible). The second level (level B) distinguishes between chemical processes occurring in a single phase (homogeneous) and processes that occur between two or more phases (heterogeneous). The third level (level C) distinguishes between chemical processes that occur predominantly at the interface between phases (surface) and those that are not restricted to phase interfaces (classical). This classification scheme defines six general classes to which individual chemical processes may be assigned. Because these classes reflect different reaction properties, the mathematical formulation of solute-transport equations is different for each class.

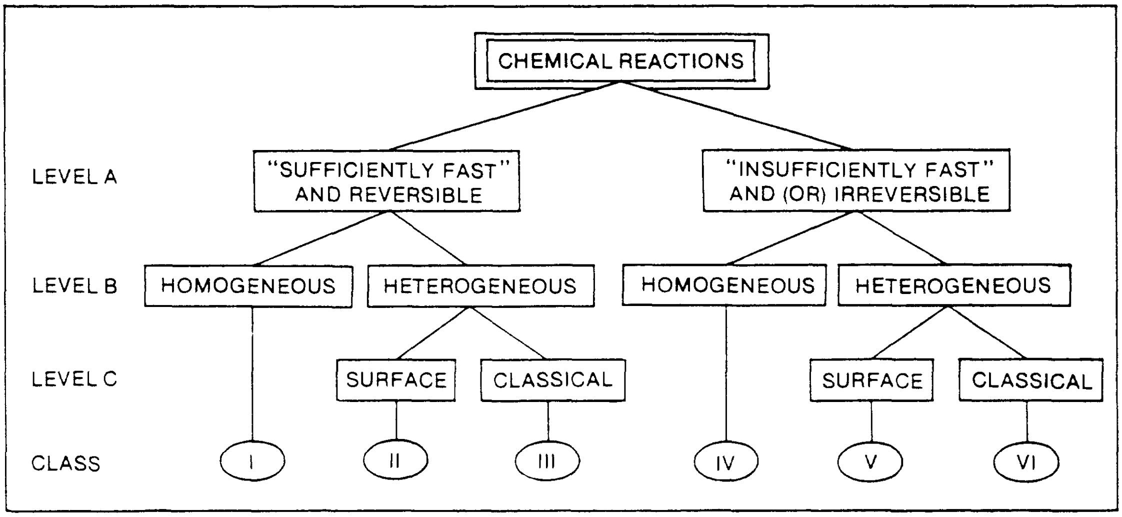

Figure A-1.--Classification of chemical reactions useful in solute-transport analyses (modified from Rubin, 1983, p. 1232).

The approach described by Rubin (1983) can be illustrated with the following example. Consider two solutes, $c_1$ and $c_2$, that react quickly and reversibly to form a third solute, $c_3$.

$$c_1 + c_2 \rightleftharpoons c_3 \qquad (2)$$

According to figure A-1, this reaction is classified as homogeneous (the reaction involves only one phase; in this case, the aqueous phase), is sufficiently rapid, and is reversible. Because the reaction is rapid, it is reasonable to assume equilibrium conditions at each point in the system. Rubin (1983) terms this the Local Equilibrium Assumption. If known concentrations of solutes $c_1$ and $c_2$ are introduced into a one-dimensional flow system at a particular time (that is, initial and boundary conditions are known), the analysis can proceed as follows: The first step is to write mass-balance equations for both $c_1$ and $c_2$ as they react to form $c_3$:

$$\theta \frac{\partial c_1}{\partial t} + \theta \frac{\partial c_3}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} - Q \frac{\partial c_1}{\partial x} + D \frac{\partial^2 c_3}{\partial x^2} - Q \frac{\partial c_3}{\partial x} \qquad (3)$$

and

$$\theta \frac{\partial c_2}{\partial t} + \theta \frac{\partial c_3}{\partial t} = D \frac{\partial^2 c_2}{\partial x^2} - Q \frac{\partial c_2}{\partial x} + D \frac{\partial^2 c_3}{\partial x^2} - Q \frac{\partial c_3}{\partial x} \qquad (4)$$

Equations 3 and 4 have three variables, $c_1$, $c_2$, and $c_3$, associated with them. A third equation is obtained by assuming local equilibrium throughout the system. At equilibrium, the relationship between $c_1$, $c_2$, $c_3$, and the equilibrium constant for the reaction is given by

$$\frac{[c_1][c_2]}{[c_3]} = Ke \qquad (5)$$

Equations 3, 4, and 5 are a system of three equations in three unknowns that can be solved simultaneously to give $c_1$, $c_2$, and $c_3$ as a function of space and time if boundary and initial conditions are specified. This is generally accomplished by making numerical approximations to the equations and solving them with the help of a computer.

The development of equations 3, 4, and 5 is presented to point out several important aspects of these problems:

1. The nature of the operative chemical reactions must be known explicitly <u>before</u> the mathematical analysis can be performed.

2. The mathematical formulations will be different for different chemical processes.

3. The number of chemical species that can be considered is limited by the complex nature of the resulting simultaneous partial differential equations.

4. Systems characterized by several different classes of reactions--that is, fast reversible reactions occurring simultaneously with slow irreversible reactions--cannot be treated simply.

5. Well-defined boundary and initial conditions are needed to obtain solutions.

In many systems, the practical problems of determining the chemical reactions among a large number of solute species, with several classes of reactions operating simultaneously or with indefinable boundary and initial conditions, may preclude the use of the boundary-value problem approach. In cases where this approach is not practical, other more semiquantitative or even qualitative procedures may be useful.

## Semiquantitative Evaluation of Geochemical Processes

In the previous section, it was shown that the transport of some reacting solutes may be described quantitatively in terms of boundary-value problems. However, if a large number of reacting solutes are present or if boundary and initial conditions cannot be specified, meaningful solutions to these problems may not be feasible. In such cases, semiquantitative or even qualitative descriptions of geochemical processes can be useful. To illustrate how such semiquantitative evaluations may be used, two important types of geochemical processes are considered in detail; these are chemical-speciation reactions and dissolution-precipitation reactions.

The term "semiquantitative" is appropriate in this context for several reasons. First, these types of calculations are often based on the principles of equilibrium chemistry. Although this approach can be a powerful tool, the results depend, among other things, upon (1) the accuracy of available thermochemical data, and (2) the degree to which a specified system approaches equilibrium. Because the thermochemical data for many substances of interest in hazardous-waste studies are uncertain, the accuracy of equilibrium calculations are commonly uncertain. Also, equilibrium chemistry does not evaluate the <u>rate</u> at which chemical processes operate. In some cases, it may not be reasonable to assume equilibrium conditions. These factors must be carefully considered when applying these techniques.

### Chemical Speciation

The geochemistry of metals, particularly transition metals, in aqueous solutions is extremely complex. Much of this complexity arises from the many different dissolved metal species that may exist at equilibrium. Depending on solution ionic strength, pH, and redox conditions, several dissolved species of the same element may coexist. It is important to realize that most chemical analysis techniques for metals gives the sum of <u>all</u> species present. Thus, it is impossible to determine metal speciation from the water analysis alone. Because different species may exhibit different properties, however, information on metal speciation is extremely important.

Because it is difficult to measure metal speciation, how is this problem evaluated? One commonly used approach in the geochemical literature is to calculate a speciation on the basis of equilibrium chemistry. The following example of this approach is paraphrased from Nordstrom and others (1979).

Assume that radioactive strontium ($^{90}Sr$), which is an unstable isotope that is present in some types of radioactive hazardous wastes, is present in solution and that it forms free $Sr^{2+}$ ions and the ion pair $SrCO_3{}^{o}$. The solution also contains free $CO_3{}^{2-}$ ions. If a water analysis is available, the molality of total strontium ($mSr_{tot}$) and the molality of total carbonate ($mCO_{3\,tot}$) are known. The question is, how much $Sr^{2+}$ and how much $SrCO_3{}^{o}$ are present simultaneously in the solution? If the solutions are dilute and molalities are approximately equal to activities, the analysis can proceed as follows:

The mass balance of this system is given by

$$mSr_{tot} = mSr^{2+} + mSrCO_3^{o} \tag{6}$$

and

$$mCO_{3\,tot} = mCO_3^{2+} + mSrCO_3^{o} \tag{7}$$

At equilibrium, the condition

$$K_{eq} = \frac{(mSrCO_3^{o})}{(mSr^{2+})(mCO_3^{2-})} \tag{8}$$

also applies. Solving equation 8 for $mSrCO_3^{o}$ gives

$$mSrCO_3^{o} = K_{eq}\ (mSr^{2+})(mCO_3^{2-}) \tag{9}$$

Substituting equation 9 into equations 6 and 7 gives

$$mSr_{tot} = mSr^{2+} + K_{eq}(mSr^{2+})(mCO_3^{2-}) \tag{10}$$

and

$$mCO_{3\,tot} = mCO_3^{+} + K_{eq}(mSr^{2+})(mCO_3^{2-}) \tag{11}$$

Because $mSr^{2+}_{tot}$, $mCO^{2-}_{3\,tot}$, and $K_{eq}$ are known, the concentrations of $mSr^{2+}$ and $mSrCO_3^{o}$ can be calculated by simultaneous solution of equations 10 and 11. This is generally accomplished by an iterative procedure based on successive approximations. In dealing with most natural waters, equating the molalities and activities of dissolved components is a poor approximation. In actual practice, therefore, activity coefficients are calculated for each dissolved species, and this problem is solved in terms of activities.

In natural systems, more than two strontium species may be present. The total number of simultaneous equations therefore depends on the number of species considered. Several different chemical equilibrium models (such as WATEQ), which use computers to calculate activity coefficients and to solve the simultaneous equations, are currently available (Nordstrom and others, 1979). The accuracy of the calculated speciation depends on several factors:

1. The accuracy of available chemical analyses.

2. The accuracy of calculated activity coefficients.

3. The accuracy of thermochemical data used to calculate equilibrium constants.

4. The degree to which the natural system has approached equilibrium.

Each of these factors presents difficulties that depend on the metals under consideration.

## Dissolution-Precipitation Reactions

In hazardous-waste studies, questions are frequently asked concerning the "solubility" of metal compounds. This really is a two-part question because metal solubilities are determined by chemical speciation (see the previous section) and by the stability of aqueous species with respect to a solid metal phase. In practical terms, an equilibrium concentration of aqueous metal species must be defined in terms of one particular solid metal phase. If more than one solid substance that contains the metal is present (such as zinc oxide coexisting with zinc hydroxide), then a unique equilibrium concentration of dissolved zinc is difficult to define. In these cases of competing equilibria, reaction kinetics must be considered. The following example of the equilibrium approach is paraphrased from Stumm and Morgan (1981).

Many metal-treatment processes involve the use of zinc compounds; thus, the waste materials of these processes commonly contain zinc oxides. The question, therefore, is what concentration of dissolved zinc may occur in equilibrium with ZnO? For this type of problem, it is convenient to construct stability diagrams for the system under consideration. To do this, the possible reactions of the solid phase (ZnO) with solute species are written with the pertinent thermochemical data.

$$ZnO_{(s)} + 2H^{+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + H_2O_{(L)} \qquad \log K_1 = 11.2 \tag{12}$$

$$ZnO_{(s)} + H^{+}_{(aq)} \rightleftharpoons ZnOH^{+}_{(aq)} \qquad \log K_2 = 2.2 \tag{13}$$

$$ZnO_{(s)} + 2H_2O_{(L)} \rightleftharpoons Zn(OH)^{-}_{3(aq)} + H^{+}_{(aq)} \qquad \log K_3 = -16.9 \tag{14}$$

$$ZnO_{(s)} + 3H_2O_{(L)} \rightleftharpoons Zn(OH)^{2-}_{4(aq)}{}^{2} + 2H^{+}_{(aq)} \qquad \log K_4 = -29.7 \tag{15}$$

Forming the reaction quotients of these equations gives

$$K_1 = \frac{(aZn^{2+})(aH_2O)}{(aZnO)(aH^{+})^2} \tag{16}$$

$$K_2 = \frac{(aZnOH^{+})}{(aZnO)(aH^{+})} \tag{17}$$

$$K_3 = \frac{(aZn(OH)^{-}_3)(aH^{+})}{(aZnO)(aH_2O)^2} \tag{18}$$

$$K_4 = \frac{(aZn(OH)_4^{2-})(aH^+)_3^2}{(aZnO)(aH_2O)} \qquad (19)$$

Setting the activities of solid ZnO and liquid $H_2O$ equal to 1, taking logs, and rearranging, gives

$$\log aZn^{2+} = \log K_1 + 2 \log aH^+ \qquad (20)$$

$$\log aZn(OH)^+ = \log K_2 + \log aH^+ \qquad (21)$$

$$\log aZn(OH)_3 = \log K_3 - \log aH^+ \qquad (22)$$

$$\log aZn(OH)_4{}^{2-} = \log K_4 - \log 2aH^+ \qquad (23)$$

These equations are linear in log-log space and can be used to construct a stability diagram. Figure A-2 shows a stability diagram constructed by plotting these equations. This diagram illustrates that for pH less than 7.0, concentrations of total dissolved zinc greater than $10^{-2}$ molar (650 mg/L) can exist in aqueous solution at equilibrium. However, at a pH of 10.0, concentrations of total dissolved zinc will not exceed $10^{-7}$ molar (0.065 mg/L) at equilibrium.

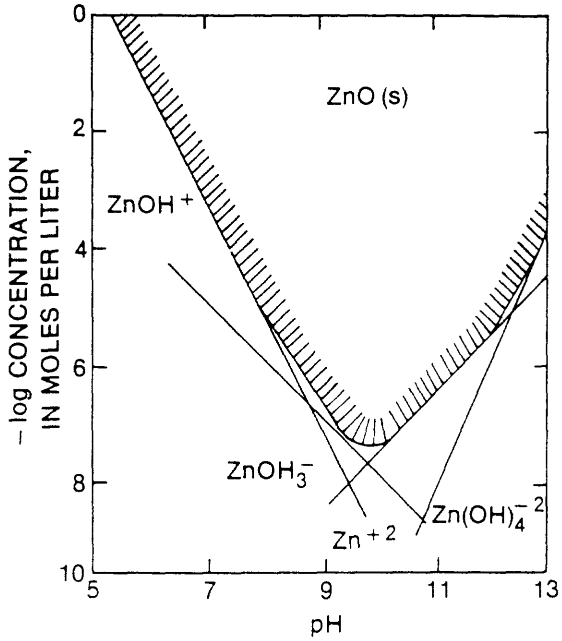

Figure A-2.--Concentrations of $Zn^{2+}$ species in equilibrium with solid ZnO in relation to pH. (Modified from Stumm and Morgan, 1981, p. 173. Copyright 1970, John Wiley, Inc.; reproduced by permission.)

The extent to which calculations such as these can be applied to real systems depends on the nature of the specific problem. Obviously, if the reactions are extremely slow, assumption of equilibrium with respect to a particular solid phase may not be valid. In some cases, however, this type of approach may be useful.

## CONCLUSIONS

An understanding of geochemical processes can significantly aid hazardous-waste studies. In some instances, diffusion-dispersion and chemical equations may be coupled to describe solute transport in space and time. If a system is too complex for this treatment, or if boundary and initial conditions cannot be adequately defined, useful information may still be obtained from chemical equilibria or chemical-kinetics considerations. In every case, treatment of hazardous-waste problems requires an explicit understanding of the geochemical system. This includes understanding the natural (unstressed by human activity) water chemistry, lithology, and mineralogy, and the chemical nature of the waste materials.

Because of the complex nature of water chemistry problems, no single approach can be applied to all problems. However, the following sequence of data-gathering and professional judgments can be recommended for any given problem:

1. Document the nature of naturally occurring chemical processes.

2. Document the nature of the waste materials or waste-generating processes.

3. On the basis of steps 1 and 2, make a judgment as to the specific class or classes of reactions (fig. A-1) that solute species are subject to (that is--fast, homogeneous, irreversible, and so on), and develop a conceptual model of the chemical processes involved in the problem.

4. From step 3, judge whether a quantitative approach is feasible and, if so, select the appropriate mathematical treatment. Transport equations can then be formulated and solved subject to particular boundary and initial conditions.

5. If a quantitative approach is not feasible (as is commonly the case), select an appropriate semiquantitative or qualitative treatment based on chemical equilibria or chemical kinetics.

In this sequence, completion of step 1 is almost always achievable. Steps 2 and 3 usually, and step 4 rarely, are achievable. Step 5, in either semiquantitative or qualitative form is frequently the most feasible approach. Most work dealing with the geochemistry of hazardous wastes is largely qualitative because of the vast complexities. Thus, while striving for a quantitative treatment, it is important to make use of more qualitative information where necessary.

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# CHAPTER B

# AN OVERVIEW OF ORGANIC COMPOUNDS IN GROUND WATER

By Anne C. Sigleo, Reston, Va.

## ABSTRACT

The majority of organic chemicals in ground water can be grouped into two major categories: (1) biochemicals--the natural products of biological processes, and (2) synthetic organic chemicals derived from a variety of manmade sources. The manmade sources include landfills, industrial wastes, mining activities, sewage, and agriculture. The transport and fate of organic pollutants in ground water are influenced by the processes of dispersion, chemical hydrolysis, sorption/desorption, and biological degradation. Despite the complexity of these processes, progress in the understanding of the transport and fate of organic pollutants continues, as indicated by a series of examples in the text.

## INTRODUCTION

The concentrations of dissolved constituents in ground water are controlled by the composition of the soils and rock through which the water passes and by various geochemical, physical, and biochemical processes. The redox conditions in ground water are most affected by oxygen-consuming reactions involving the oxidation of reduced inorganic species and, particularly, the breakdown of organic materials. These organic materials and their sources, reactions, and fate, are the subjects of this paper.

Organic chemistry is the chemistry of the compounds of carbon. The number of compounds that contain carbon is far greater than those that do not; the chemical registry lists approximately 600,000 organic compounds at the present time. This staggering number includes biochemicals, industrial chemicals, and pharmaceuticals. Although many of these compounds will never be seen outside a laboratory, an increasing number are being reported in surface and ground waters.

Carbon is unique in that one of the four outer electrons can form a single covalent bond with another element, two electrons can pair to form a double bond, or, less commonly, three electrons can form a triple bond. These bonds are represented graphically in atomic-structure diagrams by a single line, a double line, and a triple line, respectively. Compounds in the form of a ring containing alternating single and double bonds are referred to as aromatics; all others are referred to as aliphatic. The simplest carbon molecules are hydrocarbons containing only hydrogen and carbon. These include methane, petroleum fuels, and waxes. The addition of oxygen to the hydrocarbon can form an alcohol (-OH), an aldehyde (-CHO), a ketone (-CO-) or an ether (-O-) (table B-1). A second oxygen is required to form an acid (-COOH) or an ester (-COO-). Nitrogen-containing organic compounds include amines ($-NH_2$) and nitro compounds ($-NO_2$). As the name suggests, halogenated compounds contain one or more chlorine, bromine, iodine, or fluorine atoms. The atom or group of atoms that defines a particular class of organic compounds and determines the chemical properties of the compounds, is called the functional group. The functional group is the <u>reactive</u> part of an organic molecule and, from a geochemical perspective, it is the most important. More complex combinations of these basic functional groups form the primary biological building blocks--amino acids (the components of proteins), sugars (carbohydrates), and lipids (fatty acids) (fig. B-1).

Table B-1.--Classes of organic compounds

| Class | Functional group | Example | |
|---|---|---|---|
| | | Formula | Name |
| Hydrocarbon | $-\overset{H}{\underset{H}{C}}-H$ | $CH_4$ | Methane |
| Alcohol | $-OH$ | $CH_3OH$ | Methyl alcohol (methanol) |
| Aldehyde | $-\overset{O}{\overset{\|}{C}}-H$ | $CH_3CHO$ | Acetaldehyde (ethanol) |
| Ether | $-O-$ | $CH_3OCH_3$ | Dimethyl ether |
| Ketone | $-\overset{O}{\overset{\|}{C}}-$ | $CH_3COCH_3$ | Acetone (2-propanone) |
| Carboxylic acid | $-\overset{O}{\overset{\|}{C}}-OH$ | $CH_3COOH$ | Acetic acid |
| Ester | $-\overset{O}{\overset{\|}{C}}-O-$ | $CH_3COOCH_3$ | Methyl acetate |
| Amine | $-NH_2$ | $CH_3NH_2$ | Methyl amine |
| Nitro compound | $-NO_2$ | $CH_3NO_2$ | Nitromethane |
| Halogen | -Cl, -Br, -F, -I | $CH_3Cl$ | Methyl chloride (chloromethane) |

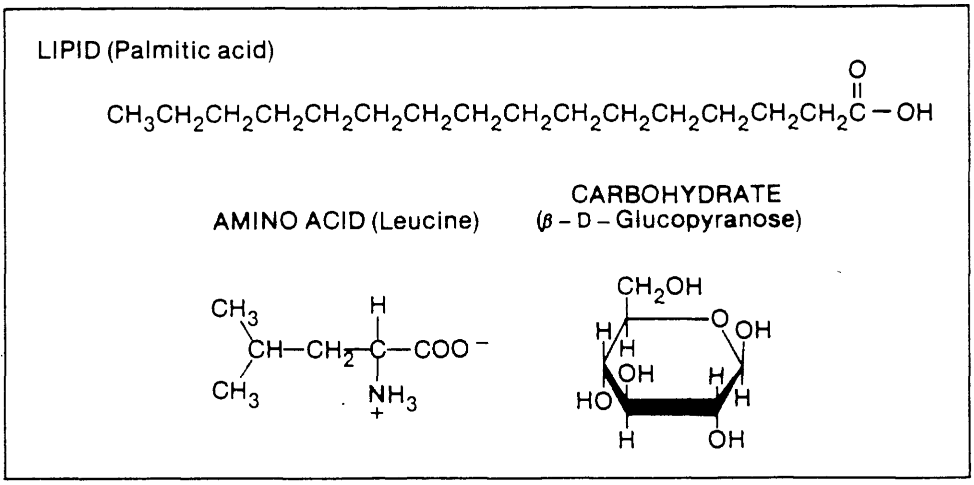


Figure B-1.--Examples of primary biological building blocks--lipids, amino acids, and carbohydrates (sugars).

## SOURCES OF ORGANIC COMPOUNDS IN GROUND WATER

Organic compounds in ground water can be grouped into biochemicals (formed by biological processes) and synthetic organic chemicals. Naturally occurring organic chemicals from biological processes can be leached or derived from the overlying soil zone during infiltration, formed by microbial processes within the aquifers, or leached from the surrounding rock matrix (Whitelaw and Edwards, 1980; Dunlap and Shew, 1981; Fazio and others, 1982; Foster and others, 1985). Several recent studies indicate that the naturally occurring organics include low molecular weight alcohols, hydrocarbons, organic acids, carbohydrates (polysaccharides), and amino acids (protein derivatives).

Natural carbon compounds such as carbohydrates are important as substrates for microbial activity within an aquifer. The presence or absence of a food source strongly influences the biodegradability of pollutants. For example, a recent study of the Chalk aquifer in England found high concentrations of nitrate at shallow depths in the unsaturated zone below arable fields (Whitelaw and Edwards, 1980; Foster and others, 1985). The carbohydrate concentrations in the pore waters varied between 2 and 10 mg/L. In the aquifer matrix, the carbohydrates decreased from 500 mg/kg near the surface to less than 100 mg/kg at a depth of 8 meters. In the same depth interval, nitrate decreased from a near-surface high of 15 mg/L to less than 2 mg/L (fig. B-2). These data indicate a close relationship between carbohydrate concentrations and nitrate concentration. The authors suggest that microbial activity is responsible for removing the infiltrating nitrate, and that carbohydrates are being utilized by nitrate-reducing organisms as a nutrient source.

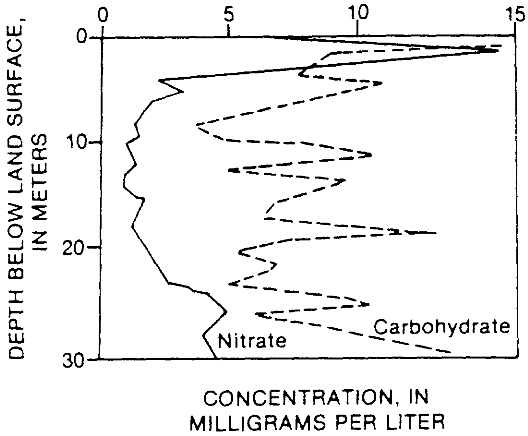


Figure B-2.--Carbohydrate and nitrate concentrations as a function of depth in porewaters in the Chalk aquifer, England. (Modified from Whitelaw and Edwards, 1980, p. 284. Copyright 1980, Elsevier; reproduced by permission.)

The amount of nitrate that can be reduced to $N_2$ depends on the type and quantity of oxidizable organic substrate available and on the establishment of anaerobic conditions. The amount of reducing equivalents ($H^+$)

generated by a carbohydrate such as glucose would be 24 hydrogen ions on complete oxidation, and 1 g would be sufficient to reduce approximately 0.4 g N 95 nitrate (Foster and others, 1985). Although the authors conclude that there is sufficient carbohydrate to serve as a substrate for nitrate-reducing organisms for many years at these sites, the examples illustrate a delicate balance between contaminant source and removal.

Bacteria may be a major source of ground-water carbohydrates and organic acids. Balkwill and Ghiorse (1985) report that many subsurface bacteria are surrounded by polysaccharide-based capsules and glycocalyx layers (also polysaccharide based). The polysaccharide strands of these structures commonly extend great distances from the cell surfaces to abiotic materials and provide a means of attachment (Balkwill and Ghiorse, 1985). These exopolysaccharides regulate the ionic traffic at the cell surface and concentrate nutrients such as amino acids, phosphates, and silica. They also protect microbes from toxic heavy metals and antibacterial agents such as those used in antifouling treatments. In aqueous environments, the outer molecules are continually being shed into the surrounding waters and may be a significant source of dissolved carbohydrates (Fazio and others, 1982).

Quantitative data on carbohydrates in ground water are scarce. A study near Hamburg, Germany, found that carbohydrate concentrations averaged 100 μg/L (Spitzy, 1982). These values are considerably less than those in areas of nitrate reduction in the Chalk aquifer in England (up to 10 mg/L). Preliminary data on concentrations of dissolved free amino acids in ground water were obtained from two observation wells during the summer of 1983 at Otis Air National Guard Base on Cape Cod, Mass. The concentrations increased from 117 μg/L in the sewage effluent to 373 μg/L approximately 50 meters away. Peptides, or combined amino acids, however, decreased markedly from 372 μg/L at the sewage outfall to 49 μg/L and 20 μg/L in the two wells (table B-2). Furthermore, the relative amounts of individual amino acids changed markedly from the proportions typical of algal protein at the sewage outfall to a composition dominated by serine, a component often associated with bacteria. These results suggest that the higher concentrations of free amino acids may be due to microbial activity. The Otis site is unusual in that it contains elevated concentrations of organic nitrogen, and the observed amino-acid concentrations may be correspondingly high relative to average ground water. In contrast to the Otis data, dissolved free amino-acid concentrations in waters from four wells in southern Florida ranged from 35 to 38 μg/L (SigLeo, written commun., 1982), and combined amino acids ranged from 21 to 367 μg/L in ground water near Hamburg, Germany (Spitzy, 1982).

Table B-2.--Amino acid concentrations in a sewage plume, Otis National Guard Base, Cape Cod, Massachusetts, 1983

[Values in micrograms per liter]

| Source or location | Dissolved free amino acids | Combined amino acids | Total amino acids |
|---|---|---|---|
| Sewage | 117 | 372 | 489 |
| Well FSW 230 | 74 | 49 | 123 |
| Well FSW 232 | 373 | 20 | 393 |

Domestic-waste disposal is a major source of proteins (amino acids) and other biochemicals. A leachate from a sanitary landfill site in Delaware had a high dissolved organic carbon (DOC) concentration (3,700 mg/L), which decreased rapidly downgradient to less than 20 mg/L as organic compounds were degraded and the leachate was diluted. In addition to the low-molecular-weight hydrocarbons methane, ethane, and ethene, eight organic acids (470 mg/L total) ranging from two to eight carbons per molecule were identified (Baedecker and Back, 1979). Volatile organic acids (two to six carbons per molecule) formed more than 95 percent (17,000 mg/L) of the total organic carbon (TOC) in a leachate collected from a municipal waste site in The Netherlands (table B-3). Volatile amines and ethanol also were present (0.8 and 0.7 percent of the TOC, respectively). Alcohols, hydrocarbons, esters, terpenes, and phthalates were identified in trace amounts in a hexane extract of the leachate (Harmsen, 1983).

Table B-3.--Concentration of major biochemical compounds in leachate from a municipal waste-disposal site in The Netherlands

[Data from Harmsen, 1983]

| Component | Acidification-stage leachate Concentration (mg/L) | | Acidification-stage leachate Total organic carbon (mg/L) |
|---|---|---|---|
| Free volatile fatty acids | | | |
| Acetic acid | 11,000 | | 4,400 |
| Propanoic acid | 3,760 | | 1,829 |
| 2-Methyl-propanoic acid | 520 | | 284 |
| Butanoic acid | 9,890 | | 5,395 |
| 2-Methyl-butanoic acid | 350 | | 206 |
| 3-Methyl-butanoic acid | 320 | | 188 |
| Pentanoic acid | 2,510 | | 1,476 |
| 4-Methyl-pentanoic acid | 70 | | 43 |
| Hexanoic acid | 5,770 | | 3,581 |
| | | Subtotal | 17,402 |
| Volatile amines | | | |
| Methylamine | 6 | | 2 |
| Trimethylamine | 83 | | 51 |
| t-Butylamine | 41 | | 28 |
| sec-Butylamine | 102 | | 67 |
| sio-Butylamine | 32 | | 21 |
| | | Subtotal | 169 |
| Alcohol | | | |
| Ethanol | 277 | | 145 |
| | | Subtotal | 145 |

The presence of most biochemicals, such as the compounds listed above, is considered harmless, although water companies prefer to remove the color, taste, and odor for esthetic reasons (Rook and others, 1982). Synthetic organic chemicals such as chlorinated hydrocarbons, however, can cause health problems ranging from nausea, dizziness, tremors, and blindness, to impairment of the central nervous system from high doses. When contaminants affect water-supply wells, they usually are present in concentrations that may cause long-term chronic illness rather than acute poisoning (Pye and others, 1983).

In contrast to most naturally occurring organic compounds, many of the synthetic organic pollutants are relatively resistant to degradation in the environment. They are more likely to resist biochemical processes in the soil zone and to be transported intact into the underlying ground water. Dunlap and Shew (1981) attribute the relative lack of knowledge concerning the probable influence of synthetic organics on ground-water quality in part to a preoccupation with the more visible problems of surface-water pollution and to a false sense of security concerning the protection afforded ground water by the overlying soil. In addition, it has only recently become possible to identify and quantify a large number of specific organic pollutants at the trace levels typically present in ground waters. Major analytical advances in techniques of compound separation (high-resolution gas and liquid chromatrography) and in methods of identification (computerized mass spectrometry and selective detectors) have been responsible for this development. The result has been a significant increase in the number of papers dealing with trace contaminants and an awareness that the inability to detect contaminants does not necessarily mean that they are not present.

It has been estimated that approximately 1 percent of the ground water in the United States is permanently contaminated, and more is likely to be unless planning and foresight are used in the disposal of wastes (Pye and others, 1983). Yet, in most areas, ground water is assumed to be relatively uncontaminated by toxic substances compared with surface water. To test this assumption, Page (1981) compiled data on the concentrations of 56 toxic substances in samples of ground water and surface water from New Jersey (table B-4). His data indicate that, in New Jersey, some ground waters and surface waters have similar patterns of contamination by toxic substances (Page, 1981). Of the 39 compounds listed by Page, 13 compounds show no significant concentration difference between surface and ground water, one compound (diiodomethane) has a higher probability of being found in ground water, and 25 compounds are more likely to be detected in surface waters. Although the long-term health effects of low-level exposure to carcinogenic and toxic substances in water supplies is unknown, ground-water-resource planners should be cognizant of the potential risks. As a general rule, hazardous, nondegradable organic chemicals that are only weakly hydrophobic (defined as having a solubility of less than a few milligrams per liter in water) appear to pose the greatest problem in water supply. Such compounds tend to be transported rapidly in ground water and are poorly removed during treatment (Schwarzenbach and others, 1983). Many of these persistent organic chemicals are solvents used in large quantity; they include the first 17 compounds listed in table B-4.

Table B-4.--Probability of detecting toxic compounds in New Jersey ground water and surface water

[Data after Page, 1981]

| Compound | Probability of detection<br>Ground water | <br>Surface water | Significantly different at 0.05 level |
|---|---|---|---|
| Fluoroform | 0.03 | 0.08 | yes |
| Methyl chloride | 0.01 | 0.04 | yes |
| Vinyl chloride | 0.01 | 0.03 | yes |
| Methylene chloride | 0.23 | 0.45 | yes |
| Chloroform | 0.64 | 0.64 | no |
| 1,2-Dichloroethane | 0.10 | 0.12 | no |
| 1,1,1-Trichloroethane | 0.78 | 0.79 | no |
| Carbon tetrachloride | 0.64 | 0.68 | no |
| 1,1,2-Trichloroethylene | 0.58 | 0.56 | no |
| Dichlorobromoethane | 0.34 | 0.43 | yes |
| 1,1,2-Trichloroethane | 0.07 | 0.09 | no |
| Dibromochloromethane | 0.14 | 0.18 | yes |
| 1,2-Dibromoethane | 0.08 | 0.06 | no |
| 1,1,2,2-Tetrachloroethylene | 0.43 | 0.88 | yes |
| Bromoform | 0.22 | 0.33 | yes |
| 1,1,2,2,-Tetrachloroethane | 0.06 | 0.11 | yes |
| Diiodomethane | 0.06 | 0.02 | yes |
| Total dichlorobenzene | 0.03 | 0.07 | yes |
| m-Dichlorobenzene | 0.02 | 0.04 | yes |
| p-Dichlorobenzene | 0.03 | 0.06 | yes |
| o-Dichlorobenzene | 0.03 | 0.03 | no |
| Aroclor 1242 | 0.11 | 0.08 | no |
| Aroclor 1248 | 0.06 | 0.14 | yes |
| Aroclor 1254 | 0.03 | 0.14 | yes |
| gem-Dichloroethylene | 0.44 | 0.65 | yes |
| Dibromomethane | 0.12 | 0.28 | yes |
| trans-Dichloroethylene | 0.51 | 0.63 | yes |
| Bromodichloroethane | 0.18 | 0.06 | no |
| BHC-alpha | 0.16 | 0.39 | yes |
| Lindane | 0.21 | 0.34 | yes |
| BHC-beta | 0.50 | 0.60 | yes |
| Heptachlor | 0.21 | 0.34 | yes |
| Aldrin | 0.26 | 0.24 | no |
| Heptachlor epoxide | 0.26 | 0.40 | yes |
| Chlordane | 0.40 | 0.56 | yes |
| O,p'-DDE | 0.19 | 0.44 | yes |
| Dieldrin | 0.17 | 0.39 | yes |
| Endrin | 0.11 | 0.14 | no |
| DDT | 0.09 | 0.18 | yes |

The principal sources of organic contaminants in ground water are sanitary-landfill leachates, industrial waste-disposal sites, mining activities, petroleum use and storage areas, chemical spills, pesticides and fertilizers, septic tanks, leaky sewers, and chlorination of otherwise natural products (Rook and others, 1982; Pye and others, 1983).

Compounds originating from obvious point sources of synthetic chemicals, such as landfills, industrial disposal sites, and chemical spills can range from benign to hazardous. The latter have received considerable publicity and form the basis for the U.S. Environmental Protection Agency (USEPA) Priority Pollutant List (Keith and Telliard, 1979).

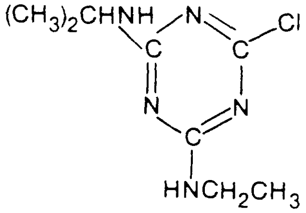
Fossil-fuel combustion, coal mining, and crude-oil processing all produce undesirable and commonly toxic products that can eventually be transported to aquifers in trace amounts. .Recently, underground coal gasification and oil-shale retorting have been considered as alternative fuel-extraction methods. The application of these techniques in the subsurface has caused concern that local ground water would be contaminated with leachates of the residual material that remains in the gasification or retort cavity, and with volatile organics that escape the underground formation (Leenheer and others, 1982; Stuermer and others, 1982). A detailed analysis of ground water collected near two underground gasification sites 15 months after the end of gasification indicated contaminant concentrations that ranged up to 50 mg/L (Stuermer and others, 1982). The 135 compounds identified included phenols, aromatic carboxylic acids, aromatic hydrocarbons, ketones, aldehydes, and the nitrogen-containing pyridines, quinolines, isoquinolines, and aromatic amines. Many of these compounds are on the USEPA Priority Pollutant list (Keith and Telliard, 1979).

Aquatic organisms and their natural products are precursors for some ground-water contaminants at river-infiltration sites (Oliver, 1983). The classic examples of these products are formed by decarboxylation and deamination of proteins during chlorination of drinking and cooling water, and during sewage disinfection (Rook and others, 1982; Helz and others, 1983). These products include halogenated organics such as chloroform, methyl chloride, and chloroamines. All of these compounds, as well as dihaloacetonitriles, have been reported in drinking water and can be formed experimentally by aqueous-solution chlorination of amino acids and by chlorination of algae under conditions similar to those used for water treatment (Oliver, 1983).

The most prevalent nonpoint source of ground-water contamination is from agriculture (Pye and others, 1983). Fertilizer residues, herbicides, insecticides, and fumigants have been reported in ground water worldwide (Whitelaw and Edwards, 1980; Nelson and others, 1981; Stibral and Vrba, 1981; Wehtje and others, 1981; Zoeteman and others, 1981; Pye and others, 1983; Foster and others, 1985). As illustrated in the earlier case of nitrate from fertilizers, however, quantities of carbohydrates generated either in the soil zone or aquifer matrix are often sufficient to provide a substrate for nitrate-reducing bacteria to eliminate the contaminant before it reaches the water table (Whitelaw and Edwards, 1980; Foster and others, 1985).

Pesticides in the environment are far more insidious. Chosen originally for their toxic qualities, these compounds typically degrade slowly and are persistent in soils, which results in ground-water contamination in rural areas. For example, the persistence of the soil fumigant DBCP (1,2-dibromo-3-chloropropane) resulted in its ban in 1977. In one study, 6 to 7 years after application in California, all wells sampled within 5 km of application had some contamination, and over 50,000 people were continuously or intermittently consuming water with DBCP concentrations that exceeded California State Health recommendations (Nelson and others, 1981). Some pesticides, such as atrazine (fig. B-3), are subject to chemical hydrolysis (rate = 5 percent per year) in which the chlorine is replaced by an OH radical and the compound is detoxified (Wehtje and others, 1981). Still others are subject to biodegradation, which is discussed in later sections.

Figure B-3.--Structure of the herbicide atrazine, which can be detoxified through replacement of the -Cl by -OH radical through hydrolysis.



## TRANSPORT AND FATE OF SYNTHETIC ORGANIC CHEMICALS

The transport and fate of organic pollutants in ground water are influenced by the processes of dispersion, hydrolysis, sorption/desorption, and biological degradation (Roberts and Valocchi, 1981). The fate of hydrophobic organics is influenced primarily by their sorption behavior and biodegradability.

### Sorption

The sorption of organic materials by sediments and soils is dependent on the properties of the adsorber and the adsorbant. A number of sediment/soil properties have been related to the sorption of hydrophobic organics; these include organic-carbon content, clay-mineral content, and pH. Research in several laboratories has demonstrated that the sorption behavior of nonpolar, hydrophobic organics can be related primarily to the organic-carbon content of sediments (Chiou and others, 1979; Karickhoff and others, 1979; Means and others, 1979; 1982), and of colloidal materials in surface waters (Means and Wijayaratne, 1982; Wijayaratne and Means, 1984) and aquifers (Means, 1983). For this reason, the amount of sorbed compound is commonly reported in terms of the amount sorbed per gram of organic carbon ($K_{oc}$ values). The sorption constants ($K_{oc}$) correspond to the slopes of adsorption isotherms that follow the equation:

$$C_s = K_{oc} Cw \qquad (1)$$

where: $C_s$ = amount of substrate sorbed,
$C_w$ = equilibrium concentration of substrate in solution, and
$K_{oc}$ = distribution coefficient or slope (fig. B-4).

For the sorption isotherms illustrated in figure B-4, substrate 8 contains the least amount of carbon, and substrate 23, which has the highest sorptive capacity, contains the largest amount of organic carbon (Means and others, 1982). All of the sorption reactions were reversible. Sorption coefficients have been determined for a number of organic pollutants, including chlorinated hydrocarbons, substituted polynuclear aromatic hydrocarbons (fig. B-4), acetophenone, aromatic amines, and the pesticides atrazine and linuron (Chiou and others, 1979; Karickhoff and others, 1979; Means and others, 1979; 1982, Schwarzenbach and Westall, 1981; Means and Wijayaratne, 1982; Means, 1983). A comparison of sorption characteristics of soils as a function of surface-water organic colloidal material (less than 0.40 m) indicates that, if normalized according to organic carbon content, the colloidal material can be up to 35 times better as a sorptive substrate for the herbicides atrazine and linuron than sediment or soil organic matter (table B-5). Means and Wijayaratne (1982) suggest that the increased sorptive capacity is due to increased exposed organic surface area in the aquatic colloids relative to soil organic matter. Further studies suggest that colloidal organic matter can enhance the solubility of hydrophobic organic pollutants by incorporation into highly soluble, stable complexes that can be transported great distances (Wijayaratne and Means, 1984).

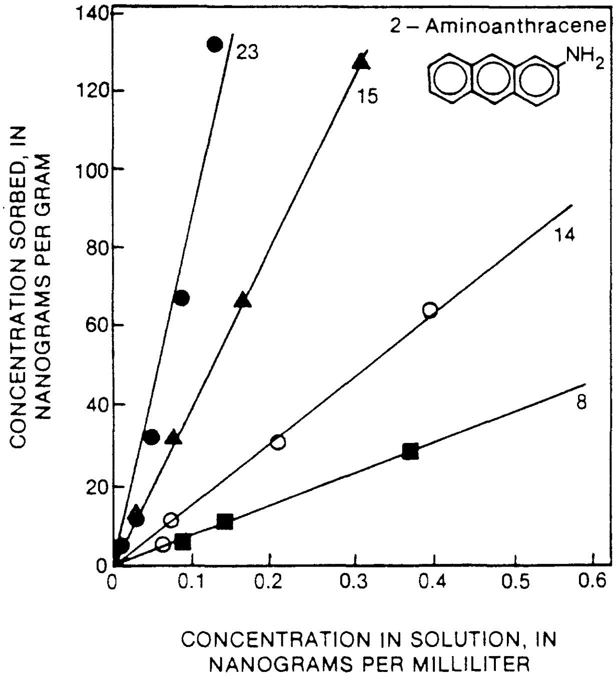


Figure B-4.--Concentration of 2-amino-anthracene sorbed onto four soils. (Modified from Means and others, 1982, p. 95. Copyright 1982, American Chemical Society; reproduced by permission.)

Table B-5.--Comparison of sorption constants for atrazine and linuron

[Data from Means and Wijayaratne, 1982]

| Substance and source | Range of distribution coefficients ($K_{oc}$) |
|---|---|
| Atrazine | |
| Soils | 47-390 |
| Colloidal dissolved organic carbon | 1,700-14,000 |
| Linuron | |
| Soils | 124-2,680 |
| Colloidal dissolved organic carbon | 6,200-6,800 |

To assess the sorption potential of organic colloids present in subsurface waters, sorption experiments were performed with the aromatic amines aniline, 4-chloroanaline, and 2, 4-dichloroanaline. Preliminary results indicate that the sorptive capacities of ground-water colloids are similar to those of surface-water colloids (Means, 1983).

The sorption coefficient is generally considered equivalent to a retardation factor for the movement of hydrophobic materials in an aquifer. However, organic matter, measured collectively as TOC, decreases·primarily in the vicinity of recharge during flow through an aquifer (Roberts and Valocchi, 1981; Schwarzenbach and others, 1983). For several sites, the average TOC values decreased from 2.8 to 1.3 mg/L during flow through 40 m of aquifer, and half the decrease was in the first 10 m. The fraction of TOC that was not degraded appeared to be transported as rapidly as a conservative tracer (Roberts and Valocchi, 1981). If this observation is considered with the sorption data discussed earlier, the conclusion is that a hydrophobic toxic compound assumed to be relatively immobile in the environment can, in fact, become soluble and be transported by sorption to soluble organics compounds.

## Biodegradation

Biodegradation refers to the removal of an organic solute from solution when the solute is utilized by micro-organisms as a substrate for energy and growth. Several factors affect this process, including sorption/desorption, critical-concentration effects, aerobic versus anaerobic conditions, preexposure, and the presence of natural biochemicals. All of these processes are interrelated, and the successful removal of an undesirable toxic component requires the establishment of a mixed microbial community capable of utilizing (or surviving) a variety of compounds. Several recent studies have focused on the biotransformation of synthetic organic compounds such as pesticides, halogenated organics, aromatics, and nitrogen-substituted aromatics (Healy and Young, 1979; Liu and others, 1981; Suflita and others, 1982; Bouwer and McCarty, 1983a; 1983b; Hallas and Alexander, 1983; Jesse and others, 1983; Spain and Van Veld, 1983; Wilson and others, 1983; Hutchins and others, 1985).

The importance of environmental conditions was shown by Nelson and others (1981) in biodegradation studies of the pesticides 2,4-D and fenitrothion. 2,4-D was found to degrade readily under aerobic conditions but not under anaerobic conditions, whereas fenitrothion was degraded faster under anaerobic conditions (Nelson and others, 1981). Anaerobic conditions also were required for a stable methanogenic bacterial community to mineralize a variety of halobenzoates to methane and carbon dioxide *in vitro* (Suflita and others, 1982).

The significance of microbial adaption was illustrated by Healy and Young (1979), who observed that anaerobic populations acclimated to a particular aromatic substrate such as vanillin could be simultaneously acclimated to other selected aromatic substrates such as cinnamic acid and the lignin products syringaldehyde, benzoic acid, and phenol. A facultative anaerobic bacterium isolated from a stream sediment was able to degrade cyanuric acid using the amino acid cysteine as a cometabolite (Jesse and others, 1983). Of particular interest was the observation that this bacterium was also capable of degrading the herbicide atrazine (fig. B-3).

## Field Studies

Several research groups have taken a multidisciplinary approach and combined hydrologic, chemical, physical, and microbiological expertise to describe organic processes under field conditions (Ehrlich and others, 1982; Schwarzenbach and others, 1983; Hutchins and others, 1985).

Phenolic compounds, polynuclear aromatic hydrocarbons (PAH), and other compounds derived from coal-tar distillates have contaminated ground water at several places in the United States (Ehrlich and others, 1982). Initial studies of one such site at St. Louis Park, Minn., indicated that phenolic compounds and naphthalene were disappearing more rapidly than expected if only dilution were occurring. The results of this study indicated that phenolic compounds in the ground water were converted to methane and carbon dioxide by anaerobic bacteria. This conclusion was based on the observations that over 95 percent of the total phenolic compounds were removed within 1,000 m of the contamination source, and that methane and methanogenic bacteria were present in the contaminated parts of the aquifer but not elsewhere. Naphthalene, on the other hand, appeared to be decreasing through sorption.

At two sites in Switzerland, Schwarzenbach and others (1983) investigated the transport and fate of organic micropollutants, including chlorinated phenols, during natural infiltration of river water to ground water. In agreement with predictions from sorption calculations, persistent organic chemicals exhibiting octanol-to-water partition coefficients ($K_{ow}$) smaller than about 5,000 moved rapidly with the infiltrating river water to the ground water. Biological processes responsible for the degradation of the alkylated and chlorinated benzenes occurred predominantly within the first few meters of infiltration. Anaerobic conditions in the aquifer near the river hindered the biological transformation of some pollutants. Compounds containing one or more halogen atoms tend to be more persistent in the environment (and more toxic) than compounds that do not. The difference in behavior of two similar compounds, dimethylbenzene and dichlorobenzene, during infiltration illustrates this point (fig. B-5). Among the compounds that were found to be persistent under any conditions were the solvents chloroform, trichloroethane, trichloroethylene, and tetrachloroethylene (fig. B-5).

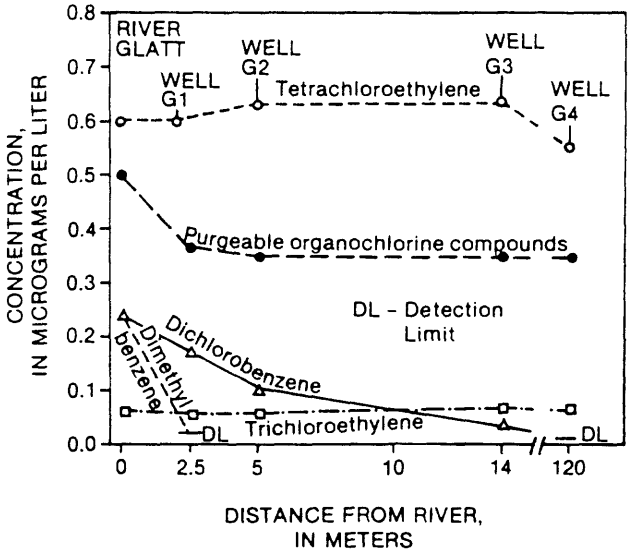


Figure B-5.--Average concentrations of selected organic micropollutants in relation to distance from river during infiltration of river water to ground water. (Modified from Schwarzenbach and others, 1983, p. 475. Copyright 1983, American Chemical Society; reproduced by permission.)

The transport of trace amounts of organic compounds through soil columns during rapid infiltration were investigated under a variety of conditions by Hutchins and others (1985). These results showed that trace-organic removal is minimal unless an adapted microbial community capable of trace-organic degradation is present. Furthermore, the extent of trace-organic removal depends not only on the nature of the compound, but also on its initial concentration. In other words, a minimum, or critical, concentration of the compound is required to initiate its microbial consumption.

## SUMMARY

Biochemicals in ground water are natural products of biological processes. Synthetic organic chemicals are derived from landfills, industrial wastes, sewage, and agricultural activities.

As a general rule, hazardous, nondegradable organic chemicals that are only weakly hydrophobic appear to pose the greatest problem in water supplies. These compounds tend to be transported rapidly in ground water, are poorly removed during treatment, and commonly are not biodegradable. Many of these persistent organic chemicals are solvents used in large quantities, thus compounding the difficulty of removal (Schwarzenbach and others, 1983).

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## CHAPTER C

# THE ROLE OF EARTH-SCIENCE CRITERIA IN THE SELECTION OF HAZARDOUS-WASTE DISPOSAL SITES

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## ABSTRACT

Earth-science criteria should be part of a rational, objective method for selecting sites for disposal of hazardous-chemical wastes on the land surface or in the subsurface. The functional requirements of the disposal system that must be met by the geologic, hydrologic, and geochemical characteristics of the site and its surroundings in degrading and isolating the wastes should be the basis for developing the criteria. These functional requirements are determined as part of an analytical process that generally involves identification and description of the waste problem, characterization of the wastes, consideration of possible alternative solutions, description of the chosen solution and its specific objectives, and description of the disposal system that must be developed to achieve the solution. Ideally, the earth-science criteria should be used in combination with criteria related to engineering, economics, and social and environmental effects of the disposal system to select sites suitable for a disposal facility. The locating of sites for nuclear-waste disposal has been approached as described above and can provide an example for disposal of other types of hazardous wastes.

Aqueous wastes that are easily degradable by oxidation and biological activity can be applied to the land surface and treated by essentially natural processes. Physical and geochemical properties of soils and near-surface geologic materials are important criteria in siting facilities for these types of degradable wastes. Nondegradable, extremely hazardous-chemical wastes require permanent isolation from the biosphere if burial or injection through wells is chosen for their disposal. Burial or injection, if it is to provide adequate safety without continuing operational or maintenance efforts, must take advantage of a site's natural geologic, hydrologic, and geochemical barriers that prevent migration of the wastes to the biosphere. Criteria for locating suitable sites should be related to attributes that favor long-term stability of the site, long paths and low velocities of ground-water flow, downward directions of ground-water flow, chemical retardation of waste movement, and deep burial.

Current burial techniques employ secure landfills and rely mainly on packaging of wastes, manmade barriers to waste movement, and effluent controls to provide isolation of the wastes from the biosphere. In many States, the requirements for site selection are related to site location (setback standards or areal exclusion criteria). A potential problem with regard to secure landfills is that when engineering measures fail in the future, many sites may not have the natural geologic, hydrologic, and geochemical barriers necessary to maintain isolation of the wastes because inadequate earth-science criteria were used during site selection.

# INTRODUCTION

Environmental law and regulation have recognized that hazardous-waste problems are not only local but also are regional, national, international, and global. Such problems are broad in scope; they cut across the full range of man's activities and affect his very well-being. Furthermore, solutions to specific waste-management problems often lead to other problems that may be quite different both in duration and character.

Disposal of wastes by means that allow releases to the atmosphere, freshwater bodies, and the ocean, often have far-reaching and unanticipated effects. Disposal in the subsurface has been commonly used, often for convenience but also with the idea that such releases may be avoided. Many subsurface disposal facilities have failed in this regard; wastes from many of them have been dispersed by soil water, ground water, and surface runoff, and have entered the environment. The worst incidences of such failures have been where pollutants from the disposal sites have been confined to plumes within ground-water systems and have affected public water supplies.

Recent legislation and regulations for waste disposal (table C-1) have focused to a large extent on land and subsurface disposal and, in particular, on protection of subsurface waters. These laws and regulations not only protect subsurface waters from pollution for use as water supplies, but also acknowledge that circulating subsurface water is a pathway by which toxic-waste materials from disposal facilities can enter the environment and the food chain of man. It is under the encompassment of a variety of laws and regulations that subsurface and land disposal of hazardous chemical wastes is being actively pursued by Federal, State, and local governments and by a host of industrial firms that produce most of the waste.

Among the available disposal technologies are methods to emplace the waste in geologic and ground-water systems through landfills and injection wells. Land-treatment facilities in which aqueous wastes are spread on the land surface or placed in shallow ponds are also used. In these facilities wastes are allowed to infiltrate into the ground and ideally are degraded to innocuous materials or are retained in the soil.

The National Research Council's Committee on Disposal of Hazardous Industrial Wastes (1983) has recommended disposal of the most hazardous wastes in mined openings in geologic environments that can isolate the wastes from the biosphere. Disposal in mined openings (repositories) is also being actively pursued for high-level radioactive wastes and spent fuel from nuclear reactors. Low-level radioactive wastes, like many hazardous wastes, are disposed of in landfills (burial grounds). In fact, though radioactive and hazardous chemical wastes are covered by different laws and regulations, technical problems of disposal are similar (Robertson, 1982). The experience with managing radioactive wastes has been long and intensive, and much can be learned from it with regard to disposal of hazardous chemical wastes.

Compared to nuclear-waste disposal, chemical-waste disposal in subsurface environments is deficient in establishing and using earth-science criteria for selecting disposal sites. Ideally, such criteria are predicated on an understanding of the character of the wastes and their behavior in a subsurface environment, so that favorable and unfavorable geologic, hydrologic, and geochemical characteristics can be determined. Identification of these characteristics provides a yardstick by which the capability of sites to isolate and degrade wastes can be appraised. When these characteristics are coupled with a disposal objective (which may allow particular concentrations or loads of wastes to be released or may call for total containment) and with a conceptual design of a disposal facility, the geologic, hydrologic, and geochemical criteria for site selection can be defined. These criteria can then be used through a screening process to identify suitable candidate sites for disposal of wastes. Once selected, a candidate site must be studied in detail to determine whether it will provide the required isolation and is indeed suitable for a disposal facility.

Table C-1.--Laws affecting ground-water contamination and protection

Federal Water Pollution Control Act of 1972
Public Law 93-523

Safe Drinking Water Act of 1974
Public Law 93-523

Federal Insecticide, Fungicide and Rodenticide Act of 1975
Public Law 92-516
Amended by Public Law 94-140

Toxic Substances Control Act of 1976
Public Law 94-469

Resource Conservation and Recovery Act of 1976 (RCRA)
or Solid Waste Disposal Act
Public Law 94-580

Surface Mining Control and Reclamation Act of 1977
Public Law 95-87

Safe Drinking Water Act as Amended November 1977
Public Law 95-190

Clean Water Act of 1977
(Federal Water Pollution Control Act as Amended)
Public Law 95-217

Clean Water Act Amendments of 1980
Public Law 96-483

Comprehensive Environmental Response, Compensation and
Liability Act of 1980 (CERCLA or Superfund)
Public Law 96-510

Executive Order 12316 of August 14, 1981

These earth-science criteria should be part of a comprehensive, rational method for selecting sites for hazardous-waste disposal. Economic, social, environmental, transportation, and possibly other criteria should also be part of the method. Using a rational method of selecting sites has several advantages. Geologically and hydrologically suitable disposal sites are more likely to be selected, and the early evaluation of environmental, social, and economic effects will help to minimize or mitigate adverse results. Unsuitable areas and sites will probably be eliminated at an early stage, which would save time and money. Persons or entities making the decision are in a more defensible position against charges of arbitrariness. The siting decision rests on a broad base and discourages one-sidedness, such as basing a decision mainly on the ability of the affected population to object, which has often been done (U.S. General Accounting Office, 1983).

## DEVELOPMENT OF SITING CRITERIA AS PART OF A PHASED RESOLUTION OF HAZARDOUS-WASTE PROBLEMS

The scale, scope, and the various interconnected issues of most hazardous-waste problems require that solutions be obtained through detailed systematic analysis. The general solutions to such problems are succinctly discussed in a report by the National Research Council's Committee on Disposal of Hazardous Industrial Wastes (1983). The solution phases depicted in figure C-1 are taken from that report.

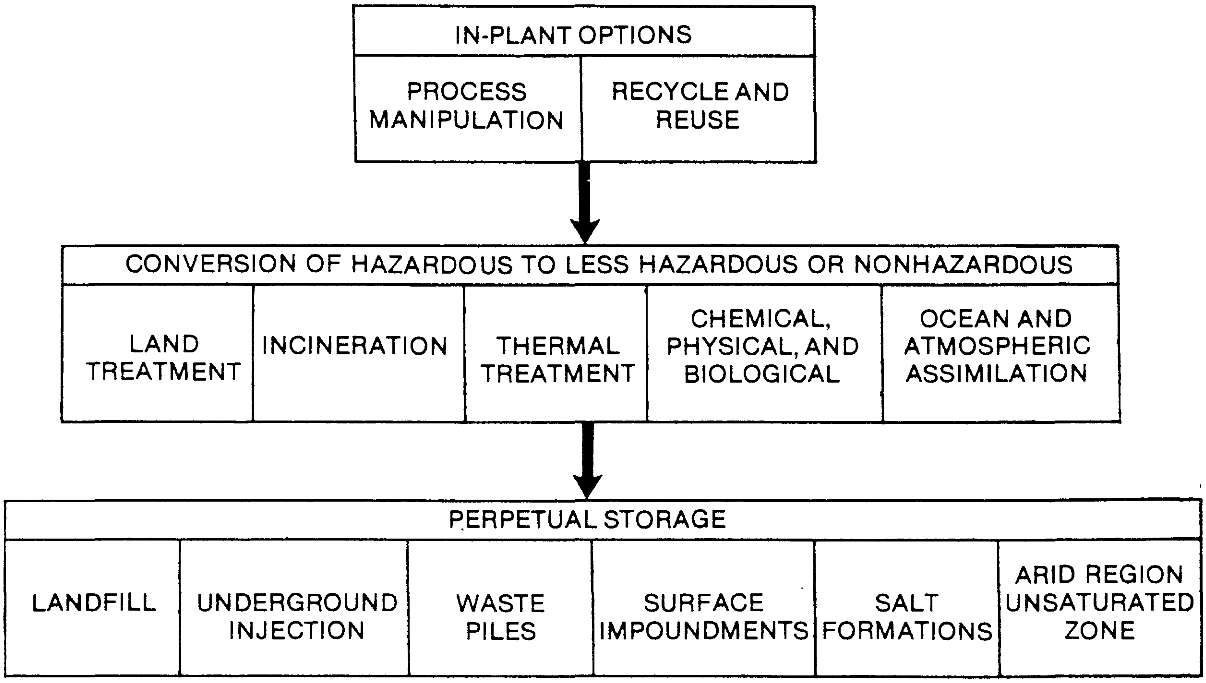


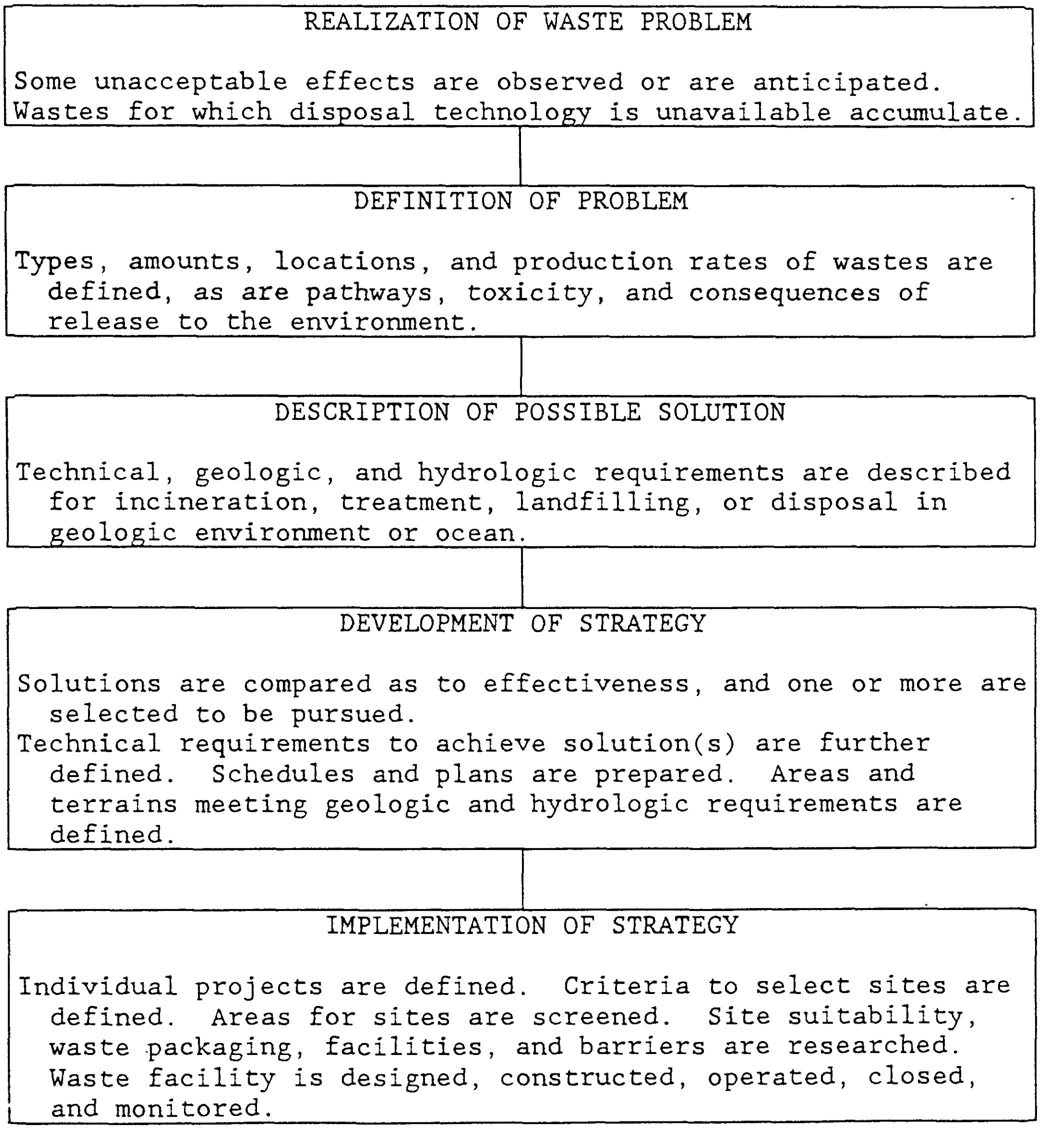
Figure C-1.--General solutions to hazardous waste problems. (From National Research Council, Committee on Disposal of Hazardous Industrial Wastes, 1983, p. 3, fig. 4.)

The first level of solution is to recycle the wastes within the plant producing them, or to manipulate processes in order to avoid producing the wastes. The second level of solution is to convert the wastes to less hazardous or nonhazardous materials. (Of the means given in figure C-1 to achieve this, only land treatment would depend heavily on the geologic, hydrologic, and geochemical character of a particular site.) The third level of solution is perpetual storage. All of the third-level solutions involve important considerations of the geology, hydrology, and geochemistry of the sites. For example, the "salt formations" and "arid region unsaturated zone" mentioned in figure C-1 refer to the proposal to emplace wastes in mined openings in these environments at depths that would prevent the wastes from reaching the surface or usable ground-water supplies. The Committee refers to recent research on radioactive-waste disposal in suggesting perpetual storage in a suitable geologic environment. The status of technology for isolating radioactive wastes in geologic repositories is discussed by Klingsberg and Duguid (1980).

A generic analysis for solving a waste problem is depicted in figure C-2. In the following discussion of the analysis, information is drawn from the U.S. Department of Energy's Civilian Radioactive Waste Management Program (formerly the National Waste Terminal Storage Program) for the purpose of demonstrating how earth-science criteria are developed and used. This program was selected as an example because it is well focused, because responsibilities for its regulation and execution are well defined, and because it is national in scope.

The initial phase of the analysis (fig. C-2) is the recognition of a problem. This recognition may come about because environmental degradation or health effects are noted. It may also come about because of accumulation of a waste product that cannot be disposed of simply without legal, social, or economic penalty. An example is spent fuel from a nuclear power reactor. Spent fuel is the most radioactive waste in existence and poses a great hazard unless well controlled. This potential hazard was recognized before the country embarked on a private nuclear-energy program. However, an interim solution was chosen to manage the spent fuel because no technology was available for disposing of it. The fuel was to be placed in water-filled pools at the reactor sites where it was produced until means became available to (1) dispose of it permanently or (2) extract unused fuel materials from it and dispose of the byproducts permanently. The means of disposal and reprocessing have not been developed, and the storage pools have been largely utilized. The need to do something with the spent fuel is therefore becoming critical. Under Federal law (the Nuclear Waste Policy Act of 1982, Public Law 97-425), a utility retains its spent fuel in a storage facility approved and licensed by the Nuclear Regulatory Commission until the Department of Energy takes custody of it for disposal or interim storage prior to disposal.

The second phase is definition of the waste problem. This involves defining the amounts and types of wastes, locations, production rates, consequences of their release to the environment, and social and legal responsibilities. The Department of Energy has continually evaluated the extent of the spent-fuel problem (U.S. Department of Energy, 1983b). The spent fuel in storage has been inventoried in relation to available pool storage, modifications that could be made to the storage pools to increase capacity, and additional interim storage facilities that may be required. The radionuclide and elemental contents have been determined for specimens typical of various types of fuel. Future production rates and schedules have been estimated, as well as a schedule at which the Department of Energy must receive the spent fuel. Transportation requirements and hazards are being evaluated (Klein, 1984; McSweeney and others, 1984). To an extent, the hazardous-waste problem is being defined with regard to existing waste sites under Public Law 96-510 and other laws. Unlike nuclear-waste problems, however, no comprehensive studies of all phases of hazardous-waste problems are in progress. The definition of problems is more difficult with hazardous than with radioactive wastes because of the much larger volumes and greater varieties of hazardous wastes, the many closed and operating disposal sites, and the many producers of wastes.



REALIZATION OF WASTE PROBLEM

Some unacceptable effects are observed or are anticipated.
Wastes for which disposal technology is unavailable accumulate.

DEFINITION OF PROBLEM

Types, amounts, locations, and production rates of wastes are defined, as are pathways, toxicity, and consequences of release to the environment.

DESCRIPTION OF POSSIBLE SOLUTION

Technical, geologic, and hydrologic requirements are described for incineration, treatment, landfilling, or disposal in geologic environment or ocean.

DEVELOPMENT OF STRATEGY

Solutions are compared as to effectiveness, and one or more are selected to be pursued.
Technical requirements to achieve solution(s) are further defined. Schedules and plans are prepared. Areas and terrains meeting geologic and hydrologic requirements are defined.

IMPLEMENTATION OF STRATEGY

Individual projects are defined. Criteria to select sites are defined. Areas for sites are screened. Site suitability, waste packaging, facilities, and barriers are researched. Waste facility is designed, constructed, operated, closed, and monitored.

Figure C-2.--Phases in identification and solution of a waste problem.

The third phase is identification and description of possible solutions. In the civilian high-level radioactive waste program, some of the solutions considered were geologic disposal in a mined repository, very deep drill holes to emplace waste in the earth, emplacement of packaged wastes in the seabed, transmutation of the radioactive elements in nuclear reactors, and transporting the wastes into space (Interagency Review Group on Nuclear Waste Management, 1978; 1979; U.S. Department of Energy, 1980b, p. 1.16-1.120). Solutions to hazardous-chemical-waste problems probably would include incineration and land treatment but doubtless would exclude disposal in space. Conceptual engineering studies and appraisal of natural-system requirements (including geologic, hydrologic, and geochemical factors) are part of the descriptions of the solutions. In the Department of Energy's Civilian Radioactive Waste Management Program, the attributes related to public safety and the earth-science characteristics that should be present at a site were determined after a lengthy period involving many interactions within the technical and scientific communities, Department of Energy, the U.S. Environmental Protection Agency, the Nuclear Regulatory Commission, and the U.S. Geological Survey. These attributes have been formalized in rules and other documents (U.S. Environmental Protection Agency, 1984; U.S. Department of Energy, 1980c; 1983a; U.S. Nuclear Regulatory Commission, 1982, 1984). In addition to this identification of requirements, some appraisal must be made of the possibility of finding sites that have the characteristics to provide the required performance. It is at this time that siting criteria begin to take shape.

The fourth phase is development of a strategy. Solutions are compared as to effectiveness, technological development needed, and time and cost requirements and one or more solutions are selected to be pursued. The requirements to achieve the selected solutions are further defined, and schedules and plans to implement the strategy are prepared (U.S. Department of Energy, 1980a: 1982). For the disposal of civilian high-level radioactive waste, President Carter (1980) adopted the recommendation of the Interagency Review Group on Nuclear Waste Management (1979, p. 610) that mined repositories be the primary solution.

Geologic disposal in mined repositories requires earth-science criteria for selecting sites. In developing the criteria for siting a geologic repository, the Department of Energy drew upon general requirements and guidelines that previously had been set forth. For instance, a report by a National Academy of Sciences committee on geologic disposal (1957) recommended consideration of salt as a disposal medium. The U.S. Geological Survey (Pierce and Rich, 1962) made an initial study of salt deposits and recommended areas for further consideration on the basis of some broad requirements. The Department's strategy with regard to siting was to pursue a nationwide screening of salt deposits and to investigate Department-owned lands as to their suitability for geological disposal. These efforts were directed toward developing an initial repository. A second repository would be needed later; thus, the Department included crystalline rocks in its considerations of suitable disposal media to obtain a wider choice of location and hydrogeologic settings.

The fifth phase is implementation of the solution. Development of the performance requirements of the disposal system continue, and the end result is determination of the characteristics of the system necessary to isolate and allow for degradation of the wastes. Parametric limits must be placed on at least some geologic criteria; however, a more difficult task is translating the criteria into a set of characteristics that can be used to screen areas for suitable sites and, finally, to select a site for the disposal facility. An intensive effort is made at geologic and hydrologic characterization in order to classify areas as to their suitability for a disposal site from the criteria and parametric limits placed on them. For the Department of Energy's Civilian Radioactive Waste Program, the screening of large regions to identify sites suitable for a repository was approached under a published set of criteria that include environmental and socioeconomic consideration as well as geologic, hydrologic, and geochemical consideration (U.S. Department of Energy, 1980a). Following passage of the Nuclear Waste Policy Act of 1982, much more detailed criteria (termed "guidelines" in the Act) were developed that will be used in the final selection of a site from among several sites that have been identified (U.S. Department of Energy, 1983a). The selection of a site makes possible the final design of the disposal system. In the case of the Civilian Radioactive Waste Program, this system must be licensed by the Nuclear Regulatory Commission. During the course of the licensing, an independent review is made of the data, analyses, and designs supporting the qualifications of the site and disposal system. Only after the site is licensed can construction begin. An operating license is issued only after construction has been demonstrated to be satisfactory.

Robertson (1982) has pointed out that although technical problems of disposal of hazardous and radioactive wastes are similar, there are important differences in the legal and institutional approaches to management and in the quantities and numbers of locations at which the wastes are produced and stored. The Federal Government has the responsibility for disposal of high-level radioactive wastes and for regulation of the relatively few generators of the waste. Responsibility for hazardous chemical wastes is more diffuse, and generators are responsible for disposal in most cases. No nationwide, planned effort to achieve disposal of hazardous chemical wastes has yet appeared, even though these wastes are ubiquitous and a national problem. Criteria for selecting sites for hazardous-waste disposal are being developed mainly by the States, and in some States do not include geologic, hydrologic, or geochemical considerations.

## PROCESSES OF LOCATING SITES FOR HAZARDOUS-WASTE DISPOSAL

The National Research Council's Committee on Disposal of Hazardous Wastes (1983, p. 65) points out that:

> "From the public perspective, burial and isolation of hazardous wastes are commonly viewed as fundamentally the same; they are not. Burial of wastes is not a difficult technical problem. Wastes can be buried in essentially any location desired. However, providing the long term isolation of hazardous materials from the biosphere is more difficult. This concern for providing isolation is predicated on what is considered to be one unalterable fact. After all efforts have been expended to render hazardous wastes nontoxic, to reduce them in volume, to recycle or reuse them, etc., most of the remaining nonreducible toxic

> materials ultimately will be disposed of by burial in the deep subsurface, thereby isolating them from the biosphere. This is the final step in disposal. Few other options for handling such wastes are available."

Wastes generally are buried in secure landfills (landfills containing an impermeable barrier) whose siting requirements may include few earth-science criteria; this may be because most earth-science considerations are considered irrelevant from the standpoint of design and construction or because they are not specified in environmental regulations. A secure landfill is essentially dependent on engineering measures (U.S. Environmental Protection Agency, 1984). The National Research Council Committee (1983, p. 63) points out drawbacks and unknowns with regard to risks to the public and to long-term projections of performance (greater than 500 years) when engineering measures may no longer be effective. On the other hand, the Committee (1983, p. 63-71) turns to permanent burial in mined-out areas and solution cavities in salt as providing a possible solution to the hazardous-waste problem. Many of the ideas the Committee puts forth have been investigated for high-level radioactive waste disposal; thus, it is fruitful to review what has been done for high-level radioactive waste disposal under the Department of Energy's Civilian Radioactive Waste Management Program as we consider the application of earth-science criteria to the siting of disposal facilities.

## Screening for Mined Repositories

Legislation and Federal regulations recognize that the only satisfactory approach to the siting of high-level radioactive waste disposal facilities is to establish rational criteria that consider a large variety of factors pertaining to health and safety, socioeconomic effects, and environmental quality. Earth-science siting criteria enter under health and safety factors because it is in reference to these criteria that the ability of a site to isolate wastes is appraised.

The U.S. Department of Energy used earth-science and other criteria to screen the United States to select a site underlain by rock salt that would be suitable for constructing a mined repository for spent fuel and high-level radioactive waste. This search had its origins in a recommendation of a panel of the National Academy of Sciences (1957) that salt deposits should be investigated for the disposal of radioactive waste. Attention was focused early in the investigation on a salt mine at Lyons, Kansas. Much was learned of the mechanical behavior of salt in relation to the safety of waste emplacement from tests that were done in this mine. When the Energy Resources and Development Agency (ERDA), a predecessor agency of the Department of Energy, decided to proceed to use the mine for disposal, objections were brought forth on hydrologic disabilities of the site. The principal objection was that the many boreholes drilled in the area posed the potential of connnecting overlying aquifers with the disposal facility and provided a means of dissolving the salt and allowing wastes to move to the environment. In 1972, the proposal to dispose of wastes at Lyons was withdrawn. A more systematic and rational quest was needed to find a suitable site underlain by salt deposits.

During 1972-76, ERDA conducted geological reconnaissances in the Permian basin of Texas and Oklahoma (Johnson, 1976) and the Paradox basin of Utah and Colorado (Hite and Lohman, 1973). Earlier work by the U.S. Geological Survey (Anderson and others, 1973) was the basis for further screening of the Gulf Coast salt domes. In 1976, the National Waste Terminal Storage Program was initiated to conduct the investigations required to select a disposal site. Criticism of the program resulted in establishment of the Interagency Review Group on Radioactive Waste Management by President Carter. The work of the Interagency Review Group was noteworthy in bringing a systems-analysis approach to the program and defining technical issues requiring investigation. President Carter's policy statement of 1980 laid out an interim strategy of geologic disposal that was to proceed in a rational, stepwise manner and that was aimed at defining four or five sites suitable for disposal from which a selection would be made for construction of a mined repository. The stepwise approach, illustrated in figure C-3, uses geologic and hydrologic criteria as well as socioeconomic and environmental criteria. The process is explained using the Permian region of Texas (fig. C-4) as an example.

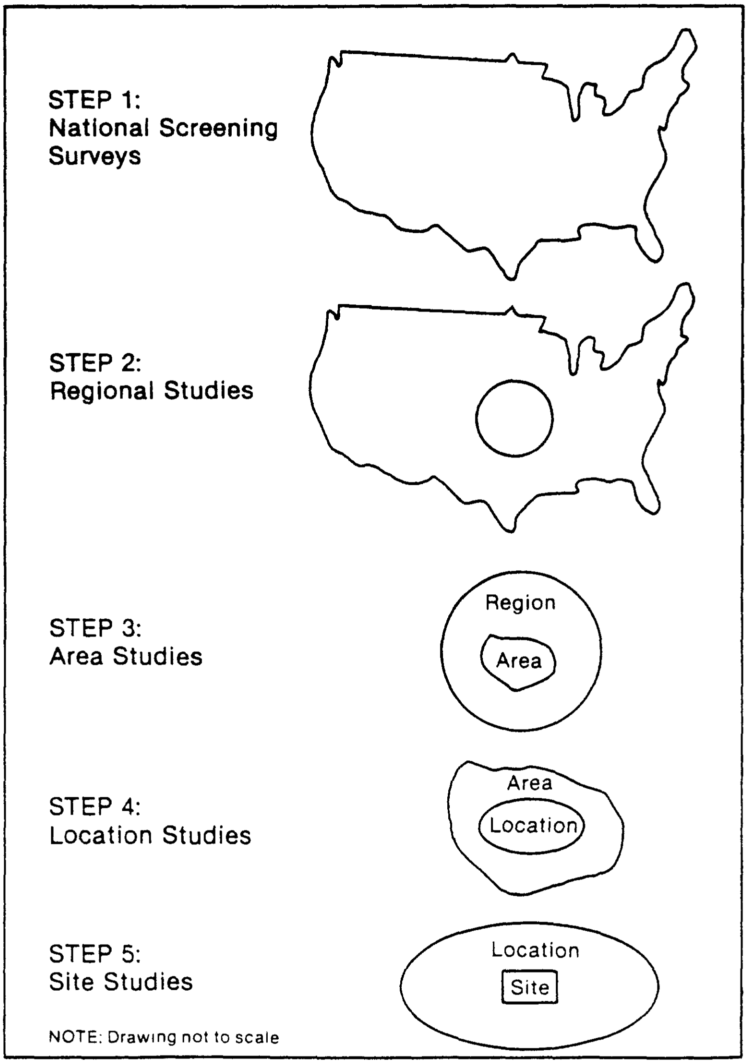


Figure C-3.--The site-selection process for a nuclear-waste repository. (From Office of Nuclear Waste Isolation, 1983, fig. 2.1.)

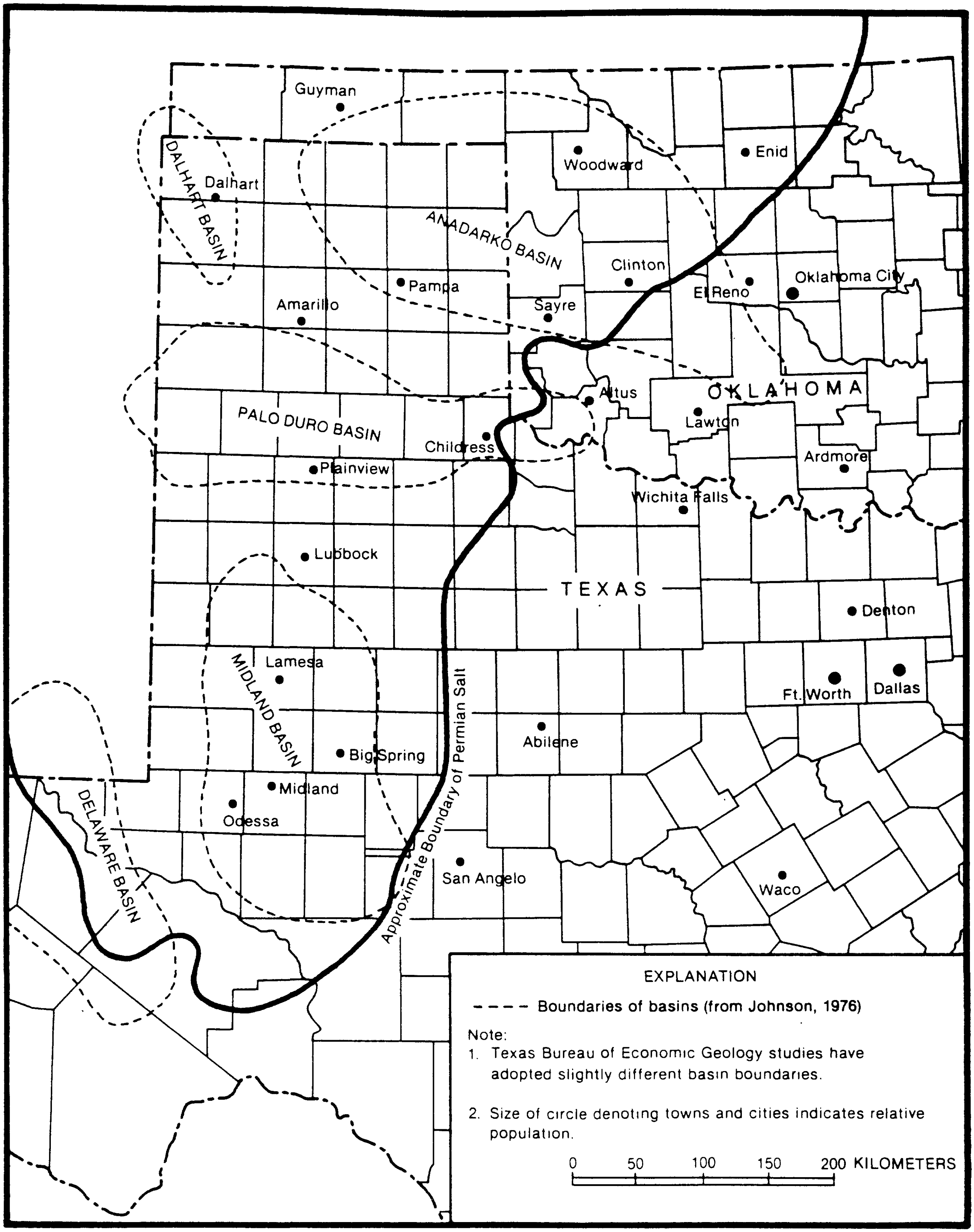


Figure C-4.--Permian region of study in Texas and Oklahoma for siting a nuclear-waste repository. (Modified from NUS Corporation, 1983, fig. 1-2.)

On the basis of work by Pierce and Rich (1962), and from knowledge gained during the Lyons investigations and other data, ERDA conducted a regional geologic characterization of the Permian region in Texas and Oklahoma (Johnson, 1976) because this region (fig. C-4) appeared to contain deposits suitable for construction of a mined repository. Using data from the regional geologic characterization, NUS Corporation (on behalf of the Department of Energy) used earth-science criteria to compare five basins that had been identified by Johnson and selected the Dalhart and Palo Duro basins for further study. The criteria used for this screening and the comparisons that were made are listed in tables C-2 and C-3. In a summary evaluation, NUS Corporation (1983, p. 50) stated,

> "While both geological and environmental factors have been considered, the geological aspects are dominant. All the basins appear to have saltbeds of thicknesses and depths of engineering interest. However, the Palo Duro and Dalhart deposits have shown far less potential for oil and gas production and consequently have been penetrated less extensively by exploratory drillings."

Geologic and hydrologic studies were then made of the area comprising the Dalhart and Palo Duro basins (fig. C-4). Table C-4 shows the criteria used for screening at the completion of these studies. Geologic and hydrologic characteristics (items I, IV, VI, and VII) were the most important considerations in selecting five locations that appeared to have suitable characteristics (fig. C-5). Qualitative comparisons were then made among these five locations, mainly on the basis of demography and some general earth-science considerations. In its summary of the comparisons, the Office of Nuclear Waste Isolation (1983, p. 74-75) stated:

> "Because each of Areas A, B, C, D, E, and F [fig. C-5] meets the adopted screening specifications [table C-4], each area is potentially adequate for repository siting and could be considered for more detailed investigation. There are, however, differences among the potential areas which make certain areas preferable. The more preferable areas are those which have the greatest likelihood of proving suitable for repository siting and of meeting U.S. Nuclear Regulatory Commission licensing requirements. They have fewer features or phenomena which are likely to become issues or concerns during facility licensing.
>
> "The five areas can be further discriminated, based on the extent to which they:
>
> - Are away from the margins of the Southern High Plains where topography is irregular, erosion rates are high, and salt dissolution may occur in the potential repository unit
>
> - Are away from known oil and gas fields
>
> - Have more than one potential repository horizon
>
> - Have salt at depths as shallow as possible while maintaining a thick rock section between the potential repository horizon and the surface

Table C-2.--Qualitative comparison of health, safety, engineering, and economic factors in the Permian subbasins

[Source: NUS Corporation, 1983, table 5-1]

| Criterion | Factor | Basin | | | | |
|---|---|---|---|---|---|---|
| | | Dalhart | Palo Duro | Anadarko | Midland | Delaware |
| Site geometry | Salt thickness | The Flowerpot and Blaine Formations make up the only salt-bearing unit that is 200 to 400 feet thick. This unit is typically 50- to 65-percent salt. | Five salt-bearing units are each more than 200 feet thick; Lower Clear Fork salt (200-500 feet thick); Upper Clear Fork salt (200 to 650); San Andreas salt (200 to 1,590); Seven Rivers salt (200 to 540); and Salado-Tansill salt (200 to 340). These units are typically 20- to 60-percent salt. | Three salt-bearing units are more than 200 feet thick; Hutchinson salt (200 to 565 feet thick); Lower Cimarron salt (200 to 420); Flowerpot salt, Blaine Formation, and Yelton salt (200 to 710). These units typically are 40- to 70-percent salt. | Two salt-bearing units are the Rustler and Salado Formations (200 to 800+ feet thick). | Three salt-bearing units are the Rustler, Salado (200 to 1,600+ feet thick), and the Castile (200 to 600+ feet thick) Formations. |
| | Salt depth | The above salt unit is 1,200 to 1,765 feet below the surface in an area of about 1,000 square miles. | The above five units are 1,000 to 3,000 feet below the surface over an area of about 12,000 square miles. | The above three units are 1,000 to 3,000 feet below the surface over an area of about 17,000 square miles. | The above salt units are 1,000 to 3,000 feet below the surface over wide areas. | The above salt units are 1,000 to 3,000 feet below the surface over wide areas. |
| Tectonic environment | Faults | Permian and younger rocks are not fractured or otherwise deformed. | Permian and younger rocks are not significantly fractured or otherwise deformed. | Permian and younger rocks are not fractured or otherwise deformed. | Permian and younger rocks are not tectonically faulted. | Permian and younger rocks are not tectonically faulted. |
| | Seismic activity | The basin is in seismic risk zone 1. | The basin is entirely within seismic risk zone 1. | The basin is entirely within seismic risk zone 1. | The basin is entirely within seismic risk zone 1. | The basin is entirely within seismic risk zone 1. |

Table C-2.--Qualitative comparison of health, safety, engineering, and economic factors in the Permian subbasins--Continued

| Criterion | Factor | Basin |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | Dalhart | Palo Duro | Anadarko | Midland | Delaware |
|  |  | A single earthquake of MM VI has been recorded in the basin. | No earthquake of MM V or greater has been recorded in the basin. | Three earthquakes of MM V have occurred in the western part of the basin, and seven events of MM V to MM VII have occurred in and near the eastern part of the basin. | One earthquake of MM VI has occurred in the Central Basin Platform. | One earthquake of MM VI has occurred nearby to the east in the Central Basin Platform. |
| Subsurface hydrology | Aquifers | Freshwater aquifers in various areas include the Ogallala Formation, the Santa Rosa Sandstone, the Dakota and Cheyenne Sandstones, and Quaternary terrace and alluvial deposits. | Freshwater aquifers at or near surface in various areas include the Ogallala Formation, Edwards-Trinity strata, the Blaine Formation and Quaternary terrace and alluvial deposits. | Freshwater aquifers at and near the surface in various areas include the Ogallala Formation, the Elk City Sandstone, the Rush Springs Sandstone, and Quaternary terrace and alluvial deposits. | Freshwater aquifers at and near surface in various areas include the Ogallala Formation and the Edwards-Trinity (Plateau) aquifer. | Freshwater aquifers at and near surface in various areas include alluvial sand and gravel and the Edwards-Trinity (Plateau) aquifer. |
|  |  | The saltwater-bearing Glorieta Sandstone underlies the salt. | Saltwater-bearing sandstones (Tubb, Glorieta, and parts of the Artesia Group) are above or below several of the salt units in parts of basin. | The saltwater-bearing Glorieta Sandstone underlies the Flowerpot salt in the western Anadarko basin. |  |  |
|  | Salt dissolution | There is no evidence of dissolution of salt at depths of 1,260 to 1,765 feet in most of the area. | There is no evidence of dissolution of saltbeds at depths greater than about 1,000 feet. | There is no evidence of dissolution of saltbeds at depths greater than about 1,000 feet. |  |  |

Table C-2.--Qualitative comparison of health, safety, engineering, and economic factors in the Permian subbasins--Continued

| Criterion | Factor | Basin<br>Dalhart | Palo Duro | Anadarko | Midland | Delaware |
|---|---|---|---|---|---|---|
| Subsurface hydrology (continued) | Salt dissolution (continued) | Salt is dissolved in an area where it is 950 to 1,200 feet below the surface. | Salt is partially or completely dissolved by circulating ground water at most places where the salt is less than 500 to 800 feet below the surface, and locally the resultant brine is emitted at the surface. | Salt is partially or completely dissolved by circulating ground water at most places where the salt is less than 500 to 800 feet below the surface, and locally the resultant brine is emitted at the surface. | | |
| Geologic characteristics | Stratigraphy | Interbedded sandstone, shale, and gypsum-anhydrite layers overlie the salt units. | Some of the salt units are overlain and underlain by impermeable shales. | The salt units are generally overlain by impermeable shales. | | |
| Human intrusion | Oil and gas | Oil is produced at only a few small fields, and the basin is not considered a significant petroleum province. | Oil is produced at only a few small fields, and the basin is not considered a significant petroleum province. | The Anadarko basin and adjacent uplifts make up one of the major petroleum-producing provinces in the Nation, and continued exploration is anticipated in all parts of the basin. | Extensive oil and gas production and exploration. | Extensive oil and gas production and exploration. |
| | Other energy and mineral resources | Excluding petroleum and salt, there are no known significant mineral deposits within or below salt units. | Excluding salt, there are no known significant mineral deposits within or below the salt units. | Excluding petroleum and salt, there are no known significant mineral deposits within or below the salt units. | Potash deposits are associated with salt units. | Potash deposits are associated with salt units. |

Table C-2.--Qualitative comparison of health, safety, engineering, and economic factors in the Permian subbasins--Continued

| | | Basin | | | | |
|---|---|---|---|---|---|---|
| Criterion | Factor | Dalhart | Palo Duro | Anadarko | Midland | Delaware |
| | Boreholes and underground mines | Many boreholes have been drilled through the salt units in most areas. | Many boreholes have been drilled through the salt units. | Many boreholes have been drilled through the salt units in search of oil and gas. | Many boreholes have been drilled through the salt units in search of oil and gas. | Many boreholes have been drilled through the salt units in search of oil and gas. |
| | | No underground mines exist in the region. | No underground mines exist in the region. | No underground mines exist in the region. | | |
| | | | | Brine wells and LPG-storage facilities have been developed in the salt units at six widely scattered localities. | | |
| Surface characteristics | Conflicting land use | No alert, restricted, or military operations areas are located within the basin. | A small part of the basin included in alert, restricted, or military operations areas. | Two small sections of the basin are within alert, restricted, or military operations areas. | A large portion of the basin is within alert, restricted, or military operations areas. | A part of the basin is within alert, restricted, or military operations areas. |

Table C-3.--Qualitative comparison of environmental and socioeconomic factors in the Permian region

[Source: NUS Corporation, 1983, table 5-2. SMSA = Standard Metropolitan Statistical Area]

| Characteristics of area | Basin | | | | |
|---|---|---|---|---|---|
| | Dalhart | Palo Duro | Anadarko | Midland | Delaware |
| Excluded natural areas, historic sites, and parks. | Most favorable<br>One National Register site in entire area. | Favorable<br>Few National Register sites. Some State parks and a wildlife refuge is in the area. | Less favorable<br>The Oklahoma portion has numerous National Register sites within the area and many adjacent. | Favorable<br>Few National Register sites or other natural historic sites within the area. | Most favorable<br>One National Register site on edge of area. |
| Urban population | Most favorable<br>No SMSA counties. All counties average less than five persons per square mile. | Favorable<br>Area includes one county of Amarillo SMSA. Population density ranges from less than 5 to 99.9 persons per square mile. | Favorable<br>One small corner of Oklahoma City SMSA. Population density within most of the area is from 5 to 25 persons per square mile. | Less favorable<br>Area includes counties of Midland-Odessa, one county of Lubbock SMSA and a portion of San Angelo SMSA. Population density ranges from less than 5 to 250 persons per square mile. Most of the area has between 5 and 15. | Most favorable<br>No SMSA areas. Population ranges from 5 to 25 persons per square mile. Much of the area is less than five persons per square mile. |
| Valuable agricultural lands | Most favorable<br>No part of the area has a level of agricultural-product value that is more than twice the State average. | Less favorable<br>About half of the area has a level of agricultural-product value per acre that is more than twice the State average. | Favorable<br>A small portion of the area has an agricultural-product value per acre that is more than twice the State average. | Favorable<br>A part of the area has an agricultural-product value per acre that is more than twice the State average. | Most favorable<br>No part of the land has a level of agricultural-product value per acre that is more than twice the State average. |
| Recreation and natural areas | Less favorable<br>A large area is part of a National Grassland. | Most favorable<br>One natural wetland. | Favorable<br>Few scattered natural areas and recreation sites. | Most favorable<br>None within the area. | Most favorable<br>None within the area. |

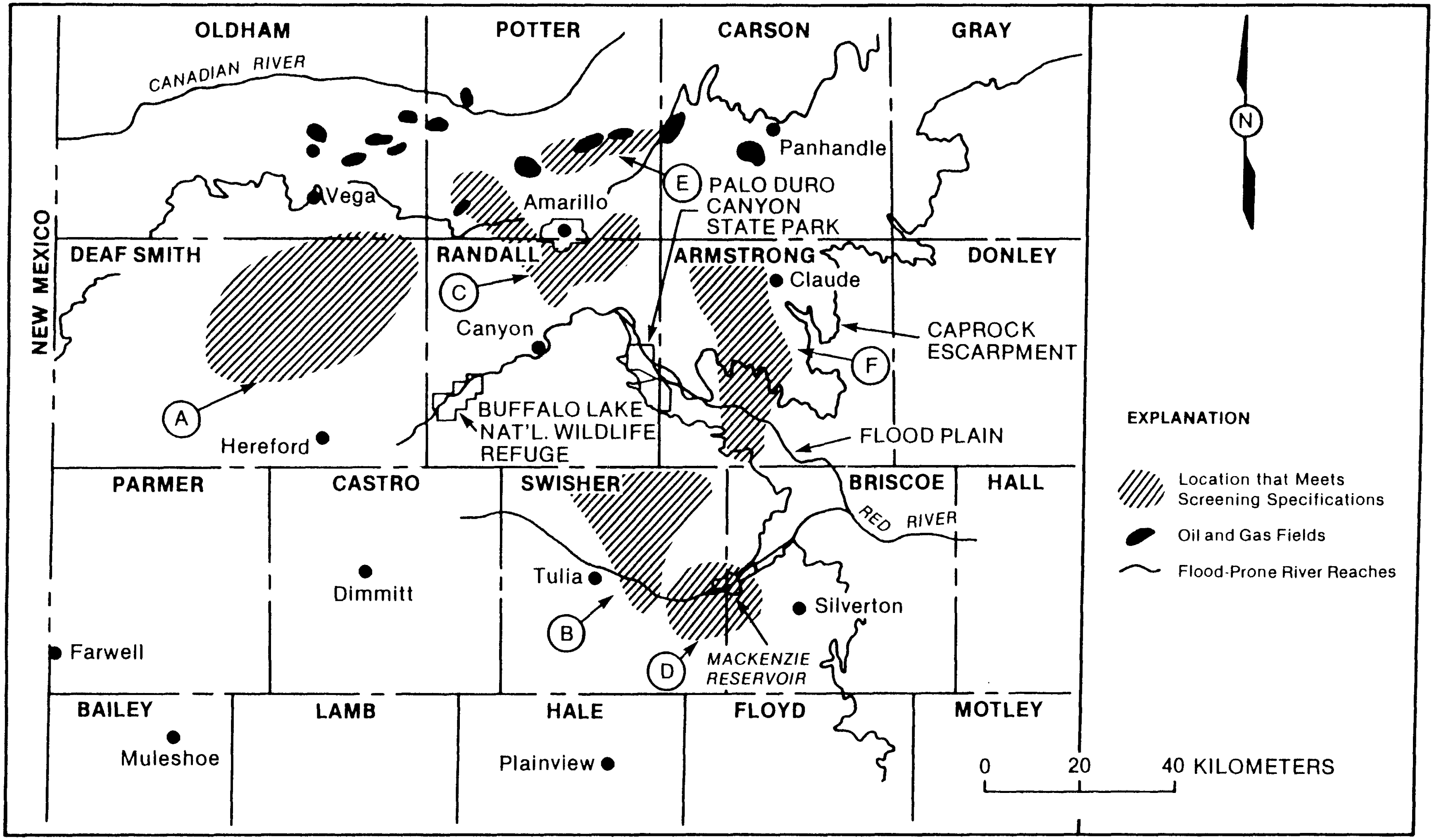


Figure C-5.--Locations meeting initial earth-science screening specifications in Palo Dura and Dalhart basins, Texas. (Location is shown in fig. C-4.) (Modified from Office of Nuclear Waste Isolation, 1983, fig. 6-2.)

Table C-4.--Screening specifications for locations in the Palo Duro and Dalhart basins, Texas

[Locations are shown in figure C-4. From Office of Nuclear Waste Isolation, 1983, p. 70]

| | Criterion | Subcriterion | Screening specification |
|---|---|---|---|
| I. | Site geometry (host rock) | 1. Minimum depth<br>2. Maximum depth<br>3. Thickness | 305 m (1,000 feet)<br>915 m (3,000 feet)<br>38 m (125 feet) |
| IV. | Geologic characteristics | Host rock characteristics | Gamma-ray geophysical log response of 15 API units or less (indicative of "massive salt") |
| VI. | Human intrusion | Oil or gas resources | Avoid existing/abandoned fields |
| VII. | Surface characteristics | Flooding | Defer 1.6 km (1 mile) on either side of perennial streams |
| VIII. | Demography | Urban areas | Exclude Standard Metropolitan Statistical Areas (SMSA) |
| IX. | Environmental protection | Conflicting land use | Avoid wildlife refuges, reservoirs |

- Have relatively few boreholes which penetrate the potential repository horizon
- Comprise a large continuous geographic area to provide flexibility in siting
- Have low population densities
- Have no unique land use conflicts.

> "Areas A and B have most of these favorable characteristics and no obvious unfavorable characteristics. Relative to Areas C, D, E, and F, they are the preferred locations for additional study."

The two preferred locations, in Deaf Smith and Swisher Counties, were selected for further study (fig. C-6). Additional fieldwork has been done in both counties, and the Department of Energy is currently selecting a site within each location to compare with other sites identified as candidates for construction of a repository. The entire process is summarized in figure C-7, and is described in detail in the Department of Energy's National siting plan for radioactive waste repositories (U.S. Department of Energy, 1982).

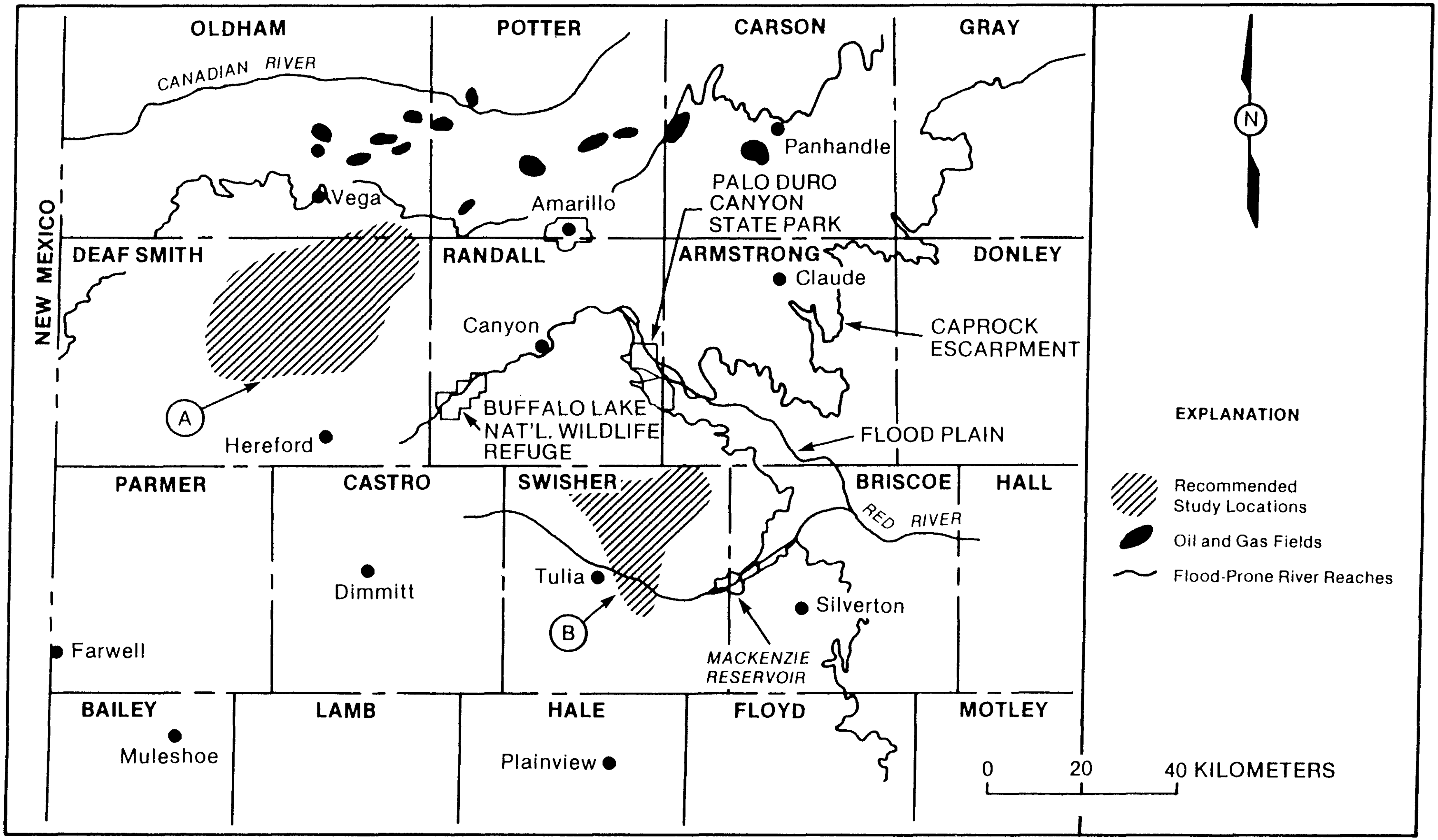


Figure C-6.--Locations recommended for further study in the Permian basin, Texas, following qualitative comparison on demographic and additional earth-science criteria. (Modified from Office of Nuclear Waste Isolation, 1983, fig. 6-3.)

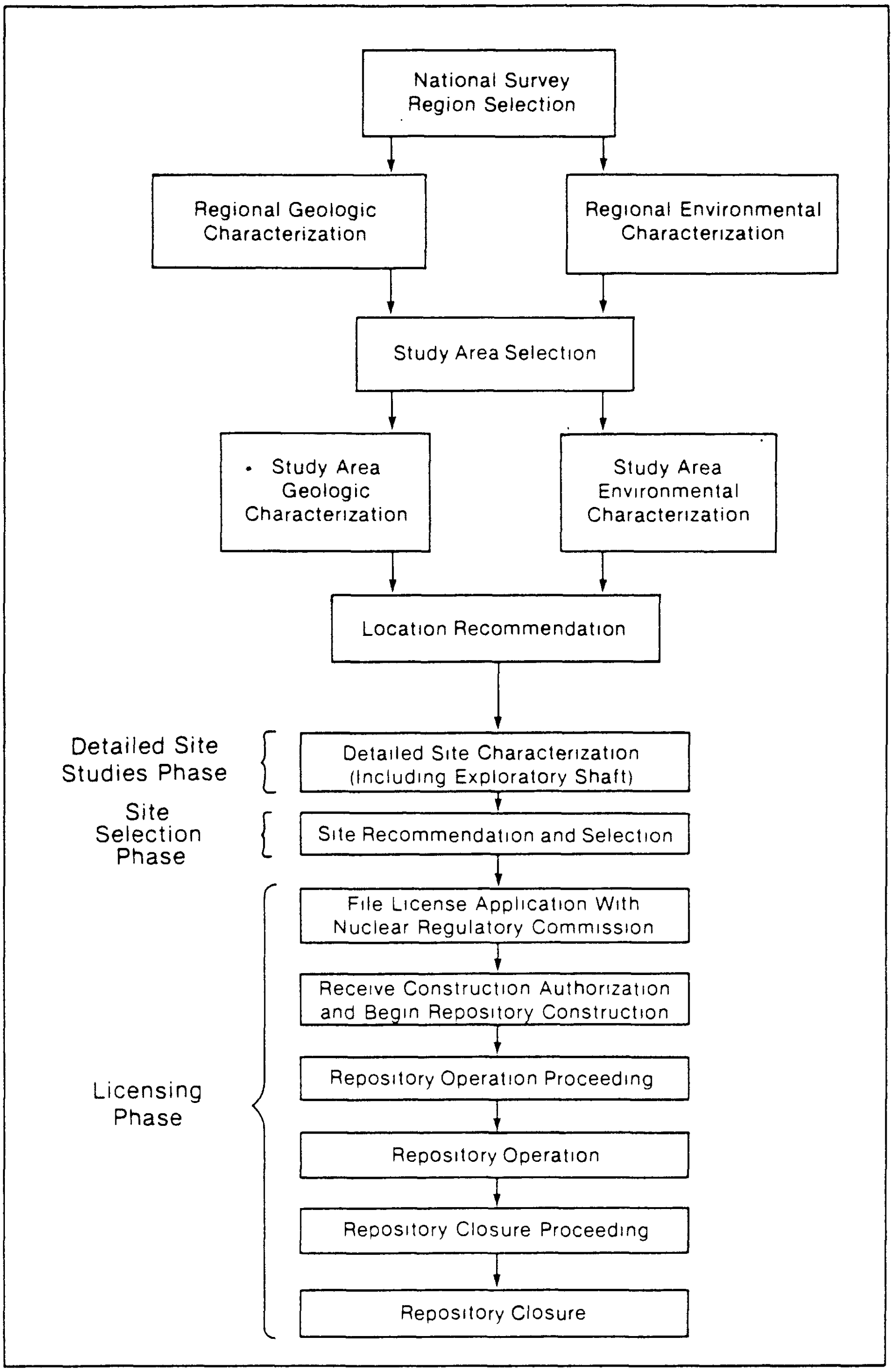


Figure C-7.--Process for siting, site characterization, and construction and operation of a nuclear-waste repository in the Permian region, Texas. (Modified from Office of Nuclear Waste Isolation, 1983, fig. 3-1.)

The siting criteria used in the Department of Energy's program are, of course, related to system performance. However, they are far removed from an actual systems analysis of how a particular hydrogeologic environment would contain and isolate wastes. The Department's intention is to use systems analysis (in particular, hydrologic and waste-transport modeling) to determine the suitability of the sites selected as candidates for the construction of a repository, but not as a site-selection method.

A different approach was taken by the U.S. Geological Survey in a study screening the Great Basin region for areas suitable for a nuclear-waste repository. The method of the study is based on recommendations made by a subgroup of the Interagency Review Group on radioactive waste appointed by President Carter (U.S. Geological Survey, 1980). The study focused on comparing the relative transport times of different ground-water systems within the region. It did not focus on a particular rock type for repository construction as does the Department of Energy's program. It used available data to define the boundaries of large ground-water flow systems, hydraulic gradients and flow directions, and geochemical data. Generalized digital models of these ground-water flow systems were used to compute traveltimes of ground water, which could then be applied to estimate transport rates of wastes from rock units that could be used for waste emplacement. Criteria also were used for other factors that could compromise the isolation capability, such as natural resources that might cause human intrusion or tectonic features that might cause disruption of a repository (Bedinger and others, 1983).

## Locating Low-Level Radioactive Waste Sites

States, either individually or in compact with other States, have the responsibility for disposing of low-level radioactive wastes under Public Law 96-573, the Low-Level Radioactive Waste Policy Act. The U.S. Nuclear Regulatory Commission has responsibility for licensing disposal sites and regulating operations and final closure of a site. The rule divides the wastes into three classes according to radioactivity levels, and defines what wastes are suitable for near-surface disposal. The performance objective is that the two classes of wastes that are less hazardous will be contained for 150 years. The third class of waste, called intruder wastes, must be at least 5 meters below the surface of the burial ground or must be disposed of with natural or engineered barriers that will protect against an inadvertent intrusion for at least 500 years.

The Nuclear Regulatory Commission rule (1981) sets forth technical requirements that should be present for the site to meet the above performance objectives. The earth-science-related requirements of that part of the rule are paraphrased in table C-5.

It is apparent that if the States are to pursue a rational site-selection plan for low-level radioactive-waste disposal, they are faced with developing suitable exploration or screening criteria from these technical requirements. These requirements must be translated into quantitative and (or) mappable characteristics that can be compared with regional maps, statewide maps, or other information to delineate areas where favorable conditions may exist. These areas must then be further screened on the basis of appropriate criteria to select sites where field investigations can be focused.

Table C-5.--Technical earth-science requirements established by the U.S. Nuclear Regulatory Commission for low-level radioactive waste burial grounds

- The disposal site shall be capable of being characterized, modeled, analyzed, and monitored.
- Areas must be avoided having economically significant natural resources which, if exploited, would result in failure to meet the performance objectives of Subpart C of this part.[1]
- The disposal site must be generally well drained and free of areas of flooding or frequent ponding. Waste disposal shall not take place in a 100-year flood plain, coastal high-hazard area, or wetland.
- Upstream drainage areas must be minimized to decrease the amount of runoff that could erode or inundate waste disposal units.
- The disposal site must provide sufficient depth to the water table that ground-water intrusion into the waste, perennial or otherwise, will not occur. The Commission will consider exceptions to this requirement if it can be conclusively shown that disposal-site characteristics will result in diffusion being the predominant means of radionuclide movement and the rate of movement will result in the performance objectives of Subpart C of this part being met.[1]
- Any ground-water discharge to the surface within the disposal site must not originate within the hydrologic unit used for disposal.
- Areas must be avoided where tectonic processes such as faulting, folding, seismic activity, or volcanism may occur with such frequency and extent so as to significantly affect the ability of the disposal site to meet the performance criteria.
- Areas must be avoided where surface geologic processes such as mass wasting, erosion, slumping, landsliding, or weathering occur with such frequency and extent so as to significantly affect the ability of the disposal site to meet the performance objectives of Subpart C of this part, or may preclude defensible modeling and prediction of long-term impacts.[1]
- The disposal site must not be located where nearby facilities or activities could adversely impact the ability of the site to meet the performance objectives or significantly mask the environmental monitoring program.
- Covers must be designed to prevent water infiltration, to direct percolating or surface water away from the buried waste, and to resist degradation by surface geologic processes and biotic activity.
- The disposal site must be designed to eliminate the contact of water with waste during storage, the contact of standing water with waste during disposal, and the contact of percolating or standing water with wastes after disposal.

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[1] Subpart C--Performance Objectives--of 10 CFR 61 sets a minimum exposure level for radioactivity for any member of the public both through transport of materials from the site through environmental pathways and through inadvertent intrusion. The site must also achieve long-term stability of the wastes.

## Selecting Sites for Hazardous-Chemical-Waste Disposal

For hazardous chemical wastes, the criteria for siting and site evaluation are not as well developed as those for radioactive wastes. As described earlier, some degradable wastes may be disposed of at land-treatment sites. The U.S. Environmental Protection Agency (1983) has provided guidelines for land-treatment sites that apply mainly to infiltration properties of soils and porous geologic materials and with precipitation and temperatures.

Secure landfills are used for the disposal of more hazardous materials. They pose a far different problem of siting than do land-treatment sites. Because landfills may receive extremely hazardous and long-lived wastes, the National Research Council's Committee on Disposal of Hazardous Industrial Wastes (1983, p. 6-7) addressed the problem of criteria for landfills related to their long-term safety. Regulations under the Resource Conservation and Recovery Act (Public Law 94-580) establish a 30-year period of concern for these landfills. It is apparent to the Committee that the period of concern is more like 500 years. If artificial barriers, such as liners, are designed to meet this 30-year period, they are likely to fail while the wastes are still hazardous. When the artificial barriers fail, the site's natural barriers must be depended on to provide safety. The Committee (1983, p. 64) has recommended research on hydrogeologic factors that bear on the transport of wastes leaking from landfills. The transport of low-level radioactive wastes from burial grounds takes place under conditions similar to those at landfills leaking chemical wastes. Studies done at low-level waste-burial grounds and the Nuclear Regulatory Commission's technical requirements (table C-5) provide a basis on which to investigate the adequacy of landfills to contain hazardous-chemical wastes and to develop criteria for siting. A prototypic study by Papadopulos and Winograd (1974) is a good example of the investigations that can be done for landfills. These authors investigated various hydrogeologic and geochemical factors and appraised their effects on the movement of radioactive wastes from burial grounds. The study was based on theoretical modeling, literature on radionuclide behavior, and a field study of an operating radioactive-waste burial ground. Studies of similar design could be used to address siting criteria and performance appraisal of hazardous-waste landfills in various geologic and hydrologic environments.

In summary, it should be noted that the criteria for disposal of long-lived (high-level) radioactive wastes are very different from those for short-lived (low-level) wastes, most notably in the depth of burial (greater than 1,000 feet for high-level wastes and less than about 50 feet for low-level wastes). For high-level wastes, low-permeability material (salt for instance) is also specified, and there is little reliance on engineering measures for long-term containment (1,000 years or more). This is in marked contrast to the emplacement of some long-lived hazardous chemical wastes in shallow landfills with almost total reliance on engineering measures for containment. The National Research Council's Committee on Disposal of Hazardous Industrial Wastes is concerned about the dependence in landfills upon engineering measures that can be effective for only a limited time. The Committee (1983, p. 67-68) has recommended that the long-lived wastes be disposed of in deep geologic formations offering containment from the natural systems. Other authors are concerned about the potential of ground-water pollution from hazardous waste landfills. Langerman (1983), in a report for the Heritage Foundation, writes that water moving through toxic-waste landfills annually discharges over 800 billion gallons of contaminated water into the ground and he recommended that States ban the use of landfills for toxic-waste disposal to protect ground-water supplies from pollution.

## CONCLUSIONS

The safe, permanent disposal of hazardous wastes requires sites at which the natural system, as opposed to engineered systems, will provide long-term isolation. As a first step to achieving the required isolation, the wastes must be well understood and characterized, a proper waste form must be developed (by concentration, treatment, or encapsulation), and pathways by which the wastes can escape from the disposal site to the environment must be understood. This understanding of the wastes leads to development of a performance objective for the disposal system, namely, what degree of isolation is necessary for health and safety. The general criteria for geologic, hydrologic, and geochemical characteristics necessary to meet the performance requirements can then be determined. These are in the form of guidelines from which specific siting criteria can be developed for application to large areas on the basis of available data. Increasingly specific siting criteria can be adopted as screening proceeds through a stepwise process that finally identifies sites potentially suitable for waste-disposal facilities. Ultimately, detailed studies and systems analysis of each potential site are required in order to prove the safety of the site.

Such stepwise processes for selecting radioactive-waste sites have been carried out, and they provide examples of applying uniform criteria to examine large areas to select potentially safe disposal sites.

Secure landfills are widely used to dispose of long-lived toxic wastes. The long-term safety of these landfills is doubtful because of the dependence on engineering measures to assure isolation, as opposed to dependence on natural barriers that could be present at a carefully selected site. Factors of geology, hydrology, and geochemistry pertinent to the long-term safety of these sites should be investigated to appraise the future functioning of present landfills and the conditions under which this technology should continue to be used for disposal, if at all.

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## CHAPTER D

# CAPACITIES AND MECHANISMS OF SORPTION OF ORGANIC COMPOUNDS BY WATER-SATURATED AND UNSATURATED SOILS

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## ABSTRACT

To characterize the transport of organic contaminants through water-saturated and unsaturated zones, the sorptive behavior of organic compounds from aqueous and organic solutions and from vapor phase was analyzed in terms of soil composition, effect of solvent polarity, and soil-water content. Characteristic differences in soil sorption of parathion and lindane from aqueous and hexane solutions, and of benzene and m-dichlorobenzene from water and from vapor phase at different humidities, are illustrated and rationalized. For water-saturated soils, the soil uptake is determined primarily by chemical partition, rather than adsorption, into the soil organic phase, in keeping with thermodynamic criteria. Adsorption by soil minerals is relatively insignificant with wet soils, presumably because water is preferentially adsorbed through its strong dipole interactions with soil minerals. By contrast, the soil uptake from hexane and from vapor phase at low soil-moisture content is effected mainly through adsorption by soil minerals, as supported by data characteristic of adsorption phenomena. The capacity of uptake of unsaturated soil is markedly greater than the capacity of saturated soil.

## INTRODUCTION

The mobility of a chemical in hydrologic and geologic environments is determined to a large extent by its sorptive interaction with soil constituents. The functionality of soil constituents in sorption has been a subject of active investigation because the uptake of a chemical by soil critically depends on the composition of the soil and the medium from which the chemical is sorbed. Earlier studies indicated that the extent of uptake of nonionic organic compounds from water by a great variety of soils is closely related to soil organic-matter content (Kenaga and Goring, 1980; Chiou, 1981; Karickhoff, 1981). Chiou and others (1979; 1983) showed that sorption isotherms of nonionic organic solutes are linear over a wide range of aqueous concentrations relative to solute solubilities, and that soil uptake of organic solutes exhibits a small heat effect (that is, the heat of sorption is less exothermic than the heat of solute condensation from water) and also shows no apparent solute competition.

The uptake of organic compounds from nonaqueous systems has fundamentally different characteristics. Hance (1965) noted that the sorptive capacity of a mineral-rich soil for a pesticide (diuron) in a petroleum solution is considerably greater than that for diuron in an aqueous solution, whereas the reverse is true for the sorptive capacity of the soil organic matter. Yaron and Saltzman (1972) observed that the sorption of parathion by dry soils from hexane is most effective, but from polar solvents is practically ineffective. Moreover, the sorption of parathion from hexane was found to be strongly suppressed by soil water, and to exhibit an "endothermic effect" when the soil was partially hydrated (that is, with water content below saturation). Similarly, Spencer and Cliath (1970) showed that the sorption of lindane on soil is suppressed by the soil moisture, and that the temperature coefficient (that is, the heat effect) of lindane vapor in equilibrium with fully hydrated soils is smaller than that of the vapor in equilibrium with its own pure phase. These observations suggest that the role of soil humus and minerals in the soil's uptake of organic compounds from aqueous systems differs from that in nonaqueous systems, and that their relative significance is affected by the soil-water content and by the medium from which the solutes are removed.

On the basis of the observed dependence of soil uptake on humic content and other isotherm characteristics in soil-water equilibria, Chiou and others (1979; 1983) suggested that the sorption of nonionic organic compounds from water consists primarily of solute partition (dissolution), rather than adsorption, into the soil humic phase. Adsorption of these compounds by soil-mineral surfaces is considered to be relatively insignificant in wet soils, presumably because water is preferentially adsorbed by minerals. With this hypothesis, it is conceivable that the uptake of organic solutes from hexane (and from other organic solvents) on dry and partially hydrated soils is effected mainly through the adsorptive contribution of soil minerals, since the partition of these compounds from hexane into soil humus would be weak (because of the high solubility of organic solutes in hexane). Thus, presumed strong adsorptivity of minerals in dry and partially hydrated soils explains the suppressive effect of water on the uptake of parathion from hexane, and on the uptake of lindane from the vapor phase. It also explains the relative effects of soil minerals and organic matter in the sorption of diuron from petroleum and aqueous solutions.

To substantiate the functions of soil humus and minerals in sorption, we have devised a series of studies to illustrate the controlling mechanism of soil sorption from aqueous and organic solutions and from vapor phase on selected soils. In the report of Yaron and Saltzman (1972), the organic contents of the selected soils happened to be closely related to the respective mineral contents; consequently, mechanistic roles of soil humus and minerals in the soil uptake of parathion from water and hexane were not immediately evident. In addition, the study of Yaron and Saltzman (1972) on the uptake of parathion from hexane was limited to a very low range of equilibrium concentrations relative to parathion solubility, which prohibited a close comparison of isotherm characteristics and sorption capacities of parathion from aqueous and hexane solutions. This present study is designed to amplify these points and to illustrate the significance of soil moisture in sorption of organic compounds from the vapor phase, in terms of the role of soil humus, the role of soil minerals, and the influence of moisture content and type of solvent on the functions of soil humus and minerals. This understanding is essential to the study of the mobility of organic pollutants in saturated and unsaturated soil zones.

## MATERIALS AND METHODS

Two Oregon soils, Woodburn silt loam and Lake Labish peat loam, were selected for study. Woodburn soil, used in a previous study (Chiou and others, 1983), is low in organic matter content (1.9 percent on dry-weight basis) and high in mineral content (9 percent sand, 68 percent silt, and 21 percent clay). Lake Labish soil is high in organic content (51 percent) and low in mineral constituents (9.8 percent sand, 36 percent silt, and 3.5 percent clay). Clay-mineral analysis by X-ray diffraction indicated that mica and kaolinite are the predominant clay types for both soils. The soils were sieved to obtain the 60/80-mesh fraction. Air-dried samples (at 45 percent relative humidity) of Woodburn and Lake Labish soils contained about 2.5 and 20 percent moisture, respectively. These soils were oven-dried at 140 °C to 150 °C for 48 h (hours) to remove moisture; resulting samples were considered "dry" soils. After oven drying, the soils were stored in a vacuum desiccator before use. Soils dried at 140 °C to 150 °C did not show significant differences in composition from the same soils dried at 105 °C.

Parathion (o,o-diethyl-o-p-nitrophenyl phosphorothioate), with a labeled purity of 98.5 percent, was purchased from Analabs. Lindane ($\gamma$-isomer of 1,2,3,4,5,6-hexachlorocyclohexane), with a labeled purity of 99+ percent, was purchased from Applied Science. Reagent-grade benzene and m-dichlorobenzene were obtained from Aldrich Chemical Co.; those compounds were used as received. The water used was distilled and filtered through an XAD-2 column to remove organic contaminants. High-purity normal hexane was purchased from Phillips Petroleum Co. and further cleaned by passing through a Linde molecular-sieve column.

Sorption experiments in aqueous and hexane systems were conducted in duplicate with 30-mL Corex glass centrifuge tubes equipped with Teflon-lined lids. Normally, 1 g of soil was mixed with 25 mL of aqueous or hexane solution containing differing amounts of test compounds. Soil slurries were equilibrated at 20 °C (or 30 °C) in a constant-temperature room for 24 h on a reciprocal shaker and centrifuged (1,560 G) at the same temperature for 1 h to spin down soil particulates. Aliquots of aqueous and hexane solutions of parathion and lindane then were removed with pipets. Aqueous samples were extracted with hexane and brought to appropriate concentrations for analysis by a Varian 3700 gas chromatograph equipped with a 63N$_i$ electron-capture detector. Hexane samples were similarly analyzed after further dilution with hexane. A glass column (2 mm x 1.8 m), packed with 3 percent SE-30 on 80/100 Chromosorb W, was used for separation and identification of the solutes; the column temperature was controlled at 200 °C. The amount of soil uptake was determined by concentration difference of the compounds in solution before and after equilibration. Results of duplicate samples were averaged.

The solubilities of parathion (at 20 °C and 30 °C) and lindane (at 20 °C) in hexane were determined by analyzing the saturated solution of each solute in hexane by gas chromatography. Samples were prepared by adding excess amounts of parathion or lindane into hexane in Corex centrifuge tubes, which were equilibrated and centrifuged according to the method described. Aliquots of the supernatant hexane phase were removed with syringes and further diluted with hexane for analysis.

Sorption of benzene and m-dichlorobenzene from the vapor phase was conducted through a dynamic-equilibrium system, as shown schematically in figure D-1. The test chemical was blended with sand and placed in a glass column that served as the chemical-vapor generator. A separate glass column filled with water was used as the moisture generator. A stream of chemical vapors and a stream of water vapors were generated by purging dry nitrogen gas through each column. Vapors exiting from the two columns were combined with a stream of make-up pure nitrogen gas to produce a final stream of vapor mixture of the test chemical and moisture, which was brought in contact with a sample of dry soil in a rotating flask. After dynamic equilibrium (4 to 8 h), soil was extracted with an acetone-hexane mixture (1:1 volume ratio). The solvent extract was further diluted with hexane and analyzed for the amount of the chemical sorbed by gas chromatography as described. Controlling the flow rate of nitrogen gas to the chemical-vapor generator and moisture generator and the flow rate of the make-up nitrogen gas gave a series of chemical-vapor concentrations at fixed relative humidity that were used to plot the vapor sorption isotherm at a fixed relative humidity.

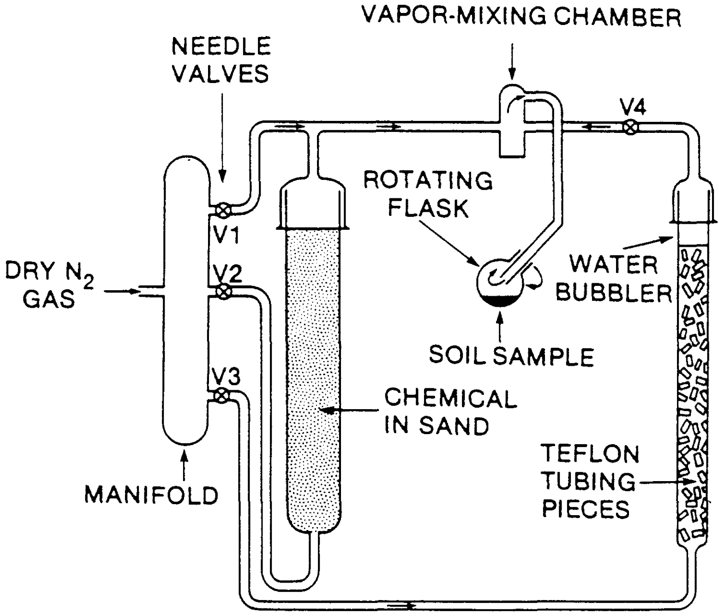

Figure D-1.--Schematic drawing of the vapor-phase sorption apparatus.

## RESULTS AND DISCUSSION

Sorption isotherms of parathion and lindane at 20 °C from water on air-dried Woodburn soil (2.5 percent moisture) are given in figure D-2. Experiments were performed with parathion and lindane both as single and binary solutes so that any competitive effect could be visualized. Observed isotherms for both parathion and lindane are essentially linear up to sufficiently high relative concentrations (ratios of equilibrium concentrations to solubility) and exhibit no obvious competitive effect between the two solutes. The linearity of parathion isotherms extends to an equilibrium concentration of $C_e = 9$ μg/mL (the upper part of the isotherm is not shown), which corresponds to about 75-percent saturation of parathion in water based on the parathion solubility of $C_s = 11.9$ μg/mL at 20 °C (Freed and others, 1979). Lindane isotherms cover about 50 percent saturation of lindane in water, based on its solubility of $C_s = 7.8$ μg/mL at 25 °C (Weil and others, 1974).

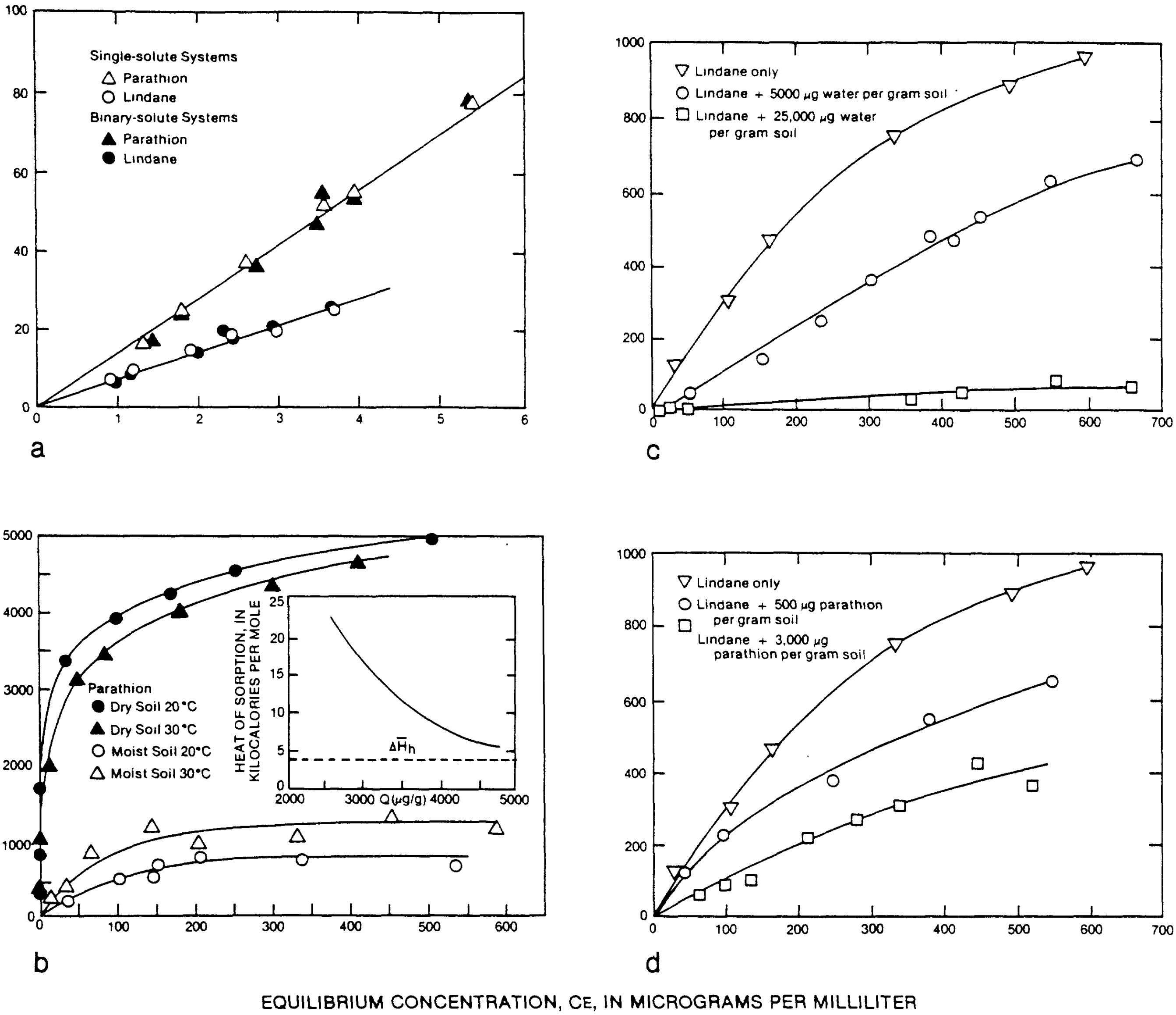

Figure D-2.--Uptake of pesticides from aqueous and hexane solutions by Woodburn soil at 20 °C in relation to: (a) parathion and lindane from water, (b) parathion from hexane on dry and moist (2.5 percent water) soils; inset shows heat of sorption with respect to soil uptake, (c) lindane from hexane on dry and moist soil, and (d) lindane from hexane in the absence and presence of parathion.

The capacity of the parathion sorption on Woodburn soil is comparable to those reported for other soils (Swoboda and Thomas, 1968; Yaron and Saltzman, 1972) when the capacity is expressed on the basis of soil organic content. The sorptive characteristics presented in figure D-2a are typical of the sorption characteristics of nonionic organic compounds from water, where the amount sorbed has been found to be closely related to soil organic content. The high isotherm linearity and lack of solute competition in this study and earlier reports (Chiou and others, 1979; 1983), and the recognized dependence of sorption on soil organic matter (Saltzman and others, 1971; Kenaga and Goring, 1980), may be taken as evidence that partitioning of the organic solute from water into the soil humic phase is the primary process of soil uptake. Analysis of thermodynamic properties that affect the sorption (partition) coefficients of organic compounds between soil organic matter and water has been presented elsewhere (Chiou and others, 1983).

By earlier rationale, one may expect to find basic differences in the characteristics of solute sorption from aqueous and organic-solvent solutions on the same soil. The sorption isotherms of parathion from hexane on dry and partially hydrated (2.5 percent water) Woodburn soils at 20 °C and 30 °C are shown in figure D-2b. Because of the high solubility of parathion in hexane ($C_s = 5.74\text{x}10^4$ mg/mL at 20 °C and $8.56\text{x}10^4$ $\mu$g/mL at 30 °C), the isotherms were extended to a sufficient range of equilibrium concentration relative to parathion solubility. In dry-soil systems, the isotherms reveal distinctive curvatures (and high heat effects, discussed later) with capacity exceeding 4,500 $\mu$g parathion per grams soil at $C_e = 500$ $\mu$g/mL (that is, at relative concentration $C_e/C_s = 0.009$ at 20 °C). These observations are not compatible with those noted in the sorption of parathion on the same soil from water; isotherm curvatures and high equilibrium heats are mechanistically consistent with phenomena of adsorption. Since the partitioning of parathion from hexane into soil humus will be relatively insignificant because of high parathion solubility in hexane (Chiou and others, 1981), the observed uptake can be ascribed to adsorption by soil minerals. The effectiveness of parathion in competing with hexane for mineral surfaces appears to be facilitated by the polarity of parathion in combination with the relative inability of nonpolar hexane to wet polar mineral surfaces. On this basis, one would expect the sorption of parathion from hexane on moist soil to be suppressed by soil-water content, as reported by Yaron and Saltzman (1972), because of the competition of highly polar water for mineral surfaces. The suppressive effect of moisture is illustrated again in figure D-2b, where 2.5 percent of water in soil (that is, the amount of water in air-dried soil at about 45 percent relative humidity) markedly reduces the parathion uptake. The observed reverse temperature dependence of parathion sorption with partially hydrated soils is, therefore, a consequence of the competitive adsorption of an energetically weaker adsorbate (parathion) against a more powerful competitor (water).

In the dry soil-and-hexane system, where physically adsorbed water is practically removed, high exothermic heats are found in support of the presumed adsorption of parathion on mineral surfaces. This is demonstrated in figure D-2b, where the isosteric heat of adsorption is calculated from the dry-soil isotherm data at 20 °C and 30 °C, by the Clausius-Clapeyron equation:

$$\Delta\bar{H}_{ads(Q)} = 2.303R \log [(C_{e,T_2}/C_{e,T_1})]/(1/T_2 - 1/T_1) \qquad (1)$$

where: $\Delta\bar{H}_{ads(Q)}$ = (molar) isosteric heat of adsorption at a sorption capacity Q ($\mu$g/g);
$R$ = gas constant;
$C_{e,T_2}$ = equilibrium concentration at temperature $T_2$ (°K) and at capacity Q; and
$C_{e,T_1}$ = the equilibrium concentration at $T_1$ (°K) and at the same capacity Q.

The calculated isosteric heat is considerably more exothermic than the heat of condensation (that is, the reverse heat of solution) of parathion from hexane ($-\Delta\bar{H}_h$), which is typical of an adsorption process (Chiou and others, 1979). The dependence of $\Delta\bar{H}_{ads}$ on Q indicates that the adsorption sites on minerals are energetically inhomogeneous, reflecting the heterogeneity of mineral surfaces in soil. The high exothermic heat and its dependence on soil loading in dry soil-hexane systems is in sharp contrast to the low and nearly constant heat of soil sorption in aqueous systems (Chiou and others, 1979), which confirms differences in sorptive mechanism of the soil in these systems.

The data on sorption of lindane from hexane onto dry and partially hydrated soils follow basically the same patterns as observed with parathion, except that the uptake capacity of lindane is significantly lower and more sharply affected by the water content (fig. D-2c). The solubility of lindane in hexane at 20 °C is determined to be $1.26 \times 10^4$ μg/mL. At $C_e = 500$ μg/mL (that is, at relative concentration $C_e/C_s = 0.04$), for example, the capacity of uptake on dry Woodburn soil is about 900 μg/g soil, which is appreciably lower than the uptake of parathion at $C_e/C_s = 0.009$. With 2.5 percent water in soil, the amount of lindane adsorbed is reduced to only about 30 μg/g at $C_e = 500$ μg/mL. These differences are consistent with the lower polarity of lindane than of parathion, which makes lindane a less potent adsorbate and thus a weak competitor against water for adsorption on mineral surfaces.

Although the water content in soil suppresses the uptake of parathion and lindane from hexane (where water can be considered as a competing solute), a similar competitive effect also occurs between parathion and lindane in their sorption from hexane on dry soil. This is illustrated in figure D-2d, in which the uptake of lindane from hexane on dry Woodburn soil decreases with an increase of parathion uptake. This finding is in agreement with the overriding effect of mineral adsorption of organic solutes from hexane on dry and partially hydrated soils, as contrasted to the partitioning of the solutes into soil humus as the dominant effect in aqueous systems.

To amplify the adsorptive contribution of soil minerals in a dehydrated soil, a further study was made on the sorption of parathion and lindane from hexane on (dry) Lake Labish peat soil, which has a low mineral content and a high organic content. Uptake capacities of both solutes on this soil (fig. D-3) are found to be considerably lower than the capacities on Woodburn soil, mainly because of differences in soil mineral content. By contrast, the sorption of parathion from water has been shown to be proportionally related to the soil organic content (Saltzman and others, 1972). These phenomena are fundamentally the same as those reported by Hance (1965) and support the proposed mechanistic roles of soil humus and minerals in sorption of organic solutes from aqueous and organic solutions.

On the basis of the proposed mechanistic roles of soil humus and soil minerals, the failure of soils to sorb nonionic organic compounds from polar organic solvents can now be explained. The high solubility of organic solutes in many organic solvents makes ineffective the partitioning of solutes into the soil humic phase. As a result, uptake of the solutes depends primarily on their ability to compete with the solvent for adsorp tion onto soil minerals. Such a competition is energetically more favorable to the solutes in nonpolar solvents, such as hexane; and is unfavorable in polar solvents, such as methanol, ethanol, chloroform, ethyl acetate, and dioxane because these can strongly adsorb onto polar inorganic minerals, thus displacing the solutes (Chiou and others, 1981). This explains why the sorption of parathion on dehydrated soils is highly favorable from hexane but practically ineffective from polar solvents (Yaron and Saltzman, 1972).

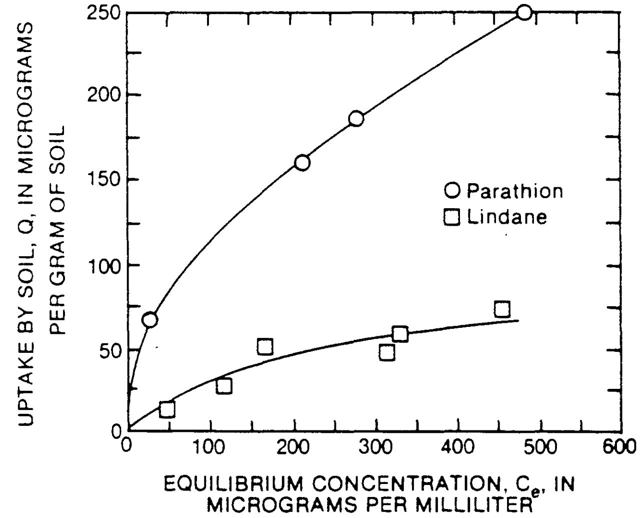

Figure D-3.--Uptake of pesticides from hexane by Lake Labish peat soil in relation to equilibrium concentration at 20 °C.

From the above analysis, one may expect the mineral fraction of dry or slightly hydrated soils to be a powerful adsorbent for organic vapor from air phase at low relative humidity (R.H.). A plot of vapor-phase sorption of benzene by Woodburn soil at different humidities against the relative vapor saturation ($P/P^o$) is shown in figure D-4a, in which P is the equilibrium partial pressure and $P^o$ is the saturation vapor pressure of the compound. A similar plot for the sorption of m-dichlorobenzene on the same soil is given in figure D-4b.

At zero and low R.H., the isotherms for both benzene and dichlorobenzene show enormously greater uptake capacities and pronounced curvatures than the respective isotherms from aqueous solutions on the same soils (plotted as capacity versus $C_e/C_s$). This finding may be attributed to the dominance of the adsorptive contribution by soil minerals (over the partition effect into soil organic matter) to the soil uptake, if the soil is relatively dry and rich in mineral content. Such behavior is much the same as noted for the uptake of parathion and lindane from hexane solution on dry and partially hydrated Woodburn soils, where adsorption by soil minerals is the dominating effect. With increasing air humidity, however, the competition of water for adsorption on soil minerals markedly reduces both the sorption capacity and isotherm curvature. At R.H. = 90 percent, the vapor-phase isotherms of these two compounds approach the respective water-phase isotherms (capacity versus $C_e/C_s$) in both capacity and linearity, presumably because the partition into soil-organic matter overrides the adsorption onto soil minerals.

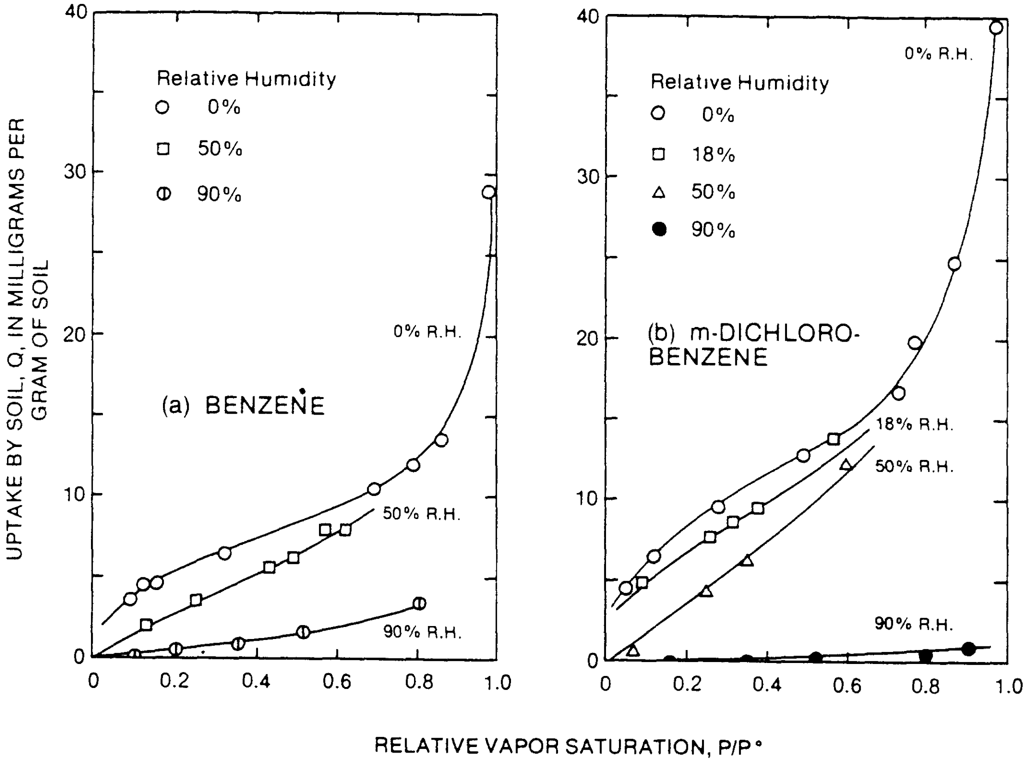

Figure D-4.--Uptake of benzene from vapor phase by Woodburn soil at 20 °C in relation to relative vapor saturation: (a) benzene, (b) m-dichlorobenzene.

## CONCLUSIONS

Characteristics of soil sorption of nonionic organic compounds vary with respect to soil composition, moisture content, and solvent medium from which the solutes are sorbed. In aqueous systems, the controlling sorptive mechanism is considered to be the solute partition into the soil humic phase, in keeping with the observations of (1) the recognized dependence of soil uptake on humic content, (2) the linearity of sorption isotherms to high relative concentrations, (3) the low equilibrium heat, and (4) the lack of apparent solute competition. When soils are fully hydrated, adsorption of the organic solutes by soil minerals becomes relatively insignificant, presumably because water is preferentially adsorbed. By contrast, the uptake of these compounds from nonpolar solvents on dry soils is effected mainly through mineral adsorption, consistent with the observed isotherm curvature, different sorptive capacity, high equilibrium heat, solute competition, and dependence of sorptive capacity on mineral content. The failure of the soil to take up organic solutes from polar organic solvents can be attributed to the inability of the solute either to effectively compete for adsorption on mineral surfaces or to effectively partition into the soil humic phase. The mineral fraction of a dry or slightly hydrated soil becomes a powerful adsorbent for organic vapors from air phase at low relative humidity, and this process may dominate in the uptake of organic compounds by unsaturated, mineral-rich soils.

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## CHAPTER E

# USE OF DETRENDED CORRESPONDENCE ANALYSIS TO IDENTIFY FACTORS THAT AFFECT THE STRUCTURE OF AQUATIC COMMUNITIES

By Harry V. Leland and James L. Carter, Menlo Park, Calif.

## ABSTRACT

Detrended correspondence analysis is an ordination method that is effective for analyzing biological-monitoring data. The method was evaluated for its usefulness in defining relationships among samples and species where an environmental gradient of copper was imposed. The method is also useful in identifying major factors that control the spatial distribution of periphyton and benthic macroinvertebrates. The method is highly sensitive to differences among samples.

## INTRODUCTION

A common objective of water-pollution investigations is to identify the factors that control spatial distributions of aquatic organisms. Biological data obtained are usually organized in the form of species x sample matrices, and measurements of potentially important environmental variables are few. Multivariate methods that summarize species x sample matrices for subsequent analysis of the distribution of community-level variables along measured environmental gradients include diversity indices, cluster analysis, and ordination. Diversity indices and cluster analysis are commonly used in water-pollution investigations. Ordination has proved effective in analyzing patterns in terrestrial vegetation and in displaying species distributions along complex environmental gradients (Whittaker, 1954; 1973; Gauch, 1982a), but its application to the study of aquatic plant and animal communities is uncommon.

Results of detrended correspondence analysis (DCA), an ordination method based on reciprocal averaging, are summarized in this report. Support data and descriptions are presented in Leland and Carter (1986) and Leland and others (1986).

## METHODS

The investigation was conducted in Convict Creek, a perennial riffle-pool stream of the eastern Sierra Nevada in California. The mainstem of Convict Creek was divided into four sections ranging from 340 to 500 m in length. (For map and description of the study area, see Leland and Carter, 1984.) A solution of cupric sulfate was continuously added to three sections of the stream from mid-September 1978 to mid-January 1979 to yield concentrations (± 25 percent) of 2.5, 7, and 15 μg/L $Cu_T$ (total filterable copper). Concentrations of 2.5, 5, and 10 μg/L $Cu_T$ (± 25 percent) were maintained from mid-August 1979 to mid-August 1980. The fourth section was a control (no copper added).

Sampling of periphyton was conducted approximately monthly from June through November each year, and aquatic insects were sampled in spring, summer, and autumn. Composite samples of periphyton were used to reduce the variation in population density of taxa having exceptionally patchy distributions. Six periphyton samples were taken from riffles in each of the four sections on each sampling date. An invertebrate box sampler (0.35-mm mesh net with an opening of 0.1 $m^2$) was used to sample aquatic insects. Three samples of the aquatic-insect community were taken from a single riffle in each stream section on each sampling date. Most diatoms were identified to species; green and blue-green algae were identified to genus. All aquatic insects were identified to the lowest taxonomic level practical (genus or species) except for the Chironomidae (family only).

Several ordination methods were applied to the species x sample matrices: detrended correspondence analysis, reciprocal averaging, polar ordination using percentage difference as a distance measure, and principal components analysis with noncentered, centered, and standardized scores. Programs for the analyses were from the Cornell Ecology Program Series (Gauch, 1982b). Variables analyzed were population densities (number of individuals per surface area) of benthic algae and aquatic insects in riffles of the four sections.

## RESULTS AND DISCUSSION

Criteria used to evaluate ordination methods were robustness, accuracy in representing data structure, and effectiveness in analyzing patterns in the species-abundance data. A major advantage of DCA over other ordination methods considered was that it consistently provided interpretable, ecologically meaningful species ordinations. DCA corrects for two major faults of the other methods that can complicate interpretation of ordination axes: (1) an arch effect caused by the quadratic relationship of axis 2 on axis 1 (Hill and Gauch, 1980), and (2) distortion of ecological distances along the axes (Hill, 1979).

Seasonal fluctuations in population density of common taxa of benthic algae and aquatic insects in Convict Creek were pronounced, and seasonality was thus a major gradient when data for all sampling dates were included. Axis 1 of the species ordination (DCA) of control samples emphasized seasonality and thus provided an objective means of ordering taxa by season of maximal abundance. The seasonal gradient complicated interpretation of the imposed copper gradient when data for all sampling dates were included.

Differences among control and copper-treated sections were determined by ordinating data for each sampling date independently. Before copper exposure, community structure in the four stream sections was similar for periphyton and aquatic insects, as evidenced by a lack of discontinuity among samples in the control and experimental sections. After several weeks of continuous copper exposure, differences existed between the control and high-treatment (5 and 10 $\mu g/L\ Cu_T$) sections. After 1 month of high stream discharge during the exposure period, discontinuities between control and high-treatment samples were less distinct, and stage of succession complicated interpretation of the copper gradient in the periphyton data.

Important factors that influence the structure of benthic communities in Convict Creek and appear as primary (axis 1) or secondary (axis 2) gradients in DCA ordinations during the preexposure period were stage of succession of periphyton, substratum composition, and biological interactions of aquatic insects. Recent studies of periphyton succession suggest that the colonization of fresh substrata may be predictable. An organic coating of bacteria and fungi is followed by low-profile diatoms and, finally, an upper story of long-stalked and large rosette diatoms and filamentous green algae (Hoagland and others, 1982; Korte and Blinn, 1983). Recolonization of substrata after disturbance is less predictable and may depend on the timing, magnitude, and spatial extent of the disturbance and the availability of nearby colonizers (Fisher, 1983). Direct evidence for autogenic succession after the initial stages of colonization in periphyton is scarce. Stage of succession was an important gradient in DCA ordinations of Convict Creek samples on most sampling dates. This ordination method may prove useful in future studies of periphyton succession.

The relative importance of predation, competition, and abiotic factors as controls on abundance and distribution of aquatic insects in streams is unknown. Most investigators have emphasized the role of abiotic factors such as current velocity, substratum composition, and detritus (Cummins and Lauff, 1969; Rabeni and Minshall, 1977). Manipulative experiments, in which abiotic factors are held constant and biological interactions are examined, indicate that competitive interactions (Hart, 1981; 1983; McAuliffe, 1986) and predator-prey interactions (Hildrew and Townsend, 1980; Siegfried and Knight, 1976) may also be important. Substratum composition was the primary (axis 1) gradient on two occasions during the preexposure period, despite the restriction of sampling to riffles of visually similar substratum particle size. Predator-prey interactions and competition among grazers were emphasized in a complex (diagonal) gradient on other preexposure sampling dates. Direct methods of evaluating the relative importance of abiotic factors, competition, and predation in structuring benthic insect communities have proved difficult. By displaying major gradients that affect the spatial distribution of species, DCA may prove useful in future microdistribution studies.

## CONCLUSIONS

Detrended correspondence analysis is an effective method of summarizing species x sample matrices of periphyton and benthic insects and of displaying major gradients that affect the structure of these communities. It is highly sensitive to differences among samples and sufficiently robust to group species in an interpretable manner.

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# CHAPTER F

# MODELING SORPTIVE PROCESSES IN LABORATORY COLUMNS

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## ABSTRACT

The differential equation that defines one-dimensional solute transport and equilibrium-controlled sorption can be written as:

$$\epsilon \frac{dc}{dt} = - \epsilon V \frac{dc}{dx} + \epsilon D \frac{d^2c}{dx^2} - \rho_b \frac{d\bar{c}}{dt} \qquad (1)$$

where:

$\epsilon$ = effective porosity;
c = concentration of the solute, $ML^{-3}$;
t = time variable, T;
V = interstitial fluid velocity, $LT^{-1}$;
x = distance variable, L;
D = coefficient of hydrodynamic dispersion, $L^2T^{-1}$;
$\rho_b$ = bulk density of the porous medium, $ML^{-1}$; and
$\bar{c}$ = concentration on the medium, $MM^{-1}$.

The first and second term on the right side of equation 1 describe the convective and dispersive fluxes, respectively. The convective flux is described by the product of the velocity and the concentration. It can be calculated in two ways. It can be calculated independently if the volumetric flow rate and the length, diameter, and porosity of the medium in the column are known; it also can be obtained by introducing a conservative (nonreacting) solute and matching a solution of equation 1 for various values of velocity and dispersivity until a best fit between the experimental results and the theoretical prediction is obtained.

The dispersive flux is computed as the product of a dispersion coefficient, D, and the concentration gradient. This flux is assumed to consist of two components, mechanical dispersion and molecular diffusion. It is described as:

$$D = \alpha V + \underline{D} \qquad (2)$$

where:

$\alpha$ = the dispersivity of the media, L; and
$\underline{D}$ = the molecular diffusion coefficient, $L^2T^{-1}$.

The dispersivity, $\alpha$, is sometimes called the characteristic length, and $\underline{D}$ is the product of the molecular diffusion coefficient in liquid and the media's tortuosity. For most experiments in which velocity through the medium is greater than $10^{-5}$ cm/s, the mechanical dispersivity is much greater than the molecular diffusion; thus, molecular diffusion can be neglected.

One of the most common types of chemical reaction to occur during the movement of solutes through porous media is sorption of the solute onto the solid surface through a physical attraction or an exchange process. When the movement of the solute is slow compared to the adsorption or exchange reaction, the sorption reaction is assumed to be equilibrium controlled, which greatly simplifies analysis. This can be illustrated as follows:

$$\frac{d\bar{c}}{dt} = \frac{d\bar{c}}{dc} \cdot \frac{dc}{dt} \tag{3}$$

where:

$\frac{d\bar{c}}{dc}$ = slope of the sorption isotherm, $L^3M^{-1}$.

The sorption isotherm is defined as a plot of the sorbed phase on the y-axis versus the dissolved phase on the x-axis. Sorption isotherms have a variety of shapes; however, they usually are defined as being either favorable or unfavorable isotherms. A favorable isotherm is convex upward, and an unfavorable one is concave upward; that is, the slope of a favorable isotherm decreases with increasing concentrations, and the slope of an unfavorable isotherm increases with increasing concentrations. The slope of the isotherm explains the shape of pulses passing through chromatographic columns. Abrupt breakthrough fronts are obtained from favorable isotherms, and diffuse breakthrough fronts from unfavorable ones. When the slope of the isotherm is constant, a pulse of solute traveling through a column should be unchanged in shape, except for a possible flattening due to the effect of dispersion. Sorption processes can be separated from simple dispersion, as the breakthrough curve of a sorbed solute will be displaced, when compared to the breakthrough curve of a nonreacting solute.

A quantitative relation between $\bar{c}$ and c is needed to evaluate the slope of isotherms. Two of the most common expressions used are the Langmuir and the Freundlich adsorption equations.

The equation that describes Langmuir adsorption is given as:

$$\bar{c} = \frac{K_1Qc}{1 + K_1c} \tag{4}$$

where:

$K_1$ = adsorption equilibrium constant, $L^3M^{-1}$; and
$Q$ = maximum number of adsorption sites, $MM^{-1}$.

The terms $K_1$ and Q can be evaluated from plots of experimental data of $c/\bar{c}$ versus c. If Langmuir adsorption applies, this should result in a straight line that has a slope of 1/Q and an intercept of $1/K_1Q$. The slope of the Langmuir isotherm is given as:

$$\frac{d\bar{c}}{dc} = \frac{K_1Q}{(1 + K_1c)^2} \tag{5}$$

For small concentrations, the slope is given by the constant $K_1Q$.

The equation that describes the Freundlich isotherm is given by

$$\bar{c} = K_fc^n \tag{6}$$

where:

$K_f$ = Freundlich adsorption equilibrium constant, $L^3M^{-1}$; and
$n$ = Freundlich exponent.

The terms Kf and n can be evaluated from plots of experimental data of ln $\bar{c}$ versus ln c. If a Freundlich isotherm applies, a straight line should result that has a slope of n and an intercept of ln $K_f$.

The slope of the Freundlich isotherm is given as:

$$\frac{d\bar{c}}{dc} = nK_f c^{n-1} \tag{7}$$

When the exponent n is equal to 1, the slope is linear (constant), independent of the concentration, and equal to $K_f$.

A computer code (Grove and Stollenwerk, 1984) is available that has numerous input and output options to compute both the effluent from a column and the concentration profile within the column. Besides the Langmuir and Freundlich sorption reactions, ion-exchange (with and without equal valence) and first-order homogeneous-rate reactions (such as radioactive decay) are included. The general equations describing the transport and reaction processes are solved by finite-difference methods with the nonlinearities accounted for by iteration. Detailed documentation and examples are included.

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## CHAPTER G

# MICROBIAL POPULATIONS AND NUTRIENT CONCENTRATIONS IN A JET-FUEL-CONTAMINATED SHALLOW AQUIFER AT TUSTIN, CALIFORNIA

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## ABSTRACT

JP-5 jet fuel has contaminated 1 hectometer of the shallow aquifer at the U.S. Marine Corps Air Station (Helicopter) in Tustin, Calif. A 1.5-meter thick clay layer at the bottom of the shallow aquifer provides a barrier to vertical migration to the deeper principal aquifer. Horizontal transport results in slow seepage from the banks of the Peters Canyon channel, which intercepts the shallow aquifer downgradient from the source of contamination.

Determinations of bacterial populations in the ground water indicate that bacterial counts are 100 to 1,000 times higher inside than outside the zone of contamination. Growth on JP-5-inoculated agar plates shows that substantial populations of JP-5-assimilating bacteria are present in the shallow aquifer. Evidence suggests that only a few species of specialized bacteria, presumably those able to assimilate JP-5, are preferentially selected for in the contaminated zone.

Laboratory enrichment experiments show that the addition of nitrate plus phosphate stimulates growth and converts a mixture of fuel and water to an emulsion. The presence of carboxylate metabolites in the ground water suggests that biotransformation of jet-fuel hydrocarbons stops short of complete mineralization to inorganic carbon, presumably reflecting oxygen limitation. These findings indicate that injection of inorganic nitrogen, phosphorus, and oxygen might enhance _in-situ_ microbial degradation of jet fuel in the shallow aquifer.

## INTRODUCTION

Jet fuel has contaminated the shallow aquifer at the MCAS(H) [Marine Corps Air Station (Helicopter)] at Tustin, Calif. (fig. G-1). Contamination is a result of leakage from unlined earthen pits used for burning waste fuel during crash-crew training exercises. Aerial photographs show that the pits have been present for at least 15 years. The periodic presence of an iridescent oil sheen in Peters Canyon channel (figs. G-2 and G-3), a result of overland flow and seepage from the channel bank, led to detection of the problem in January 1983. The U.S. Geological Survey, in cooperation with the U.S. Marine Corps, began a study to determine the areal extent of contamination, direction of contaminant migration, and the possible methods for cleanup (Ehrlich and others, 1985).

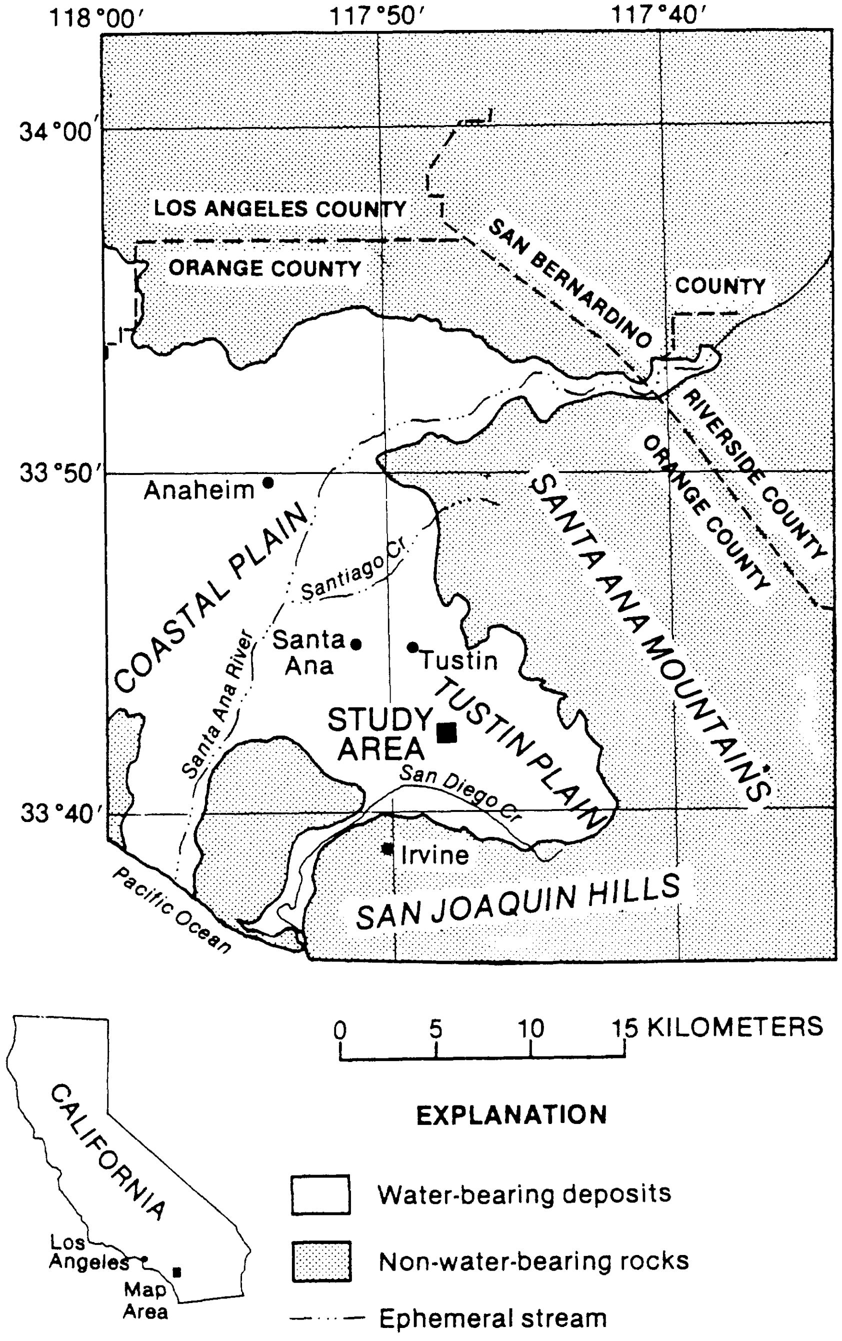

Figure G-1.--Location of the study area near Tustin, California.
(Map from Singer, 1973.)

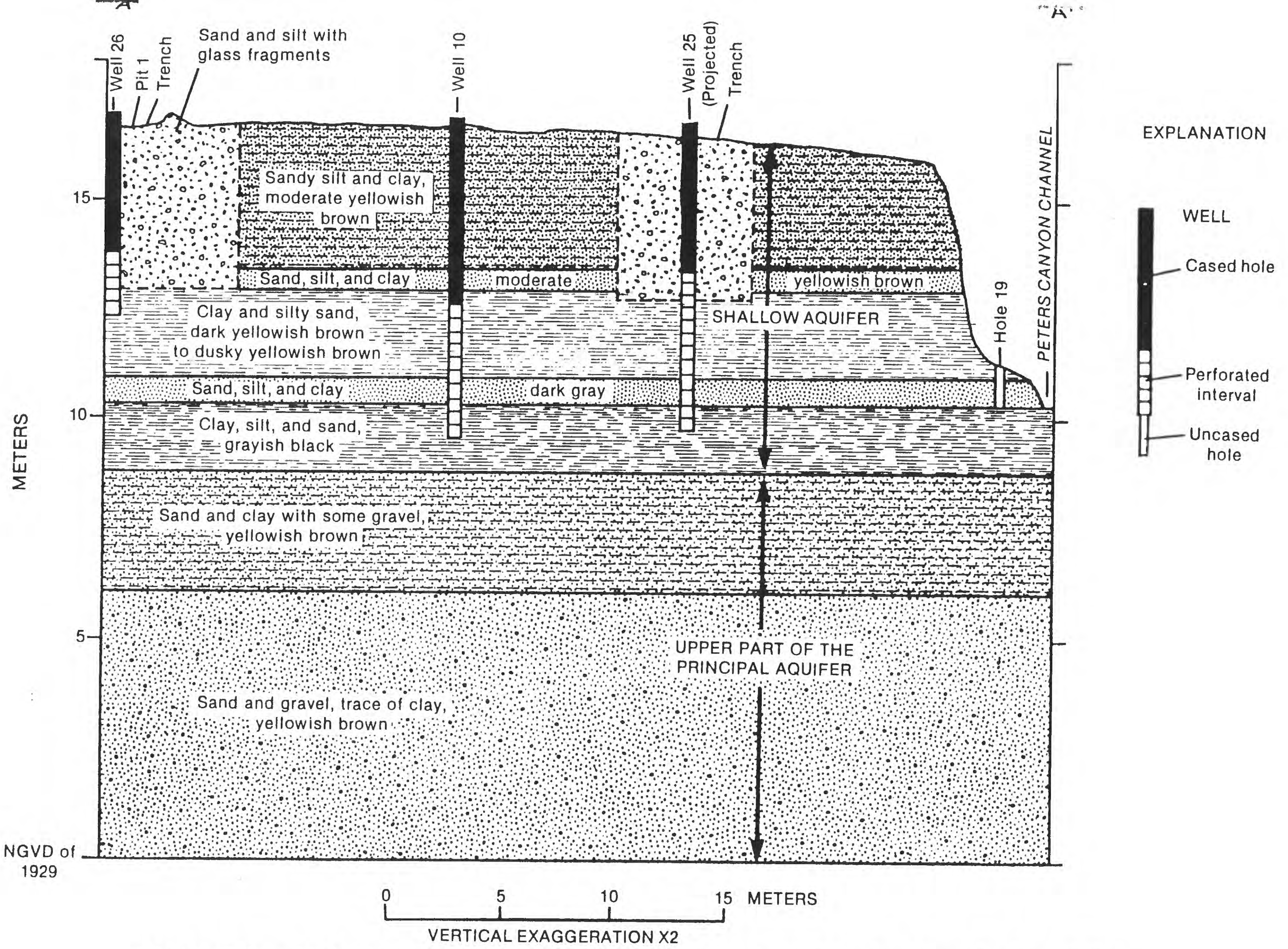

Figure G-2.--Geologic section A-A' at MCAS(H) site. (Location is shown in fig. G-3.)

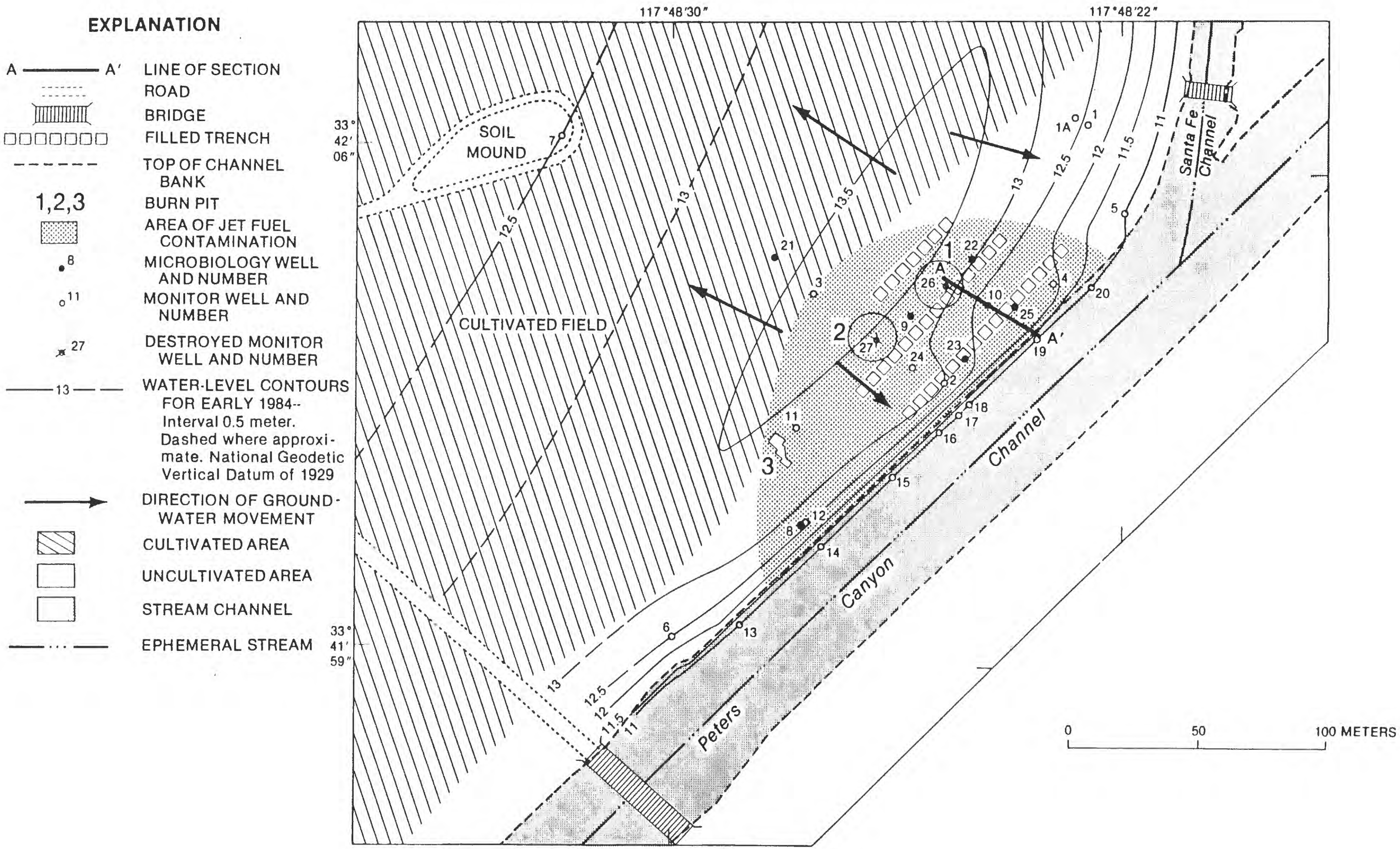

Figure G-3.--Location of monitoring wells, direction of ground-water movement, and estimated area of jet-fuel contamination.

Effective cleanup of aquifers that have been contaminated with petroleum products is often accomplished by depression pumping (de Postrovich and others, 1979). This involves creating a cone of depression in the water table near or in the contaminated zone and then removing the floating hydrocarbon phase that collects in the water columns of wells within the cone by pumping it to the surface. The shallow aquifer at the MCAS(H) site consists predominantly of low-permeability material; hence conventional depression-pumping methods alone are slow and relatively ineffective for removing the JP-5 fuel from the aquifer. Operation of a depression-pump and oil-scavenger recovery system on the site for about 2 months recovered only 100 gallons of fuel.

An alternative scheme under consideration involves coupling biochemical activity with depression pumping. Naturally occurring soil micro-organisms are known to mineralize some components of fuels (Jamison and others, 1973). Some of the micro-organisms also produce hydrocarbon emulsifiers (Gutnick and Rosenberg, 1977). These emulsifying agents could promote dispersion of pockets of trapped hydrocarbons into the ground water and might also promote desorption of hydrocarbons from the sediments. The rate of contaminant removal by depression pumping would be accelerated if dispersion and desorption effects were intensified.

This paper presents results of investigations on the indigenous hydrocarbon-degrading bacteria at the site as a background for possible development of a comprehensive remedial plan.

## Description of the Study Area

The study area is about 65 km southeast of Los Angeles in the Tustin Plain (fig. G-1). The Tustin Plain lies within the central block of the coastal plain and is bounded on the east by the Santa Ana Mountains and on the south by the San Joaquin Hills. Sediment from these highlands has created the Tustin Plain and makes up the underlying aquifer.

## Description of the Aquifer System

The water-bearing deposits in the Tustin Plain range in thickness from zero along the margins of the plain to more than 400 m in the central part. In the study area, the water-bearing deposits consist of unconsolidated Holocene alluvium from land surface to a depth of about 80 m and partly consolidated material of late Pleistocene age from about 80 m below land surface to a depth of about 300 m (Singer, 1973, p. 16). On the basis of water-level differences, the water-bearing deposits have been divided into a shallow and principal aquifer (Hardt and Cordes, 1971, p. 30).

In the study area, the shallow aquifer is present in the upper 8 m of the alluvium and is locally perched. The shallow aquifer consists predominantly of silt and clay interspersed with two thin sand lenses at about 3 and 6 m below land surface (fig. G-2). The bottom of the shallow aquifer is a 1.5 m clay layer of low permeability. The shallow aquifer is unconfined and is recharged by rainfall and irrigation-return flows.

The alluvium and late Pleistocene deposits underlying the shallow aquifer comprise the principal aquifer in the Tustin Plain. In the Tustin Plain, both the alluvium and late Pleistocene deposits consist predominantly of silt- and clay-rich sediments with occasional sand and gravel lenses. In general, little hydrologic difference exists between the alluvium and the late Pleistocene deposits (Singer, 1973, p. 13). Ground water in the principal aquifer is confined throughout most of the Tustin Plain.

### Ground-Water Movement

The spring 1984 water-level contours constructed from measurements in wells perforated in the shallow aquifer are shown in figure G-3. From the burn pits, ground water moves generally southeastward and discharges into Peters Canyon channel. West of the burn pits there is a ground-water divide; ground water west of the divide moves to the west. Ground-water movement is complicated, however, by three filled trenches that parallel the channel (fig. G-3). The buried trenches are about 3 m deep and are backfilled with material that is more permeable than the surrounding native soil. This difference in permeability causes the water-level contours to deflect in the vicinity of the trenches.

Ground-water movement in the principal aquifer in the vicinity of the study area is generally to the west during winter, when ground-water pumping is at a minimum. During summer months, ground-water pumping east of the study area causes a reversal in the ground-water gradient.

Prior to significant ground-water development in the Tustin Plain, ground water moved upward from the principal aquifer to the shallow aquifer. Ground-water pumping since 1945, however, has lowered the water level in the principal aquifer below the water table of the shallow aquifer, causing water to move downward from the shallow aquifer to recharge the principal aquifer (Hardt and Cordes, 1971, p. 8). During the study period, water-level fluctuations related to pumping in the principal aquifer were not observed in the shallow aquifer, indicating little hydraulic continuity in the study area between the shallow aquifer and the underlying heavily pumped principal aquifer.

## MATERIALS AND METHODS

### Well Construction

Wells were constructed of 5-cm-diameter polyvinyl-chloride casing that was slotted by horizontal saw cuts over the interval from about 2.5 to 6.5 m below land surface. The annulus was backfilled with quartz sand from the bottom of the hole to within 1 m below land surface and then with cement to land surface. Location of wells is shown in figure G-3.

### Microbiological Sampling

Samples for initial microbial screenings were collected from wells 8, 9, 21, 22, 23, and 25 on November 16-17, 1983. Samples from wells 21, 22, and 23 were resampled daily from January 16-20, 1984, to permit statistical determination of variation. Samples for chemical analyses were collected in the spring and summer of 1983. Approximately 24 hours prior to sampling, each well was bailed until three casing volumes of water were removed, or until the well was dry.

Water samples were collected with a glass bailer equipped with a glass ball-check valve at the bottom. Bailers were rinsed with acetone and sterilized in 0.06-percent sodium hypochlorite bleach solution immediately before use. The bailers were lowered into the water until the top of the bailer was just submerged, and then rapidly raised. Samples for enumerating anaerobic micro-organisms were immediately drawn into a sterile syringe through a 15-cm long 16-gauge steel cannula. The cannula was replaced with a hypodermic needle, and test media were inoculated in the field. Water remaining in the bailer was poured into a sterile bottle that was capped and placed in an ice chest for transport to the laboratory for other determinations. All microbiologic testing was completed within 2 hours after collection.

## Microbiological Methods

AODC (acridene orange direct counts) were done by the method described in Hobbie and others (1977).

Colony counts were made on spread plates in accordance with guidelines given by Koch (1981). The media used were SMA (standard methods agar) (BBL Microbiology Systems, Cockeysville, Md.) and mineral salts agar (Stanier and others, 1966). To determine counts of JP-5-utilizing bacteria, 0.1 mL of well water, or a dilution thereof, was spread over the surface of a sterile plate of mineral-salts agar, which was then inverted over a piece of JP-5-saturated filter paper contained in the petri-dish lid. Standard-methods agar plates were incubated at 30 °C for 48 hours. JP-5 plates were incubated at ambient conditions (18-22 °C) for 7 days.

The presence of methanogenic bacteria was determined by multiple-tube procedures according to the method of Godsy (1980). Sulfate-reducing bacteria counts were determined by multiple-tube procedures with API (American Petroleum Institute) broth (Difco, Detroit, Mich.). Heterotrophic anaerobic bacteria counts were determined by multiple-tube techniques with prereduced, anaerobically sterilized, peptone-yeast extract glucose broth (Holdeman and Moore, 1972).

## Chemical Analyses

Core-sediment and water samples were analyzed for JP-5 fuel by the U.S. Geological Survey National Water Quality Laboratory in Arvada, Colo., using methods for determination of light fuel oils described by Wershaw and others (1983). Hexane extracts were concentrated and analyzed by fused-silica capillary-column gas chromatography with flame-ionization detection. A standard was prepared by dissolving free-floating fuel from one of the wells in hexane. Quantitation was obtained by adding the area of the peaks from the sample extract and then dividing this sum by the summed area of matching peaks from the standard. Retention times had to be within ± 0.02 minute to qualify as a match. On the average, about 50 peaks fulfilled this requirement. Spikes with the jet-fuel standard and $C_{20}$-hydrocarbon indicated that extraction efficiencies were about 80 percent.

Dissolved methane was determined by the procedure described by the American Public Health Association and others (1976). Inorganic nutrients were determined by wet-chemical colorimetric methods described in Skougstad and others (1979).

Fatty-acid analyses were done on a Finnegan 4500 fused-silica capillary-column gas chromatograph-mass spectrometer (GC/MS) data system. The pH of 5-mL samples of well water or cell-free laboratory culture fluid was adjusted to 12 with 7N KOH solution and extracted with 5 mL of dichloromethane. The phases were separated, and the aqueous phase was acidified with 10N $H_2SO_4$ to a pH less than 2. Two mL of the acidified aqueous phase were extracted with 1.0 mL of diethyl ether. Diethyl ether extracts were dried over sodium sulfate before analysis.

## RESULTS AND DISCUSSION

### Zone of Contamination

The approximate boundary of contamination is shown by the shaded area in figure G-3 and is based on analysis for JP-5 fuel in samples from 20 monitor wells and 8 shallow hand-augered holes. The contaminated area includes about 1 $hm^2$ between the burn pits and Peters Canyon channel.

Results of semiquantitative analyses for JP-5-fuel content of soil cores collected during the construction of the monitor wells indicate that the contamination extends from about 2 m below land surface to the top of the 1.5-m clay layer at about 6.5 m below land surface (fig. G-2). JP-5 fuel was not found in the clay layer, which indicates that the clay layer is an effective barrier to the vertical movement of contamination.

Significant concentrations of JP-5 fuel were identified in soil-core samples collected below the present-day water table. The presence of the jet fuel below the water table suggests that the water level has been lower in the past. Water levels have declined from about 2.5 m below land surface in spring 1983 to about 4.0 m below land surface in spring 1984. Even larger water-level fluctuations may have occurred in the past, which would have allowed JP-5 fuel to contaminate the entire vertical profile of the shallow aquifer above the clay layer. The low permeability of the shallow aquifer, has kept some JP-5 fuel trapped below the present water table.

Among the wells sampled for microbiological analyses, wells 9, 22, 23, and 25 contained thin, free-floating fuel layers and dispersed fuel droplets. No free fuel layer was noted in well 8, but the JP-5 concentration of well 8 water was 19 mg/L, which is probably its solubility in water. By mid-1984, 2 m of JP-5 was present in well 8, indicating the capricious nature of fuel movement in the shallow aquifer. Similar, though less dramatic, changes were observed in several monitor wells.

GC/MS analysis of JP-5-contaminated soil from the trenches and beneath the burn pits found no extractable organic "priority pollutants" in concentrations exceeding the detection limit of 0.2 mg/kg. Organochlorine pesticides and polychlorinated biphenyls, analyzed by gas chromatography with electron-capture detection, were also not found (detection limit of 0.01 mg/kg). Volatile organic priority pollutants are present in low concentrations. Highest concentrations measured were about 50 mg/L for common organochlorine solvents, such as dichloroethane and dichloroethylene, from fuel layers in monitor wells. These compounds partition into the ground water resulting in concentrations of several micrograms per liter.

## Nutrient Concentrations

Phosphorus, nitrogen, and oxygen concentrations were determined in water samples from most of the monitor wells in the study area. These macronutrients were measured to establish whether they were affected by microbial degradation of the jet fuel.

The concentration of dissolved phosphate ($PO_4$) was generally a few tenths milligram per liter but was highly variable. Variations show no apparent relation to the jet-fuel concentration. Because phosphate has a strong affinity for mineral surfaces, sorption on aquifer soils is probably the major control of $PO_4$ concentrations in the ground water.

The concentration of nitrate-nitrogen ($NO_3$-N) ranged from 50 mg/L in samples from well 21 to less than 0.1 mg/L (detection limit) in samples from wells containing jet fuel. Well 21 is surrounded by a cultivated field; therefore, the high nitrate probably reflects the use of fertilizer on the field. Samples from wells outside the cultivated field and outside the area of jet-fuel contamination (unshaded area in fig. G-3) had $NO_3$-N concentrations ranging from 1 to 5 mg/L. Evidently nitrate is completely consumed by microbial populations degrading the jet fuel.

In surface-water sediments ammonium normally increases while nitrate decreases as the sediments become more anaerobic. However, ammonium-nitrogen ($NH_4$-N) concentrations were less than 0.1 mg/L throughout the study area except in the filled trenches, where concentrations ranged from 1 to 2 mg/L. The ammonium ion is strongly sorbed to particle surfaces and exchangeable clays, so the higher concentrations within the trenches might be due to less sorption on the comparatively larger particle-size material (with less surface area) that fills the trenches.

Oxygen concentration was 3 to 5 mg/L in samples from wells outside the area of jet-fuel contamination but was zero in wells containing jet fuel. The absence of oxygen was accompanied by a strong odor of hydrogen sulfide in wells located in the trenches, and sometimes by a faint odor in contaminated wells outside the trenches. Evidently, aerobic bacteria that use jet fuel as an energy source rapidly consume all the available oxygen.

The absence of nitrate and oxygen in the ground water contaminated by jet fuel suggests that jet-fuel degradation might be enhanced if additional oxygen and inorganic nitrogen were available.

## Microbiological Test Results

Results of microbiological determinations are given in tables G-1 and G-2. It can be seen that AODC values and SMA and JP-5 agar plate counts were highest in the wells with free fuel layers. AODC values ranged from nearly $1x10^6$ cells/mL to slightly more than $1x10^7$ cells/mL in this group of wells, but AODC values in uncontaminated well 21 were less than $2x10^4$ cells/mL--roughly forty-fold less than the lowest value for a well with a free fuel layer. The AODC value for well 8, which is near the edge of the fuel plume, was $2.2x10^6$ cells/mL. This is near the low end of the range for the contaminated zone but more than 100-fold greater than in uncontaminated well 21.

Table G-1.--JP-5 fuel concentrations and bacterial counts in ground-water samples from MCAS(H) site, Tustin, California, 1983-84

[AO, acridene orange; SMA, standard methods agar; cfu, colony-forming units. Well locations shown in figure G-3.]

| Well No. | JP-5 concentration[1] (mg/L) | Microbiological sampling dates | AO direct counts (cells/mL) times $10^3$ | Aerobic plate counts<br>SMA (cfu/mL) times $10^3$ | Aerobic plate counts<br>JP-5 fuel (cfu/mL) times $10^3$ |
|---|---|---|---|---|---|
| 8 | 19 | Nov. 16-17, 1983 | 2,200 | 62 | 62 |
| 9 | [2]13,000 | Nov. 16-17, 1983 | 13,000 | 1,200 | 1,300 |
| 21 | <0.2 | Nov. 16-17, 1983 | 1.3 | <1 | <1 |
| | | Jan. 16-20, 1984 | 19±8 | 0.35±.21 | 0.33±.18 |
| 22 | [2]16,000 | Nov. 16-17, 1983 | 6,600 | 900 | 1,400 |
| | | Jan. 16-20, 1984 | 5,600±1,200 | 1,200±600 | 1,000±700 |
| 23 | 130 | Nov. 16-17, 1983 | 1,000 | 90 | 90 |
| | | Jan. 16-20, 1984 | 700±100 | 110±80 | 70±10 |
| 25 | 820 | Nov. 16-17, 1983 | 7,600 | 710 | 1,300 |

[1] Sampled spring 1983.
[2] Fuel layer present.

AODC values are greater than the SMA and JP-5 agar plate counts by factors of about 10 or less for wells 9, 22, 23, and 25, which all have free fuel layers, but are significantly larger than the counts for uncontaminated well 21 (table G-1). The results of the JP-5 agar plate counts indicate that substantial populations of JP-5-assimilating bacteria exist within the shallow aquifer. Interestingly, the counts on JP-5 agar and SMA were similar even though the compositions of these two media differ greatly. SMA is a mixture of polypeptides, glucose, and a few inorganic salts, whereas the only energy sources in the JP-5 agar are the hydrocarbons of the fuel.

Table G-2.--Anaerobic bacterial indicators in ground water at MCAS(H) site, Tustin, California

[--, not detected; NA, not analyzed; +, present; MPN, most probable number. Well locations shown in figure G-3]

| Well No. | Date (1983) | Anaerobes (MPN/mL) | Sulfate reducer | Methanogens | Methane concentration (mg/L) |
|---|---|---|---|---|---|
| 8 | Nov. 16 | <30 | + | -- | -- |
|  | Nov. 17 | 150 | + | -- | + |
| 9 | Nov. 16 | <30 | + | -- | + |
|  | Nov. 17 | <30 | + | -- | + |
| 21 | Nov. 16 | <30 | -- | -- | NA |
|  | Nov. 17 | <30 | -- | -- | -- |
| 22 | Nov. 16 | 210 | + | -- | + |
|  | Nov. 17 | 750 | + | -- | + |
| 23 | Nov. 16 | 2,400 | + | + | 6 |
|  | Nov. 17 | 430 | + | + | 5 |
| 25 | Nov. 16 | 150 | + | + | 1 |
|  | Nov. 17 | 2,100 | + | + | 1 |

Methane-producing bacteria and dissolved methane were detected in water samples from only wells 23 and 25 (table G-2) and their presence was surprising. It was expected that any methane-producing bacteria that might be present would perish as a result of exposure to oxygen during well recovery after bailing. However, Patel and others (1984) reported that methane-producing bacteria may be less sensitive to oxygen toxicity than is commonly supposed. In their study, stationary-phase cells of three species of methanogenic bacteria were aerated in the absence of reducing agents. Exponential death rates were observed, but the times required to destroy 90 percent of the bacterial standing crop ranged from 3.5 to more than 9 hours. The density of methanogenic bacteria in the saturated zone may be sufficiently high that a small number of them survive even after several hours of exposure to oxygen.

## Carboxylate Metabolites

Results of fatty-acid analyses of samples from wells 21, 22, 23, and 25 are given in table G-3. Only formate, acetate, propionate, and benzoate were found; higher molecular-weight acids and alcohols were not found. Anaerobic bacteria are generally unable to utilize the compounds in crude oil and its refined derivatives as nutrients. Methane-producing bacteria can assimilate only a limited range of compounds. They are capable of autotrophic growth with $H_2$ and $CO_2$, and some species can use formate and acetate as growth substrates. Sulfate-reducing bacteria can utilize certain fatty acids, including acetate (Widdle and Pfennig, 1981). The presence of fatty acids and benzoate in water from wells 22, 23, and 25 suggests that biotransformations of hydrocarbons is occurring in the shallow aquifer, but complete oxidation of hydrocarbons to $CO_2$ and $H_2O$ by microbial metabolism does not occur. This incomplete mineralization presumably reflects an oxygen limitation.

Table G-3.--Concentration of carboxylates in ground water at MCAS(H) site, Tustin, California, and in laboratory test solutions

[Concentrations in mg/L. Well locations shown in figure G-3]

| Well No. | Formate | Acetate | Propionate | Benzoate |
|---|---|---|---|---|
| 21 | <0.1 | <0.1 | <0.1 | 0.6 |
| 22 | <.1 | .8 | <.1 | .9 |
| 23 | .2 | .3 | <.1 | <.1 |
| 25 | 2.4 | .9 | <.1 | 1.3 |
| Laboratory test | 9.0 | 36.7 | .2 | 14.0 |

## Nutrient Addition

A series of laboratory experiments with shaking flasks was done to determine if adding nitrogen or phosphorus to a sample of water from well 22 would enhance microbial growth. The control test used a mixture of well 22 water and 1 mL of JP-5 fuel inoculated with a culture of hydrocarbon-degrading bacteria derived from well 22. After 7 days the SMA plate count reached $2.6 \times 10^5$ cfu/mL (colony forming units) and then declined to $4.1 \times 10^4$ cfu/mL after 14 days. Comparable results were obtained when well 22 water and JP-5-inoculated water were each enriched with potassium phosphate to a phosphorus level of 100 mg/L (as $PO_4$-P) or with potassium nitrate to a nitrogen level of 100 mg/L (as $NO_3$-N). When both potassium phosphate and potassium nitrate were added to the same solution, the SMA count reached $4.5 \times 10^8$ cfu/mL after 7 days. Furthermore, the fluid in the shaking flask became a milky white, presumably through emulsification of the hydrocarbon phase. With the addition of either phosphate or nitrate, but not both, the JP-5 remained in the form of isolated globules floating on the surface of the water. Evidently, the addition of both is required to enhance microbial growth and cause emulsification of the fuel and water mixture.

Results of analyses for fatty acids in an inoculated sample of well 22 water that had been enriched with phosphate plus nitrate, and shaken for 7 days, is shown in table G-3. It can be seen that substantial amounts of formate, acetate, and benzoate are present, even in this well-aerated sample. This suggests that total mineralization may occur only slowly in the presence of free hydrocarbon, even under aerobic conditions.

## SUMMARY AND SUGGESTIONS FOR FUTURE WORK

The results presented show that the presence of JP-5 fuel supports a significant population of hydrocarbon-assimilating organisms in the shallow aquifer at the MCAS(H). The presence of methane-producing bacteria suggests that oxygen limitation may be a control on growth of the populations of aerobic hydrocarbon-degrading bacteria. The sulfate-reducing bacteria and methane-producing bacteria are apparently using fatty acids that result from the biotransformation of aliphatic and aromatic hydrocarbons in the JP-5 fuel. The results of laboratory shaking-flask experiments indicate that microbial growth in the contaminated part of the shallow aquifer is limited by the availability of inorganic nitrogen and phosphorous.

On site microbial biodegradation has been considered to be a promising process for removal of contaminants from ground water. Examples of _in-situ_ microbial activity as an aid to ground-water cleanup are given by McKee and others (1972), Jamison and others (1973), and Van Loocke and others (1975). Jamison and others (1973) observed that bacterial counts in well-water samples from a gasoline-contaminated aquifer increased by 10- to 100-fold after injection of ammonium sulfate solution into the aquifer near the wells. They also speculated that additional oxygen would be needed to achieve the maximum benefit of _in-situ_ microbial degradation of fuel.

These preliminary findings suggest that injection of soluble nitrogen and phosphorous compounds into the contaminated shallow aquifer could stimulate microbial growth and increase biotransformation of contaminating JP-5 fuel. Evidence for oxygen limitation as a control on microbial growth in the shallow aquifer already exists. Injection of hydrogen peroxide might prove beneficial if, as a result of its chemical or microbial breakdown, a supply of oxygen were released to the ground water.

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## CHAPTER H

# ADSORPTION AND DESORPTION OF HEXAVALENT CHROMIUM IN AN ALLUVIAL AQUIFER NEAR TELLURIDE, COLORADO

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## ABSTRACT

A laboratory investigation was conducted to evaluate reactions of hexavalent chromium Cr(VI) with alluvium in an aquifer near Telluride, Colo., and to determine the mechanisms for these reactions. The problem was discovered in 1978 when two domestic water wells were drilled in alluvium approximately 400 m downvalley from the base of a tailings pond. Water in the tailings pond contained 8.8 mg/L Cr(VI); concentrations as high as 0.65 mg/L were measured in the wells. Discharge of Cr(VI) to the tailings pond was stopped shortly after a contaminated plume was discovered; however, a significant quantity was already present in the ground water, thereby preventing the use of ground water as a potable water supply.

Chromium in natural waters exists in the +3 and +6 oxidation state; the presence of Cr(VI) is generally indicative of industrial pollution. Hexavalent chromium occurs as an anion in aqueous solution. Dichromate ($Cr_2O_7^{2-}$) predominates in acidic solutions at concentrations $>10^{-2}M$, whereas $HCrO_4^-$ and $CrO_4^{2-}$ are the stable species at lower concentrations. The ionization constant for $HCrO_4^-$ is 6.5.

Adsorption can be an important mechanism for removing Cr(VI) from solution. At least two different mechanisms, nonspecific and specific, are responsible for adsorption of anions. Nonspecific adsorption refers to the anions being retained as counter ions in the diffuse layer, opposite a net positively charged surface. Specific anion adsorption occurs when anions coordinate directly with the metal ion of a mineral surface by ligand exchange (Hingston, and others, 1967). Given appropriate conditions, Cr(VI) may also be reduced to Cr(III) (Ross, and others, 1981).

Uncontaminated alluvium and ground water (spiked with $CrO_4^{2-}$) from the study site were used in batch and column experiments. Batch experiments indicate that approximately 3 days are required to achieve equilibrium between Cr(VI) and alluvium.

Results show that alluvium from the aquifer has a finite capacity for removing Cr(VI) from ground water. In a column experiment, all Cr(VI) in the first seven pore volumes of ground water which contained 50 mg/L Cr(VI), was removed by the alluvium (fig. H-1). At an initial Cr(VI) concentration of 0.5 mg/L, complete removal of Cr(VI) from ground water was achieved for more than 80 pore volumes (data not shown).

The zero point of charge for the alluvium occurred at a pH of approximately 8.3, and the alluvium had a positive net charge at the ground-water pH of 6.8. Visual and chemical evidence indicated that iron oxide and hydroxide coatings on the alluvial particles principally were responsible for the adsorption of Cr(VI).

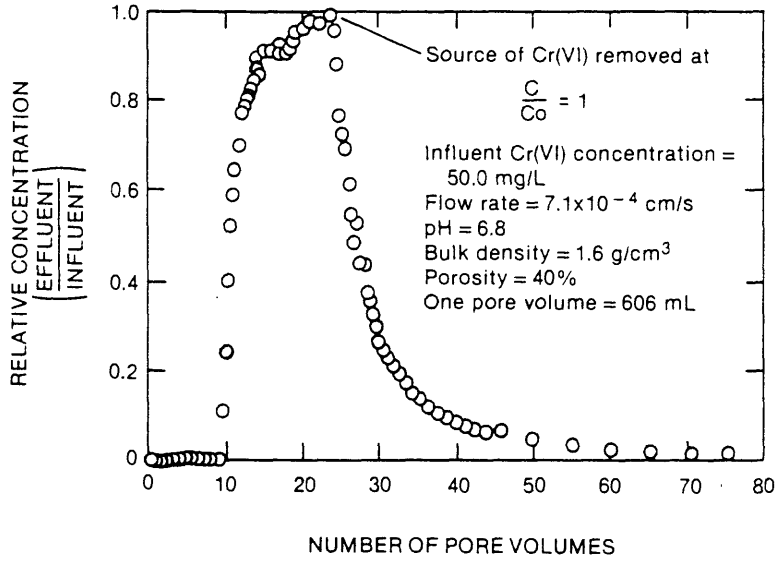

Figure H-1.--Relative concentration ($C/C_o$) of hexavalent chromium in alluvium with respect to number of pore volumes during column experiment.

A significant result from this study concerns desorption of Cr(VI) from alluvium after the contaminated plume has passed. Data in figure H-1 are typical of results obtained in other column experiments at a variety of concentrations. Initially, desorption of Cr(VI) is rapid; this is followed by a steadily decreasing rate until the desorption curve becomes almost level. For the desorption curve in figure H-1, almost 16 percent of the adsorbed Cr(VI) was still associated with the alluvium when the experiment was stopped after 80 pore volumes (232 days). The concentration of Cr(VI) in the effluent was still 0.15 mg/L, three times the drinking-water standard of 0.05 mg/L. In other column experiments, more than 320 pore volumes were required to reduce the concentration of Cr(VI) to 0.05 mg/L.

Alluvium from the column (fig. H-1) was removed and subjected to a variety of extraction procedures. Approximately 10 percent of the Cr(VI) was extractable by anion exchange with $HPO_4^{2-}$ + $H_2PO_4^-$; however, reduction of iron oxide and hydroxide coatings with sodium dithionite was required to remove all Cr. This suggests that some Cr(VI) initially adsorbed by the alluvium was incorporated into the structure of iron oxides either as Cr(VI) or as Cr(III).

Distribution coefficients ($Kd_{Cr}$) obtained from batch experiments ranged from 52 mL/g for an initial Cr(VI) concentration of 0.2 mg/L to 1.7 mL/g for an initial Cr(VI) concentration of 100 mg/L. Langmuir plots of the batch adsorption data are linear from 0.2 to 3 mg/L and from 3 to 100 mg/L. This kind of result is often interpreted to represent two different adsorption mechanisms (Harter and Baker, 1977). It is possible that the two linear Langmuir plots represent specific and nonspecific adsorption of Cr(VI) by the alluvium.

Cr(VI) adsorption is dependent on the type and concentration of other ions in solution. The data in figure H-2 show the effect of various concentrations of $Cl^-$, $NO_3^-$, $SO_4^{2-}$, and $H_2PO_4^-$ + $HPO_4^{2-}$ on adsorption of Cr(VI) by Telluride alluvium. A mixture of 50 percent $H_2PO_4^-$ and 50 percent $HPO_4^{2-}$ inhibited adsorption of Cr(VI) to the greatest extent. Sulfate also prevented a significant amount of Cr(VI) adsorption. The effects of $Cl^-$ and $NO_3^-$ are similar and are significantly less than those of $SO_4^{2-}$ and $H_2PO_4^-$ + $HPO_4^{2-}$.

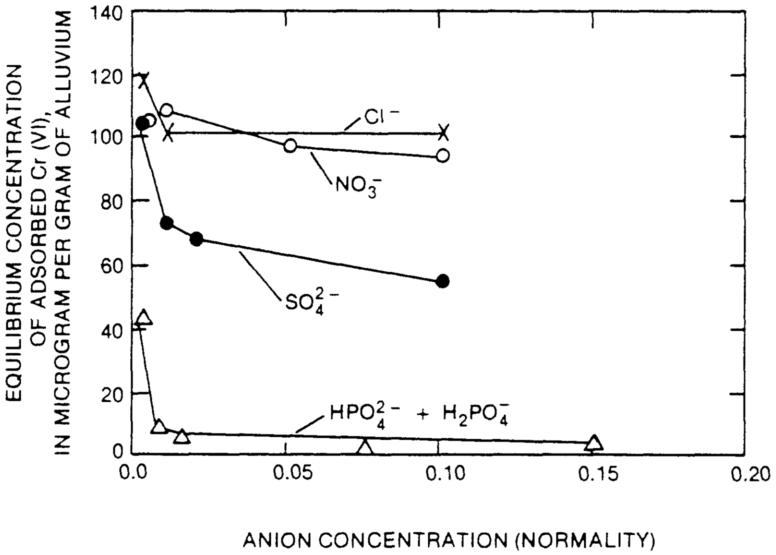

Figure H-2.--Equilibrium concentration of adsorbed hexavalent chromium in alluvium with respect to concentration of competing anions.

Part of the reason that some anions are more effective than others in preventing adsorption of Cr(VI) is probably related to the charge distribution around the ion, which in turn is related to molecular structure of the anion. The tetragonal shape of $SO_4^{2-}$, $PO_4^{3-}$, and $CrO_4^{2-}$ is apparently more favorable for adsorption than the planar $NO_3^-$ and spherical $Cl^-$. Thus, $SO_4^{2-}$, $H_2PO_4^-$, and $HPO_4^{2-}$ may act to prevent adsorption of Cr(VI) by direct competition for specific surface sites. The greater effectiveness of $H_2PO_4^-$ + $HPO_4^{2-}$ than of $SO_4^{2-}$ may be related to the presence of $H^+$ and hydrogen bonding or to precipitation of an Fe phosphate mineral.

Davis and Leckie (1980) calculated that an increase in solution concentration of an indifferent electrolyte, such as $NO_3^-$ or $Cl^-$, caused a reduction in electrostatic potential near the surface of a charged particle. This fact would result in less adsorption of specific anions, such as Cr(VI). Anions, such as $SO_4^{2-}$ and $HPO_4^{2-}$ can also inhibit adsorption of $CrO_4^{2-}$ by reducing the electrostatic potential in addition to direct competition for specific adsorption sites.

In summary, Cr(VI) in alluvium near Telluride, Colo., is adsorbed by specific and nonspecific mechanisms. Cr(VI) adsorbed by nonspecific processes is readily desorbed by Cr-free ground water. Stronger bonds formed between Cr(VI) and alluvium during specific adsorption result in very slow release of this fraction. Thus, the adsorbed Cr(VI) will serve as a secondary source of contamination long after the original plume is gone.

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# CHAPTER I

# EFFECTS OF PENTACHLOROPHENOL ON THE METHANOGENIC FERMENTATION OF PHENOL

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## ABSTRACT

The methanogenic fermentation of phenol at a concentration of 200 mg/L was investigated in the presence of pentachlorophenol (PCP) ranging in concentration from 0.01 to 5.0 mg/L in laboratory digestors. The digestors contained a mixture of mineral salts in a solution and settled sludge from a bench-scale anaerobic digestor (10:1,v/v). The mean rates of methane gas evolution from the digestors indicated that a concentration of 0.05 mg/L PCP or less had no effect on methanogenesis. PCP concentrations of 0.1 and 0.5 mg/L delayed the onset of methanogenesis but did not affect the overall rate. Methanogenesis of phenol did not occur at PCP concentrations greater than 1.0 mg/L. Results of high-performance liquid chromatography analysis of the culture solutions, biomass, and the inner walls of the digestors indicated that PCP was partially biodegraded when the initial concentration was 1.0 mg/L, and was completely biodegraded when the concentration was 0.5 mg/L or less. PCP was not biodegraded at a concentration of 5.0 mg/L. Results indicate that the observed delay before the onset of phenol biodegradation, when the PCP concentrations were between 0.1 and 0.5 mg/L, was relieved by the biodegradation of PCP.

## INTRODUCTION

According to the U.S. Environmental Protection Acency, PCP and creosote are the two pesticides used in largest volume in the United States (Chemical and Engineering News, 1978). It has been estimated that more than 500 wood-preserving operations in the United States that collectively use more than 36 million kg of PCP and 454 million kg of creosote annually (Cirelli, 1978).

Creosote is a complex mixture of chemical compounds and typically consists of about 85 percent polynuclear aromatic hydrocarbons (PAH) and 2 to 7 percent phenolic compounds; the remainder consists of nitrogen- and sulfur-containing heterocyclic compounds. Phenolic compounds are more soluble than the other compounds of creosote; therefore, when creosote is mixed with water, two separate phases result: (1) an aqueous phase rich in phenolic compounds, and (2) a dense hydrocarbon phase rich in PAH. When ground water moves through an area contaminated by creosote, the water-soluble phenols dissolve and are transported downgradient in the flow.

PCP is usually applied to wood products as a 5-percent solution in such solvents as mineral spirits, no. 2 fuel oil, kerosene, or sometimes as aqueous solutions of the sodium salt (NaPCP). The solubility of PCP in water is 20 to 25 mg/L, whereas the solublity of NaPCP in water is 5 to 7 g/L (Bailey and White, 1965). It has been estimated that more than 200 sites in the United States use both PCP and creosote (Cirelli, 1978). At many of these sites, contamination of the ground water by PCP and phenolic compounds from creosote has occurred as a result of improper storage and disposal of these compounds. As these compounds migrate in the ground water, they are susceptible to biodegradation.

The biodegradation pathways of phenols, chlorophenols, and PCP in anoxic environments have been studied individually (Ide and others, 1972; Ehrlich and others, 1982; Godsy and others, 1983; Boyd and Shelton, 1984) but few, if any, studies have examined possible interactions when both materials are present in an anoxic environment.

This study evaluated the interactions of PCP and phenol, one of the major water-soluble, anaerobically biodegradable components of creosote, in anaerobic laboratory digestors. Results demonstrated that PCP was inhibitory to the methanogenic fermentation of phenol and that this inhibition could be relieved if the PCP concentration was low enough to undergo biodegradation.

## MATERIALS AND METHODS

The study was conducted in 16 butyl-rubber-capped 125-mL serum bottles with aluminum crimp seals. All operations were carried out in an anaerobic glove box in an atmosphere of 90 percent Ar and 10 percent $H_2$.

Each bottle contained 100 mL of a mixture of mineral salts solution and settled sludge from a bench-scale anaerobic digestor (10:1, v/v). Phenol was added to 14 of the bottles to result in a final concentration of 200 mg/L (2.1 m*M*). PCP was added in duplicate to bottles containing phenol solution to produce final concentrations of 0.01 mg/L (0.04 m*M*), 0.05 mg/L (0.19 m*M*), 0.1 mg/L (0.38 m*M*), 0.5 mg/L (1.0 m*M*), 1.0 mg/L (3.8 m*M*), and 5.0 mg/L (19 m*M*). The serum bottles were maintained for 150 days at ambient temperature (19-22 °C), and were shaken once daily.

The mineral salts solution contained: $KH_2PO_4$, 0.75 g/L; $K_2HPO_4$, 0.9 g/L; $MgCl \cdot 6H_2O$, 0.36 g/L; $NH_4Cl$, 0.9 g/L; trace-metal solution (Zeikus, 1977), 9.0 mL; and vitamin solution (Wolin and others, 1963), 5.0 mL. After the pH was adjusted to 7.2 with 1 normal NaOH, the solution was boiled to remove dissolved $O_2$ and cooled under $O_2$-free Ar. The solution was then placed into the glove box and allowed to equilibrate with the glove-box atmosphere for a minimum of 2 days. Just before the test, 0.5 g of $Na_2S$ was added as a reducing agent.

Volatile fatty acids (VFA) in the mixture of mineral salts solution and sludge were determined by high-performance liquid chromotography (HPLC) by the method of Ehrlich and others (1981). The initial biomass in the serum bottles was determined by drying a measured volume of the mineral salts solution and sludge mixture to a constant weight at 105 °C (Gerhardt, 1981). Each serum bottle contained 0.2 mg/L formate, 5.9 mg/L acetate, 11.6 mg/L propionate, and 727 mg/L biomass.

Gas production in the serum bottles was measured by displacement of the plunger in a water-wetted 10-mL glass hypodermic syringe. Methane concentration in the head space was determined by the gas chromatographic method described by Godsy and others (1983).

At the conclusion of the experiment, 20.0 mL of the mixed suspension from each serum bottle was centrifuged at 10,000 x gravity for 5 min. The supernatent fluid was removed and filtered through a 0.4 μm polycarbonate filter (Nucleopore Corp., Pleasonton, Calif.). Concentrations of phenol and chlorophenols in the filtrate were determined by HPLC through the method of Goerlitz (1982). The cell pellet was mixed with 2.0-mL of methanol-KOH solution (50.0 g KOH/L methanol) and digested at 70 °C for 1 hour. Five mL of water was then added, and the tube was heated at 100 °C for 15 min. to remove the methanol. Cell debris was removed by centrifugation. The supernatant was removed and the pH adjusted to 7.0 with glacial acetic acid. The neutralized solution was filtered through a 0.4-μm polycarbonate filter before HPLC analysis for phenol and chlorophenols. Finally, the serum bottles were emptied and their inner surfaces rinsed with 4.0 mL of the methanol-KOH solution. Ten mL of water was added to the wash solution, and the methanol was removed by heating as described above. After pH adjustment and filtration, the concentrations of phenol and chlorophenols were determined by HPLC analysis.

## RESULTS

The mean rates of gas evolution from the duplicate serum bottles are shown plotted in figure I-1. Individual values of gas production from the duplicate serum bottles were within 5 percent of the average values shown. Methane production in the early part of the experiment resulted largely from the VFA introduced with the sludge. The rates of methanogenesis were unaffected at PCP concentrations of 0.1 mg/L or less. Marked reductions occurred at levels of 0.5 and 1.0 mg/L, and methanogenesis virtually stopped at 5.0 mg/L.

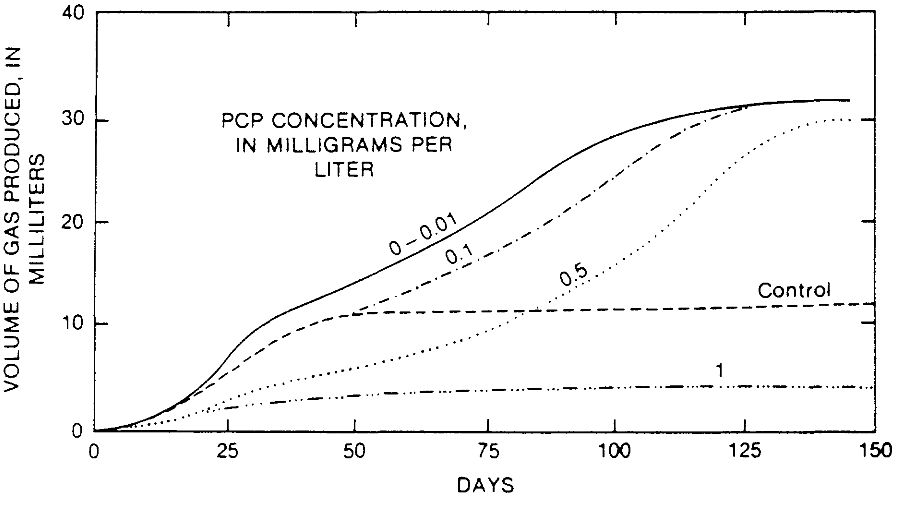

Figure I-1.--Volume of methane produced during methanogenesis of phenol in mineral-salt and anaerobic-digestor sludge solution in presence of pentachlorophenol (PCP) at selected concentrations.

Methanogenesis from phenol also began to occur at the same time as the VFA, but at a slower rate. This was verified by weekly analysis of phenol concentrations and of $CH_4$ in the head space. The methanogenic fermentation of phenol was inhibited longer in the presence of low PCP concentrations than the methanogenic fermentation of the VFA. Interestingly, once methanogenesis began, the rate was not affected by the presence of PCP. Methanogenesis of phenol did not occur at PCP concentrations greater than 1.0 mg/L.

Results of the HPLC analysis of the culture solutions are given in table I-1. Phenol, PCP, and other chlorophenols were not found if the initial PCP was less than 0.5 mg/L. At an initial PCP concentration of 1.0 mg/L, no decrease in the phenol concentration was apparent, the PCP had disappeared, and several chlorophenols that were absent in the starting mixture were present. After 150 days, the PCP concentration in the serum bottle, which had originally been 5.0 mg/L, was reduced to 3.4 mg/L.

Table I-1.--Concentration of phenol and chlorophenols in digestors after 150 days

[ND, not detected (<0.001 mg/L); TR, trace (~0.002 mg/L)]

| Compound | Initial PCP concentration (milligrams per liter) | | |
|---|---|---|---|
| | 0-0.5 | 1.0 | 5.0 |
| Phenol | ND | 200 | 200 |
| PCP | ND | ND | 3.4 |
| Tetrachlorophenols | ND | 0.09 | ND |
| Trichlorophenols | ND | TR | ND |
| Dichlorophenols | ND | 0.5 | ND |
| Chlorophenols | ND | .05 | ND |

Results of the HPLC analysis of biomass extracts and serum-bottle wall washings are given in table I-2. Low PCP levels caused no apparent uptake of PCP into the cells or sorption to the serum-bottle walls. In serum bottles with an initial PCP level of 1.0 mg/L, only a fraction of the PCP was recovered from the biomass. At an initial level of 5.0 mg/L, appreciable amounts of PCP were recovered from the biomass, but the total recovery was only 74 percent of the amount initially added. We are unable to account for the remainder at this time.

Table I-2.--Recovery and distribution of PCP in laboratory digestors

[ND, not detected (<0.001 mg/L); all values are in micrograms]

| Initial PCP mass in digestors | Mass of PCP | | | Percent recovery |
|---|---|---|---|---|
| | Cells | Liquid | Glass | |
| 1 | ND | ND | ND | 0 |
| 10 | ND | ND | ND | 0 |
| 50 | ND | ND | ND | 0 |
| 100 | 0.8 | ND | ND | .8 |
| 500 | 30 | 340 | ND | 74 |

## DISCUSSION AND CONCLUSIONS

PCP and other halogenated aromatic compounds have been shown to be susceptible to reductive dechlorination and degradation by bacteria under anoxic conditions. Hakulinen and Salkinoja-Salonen (1982) demonstrated that PCP was biodegraded in an anaerobic fluidized-bed reactor that treated paper- and pulp-mill effluents. Ide and others (1972) reported that PCP was converted to 2,3,4,5- and 2,3,4,6-tetrachlorophenol, 2,4,5- and 2,3,5-trichlorophenol, 3,4- and 3,5-dichlorophenol, and 3-chlorophenol after incubation for several weeks in a paddy soil. Boyd and Shelton (1984) investigated the anaerobic biodegradation of mono- and dichlorophenols to $CH_4$ and $CO_2$ by anaerobic sewage sludge. Biodegradation was evaluated by monitoring substrate disappearance and, in selected cases, by production of $^{14}CH_4$ from labeled substrates.

Both Boyd and Shelton (1984) and Horowitz and others (1983) found that methanogenic fermentation of chlorinated aromatics requires complete removal of the halogen as a first step. Our results demonstrate dechlorination of PCP at initial PCP levels below 5 mg/L PCP. Presumably, at higher levels, PCP is toxic to the dechlorinating organisms. The fact that PCP was partially dechlorinated in the digestors with an initial PCP concentration of 1.0 mg/L, and also that phenol, PCP, or other chlorophenols were not found in digestors with an initial PCP concentration at or below 0.5 mg/L, demonstrates that PCP was totally biodegraded to $CH_4$ and $CO_2$.

These results suggest that the dechlorinating component of the microbial consortium may be distinct from the components that effect ring reduction, ring cleavage, and the other intermediate steps incident to production of one-carbon compounds, acetate, $H_2$, and $CO_2$--the immediate precursors of $CH_4$.

The time required before the onset of phenol biodegradation in digestors with initial PCP concentrations of 0.1 and 0.5 mg/L is the time required to effect the dechlorination of PCP to a nontoxic level. At this time, methanogenic fermentation of phenol can begin.

The effect of this process in ground water contaminated by both PCP and phenol would be to enlarge the extent of contamination where the PCP concentration was greater than 5.0 mg/L. In areas where the PCP concentration was approximately 1 mg/L or less, dechlorination of the PCP to a nontoxic level would allow for complete bioconversion of phenol and PCP to $CH_4$ and $CO_2$--if there are no other limiting environmental factors.

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## CHAPTER J

# THE ROLE OF COMPLEXATION AND ADSORPTION PROCESSES IN TOXIC METAL TRANSPORT

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## ABSTRACT

A detailed laboratory study of cadmium uptake onto a calcareous, sandy aquifer material is being conducted to elucidate the mechanisms of adsorption and the role of specific mineral phases. The study has shown the importance of aqueous speciation on the adsorption behavior of cadmium, using EDTA as a strong chelating agent to compete with surface binding. The presence of a strong complexing agent precludes the use of the classical distribution coefficient in transport models; a binding constant based on the computed free metal ion concentration can be determined instead. With this constant, the transport equation can be modified to account for aqueous complexation. The general concepts developed from the laboratory study should have significant transfer value to field studies of toxic metal transport, including metals other than cadmium. A field study has begun that will test the hypotheses and conclusions reached from the laboratory work and will examine the applicability of the local equilibrium assumption in solute transport models.

## INTRODUCTION

The transport of toxic metals in ground-water systems is an important water-quality issue in the United States and other developed nations. Most inorganic solutes that are toxic or hazardous to human health contain elements with an atomic number greater than 27. These elements are often highly reactive with mineral surfaces. Solute-transport models for such elements must therefore include a term to describe the surface reaction of the element with the host rock or porous medium of the specific aquifer being examined.

The transport of solutes that participate in ion-exchange or adsorption reactions can be described by the familiar convective-dispersive equation with a term included to describe adsorption, for example:

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2} - Q \frac{\partial c_i}{\partial x} + \frac{\rho_b}{n} \frac{\partial \Gamma_i}{\partial t} \qquad (1)$$

where: $n$ = volumetric water content, porosity;
$C_i$ = concentration of solute i in moles per unit volume of water;
$D$ = constant coefficient of longitudinal dispersion;
$Q$ = constant volume flux of water;
$\rho_b$ = bulk density of the porous medium;
$_i$ = adsorption density (mass of solute i bound to the solid phase per unit mass of the solid phase);
$\partial t$ = change in time; and
$\partial x$ = change in distance.

If the surface reaction is rapid relative to the flow velocity (and thus approaches an equilibrium condition), the adsorption density derivative may be rewritten as follows:

$$\frac{\partial\Gamma_i}{\partial t} = \frac{\partial\Gamma_i}{\partial c_i} \times \frac{\partial c_i}{\partial t} \qquad (2)$$

An important problem in developing the transport model is to determine the adsorption isotherm, $\partial\Gamma_i/\partial c_i$. The relationship used most frequently in solute transport models to date has assumed a simple linear isotherm, for example:

$$\Gamma_i = K_D C_i \text{ or } \frac{\partial\Gamma_i}{\partial c_i} = K_{D_i} \qquad (3)$$

where $K_{D_i}$ is known as the distribution coefficient in liters per gram, that is;

$$K_{D_i} = \frac{\text{mass of solute i on the solid phase unit per mass of solid phase (milligrams per gram)}}{\text{concentration of solute i in water (milligrams per liter).}}$$

The justification for the use of this isotherm is derived from ion-exchange theory, and the equation is generally well suited for applications involving ion-exchange reactions. From the above, one can derive what is commonly known as the retardation equation:

$$\frac{\bar{V}}{\bar{V}_i} = 1 + \frac{\partial_b}{n} K_{D_i} \qquad (4)$$

where: $\bar{V}$ = average velocity of the ground water (and nonreactive solutes being transported), and

$\bar{V}_i$ = average velocity for the reactive (or retarded) solute i.

Figure J-1 is a schematic diagram of the relative transport of such species through a hypothetical column containing the porous medium.

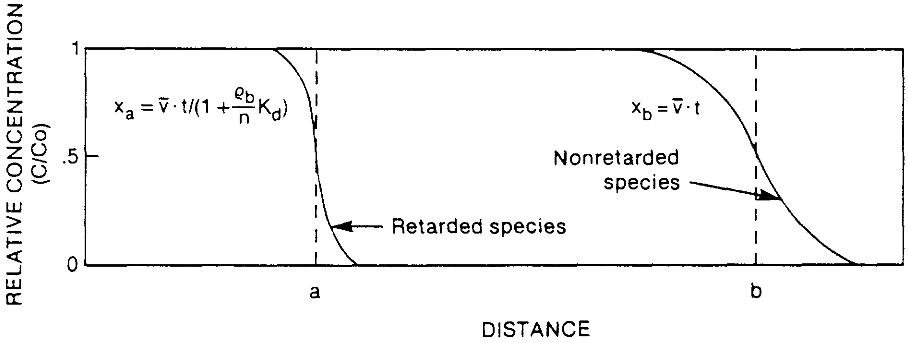

Figure J-1.--Advance of adsorbed and nonadsorbed solutes through a column of porous materials. Partitioning of adsorbed species is described by $K_d$. Relative velocity = $1/[1 + (\rho_b/n)K_d]$. Solute inputs are at concentration $C_o$ at $t > 0$.

## GENERAL APPROACH TO TOXIC METAL TRANSPORT

The preceding summary represents the classical treatment given for reactive solutes and their inclusion in solute-transport models. As will be shown, the general assumptions of this classical treatment are inappropriate for the most common situations where toxic metals will be mobile. The most important failures of the classical treatment are discussed below.

### Complex-Adsorption Isotherms

The metals or radionuclides that are toxic or hazardous to human health are often highly surface-active solutes; that is, they are strongly partitioned to the solid phase. The chemical bonding that binds the solute to a mineral surface in this case is usually dominated by covalent bonding rather than electrostatic attraction, which is the usual case for ion-exchange reactions. The isotherms that result from covalent bonding to mineral surfaces are often nonlinear, as in the Freundlich isotherm,

$$\Gamma_i = aC_i^b \tag{5}$$

and apply only at a single pH value. Thus, a general model for toxic-metal transport should be capable of handling nonlinear isotherms and changes in pH values within the range of interest for specific field applications.

### Transport of Metal Complexes

Because these solutes are strongly partitioned to the mineral surface, it is often assumed that the solutes are highly retarded or even "immobile," since the retardation factor may be quite large. However, as has been documented in field situations, the mobility of toxic metals may be quite high in the presence of strong complexing agents. If the aqueous speciation of a toxic metal is dominated by a complex, one must evaluate the meaning of the variable $c_i$ in equations 1 and 5. In many situations, a complexed metal will not bond to mineral surfaces. Figure J-2 illustrates an example for the interactions between $Cd^{2+}$ ion, EDTA (a synthetic complexing agent), and a mineral surface. The EDTA and its complexes remain in the water and do not interact with the mineral surface. Chemical equilibrium is maintained between the free $Cd^{2+}$ ion and the CdEDTA complex. The free $Cd^{2+}$ ion, in turn, reacts with the mineral surface through adsorption. Thus, the concentration term, $c_i$, in equation 5 should refer to the <u>free metal-ion concentration</u>, that is $Cd^{2+}$, which may be very small in comparison to the total dissolved cadmium concentration. One can then rewrite equation 1:

$$\frac{\partial c_i(aq)}{\partial t} = D\frac{\partial^2 c_i(aq)}{\partial x^2} - Q\frac{\partial c_i(aq)}{\partial x} + \frac{\rho_b}{n}\frac{\partial \Gamma_i}{\partial t} \tag{6}$$

where $c_i(aq)$ means the total dissolved cadmium concentration, including $Cd^{2+}$ and all Cd complexes. The adsorption isotherm, however, is written as:

$$\Gamma_i = ac_i^b(ads) \tag{7}$$

where $c_i$(ads) refers to only those dissolved cadimum species that will adsorb. For the example above, $c_i$ would be the free Cd$^{2+}$ ion concentration.

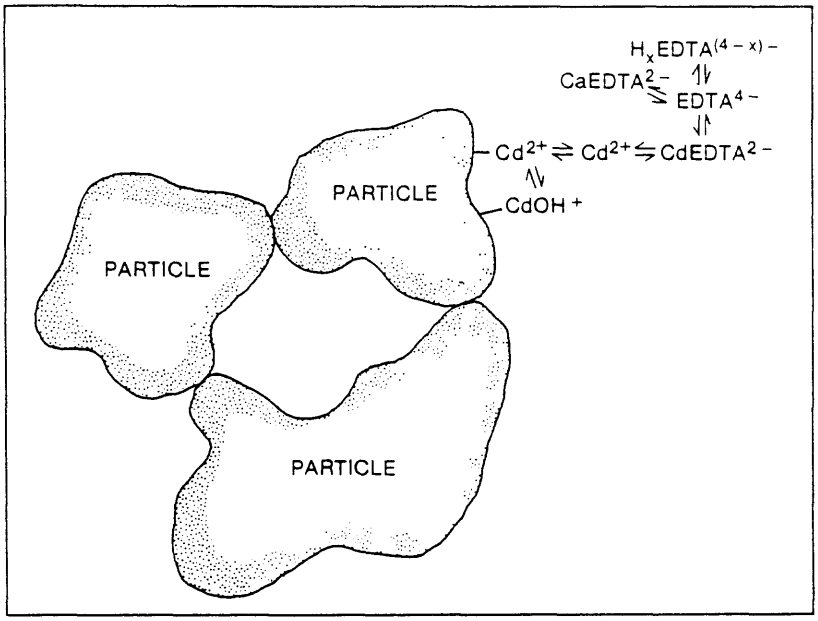

Figure J-2.--Interactions between Cd$^{2+}$, EDTA, and particle surfaces in the saturated zone of an aquifer.

The retardation concept does not apply in this case because the CdEDTA complex is transported at the same velocity as other nonreactive solutes. Moreover, it is not possible to derive a constant distribution coefficient, $K_D$, from the total dissolved cadmium concentration. This coefficient varies with the EDTA concentration: thus, the physical process of dispersion would create a situation where the $K_D$ value could vary by orders of magnitude over very short distances. As will be shown later, however, it is possible to derive a more meaningful term, $K_{ADS}$, which is an adsorption coefficient based on the free Cd$^{2+}$ ion concentration only.

## Local Equilibrium Assumption

A major problem with the classical treatment is the assumption that the adsorption process is rapid relative to the flow velocity. Ion-exchange reactions are rapid at particle surfaces, but they may not approach complete equilibrium if the process requires diffusion into long, tunnel-like pores. Likewise, the adsorption of heavier elements to nonporous hydrous oxides is rapid, but porosity, solid solution formation, or slow dissolution processes may create complex situations for which the local equilibrium assumption is no longer valid. The mathematical formulation of the transport equation then requires more information about the rates of reaction.

## PRELIMINARY RESULTS

In early 1983, a laboratory and field study began in collaboration with John Cherry of the University of Waterloo at the Borden landfill site in northern Ontario, Canada, to demonstrate the concepts discussed above. The choice of site was based on several factors including the great amount of study that has already taken place at the site, the relatively simple hydrology and mineral chemistry of the unconfined aquifer, and the capability of injecting radioisotopes as chemical tracers. The solutes chosen for study were Cd(II) and Cr(VI). EDTA was chosen as a strong complexing agent that, at very low concentrations, would increase the mobility of Cd(II).

The objectives of the study were as follows:

1. Determine the mechanism of Cd adsorption onto the Borden sand, especially at the field pH, by detailed laboratory experiments with Cd(II) and EDTA.
2. Study the kinetics of the Cd adsorption reactions in the laboratory to determine the applicability of the local equilibrium assumption.
3. Demonstrate the important concepts of metal transport governed by strong complexation and adsorption reactions by studies in the field and laboratory.

The major mineralogical composition of the Borden sand and chemical constituents of the ground water are summarized in table J-1. Cores of the sand were taken from the location in the landfill where the field experiment would be conducted. These cores were combined and air-dried for use in laboratory batch-adsorption experiments with a synthetic ground water that matched the composition shown in table J-1. Mixtures of sand and ground water were equilibrated with a specific $pCO_2$ gas mixture to obtain the desired pH. Cd(II) and EDTA were then added to the sand-and-ground-water mixture at the beginning of the experiment, usually to a concentration of about 1x10$^{-6}$ molar (M). A slight excess of EDTA was always present (for example, 1.5x10$^{-6}$M); to ensure that the dissolved Cd(II) would be present predominantly (>98 percent) as a CdEDTA complex.

Table J-1.--Chemical and physical characteristics of aquifer sand and chemical composition of ground water at Borden landfill, Ontario, Canada

| Borden sand | | | Ground water | |
|---|---|---|---|---|
| Mineral composition | Weight percent | Physical characteristics | Species | Concentration (M) |
| Quartz | 58 | Surface area: 0.8 m$^2$/g | $Cl^-$ | 8x10$^{-5}$ |
| Feldspars | 19 | Cation-exchange capacity: | $SO_4^{2-}$ | 2.1x10$^{-4}$ |
| (plagioclase, | | 0.5 meq/100 g | $NO_3^{2-}$ | 1.5x10$^{-5}$ |
| orthoclase) | | Average pH (field): 7.9 | $K^+$ | 1.5x10$^{-5}$ |
| Carbonates | 14 | Bulk density: 1.7 g/cm$^3$ | $Mg^{2+}$ | 1.4x10$^{-4}$ |
| Amphiboles | 7 | Porosity: 0.38 (mL | $Na^+$ | 2.2x10$^{-4}$ |
| (horneblende) | | solution/cm$^3$) | $Ca^{2+}$, | Saturated |
| Chlorite | <2 | | $HCO_3^-$ | with $CaCO_3$ |
| Magnetite | .3 | | | |

The adsorption of Cd onto the sand as a function of pH, sand concentration, and the presence of EDTA is plotted in figure J-3. As expected, Cd adsorption is much greater in the absence of EDTA than when it is present. Cd adsorption also increases in relation to the amount of sand present; the <u>in-situ</u> sand concentration is estimated to be about 4,000 g of sand per liter of water. In the absence of EDTA, Cd is almost completely removed at pH values greater than 6. In the presence of EDTA, however, the pH dependence of Cd adsorption is relatively weak.

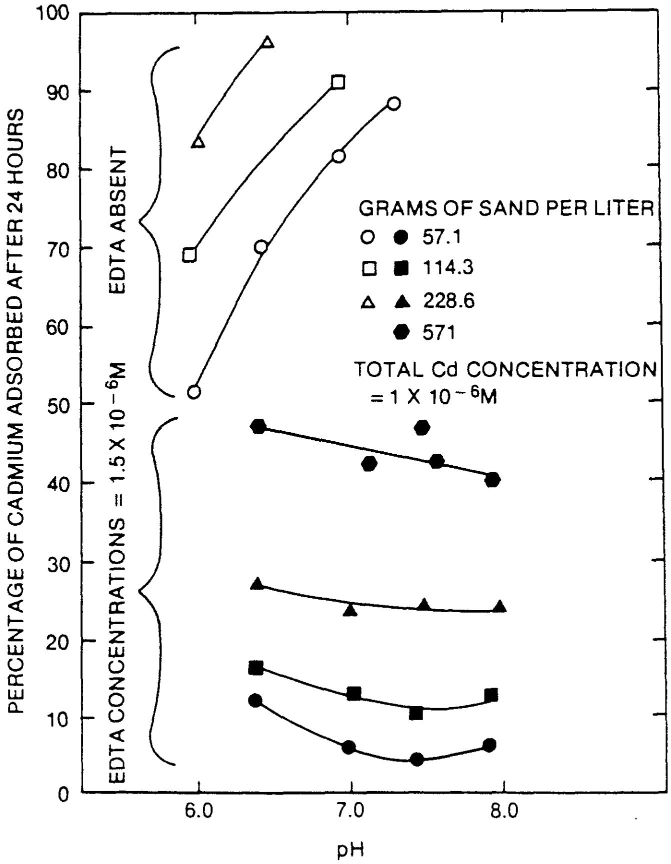

Figure J-3.--Percentage of $Cd^{2+}$ adsorbed in relation to aquifer pH at selected sand concentrations (g/L) in presence and absence of EDTA.

Figure J-4 shows that the Cd adsorption decreases as the EDTA concentration is increased. In reference to figure J-2, again, the interactions can be explained by the fact that both the sand surface and EDTA have strong reactions with $Cd^{2+}$. In effect, both the sand surface and EDTA are competing to bind $Cd^{2+}$, and, as the concentration of one or the other is increased (figs. J-3 and J-4), the percentage of Cd adsorbed adjusts accordingly. This study confirmed experimentally that the CdEDTA complex is not adsorbed. The reproducibility of the adsorption data is very good, both from material from one core or from mixtures of cores.

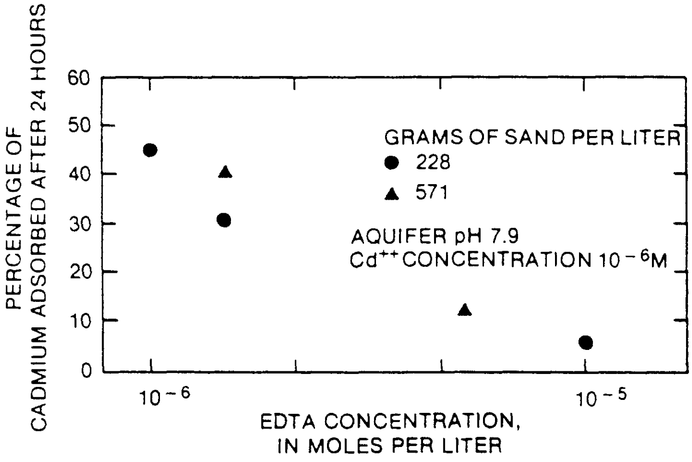

Figure J-4.--Percentage of $Cd^{2+}$ adsorbed in relation to EDTA concentrations at two selected sand concentrations.

An adsorption coefficient, $K_{ADS}$, can be derived to quantify the binding of $Cd^{2+}$ to the sand(s). The surface reaction can be modeled in the following way:

$$Cd^{2+} + S \overset{K_{ADS}}{<---->} S - Cd^{2+}$$

and thus

$$K_{ADS} = [S - Cd^{2+}]/[Cd^{2+}][S] \qquad (8)$$

where: $[S]$ = a surface binding site concentration,
$K_{ADS}$ = conditional (for example, constant pH) equilibrium constant for the reaction, and
$[S\text{-}Cd^{2+}]$ = concentration of adsorbed Cd.

We can estimate [S] from literature values or by measuring the cation-exchange capacity, $[S\text{-}Cd^{2+}]$ is measured directly, and $[Cd^{2+}]$ can be calculated for specific conditions (for example, a given EDTA concentration) through a chemical equilibrium computer program such as MINEQL or SOLMENEQ. This makes it possible to calculate $K_{ADS}$ at various pH values and solid concentrations from the data in figure J-3.

Table J-2 shows the values of leg $K_{ADS}$ at pH 7 for several solids concentrations. These were calculated from the data for systems without EDTA, and then used to predict the expected adsorption in the presence of EDTA. All data modeled are for 24-hour reaction times. The model predictions agree well with the experimental observations of $Cd^{2+}$ adsorption in the presence of EDTA and confirm that the CdEDTA complexes do not adsorb. From this type of data, one can begin to construct an isotherm of the type suggested in equation 7, one that is based on the free $Cd^{2+}$ ion concentration rather than the total dissolved Cd concentration. $K_{ADS}$ is a better term than $K_D$ in the sense that it is <u>not</u> dependent on the concentration of EDTA or any other complexing ligand in the system. However, the dependence of $K_{ADS}$ on the solids concentration (table J-2) means that the slope (b) of the isotherm (eq. 5) will not be equal to 1. Thus, the linear approximation required to establish a constant $K_D$ (eq. 3) will not be valid.

Table J-2.--Model calculations of cadmium$^{2+}$ adsorption on Borden landfill sand, Ontario

Surface reaction: $Cd^{2+} + S \overset{K_{ADS}}{<\text{----}>} S - Cd^{2+}$

Conditions: Cd concentration = $10^{-6}$

pH = 7

Total surface site concentration = $2.49 \times 10^{-5}$ moles per gram of sand

| Solid concentration (g/L) | Log $K_{ADS}$ (pH 7) |
|---|---|
| 57.1 | 3.6 |
| 114 | 3.7 |
| 229 | 3.75 |
| 571 | 3.8 |

SYSTEMS WITHOUT EDTA:

| Solids concentration | Percentage of Cd adsorbed (expt.) | Percentage of Cd adsorbed (model calculation) |
|---|---|---|
| 57.1 | 83 | 85 |
| 114 | 92 | 92 |
| 229 | >99 | 99.4 |

SYSTEMS WITH $1.5 \times 10^{-6}$M EDTA:

| Solids concentration | Percentage of Cd adsorbed (expt.) | Percentage of Cd adsorbed (model calculation) |
|---|---|---|
| 57.1 | 6 | 6 |
| 114 | 13 | 12 |
| 229 | 24 | 24 |
| 571 | 43 | 44 |

## Kinetic Studies

Figure J-5 shows the short-term and long-term kinetic behavior of $Cd^{2+}$ adsorption onto the sand. Much of the adsorption occurs within the first few minutes, but the Cd uptake continues slowly for several days afterward. The slow adsorption process also occurs in systems without EDTA, so it is concluded that the EDTA is not the cause of the slow attainment of equilibrium. The importance and the cause of the slow step in transport of Cd and the applicability of the local equilibrium assumption are not yet known.

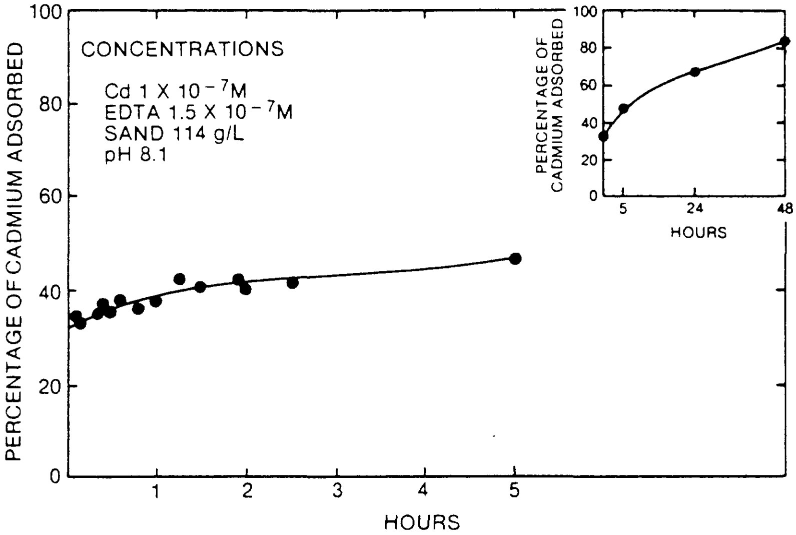

Figure J-5.--Percentage of cadmium adsorbed onto Borden sand in presence of EDTA at pH = 8.1 during 48-hour test.

We have conducted further detailed studies with other mineral components of the aquifer to determine the mechanism of adsorption and the reason for the slow uptake step. These studies are still in progress, but the following speculative statements can be made:

(1) Clean quartz adsorbs $Cd^{2+}$ too weakly to account for the behavior observed for the rapid uptake step on the sand shown in figure J-5.

(2) A magnetic fraction that contained magnetite and some hematite was separated from the sand. This fraction adsorbed very little Cd initially, but may be significant in the slow uptake of $Cd^{2+}$.

(3) Reagent-grade calcite adsorbs $Cd^{2+}$ significantly both through rapid initial uptake and continued uptake for up to 2 days. However, the pH dependence of $Cd^{2+}$ adsorption on calcite is quite different (decreasing $Cd^{2+}$ with increasing pH) than that observed for the sand. Dolomite and other slow-dissolving carbonates are present in the sand. We are continuing to study the importance of this carbonate fraction.

(4) In addition to the above, we are investigating the importance of secondary mineral phases (present as coatings on the mineral grains) as sinks for rapid Cd uptake, and diffusion into feldspar grains as a mechanism for slow Cd uptake.

### Field Experiment

In November 1983, 500 L of ground water were injected in the aquifer after addition of $Cl^-$ (320 mg/L), $Br^-$ (61 mg/L), CdEDTA ($1\text{x}10^{-6}\underline{M}$), $CrO_4^{-2}$ ($1\text{x}10^{-6}\underline{M}$), and excess EDTA ($8\text{x}10^{-6}\underline{M}$). Two millicuries (mCi) of Cd-109 and five mCi of Cr-51 were also injected as analytical tracers for the Cd and Cr. The water was injected at a rate of 1 L/min into a well screened from 1.4 to 1.9 m below land surface. The water table is between 0.5 and 1 m below land surface. Observation wells were drilled in a rectangular grid and spaced about 0.5 m apart near the injection well and 1 m apart farther away. Each observation well has eight polypropylene tubes for sampling from 1.15 to 2.2 m below land surface. The average ground-water velocity is about 0.1 m/d.

To date, the only observation is that the center of the Cd-109 activity appears to be moving at approximately the same speed as the nonreactive solutes ($Cl^-$ and $Br^-$). The decay-corrected concentration of Cd-109 at the center of the plume is decreasing at a rate greater than can be explained by dispersion, and the difference can be attributed to adsorption. The Cr-51 data have not been carefully analyzed yet, but it appears that Cr(VI) is weakly retarded. A quantitative analysis of the data is not yet possible, but results of the field experiment thus far agree with expectations.

## SUMMARY

A detailed laboratory study of cadmium uptake onto a calcareous, sandy aquifer material is being conducted to elucidate the mechanisms of adsorption and the role of specific mineral phases. The laboratory study includes an examination of the importance of aqueous speciation on the adsorptive behavior of cadmium, using EDTA as a strong chelating agent to compete with surface binding. The presence of a strong complexing agent precludes the use of the classical distribution coefficient in solute-transport models. A binding constant based on the computed free metal ion concentration can be determined instead. With this constant, the transport equation can be modified to account for aqueous complexation. The general concepts developed from the laboratory study should have significant transfer value to field studies of toxic metal transport, including metals other than cadmium. A field study has been initiated to test the hypotheses and conclusions reached from the laboratory work and to examine the applicability of the local equilibrium assumption in solute transport models.

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