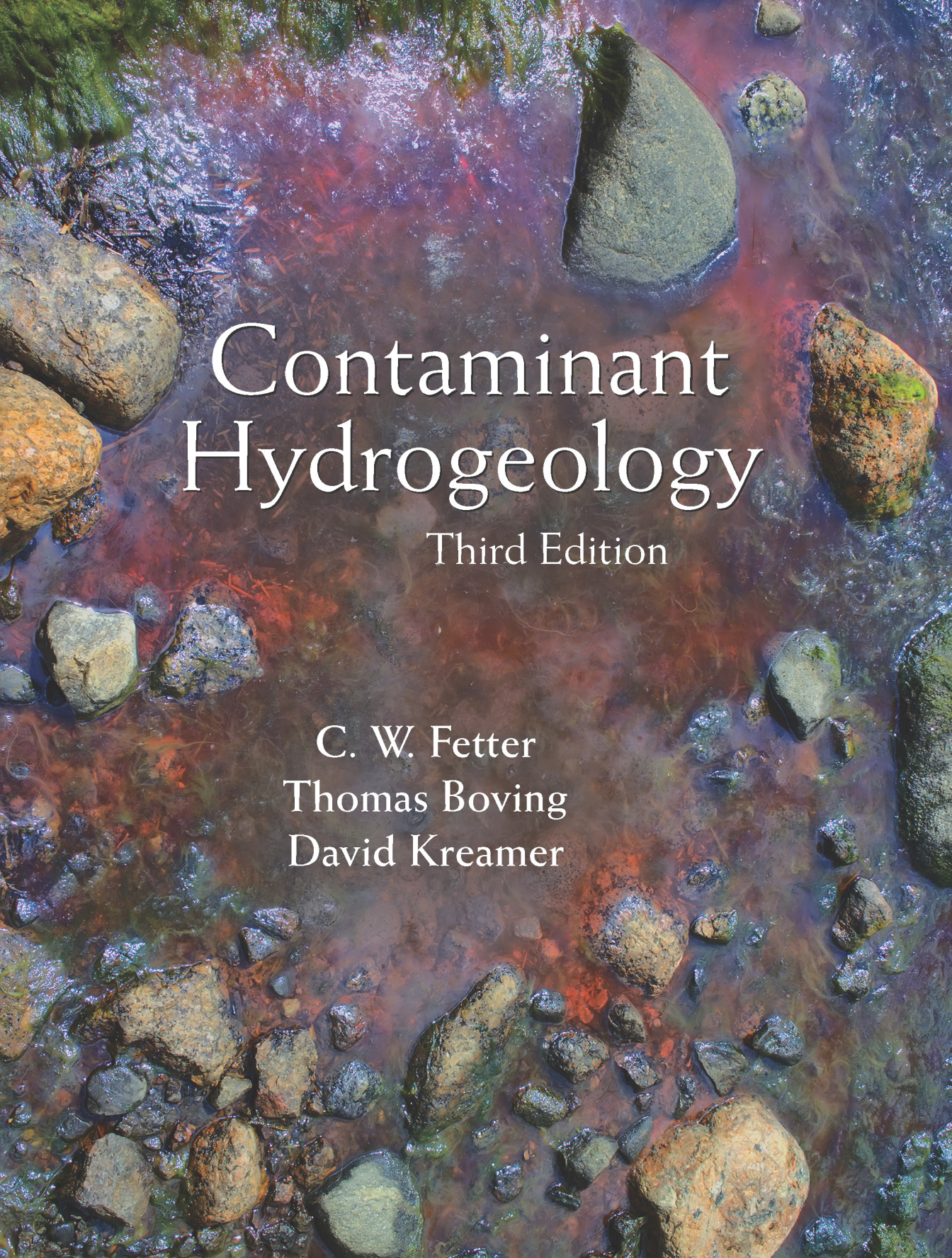

Contaminant Hydrogeology

Third Edition

C. W. Fetter
Thomas Boving
David Kreamer

Contaminant Hydrogeology

Third Edition

C. W. Fetter
late of University of Wisconsin–Oshkosh

Thomas Boving
University of Rhode Island

David Kreamer
University of Nevada, Las Vegas

Long Grove, Illinois

For information about this book, contact:
Waveland Press, Inc.
4180 IL Route 83, Suite 101
Long Grove, IL 60047-9580
(847) 634-0081
info@waveland.com
www.waveland.com

10-digit ISBN 1-4786-3279-8
13-digit ISBN 978-1-4786-3279-5

Printed in the United States of America

7 6 5 4 3 2 1

Contents

Acknowledgements and Dedication

This edition is dedicated to C.W. "Bill" Fetter, Jr., who died on September 10, 2011. Bill had an illustrious career for 25 years as a professor at the University of Wisconsin-Oshkosh, including 16 years as Department Chairman. He was a valued mentor, well-known consultant and groundwater professional, served as an expert witness in more than 200 cases concerning groundwater and contamination, and authored the first two editions of this book. Having worked with Bill personally, a coauthor of the Third Edition always found him to be a warm, personable, and thoughtful man, in addition to being a superb groundwater professional and practitioner. He is greatly missed.

The authors would also like to acknowledge the support of family and friends, and the assistance of many professionals and colleagues who helped review and inform this edition, and our students who give continuing motivation for our work. The authors would particularly like to recognize the suggestions, insights, inspiration, and efforts of our mentors and colleagues (past and present) including: Jean M. Bahr, Stanley N. Davis, Herman Bouwer, David A. Sabatini, Glenn M. Thompson, Simon Ince, Lorne G. Everett, Eugene S. Simpson, Roger DeWiest, Franklin W. Schwartz, Patrick A. Domenico, Charles J. Newell, David M. Nielsen, Beth L. Parker, Michael E. Campana, Lorne Graham "Gray" Wilson, Peter Grathwohl, William "Bill" Blanford, Craig Devine, John McCray, Geoff Tick, KC Carrol, Mark Brusseau, Dakota West, and Don Rosso.

We would also like to recognize R. Allan Freeze and John A. Cherry, who, from the very front cover of their textbook to their inspiring work in the field, have shown us that looking at things from a different angle is not a bad thing.

It is impossible for the authors to acknowledge all those who contributed either directly or indirectly to this edition, and to all those unmentioned colleagues who we might have missed, our apologies.

Preface

Dr. C. W. Fetter, Jr., was an internationally recognized expert in hydrogeology and Emeritus Professor of Geology, University of Wisconsin Oshkosh. He passed away in September 2011. His legacy encompasses textbooks on the subject of applied hydrogeology, including the standard textbook on contaminant fate and transport in soil and groundwater, titled *Contaminant Hydrogeology*. Last updated in 1998 (the second edition), the *Contaminant Hydrogeology* textbook has been the go-to reference for generations of students in geology, civil and environmental engineering, environmental sciences, and agricultural engineering. The book is also found on the shelves of many professionals working in the field of contaminant site investigation and remediation as well as in the offices of the regulating agencies overseeing environmental clean-up and restoration.

Since Dr. Fetter authored the previous editions of *Contaminant Hydrogeology*, the interest in and importance of contaminant hydrogeology has been greater than ever, particularly in regions around the world where the extent of pollution of soil and groundwater is being recognized only very recently. Unprecedented advances in remediation technology and new concepts for dealing with soil and groundwater contamination problems made it necessary to take a critical look at the models and practices introduced by Fetter two decades earlier. When our publisher first approached us with the proposal to bring the *Contaminant Hydrogeology* textbook into the twenty-first century, we were both honored and humbled to build on Fetter's prior work. Our goal was to not entirely rewrite the book, but to revise, update, and expand on the materials originally developed. In particular, we recognized that a great deal of the most exciting research into the fate and transport of contaminants is now happening outside the United States, which in the past has been the driving force behind much of environmental innovation. Regions like Europe or East Asia are now important centers of environmental research and many of today's most pressing soil and groundwater pollution problems are found outside the United States. We intended to highlight this development by including examples and references from around the globe.

Major changes have been made to all chapters. In Chapter 1, we have expanded the discussion of contaminants, including an introduction to "emerging contaminants" whose risk to health and the environment is not completely understood, and new discussion of potential contaminant sources which are receiving increasing attention, such as deep well injection, fracking fluids, and newer mining methods, such as *in situ* leach mining. In Chapter 2's presentation of mass transport in the saturated zone,

we added a section on statistical tools (Moment analysis) and expanded the discussion of deterministic models of solute transport, including in fractured matrices, while cutting the discussion of the fractal mathematics, geometry, and scaling of transport parameters. In Chapter 3, which focuses on transformation, retardation, and attenuation of solutes, we added sections covering BET and Polanyi adsorption potential theory, expanded on kinetic models, quantitative structure-property relationships, and colloid-facilitated contaminant transport. Chapter 4's discussion of vadose zone contaminant migration includes a new section on vapor transport theory, among other additions. Major changes to Chapter 5 (multi-phase flow) include the introduction of the Capillary and Bond Numbers and the partitioning interwell tracer testing technique for investigating NAPL sites. Chapter 6 expands the description of distribution, movement, and impact of inorganic contaminants and radionuclides. On the topic of organic compounds, additions to Chapter 7 include a more detailed discussion of chemical structures and functional groups, as well as adapting the line form for showing the chemical structure of organic compounds. We also expanded or replaced the list of chemical compounds typically found in contaminated soil and groundwater, including a discussion of emerging contaminant characteristics and updated pollutant transformation pathways. Chapter 8 focuses on site assessment and has major additions and reorganization, proceeding from basic principles and general approaches, to noninvasive techniques, rapid field screening, invasive techniques, and monitoring well construction, to forensic techniques. New sections of this chapter include: aerial photographic interpretation, geophysics, immunological surveys, high resolution vertical sampling, flexible liner systems, directional drilling, sampling frequency considerations, groundwater tracers, isotopic identification of groundwater pollution and groundwater pathways, and genome sequencing of subsurface microbes. Finally, the substantial additions to Chapter 9 reflect the immense progress that has been made in the field of remediation technologies.

Similar to the prior editions, the third edition of *Contaminant Hydrogeology* is intended as a textbook in a graduate level course in mass transport and contaminant hydrogeology. We assumed that our readers have some basic course work in hydrogeology, mathematics and statistics, chemistry and physics, and are comfortable with spreadsheet software, like Excel.

Tom Boving and Dave Kreamer
September 2017

1

Introduction

1.1 Groundwater as a Resource

Groundwater is the source of drinking water for many people around the world, especially in arid regions, rural areas, and increasingly in urban and suburban environments. It is the most abundant, available source of freshwater and most extracted raw material on earth, representing about 97% of nonfrozen fresh water with withdrawal rates near 982 km^3/yr. Worldwide, groundwater accounts for approximately 35% of all water withdrawals by human populations. Groundwater supplies an estimated 38–42% of the global water used for irrigation, approximately 36% of the water resources needed for households, and roughly 27% of the water needed for industry and manufacturing (Döll et al. 2012; Siebert et al. 2010; Margat and van der Gun 2013; National Ground Water Association 2015). Excessive groundwater abstraction, where withdrawals exceed recharge over time, can have many negative consequences, and about 1.7 billion people live in areas where groundwater resources are under threat. Exploitation of limited groundwater can stress aquifers used for water supply, produce ground subsidence, increase saline water intrusion in coastal regions, contribute to sea-level rise, and reduce water supply to groundwater-dependent ecosystems surrounding springs, rivers, estuaries, and wetlands. (Gleeson et al. 2012; Konikow 2011; Wada et al. 2010). Tables 1.1 and 1.2 show the percentage portion of the world population and total population estimates respectively for those obtaining drinking water from dug holes and boreholes in 1990 and 2010.

In the United States, groundwater accounts for nearly 25% of all freshwater withdrawals and 43% of the water used for agriculture. Virtually all the homes that supply their

TABLE 1.1 Proportion of the population obtaining drinking water from boreholes and dug wells, urban and rural, 1990 and 2010 (percent).

	Urban Percent		Rural Percent		Total Percent	
	1990	**2010**	**1990**	**2010**	**1990**	**2010**
Boreholes	6	8	29	30	19	18
Dug Wells	5	4	27	19	18	12
Total	**11**	**12**	**56**	**49**	**37**	**30**

Source: UNICEF 2012.

TABLE 1.2 World population obtaining drinking water from boreholes and dug wells, 1990 and 2010 (population in millions).

	Urban			Rural			Total		
	1990	**2010**	**Percent change**	**1990**	**2010**	**Percent change**	**1990**	**2010**	**Percent change**
Boreholes	138	255	+84.8	878	996	+13.4	1,016	1,251	+23.1
Dug Wells	111	151	+36.0	843	656	−22.2	954	807	−15.4
Total	**249**	**406**	**+63.1**	**1,721**	**1,652**	**−4.0**	**1.970**	**2,058**	**+4.5**

Source: UNICEF 2012.

own water have wells (98%) and use groundwater. Approximately 115 million people rely on groundwater for drinking water, 43 million from private wells. There are more than 15.9 million water wells in the United States, and approximately 500,000 new residential wells are added each year (Maupin et al. 2014; National Ground Water Association 2015). Figure 1.1 shows groundwater withdrawals in the United States in 2010.

Inasmuch as groundwater provides drinking water to so many people, the quality of groundwater is of paramount importance. Public water suppliers in the United States are obligated by the Safe Drinking Water Act of 1986 to furnish water that meets specific drinking-water standards to their consumers. If the water does not meet the standards when it is withdrawn from its source, it must be treated. Groundwater may not meet the standards because it contains dissolved constituents coming from natural sources. Common examples of constituents coming from natural sources are total dissolved solids, sulfate, and chloride. Groundwater also may not meet the standards because it contains organic liquids, dissolved organic and inorganic constituents, excessive nutrients, or pathogens that came from an anthropogenic source. In such cases the groundwater has been contaminated by the acts of humans.

In the case of self-supplied systems, a source of uncontaminated water is of even greater importance. Such systems are typically tested initially for only a very limited range of constituents, such as coliform bacteria, nitrate, chloride, and iron. Most times groundwater contamination cannot be tasted, so that with such limited testing it is possible for a user to have a contaminated source and not be aware of it. In one example, the lack of complete water quality testing of groundwater in India and Bangladesh in the 1970s and 1980s led to the drilling of tens of thousands of shallow tube wells which were later found to be contaminated with arsenic, poisoning huge numbers of people. A 2007 study indicated that over 137 million people in more than 60 countries are likely affected by arsenic contamination of their drinking water (Ravenscroft et al. 2009). Self-supplied systems rarely undergo treatment other than softening and perhaps iron removal. There are limited options available for the homeowner who wishes to treat contaminated groundwater so that it can be consumed.

In addition to providing for the sustenance of human life, groundwater has important ecological functions. Many freshwater habitats are supplied by the discharge of springs. Springs can supply water to many sorts of ecological environments, including the gaining reaches of rivers, estuaries, and wetlands. If the groundwater supplying these springs is diminished in flow or contaminated, the ecological function of the

FIGURE 1.1 Groundwater withdrawals in the United States, 2010.

Source: Maupin et al. 2014.

freshwater habitat can be impaired with negative consequences to species diversity and sustainability (Kreamer et al. 2015).

1.2 Types of Groundwater Contaminants

A wide variety of materials have been identified as contaminants found in groundwater. These include synthetic organic chemicals, hydrocarbons, inorganic cations, inorganic anions, pathogens, and radionuclides. Table 1.3 contains an extensive listing of these compounds. Most of these materials will dissolve in water to varying degrees. Some of the organic compounds are only slightly soluble and will exist in both a dissolved form and as an insoluble nonaqueous phase, which can also migrate through the ground. Examples of the uses of these materials are also given on Table 1.3. These uses may provide help in locating the source of a compound if it is found in groundwater. The inorganic cations and anions occur in nature and may come from natural as well as anthropogenic sources. Some of the radionuclides are naturally occurring and can come from natural sources as well as mining, milling, and processing ore, industrial uses, and disposal of radioactive waste. Other radionuclides are man-made and come from nuclear weapons production and testing. There is increasing public concern over the development of new chemicals and industrial processes which have the potential to pollute groundwater. For example, current challenges include the subsurface injection of liquid wastes, circulation of geothermal energy fluids, and the use of newly developed fracking fluids for enhanced extraction of hydrocarbon fuels, combined with increasing utilization of groundwater in stressed locales.

TABLE 1.3 Substances known to occur in groundwater.

Contaminant	Examples of uses
Aromatic hydrocarbons	
Acenaphthene	Coal tar by-product
Acenaphthylene	Coal tar by-product
Acetanilide	Intermediate manufacturing, pharmaceuticals, dyestuffs
Alkyl benzene sulfonates	Detergents
Aniline	Dyestuffs, intermediate, photographic chemicals, pharmaceuticals, herbicides, fungicides, petroleum refining, explosives
Anthracene	Dyestuffs, intermediate, semiconductor research, coal tar by-product
Benzene	Detergents, intermediate, solvents, gasoline, coal tar by-product
Benzidine	Dyestuffs, reagent, stiffening agent in rubber compounding
Benzo[a]anthracene	Coal tar by-product
Benzo[a]pyrene	Coal tar by-product
Benzo[b]fluroanthene	Coal tar by-product
Benzo[g, h,i]perylene	Coal tar by-product
Benzo[k]fluoranthene	Coal tar by-product
Benzyl alcohol	Solvent, perfumes and flavors, photographic developer inks, dye-stuffs, intermediate
Butoxymethylbenzene	NA
Chrysene	Organic synthesis, coal tar by-product
Creosote mixture	Wood preservatives, disinfectants
Dibenz[a,h]anthracene	NA
Di-butyl-p-benzoquinone	NA
Dihydrotrimethylquinoline	Rubber antioxidant
4,4-Dinitrosodiphenylamine	NA
Ethylbenzene	Intermediate, solvent, gasoline, coal tar by-product
Fluoranthene	Coal tar by-product
Fluorene	Resinous products, dyestuffs, insecticides, coal tar by-product
Fluorescein	Dyestuffs
Isopropyl benzene	Solvent, chemical manufacturing
4,4-methylene-bis-2-chloroaniline (MOCA)	Curing agent for polyurethanes and epoxy resins

(*Cont'd*)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
Methylnapthalene	Coal tar by product, diesel fuel
Methylthiobenzothiazole	NA
Napthalene	Solvent, lubricant, explosives, preservatives, intermediate, fungicide, moth repellent, coal tar by product, gasoline
o-Nitroaniline	Dyestuffs, intermediate, interior paint pigments, chemical manufacturing
Nitrobenzene	Solvent, polishes, chemical manufacturing
4-Nitrophenol	Chemical manufacturing
n-Nitrosodiphenylamine	Pesticides, retarder of vulcanization of rubber
Phenanthrene	Dyestuffs, explosives, synthesis of drugs, biochemical research
n-Propylbenzene	Dyestuffs, solvent
Pyrene	Biochemical research, coal tar by-product
Styrene (vinyl benzene)	Plastics, resins, protective coatings, intermediate, gasoline
Toluene	Adhesive solvent in plastics, solvent, aviation and high-octane blending stock, dilutent and thinner, chemicals, explosives, detergents, gasoline, coal tar by-product
1,2,4-Trimethylbenzene	Manufacture of dyestuffs, pharmaceuticals, chemical manufacturing, gasoline
Xylenes (*m, o, p)*	Aviation gasoline, protective coatings, solvent, synthesis of organic chemicals, gasoline, coal tar by-product
Oxygenated hydrocarbons	
Acetic acid	Food additives, plastics, dyestuffs, pharmaceuticals, photographic chemicals, insecticides
Acetone	Dyestuffs, solvent, chemical manufacturing, cleaning and drying of precision equipment
Benzophenone	Organic synthesis, odor fixative, flavoring, pharmaceuticals
Butyl acetate	Solvent
n-Butyl-benzylphthalate	Plastics, intermediate
Di-n-butyl phthalate	Plasticizer, solvent, adhesives, insecticides, safety glass, inks, paper coatings
Diethyl ether	Chemical manufacturing, solvent, analytical chemistry, anesthetic, perfumes
Diethyl phthalate	Plastics, explosives, solvent, insecticides, perfumes
Diisopropyl ether	Solvent, rubber cements, paint and varnish removers
2,4-Dimethyl-3-hexanol	Intermediate, solvent, lubricant

(*Cont'd*)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
2,4-Dimethyl phenol	Pharmaceuticals, plastics, disinfectants, solvent, dyestuffs, insecticides, fungicides, additives to lubricants and gasolines
Di-*n*-octyl phthalate	Plasticizer for polyvinyl chloride and other vinyls
l,4-Dioxane	Solvent, lacquers, paints, varnishes, cleaning and detergent preparations, fumigants, paint and varnish removers, wetting agent, cosmetics
Ethyl acrylate	Polymers, acrylic paints, intermediate
Formic acid	Dyeing and finishing, chemicals, manufacture of fumigants, insecticides, solvents, plastics, refrigerants
Methanol (methyl alcohol)	Chemical manufacturing, solvents, automotive antifreeze, fuels
Methylcyclohexanone	Solvent, lacquers
Methyl ethyl ketone (2-Butanone)	Solvent, paint removers, cements and adhesives, cleaning fluids, printing, acrylic coatings
Methylphenyl acetamide	NA
Phenols (e.g., p-tert-butylphenol)	Resins, solvent, pharmaceuticals, reagent, dyestuffs and indicators, germicidal paints
Phthalic acid	Dyestuffs, medicine, perfumes, reagent
2-Propanol	Chemical manufacturing, solvent, deicing agent, pharmaceuticals, perfumes, lacquers, dehydrating agent, preservatives
2-Propyl-1-heptanol	Solvent
Methyl tert-butyl ether (MTBE)	Gasoline additive
Tetrahydrofuran	Solvent
Varsol	Paint and varnish thinner
Hydrocarbons with specific elements (e.g., with N, P, S, Cl, Br, I, F)	
Acetyl chloride	Dyestuffs, pharmaceuticals, organic preparations
Alachlor (Lasso)	Herbicides
Aldicarb (sulfoxide and sulfone;Temik)	Insecticide, nematocide
Aldrin	Insecticides
Atrazine	Herbicides, plant growth regulator, weed-control agent
Benzoyl chloride	Medicine, intermediate
Bromacil	Herbicides
Bromobenzene	Solvent, motor oils, organic synthesis
Bromochloromethane	Fire extinguishers, organic synthesis

(*Cont'd*)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
Bromodichloromethane	Solvent, fire extinguisher fluid, mineral and salt separations
Bromoform	Solvent, intermediate
Carbofuran	Insecticide, nematocide
Carbon tetrachloride	Degreasers, refrigerants and propellants, fumigants, chemical manufacturing
Chlordane	Insecticides, oil emulsions
Chlorobenzene	Solvent, pesticides, chemical manufacturing
Chloroform	Plastics, fumigants, insecticides, refrigerants and propellants
Chlorohexane	NA
Chloromethane (methyl chloride)	Refrigerants, medicine, propellants, herbicide, organic synthesis
Chloromethyl sulfide	NA
2-Chloronaphthalene	Plasticizer, solvent for dyestuffs, varnish gums and resins, waxes; moisture-, flame-, acid-, and insect-proofing of fibrous materials; moisture- and flame-proofing of electrical cable
Chlorpyrifos	NA
Chlorthal-methyl (DCPA, or Dacthal)	Herbicide
p-Chlorophenyl methylsulfone	Herbicide manufacture
Chlorophenylmethyl sulfide	Herbicide manufacture
Chlorophenylmethyl sulfoxide	Herbicide manufacture
o-Chlorotoluene	Solvent, intermediate
p-Chlorotoluene	Solvent, intermediate
Cyclopentadiene	Insecticide manufacture
Dibromochloromethane	Organic synthesis
Dibromochloropropane (DBCP)	Fumigant, nematocide
Dibromodichloroethylene	NA
Dibromoethane (ethylene dibromide, EDB)	Fumigant, nematocide, solvent, waterproofing preparations, organic synthesis, gasoline additive
Dibromomethane	Organic synthesis, solvent
Dichlofenthion (DCFT)	Pesticides
o-Dichlorobenzene	Solvent, fumigants, dyestuffs, insecticides, degreasers, polishes, industrial odor control

(*Cont'd*)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
p-Dichlorobenzene	Insecticides, moth repellent, germicide, space odorant, intermediate, fumigants
Dichlorobenzidine	Intermediate, curing agent for resins
Dichlorocyclooctadiene	Pesticides
Dichlorodiphenyldichloroethane (DDD, TDE)	Insecticides
Dichlorodiphenyldichloroethylene (DDE)	Degradation product of DDT, found as an impurity in DDT residues
Dichlorodiphenyltrichloroethane (DDT)	Pesticides
l,1-Dichloroethane	Solvent, fumigants, medicine
1,2-Dichloroethane	Solvent, degreasers, soaps and scouring compounds, organic synthesis, additive in antiknock gasoline, paint and finish removers
l,1-Dichloroethylene (vinylidiene chloride)	Saran (used in screens, upholstery, fabrics, carpets, etc.). adhesives, synthetic fibers
1,2-Dichloroethylene (cis and trans)	Solvent, perfumes, lacquers, thermoplastics, dye extraction organic synthesis, medicine
Dichloroethyl ether	Solvent, organic synthesis, paints, varnishes, lacquers, finish removers, dry cleaning, fumigants
Dichloroiodomethane	NA
Dichloroisopropylether (bis-2-chloroisopropylether)	Solvent, paint and varnish removers, cleaning solutions
Dichloromethane (methylene chloride)	Solvent, plastics, point removers, propellants, blowing agent in foams
Dichloropentadiene	NA
2,4-Dichlorophenol	Organic synthesis
2,4-Dichlorophenoxyacetic acid (2,4-D)	Herbicides
l, 2-Dichloropropane	Solvent, intermediate, scouring compounds, fumigant, nematocide, additive for antiknock fluids
Dicyclopentadiene (DCPD)	Insecticide manufacture
Dieldrin	Insecticides
Diiodomethane	Organic synthesis
Diisopropylmethyl phosphonate (DIMP)	Nerve gas manufacture
Dimethyl disulfide	NA
Dimethylformamide	Solvent, organic synthesis
2,4-Dinotrophenol (Dinoseb, DNBP)	Herbicides

(*Cont'd*)

TABLE 1.3 *Cont'd*

Contaminant	Examples of uses
Dithiane	Mustard gas manufacture
Dioxins (e.g., TCDD)	Impurity in the herbicide 2,4,5-T
Dodecyl mercaptan (lauryl mercaptan)	Manufacture of synthetic rubber and plastics, pharmaceuticals, insecticides, fungicides
Endosulfan	Insecticides
Endrin	Insecticides
Ethyl chloride	Chemical manufacturing, anesthetic, solvent, refrigerants, insecticides
Bis-2-ethylhexylphthalate	Plastics
Di-2-ethylexylphthalate	Plasticizers
Fluorobenzene	Insecticide and larvicide intermediate
Fluoroform	Refrigerants, intermediate, blowing agent for foams
Heptachlor	Insecticides
Heptachlorepoxide	Degradation product of heptachlor, also acts as an insecticide
Hexachlorobicycloheptadiene	NA
Hexachlorobutadiene	Solvent, transformer and hydraulic fluid, heat-transfer liquid
α-Hexachlorocyclohexane (Benzenehexachloride, or α-BHC)	Insecticides
β-Hexachlorocyclohexane (β-BHC)	Insecticides
γ-Hexachlorocyclohexane (γ-BHC, or Lindane)	Insecticides
Hexachlorocyclopentadiene	Intermediate for resins, dyestuffs, pesticides, fungicides, pharmaceuticals
Hexachloroethane	Solvent, pyrotechnics and smoke devices, explosives, organic synthesis
Hexachloronorbornadiene	NA
Isodrin	Intermediate compound in manufacture of Endrin
Kepone	Pesticides
Malathion	Insecticides
Methoxychlor	Insecticides
Methyl bromide	Fumigants, pesticides, organic synthesis
Methyl parathion	Insecticides
Oxathine	Mustard gas manufacture

(*Cont'd*)