Hydrogeology and Geochemistry of Bottled Spring Water in the United States

Francis H. Chapelle

THE GROUNDWATER PROJECT

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Published by the Groundwater Project, Guelph, Ontario, Canada, 2025.

Hydrogeology and Geochemistry of Bottled Spring Water in the United States/ Francis H. Chapelle, The Groundwater Project, 2025.
100 pages

ISBN: 978-1-77470-115-7.
DOI: https://doi.org/10.62592/DWMH1044 ↗.

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APA (7th ed.) Citation
Chapelle, F.H., (2025). *Hydrogeology and Geochemistry of Bottled Spring Water in the United States*↗. The Groundwater Project. https://doi.org/10.62592/DWMH1044 ↗.

Cover Image: Groundwater Project Original, 2024

Dedication

This book is dedicated to the memory of Rodney N. Cherry of the U.S. Geological Survey. Mr. Cherry possessed an unusual combination of abilities, being a productive and imaginative scientist as well as being an excellent administrator.

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The Groundwater Project Foreword

The United Nations (UN)-Water Summit on Groundwater, held from 7 to 8 December 2022, at the UNESCO headquarters in Paris, France, concluded with a call for governments and other stakeholders to scale up their efforts to better manage groundwater. The intent of the call to action was to inform relevant discussions at the UN 2023 Water Conference held from 22 to 24 March 2023 at the UN headquarters in New York City. One of the required actions is *strengthening human and institutional capacity*, for which groundwater education is fundamental.

The UN-Water website↗ states that *more than three billion people worldwide depend on water that crosses national borders*. There are 592 transboundary aquifers, yet most do not have an intergovernmental cooperation agreement in place for sharing and managing the aquifer. Moreover, while groundwater plays a key role in global stability and prosperity, it also makes up 99 percent of all liquid freshwater—accordingly, groundwater is at the heart of the freshwater crisis. *Groundwater is an invaluable resource*.

The Groundwater Project (GW-Project), a registered Canadian charity with its beginnings in 2018, pioneers in advancing understanding of groundwater and, thus, enables *building the human capacity for the development and management of groundwater*. The GW-Project is not government funded and relies on donations from individuals, organizations, and companies. The GW-Project creates and publishes high-quality books about *all-things-groundwater* that are scientifically significant and/or relevant to societal and ecological needs. Our books synthesize knowledge, are rigorously peer reviewed and translated into many languages. Groundwater is 'hidden' and, therefore, our books have a strong emphasis on visualizations essential to support the spatial thinking and conceptualization in space and time of processes, problems, and solutions. Based on *our philosophy that high quality groundwater knowledge should be accessible to everyone*, The GW-Project provides all publications for free.

The GW-Project embodies a new type of global educational endeavor made possible by the contributions of a dedicated international group of over 1000 volunteer professionals from a broad range of disciplines, and from 70 countries on six continents. Academics, practitioners, and retirees contribute by writing and/or reviewing books aimed at diverse levels of readers including children, youth, undergraduate and graduate students, groundwater professionals, and the general public.

The GW-Project started publishing books in August 2020; by the end of 2024, we have published 55 original books and 77 translations (55 languages). Revised editions of the books are published from time to time. In 2024, interactive groundwater education tools and groundwater videos were added to our website, gw-project.org↗.

We thank our individual and corporate sponsors for their ongoing financial support. Please consider sponsoring the GW-Project so we can continue to publish books free of charge.

The Groundwater Project *Board of Directors*, January 2025

Foreword

Nearly all people of the world drink bottled water either occasionally or all of the time. In some countries there are a few categories of bottled water, one of which is spring water that comes directly from springs, or from wells that intercept groundwater flowing to springs. This intercepted would-be-spring water is generally better than water that discharges from natural spring orifices because it is less likely to have contaminants originating from shallow sources around the springs. Much of the bottled water available in many countries is not spring water but, rather, is bottled tap water or treated surface water. Most bottled water is purchased because it is convenient or because it tastes better to the purchaser. Importantly, bottled water in some areas is the only available relatively safe drinking water. In many countries, bottled water is controversial for reasons that can include: public fear of aquifer depletion if the water comes from wells; harm of plastic to the environment; and whether there is a human right to have affordable safe drinking water. This book, however, is focused on the hydrogeological, geochemical, and historical aspects of bottled spring water in the United States. The generic aspects of the hydrological settings described in this book are generally applicable to spring water from other locations throughout the world.

In the United States and Canada, bottled water is regulated as a food (not as drinking water) so the information labeled on the bottles relates to characteristics of food, such as calorie content, which is irrelevant for water. Given that bottled water is not regulated as drinking water, the labels do not have to show information about its chemical composition. In contrast, in the European Union and most developed countries, major-ion concentrations are labeled on the bottle. Although it is not a regulatory requirement in North America, labeling may include chemical composition, especially if the bottled water is imported from Europe. Those who read this book will acquire background knowledge to appreciate this chemical information in the context of the hydrogeology of the United States, as well as knowledge of the geochemical processes that influence groundwater and hence its flavor. Purchasers of bottled water generally pay a premium for the spring water category. However, the only way to know the value gained for paying this premium is to know the chemical composition, thus the benefit of having chemical composition displayed on the label. By studying the chemical information on the label when I buy bottled spring water, I accumulate knowledge that I find interesting. This book, however, provides a scientific framework for understanding why each bottle of spring water may be especially interesting in the context of earth science. That, in turn, offers some basis for selecting between different brands of bottled spring water.

The author of this book, Francis H. Chapelle, is a distinguished emeritus scientist with the US Geological Survey who in addition to publishing many scientific articles about groundwater geochemistry has published two books for the general reader, one about the natural history of bottled spring water (Chapelle, 2005).

John Cherry, The Groundwater Project Leader

Guelph, Ontario, Canada, February 2025

Preface

The beginnings of groundwater geochemistry as a quantitative science can be traced back to the early 19th century when accurate atomic weights became available. This, for the first time in history, enabled chemists to analyze the kinds and amounts of dissolved solids present in natural water. For centuries, it had been noticed that certain spring water seemed to have medicinal properties. It's not surprising, therefore, that one of the first applications of this new chemical technology was to determine the chemical composition of spring water purported to have medicinal properties (Steele, 1819). This initiated the science of groundwater geochemistry (Davis and Davis, 1997) but it also marked the beginnings of the bottled water industry in the United States. That industry began, as it had in Europe, by putting spring water in bottles and making it available to people who otherwise had no access to them.

As the nineteenth century progressed, it became apparent that the composition of spring water varied considerably from place to place. That fact was a boon to the new bottled water industry in America, as those differences were useful in marketing bottled water from different regions of the country. It also raised the question as to *why* those differences existed in the first place. That is the question that is addressed in this book. It turns out that spring water, and its suitability for bottling, depends on geologic, geographic, climatic, and hydrologic processes and how those processes interact with each other. Explaining some of those interactions as they occur in the United States is the objective of this book.

Acknowledgments

I deeply appreciate the thorough and useful reviews of and contributions to this book by the following individuals:

- Eduardo Batista, Industrial Engineer and Hydrogeologist, Former Director (1990-2006) of "Curso Internacional de Hidrologia Subterránea", Barcelona, Spain;
- Patrick Lachassagne, Director, IRD, France;
- Miquel Salgot, Professor Emeritus, University of Barcelona, Spain;
- Jack Sharp, Professor Emeritus, Department of Geological Sciences, University of Texas at Austin, United States;

I am grateful for Amanda Sills and the Formatting Team of the Groundwater Project for their oversight and copyediting of this book. I thank Eileen Poeter (Colorado School of Mines, Golden, Colorado, USA) for reviewing, editing, and producing this book.

The sources of figures and/or tables are cited in their captions. Where a citation does not appear, the figures and/or tables are original to this book.

1 Introduction

Bottled spring water is one of the most popular beverages in the world. The reasons for this popularity include convenience, wide availability, and their perceived purity. Bottled water produced from different springs contains different kinds and amounts of dissolved minerals and gases. That is why the flavor of drinking water varies from spring to spring. Those flavors reflect the chemical composition of the rocks or sediments through which the groundwater flows, the nature of the microbial processes occurring in those rocks or sediments, and the hydrologic setting of the groundwater systems themselves. This book examines how those factors combine to produce spring s of differing chemical character and thus their desirability for bottling and human consumption.

Thousands of springs the around the world are presently sources for water-bottling operations (LaMoreaux & Tanner, 2001). For practical reasons, the scope of this investigation will be limited to the United States, with some discussion of Europe to provide historical context. However, the approach and methods illustrated here are applicable to any large region on earth. The methodology used in this book begins by defining the different groundwater regions of the United States as originally identified by Meinzer (1923) and modified by Heath (1984). Next, the geologic settings of each region are described as they affect the hydrologic and geochemical properties of the groundwater systems they contain. Finally, the unique hydrologic and geochemical characteristics of selected springs used for individual water-bottling operations are described. The selected water-bottling operations are not meant to be representative of others in that groundwater region, rather they are meant to illustrate the variety of hydrologic, biologic, and geochemical characteristics that produce water of sufficient "water quality" to make bottling operations economically feasible.

1.1 What is meant by Bottled Spring Water

One of the curious things about bottled water in America is that it is not regulated as water but as a food. Under the Federal Food, Drug, and Cosmetic Act (FFDCA) of 1938, a food is defined as "articles used for food and drink for man or other animals." Because of this, bottled water is regulated by the Food and Drug Administration (FDA), not, as might be expected, by the Environmental Protection Agency (EPA). The EPA regulates the quality of municipal tap water but not bottled water. The difference is that municipal water is deemed a *commodity* pursuant to the Safe Drinking Water Act of 1974 as amended in 1986, 1996, and 2018. Bottled water however, because of the language in the FFDCA, is deemed a *food*.

There are many different kinds of bottled water on the market. The FDA "Standard of Identity" outlined in the Code of Federal Regulations (CFR) 21 CFR 165.11a draws a basic distinction between *natural water* and *processed water*. Natural water comes from naturally occurring sources and its chemical composition has not been fundamentally changed by the bottling process. Natural bottled water includes spring water, well water, and surface water. Processed bottled water, on the other hand, has been chemically altered to make it more palatable, such as removing dissolved solids, raising the pH, or adding flavors (Table 1).

Table 1 - The different classes of bottled water. Source: International Bottled Water Association.

NATURAL WATER	
Class	*Definition*
Spring water	Water derived from an underground formation from which water flows naturally to the surface of the earth.
Groundwater	Water derived from an underground formation that is not under the direct influence of surface water.
Well water	Water derived from an underground formation tapped by a bored well.
Artesian water	Water derived from a bored well tapping a confined aquifer, but not necessarily flowing at land surface.
Surface water	Water derived from a surface water body such as a stream, river, or lake.
Mineral water	Water derived from an underground formation that has a total dissolved solids (TDS) greater than 250 mg/L and contains no added minerals.
PROCESSED WATER	
Class	*Definition*
Purified	Water whose chemical composition has been modified by artificial means that include deionization, distillation, and reverse osmosis.
Enhanced	Water with chemical composition that has been modified by artificial means including deionization, distillation, and reverse osmosis, and to which artificial mineral or flavors have been added.
Fluoridated	Water to which fluoride has been added.
Minimally treated municipal water	Municipal water that has been subjected to treatment such as chlorine removal, filtration, or ozonation.

There are obvious overlaps in the definitions of these different classes of bottled water. For example, there is no requirement that spring water be collected at a naturally occurring spring orifice. Rather, spring water can be collected through a borehole tapping the underground formation feeding a naturally occurring spring. The reason for this is that natural spring orifices are subject to contamination from the land surface. Because of that, many state health departments actually *require* that boreholes be used to collect spring water for bottling.

Although the federal government through the FDA has regulatory responsibility over bottled water, the actual enforcement is delegated to each state. The FDA provides standards of identity (CFR 165.110a), standards of quality (CFR 165.110b), and good manufacturing practices (CFR 165.110 and 129). The grassroots business of licensing and inspecting bottled water plants, however, is performed by various state agencies. Most states regulate bottled water as a food in accordance with the FDA. A few, Pennsylvania being one, regulate bottled water containers of more than one gallon in the same way they regulate municipal water supplies. In all cases, however, the foundation of the regulatory system is licensing, record keeping, and unannounced plant inspections one or more times per year. Many water bottlers belong to industry organizations, the largest being the International Bottled Water Association (IBWA), which assists members in meeting the FDA and state identity, water quality, and manufacturing standards.

The definition of "spring water" used in this book is water from an underground aquifer from which water either flows naturally to the surface of the earth or is collected from the aquifer by means of drilled boreholes.

2 What Does "Water Quality" Mean?

The term "water quality," as used above, has been in general use for the last hundred years or so, yet to many people, the meaning of this term is unclear. Does "good" water quality mean the absence of biological or chemical contaminants? Does it mean that such contaminants may be present at concentrations below maximum contaminant levels (MCLs) established by regulatory agencies? Or does it mean that it simply satisfies the expectations and needs of the people drinking it? In other words, does water quality depend on the chemical characteristics of the water itself, or is it just what people happen to like?

2.1 The Aesthetics of Water Quality

Beginning at least with the ancient Greeks, understanding what constitutes "good" or "bad" has been an active area of philosophical inquiry. In 1790, Emmanual Kant argued that assessments of quality were *judgments* based partly on objective characteristics but interpreted within the subjective framework of the observer (Kant, 2003; Wenzel, 2008). Quality, therefore, can never be solely objective or solely subjective, rather is always a combination of the two. Furthermore, because everybody's subjective framework is different, judgments of quality necessarily differ between people.

A logic diagram illustrating Kant's aesthetic framework (Figure 1) suggests why the term "water quality" can mean so many different things to different people. To take an extreme example, the notion of "good" water quality would be very different for someone casually turning on a tap of municipal water than it would be for a Bedouin nomad traveling in the desert trying to reach the next oasis. The important point is that judgments of better or poorer water quality are not static but change from person to person and from situation to situation. Although the objective characteristics of water may stay the same, the subjective expectations of humans vary enormously. Quality is more like an *event* (Pirsig, 1974) that happens when any kind of object interacts with the subjective needs or expectations of people.

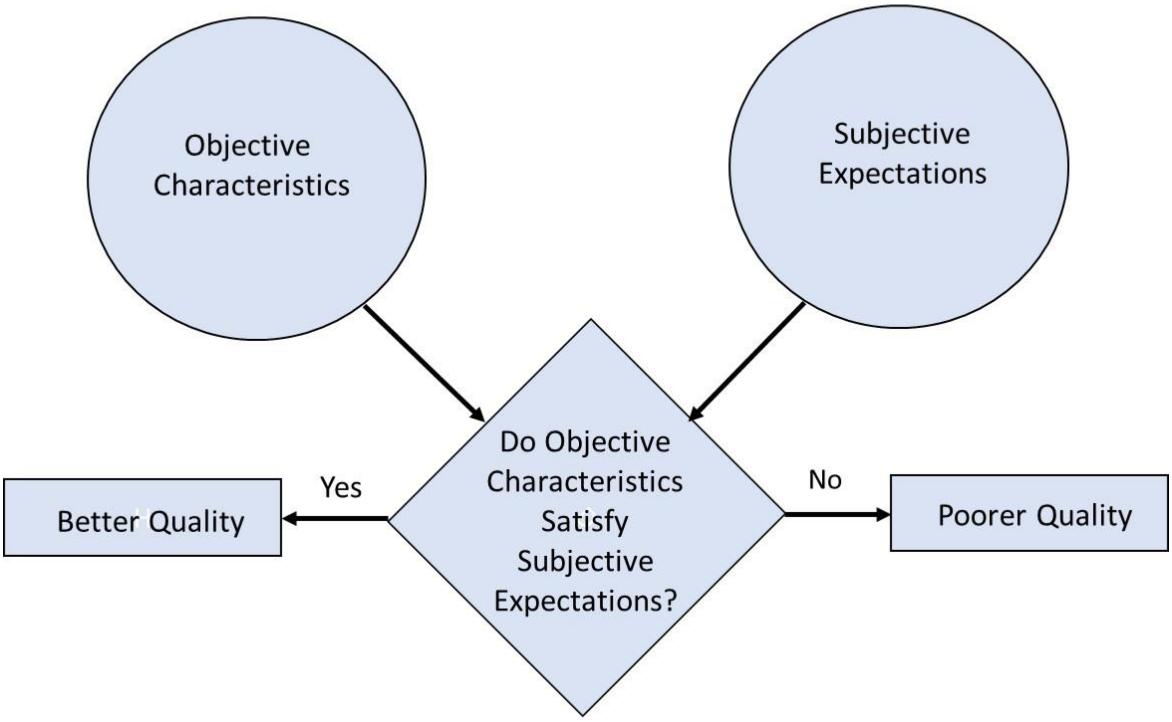

Figure 1 - Diagram illustrating Kant's conception of how judgements of better or poorer quality are made.

Water-quality standards are an example of what Kant would consider aesthetic judgments. On one hand, there are the objective characteristics of the water—e.g., concentrations of dissolved, particulate, and microbiologic matter—to consider. Having reliable analytical methods for assessing the chemistry and microbiology of water has made it possible to determine these objective characteristics accurately. However, there is always uncertainty associated with analytical methods, and so even here, complete objectivity is not possible. On the other hand, there are also the subjective needs and expectations of the people using the water to consider.

Interestingly, the regulatory process by which water-quality standards are established conforms closely to Kant's aesthetic framework. In the United States, the Safe Drinking Water Act of 1974, as amended in 1986, 1996, and 2018, gives the Environmental Protection Agency (EPA) authority to establish drinking water standards, and these standards are to be based on the use to which the water is put. In the case of water intended for human consumption, the EPA recognizes two categories of standards for water. The first are primary standards, which limit the levels of specific constituents that can adversely affect public health. In Kant's framework (Figure 1), this corresponds to the objective characteristics of water that have been shown to be detrimental to human health. *Salmonella typhi*, for example, is a water-borne pathogen that can cause deadly typhoid fever in humans. Drinking water, therefore, must not contain measurable amounts of *S. typhi*, and these primary standards are legally enforceable. The other category of standards is secondary, or aesthetic, in nature. These are non-enforceable guidelines for characteristics like taste, odor, and color that are more subjective in nature.

With respect to bottled water, perceptions of what constitutes "good" water vary tremendously. An example of this is the dichotomy between what many Europeans consider "good" bottled water as opposed to what many Americans consider "good." Probably due to the long history of Europeans visiting springs to "take the waters" for health reasons, and because mineral springs are widespread in Europe, many Europeans prefer naturally-mineralized bottled water because it is considered "healthy." In contrast, because Americans in the nineteenth century tended to view bottled water as a cleaner alternative to often polluted municipal water (prior to the invention of chlorination) they tend to prefer less-mineralized bottled water. When it comes to bottled water, perceptions of quality depend as much on the preferences and expectations of the drinker as on the characteristics of the water.

3 Historical Overview

According to legend, Hannibal and his army drank from a curious pool of water on the Languedoc plain in what is now southern France as they prepared to cross the Alps to invade Rome in 218 BCE. The pool, which was fed by a spring seeping through a small orifice in the earth's surface, had the curious property that it was naturally effervescent and was judged to be excellent for drinking. Much later, in 1884, a Dr. Louis Perrier leased the spring and began to bottle the water and sell it locally.

The desirable chemical properties of Perrier water can be traced to a highly unusual confluence of geologic circumstances. The Languedoc plain is underlain by gravels of alluvial origin that function as a productive aquifer. These gravels, in turn, are overlain by clays, which were deposited by a lake that formed after the most recent ice age ended. This clay acts as a confining bed, allowing the underlying groundwater to become pressurized. The water in the gravel aquifer has three distinct sources. One source is rainwater seeping from land surface. Another is water flowing from a fractured limestone aquifer underlying the Garrigues hills north of the Languedoc plain. Finally, hot mineralized water of volcanic origin seeps upward from a deeper source (Audemard, 1998). This hot volcanic water is saturated with carbon dioxide gas, which gives the water its natural effervescence.

If any of these three water sources were taken by themselves, they would either be unremarkable (the rainwater), undrinkable (the volcanic water) because it is highly mineralized, or usable (the fractured limestone) but hard due to high concentrations of dissolved calcium. However, when these three water sources are mixed in the proper proportions, as happens naturally in the gravel aquifer, they become a healthy and delightful drinking water.

The natural hydrologic and geologic circumstances that produce Perrier water are certainly unusual. However virtually all springs that produce high-quality drinking water are, in a variety of ways, unusual. Most springs tap shallow groundwater that is not only unremarkable in composition but can easily be contaminated by human-derived chemicals and bacteria originating at land surface. Some springs tap deeper circulating groundwater that has low concentration of dissolved organic matter, is free of fecal microorganisms, and has dissolved solids compositions that people judge to be desirable. Those deep springs provide the groundwater that is most highly prized as bottled drinking water in America.

For the last two thousand years, Europeans of means traveled to such springs to take advantage of their healthy properties. One hears a lot about "healing springs," the idea that water from certain springs can cure a variety of human ailments. It is true that some dissolved minerals may alleviate the symptoms of medical conditions such as indigestion (dissolved bicarbonate), anemia (dissolved iron), or simple goiters (dissolved iodine), but the more important characteristic was that these springs were relatively clean. They did not contain the fecal matter that laced the everyday drinking water consumed by many

Europeans. In the 1850s, an engineer named Henri Darcy solved that problem for the city of Dijon, France, by piping clean water from a spring directly into the city (Darcy, 1856). That was an elegant solution to the problem, but it was not feasible for many European cities. Furthermore, traveling to springs to "take the waters" was expensive and could only be afforded by the very wealthy. So, if most people could not come to the springs how was it possible for the water to come to the people?

That is what led to the development of the bottled water industry. Impressed with the water being bottled by Dr. Perrier, an Englishman named St John Harmsworth realized the economic potential of Perrier's operation and bought the spring in the late 1800s. Harmsworth continued using the name "Perrier" because it had acquired a considerable reputation. In the early twentieth century, the far-flung British Empire had a particularly bad problem with drinking water. Local water in India, Afghanistan, and eastern Africa was often so contaminated that it could only be rendered drinkable by mixing in a liberal dose of whiskey or gin. Harmsworth, taking advantage of the English affinity for things continental, marketed Perrier as a healthy—and high-class—drinking water. By 1930, the Perrier Company was selling 18 million bottles of water per year, much of which was being exported to expatriate Englishmen around the world. The history of Perrier bottled water has, at some level, been replicated all over the world in the modern era.

As in Europe, the bottled water industry in America originally began because of the purported medicinal properties of some spring water. In 1820, for example, an enterprising preacher named Rev. D. O. Grizwold began to bottle the naturally effervescent water of Saratoga Springs in New York State. At first, this sparkling water seems to have been used primarily as a cure for upset stomachs, and Reverend Grizwold sold the water under the name of "Doctor Clark." Gradually, as glass bottles became cheaper and more widely available in the middle 1800s, bottled spring water came to be viewed less as medicine and more as a source of relatively clean drinking water. Most city water was always more or less contaminated with various microorganisms, and epidemics of water-borne diseases such as typhoid fever and cholera were common in large cities such as Boston, New York, and Philadelphia. That being the case, bottled drinking water began to appear on the dinner tables of wealthy and not-so-wealthy city dwellers. By the end of the nineteenth century, bottled water for drinking was thought of more as a desirable amenity rather than a luxury. This affected the preferences of American consumers of bottled water, who came to prefer water with relatively low concentrations of total dissolved solids (TDS). For example, bottled water from Poland Spring in the State of Maine, with a TDS of just 40 milligrams per liter (mg/L), received a medal for its "purity and potential medicinal properties" at the Chicago Columbian Exposition of 1893. Later, at the St. Louis Louisiana Purchase Exposition in 1904, it won the Grand Prize "besting all the waters of the world."

But things were soon to change radically for the American bottled water industry. In 1913, engineers for the city of Philadelphia worked out a method for adding liquid chlorine to municipal water supplies. Free chlorine is toxic to many fecal microorganisms including *Vibrio cholera* and *Salmonella typhi*. Suddenly, safe drinking water could be had straight from the tap. As you might expect, the consumption of bottled water dropped precipitously, and within a couple of years the bottled water industry in America had virtually ceased to exist. It remained that way for the next half century. In 1960, annual sales of bottled water in America were less than 50 million dollars. Beginning about 1975, however, the American bottled water industry rebounded, largely because bottled water like Perrier and Poland Spring had become fashionable. By the year 2000, bottled water sales in the United States exceeded five billion dollars. In 2022, 60 billion liters (15.9 billion gallons) of bottled water were sold in the United States for approximately 46 billion dollars.

The American bottled water industry had recovered entirely.

4 Groundwater Regions of The United States

In 1923, O. E. Meinzer of the U.S. Geological Survey subdivided the United States into twenty-three groundwater "provinces" in which geologic, climatic, and hydrologic conditions are generally similar (Meinzer, 1923). Thomas (1952) reduced Meinzer's twenty-three provinces to ten regions by combining provinces where groundwater conditions were generally similar. Finally, Heath (1984) revised the number of groundwater regions in the United States upwards to fourteen. The regions of Heath (1984) are shown in Figure 2 and are used in this book.

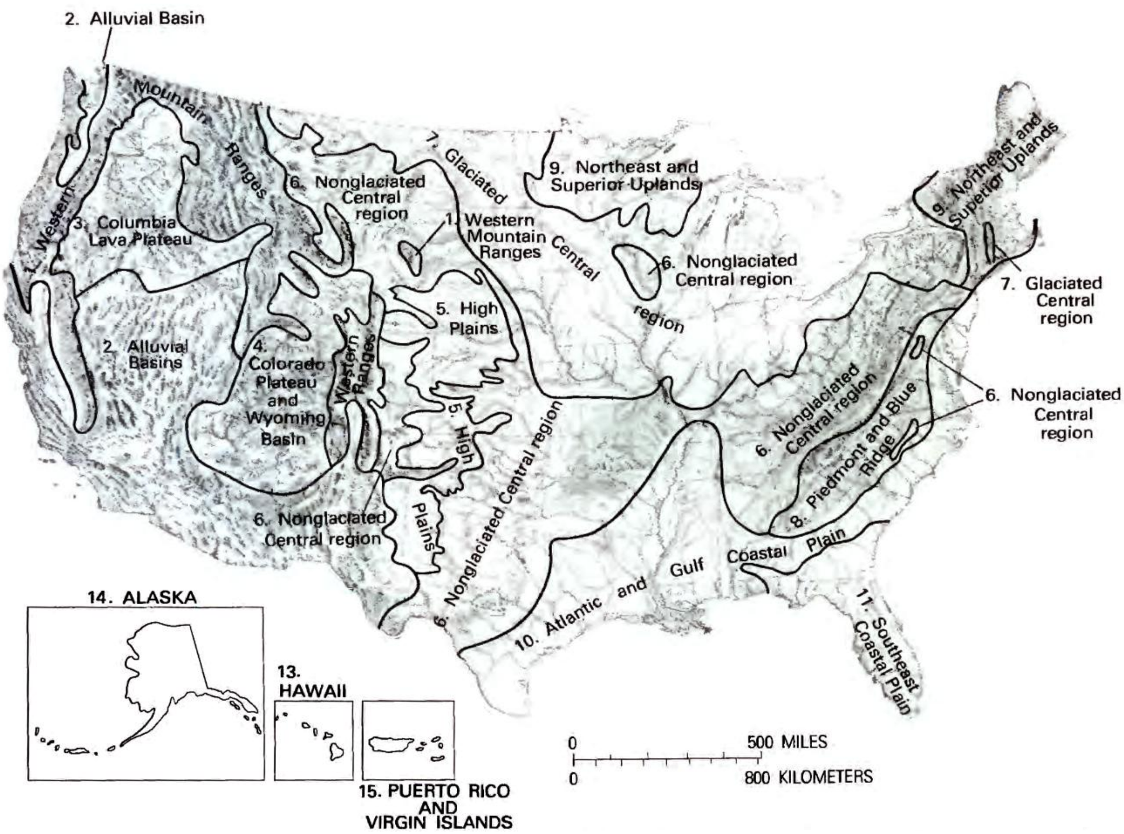

Figure 2 - The groundwater regions described by Heath (1984).

The five features used by Heath (1984) to arrive at his classification are (1) the components (geologic formations) of the system and their arrangement; (2) the nature of the water-bearing openings (porous or fractured rock) of the dominant aquifer or aquifers with respect to whether they are of primary (sand) or secondary (fractured or solution channels) origin; (3) the mineral composition of the rock matrix of the dominant aquifers with respect to whether it is soluble (carbonate) or insoluble (quartz sand or sandstone); (4) the water storage and transmission characteristics of the dominant aquifer or aquifers; and (5) the nature and location of recharge and discharge areas. We will consider examples from each of Heath's fourteen groundwater regions.

Throughout this book the regions are delineated on a base map of the USA. Some sections refer to places by the name of individual states. Figure 3 provides the names of the states.

Figure 3 - Names of the individual states of the United States.

4.1 Northeast and Superior Uplands Region

The location of the Northeast and Superior Uplands Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 4.

Begin Excerpt from Heath, 1984, pages 48–50. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by glacial deposits over fractured crystalline rocks

The Northeast and Superior Uplands region is made up of two separate areas totaling about 415,000 km^2. The Northeast Upland encompasses the Adirondack Mountains, the Lake Champlain Valley, and nearly all New England. The parts of New England not included are the Cape Cod area and nearby islands, which are included in the Atlantic and Gulf Coastal Plain region, and the Triassic lowland along the Connecticut River in Connecticut and Massachusetts, which is included in the Glaciated Central region. The Superior Upland encompasses most of the northern parts of Minnesota and Wisconsin adjacent to the western end of Lake Superior. The Northeast and Superior Uplands are characterized by rolling hills and low mountains. Land surface altitudes in the Northeast Upland range from sea level to more than 1,500 m on some of the peaks in the Adirondacks and White Mountains. In contrast to the mountainous areas in the Northeast, the Superior

Upland is in an area of rolling hills whose summits reach altitudes of only 300 to 600 m (Figure 4).

Figure 4 - The Northeast and Superior Uplands Region (based on Heath, 1984).

Bedrock in the region ranges in age from Precambrian to Paleozoic and consists mostly of granite, syenite, anorthosite, and other intrusive igneous rocks and metamorphosed sedimentary rocks consisting of gneiss, schist, quartzite, slate, and marble (Figure 5). Most of the igneous and metamorphosed sedimentary rocks have been intensely folded and cut by numerous faults.

The bedrock is overlain by unconsolidated deposits laid down by ice sheets that covered the areas one or more times during the Pleistocene and by gravel, sand, silt, and clay laid down by meltwater streams and in lakes that formed during the melting of the ice (Figure 5). The thickness of the glacial deposits range from a few meters on the higher mountains, which also have large expanses of barren rock, to more than 100 m in some valleys. The most extensive glacial deposit is till, which was laid down as a nearly continuous blanket by the ice, both in valleys and on the uplands. In most of the valleys and other low areas, the till is covered by glacial outwash consisting of interlayered sand and gravel, ranging in thickness from a few meters to more than 20 m, that was deposited by streams supplied by glacial meltwater (Figure 5). In several areas, including parts of the Champlain Valley and the lowlands adjacent to Lake Superior, the unconsolidated deposits consist of clay and silt deposited in lakes that formed during the melting of the ice sheets.

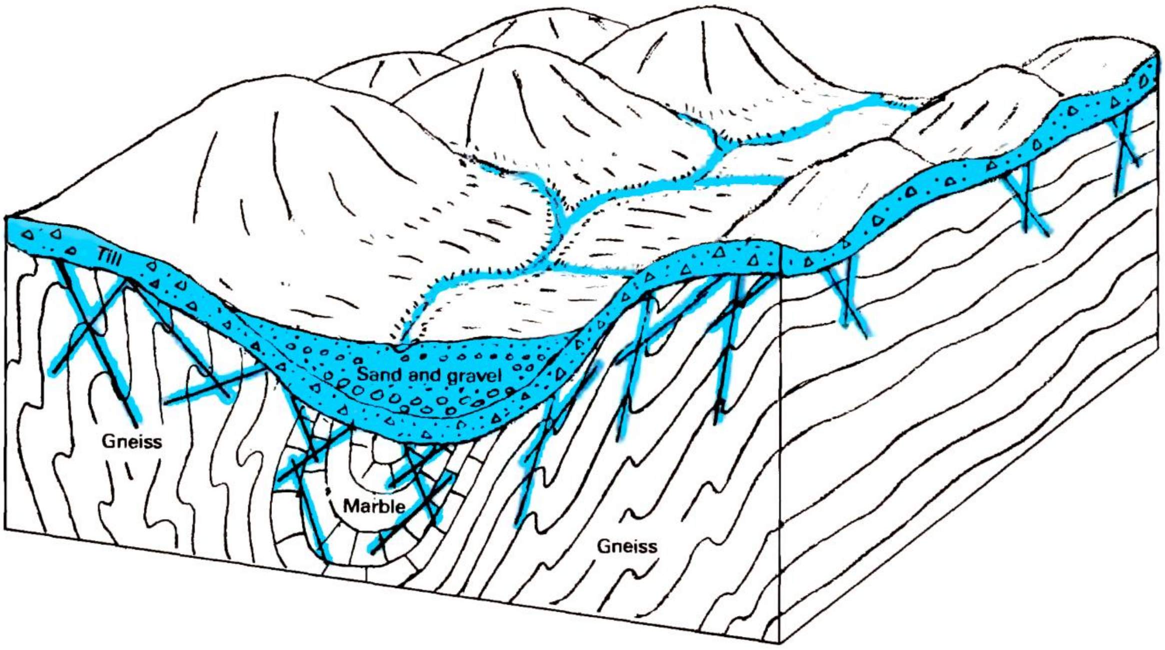

Figure 5 - Topographic and geologic features of the Northeast and Superior Uplands Region (Heath, 1984).*Blue indicates water bearing zones.

Ground-water supplies are obtained in the region from both the glacial deposits and the underlying bedrock. The largest yields come from the sand and gravel deposits, which in parts of the valleys of large streams are as much as 60 m thick. These and other valleys in the United States underlain by thick and productive deposits of sand and grave1 are covered in the discussion of the Alluvial Valleys region. Other sand and grave1 deposits, not thick or productive enough to be included in the Alluvial Valleys region, occur locally in most valley and lowland areas in the Northeast and Superior Uplands region and serve as important sources of water.

Recharge from precipitation generally begins in the fall after plant growth slows. It continues intermittently over the winter during thaws and culminates during the period between the spring thaw and the start of the growing season. Precipitation on the Northeast Upland, about 1,200 mm per year, is twice that on the Superior Upland, with the result that recharge—both to the glacial deposits and to the underlying bedrock—is largest in the Northeast. The glacial deposits in the region serve as a storage reservoir for the fractures in the underlying bedrock, in the same way the saprolite functions in the Piedmont and Blue Ridge Region. The major difference is that the glacial deposits on hills and other upland areas are much thinner than the saprolite in similar areas in the Piedmont and Blue Ridge and, therefore, have a much smaller ground-water storage capacity.

End Excerpt from Heath, 1984, pages 48–50.

4.1.1 Groundwater of the Northeast and Superior Uplands Region

Groundwater in the Northeast and Superior Uplands Region is largely produced from Pre-Paleozoic and Paleozoic basement rocks or the glacial sediments that mantle the basement rocks (Figure 5). An example of springs emanating from basement rocks is Saratoga Springs in New York. An example of springs coming from glacial sediments overlying the basement rocks is Poland Spring in Maine. These examples illustrate the much different chemistry of groundwater from the two aquifer types, and they also illustrate how the bottled water industry in America began in the nineteenth century.

4.1.2 Saratoga Springs

The ground-water chemistry characteristic of the Northeast and Superior Uplands Region is of note for this book because this was the part of the country that initiated the bottled water industry in the United States. As in Europe, the original motivation for bottling spring water in the nineteenth century was to take advantage of its purported medicinal properties. In the United States, the first mineral water to be used for medicinal purposes came from Saratoga Springs, New York (Davis & Davis, 1997). One translation of "Saratoga," a word from the Mohawk language, is "the place of the medicine waters of the Great Spirit" (Back et al., 1995). It seems the Native Americans considered the spring water to have healing qualities long before Europeans settled in New York. The first recorded European visitor to Saratoga Springs was a gentlemen named Sir William Johnson, who was taken there in 1767 by Native Americans to try and cure a leg wound. Apparently, the treatment was successful and the fame of Saratoga Springs water as a cure for just about any ailment spread rapidly. By the 1790s, an inn was built to accommodate the influx of visitors seeking to "take the waters." This inn is said to have served such notable persons as George Washington, a prodigious traveler, and Alexander Hamilton as guests (Davis & Davis, 1997). The spring water is unusual because it has very high TDS (~10,000 mg/L), and is heavily charged with carbon dioxide providing natural effervescence.

In the early nineteenth century, it was soon noticed that the water chemistry of twenty or so springs at Saratoga differed from place to place. One of the first descriptions of Saratoga Springs water, written by a physician (Stoddard, 1806), reads like a prescription (Chapelle, 2005, page 47):

> Each spring has the salts and solutions in different proportions which gives it a peculiar virtue and adapts it more particularly to certain forms of disease. Columbian Spring is a fine chalybeate tonic (high iron concentrations), gives tone and strength to the stomach, and improves the condition of the blood by increasing the number of red corpuscles. It is useful in all diseases characterized by impoverished condition of the blood. Hawthorne Spring as a cathartic is unrivaled in potency by any spring in Saratoga… It is highly beneficial in dyspepsia, chronic constipation, gout, rheumatism, and in liver and kidney difficulties.

Chemical analyses of the spring water performed by a physician named John Steel confirmed the chemical variability noticed by Stoddard (Steel, 1819). While this variability was initially of purely medical interest, it made people wonder just why this should be.

Why was it that springs or wells just a few hundred meters from each other were so different in chemical composition? Why did some springs such as High Rock Spring and Washington Spring, contain relatively high concentrations of sodium, calcium, and magnesium whereas other springs, such as Sulfur Spring, contained much less? Why did Sulfur Spring have so much more hydrogen sulfide than other springs? Why did some of the water have more natural effervescence than others? Why did water from Congress Spring contain iodine, a mineral of considerable medical interest, whereas others did not? Until quantitative chemical analyses of this water became available in the early nineteenth century, nobody even thought to ask these questions. Many more years would pass before they could be answered in any satisfactory way.

4.1.3 Hydrology and Geochemistry of Saratoga Springs

The chemical variability of water from the Saratoga Springs is due to the different geology and hydrology of the springs. The springs are in the foothills of the Adirondack Mountains along the Saratoga Fault (Figure 6). Brines upwelling along these faults from the deeply buried Appalachian Basin and Canadian Shield mix with shallower phreatic groundwater present in Cambrian sandstones and dolomites (Figure 5). Each spring has a different mixture of the four different water types which explains the observed chemical variability (Siegel et al., 2004). While solute concentrations vary from spring to spring, the proportion of each solute is similar (Figure 7).

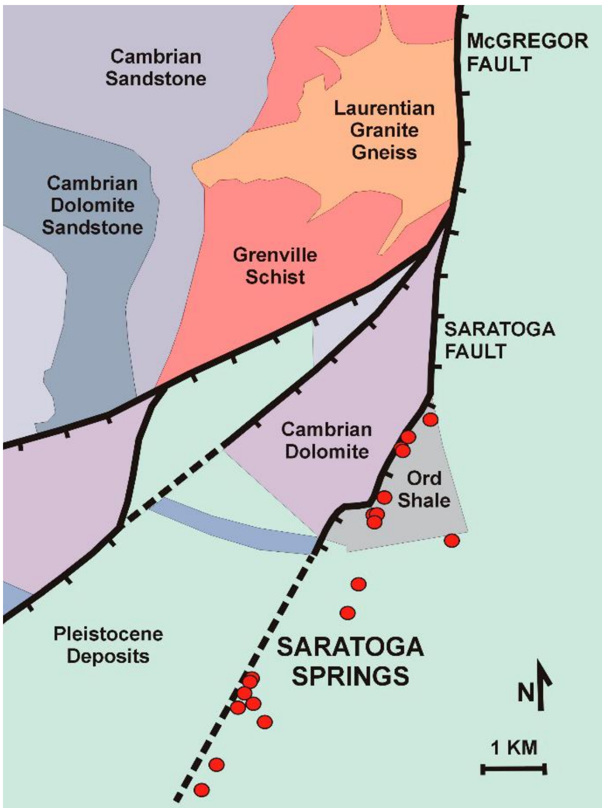

Figure 6 - Geologic Map of Saratoga Springs (Reproduced from Siegel et al., 2004).

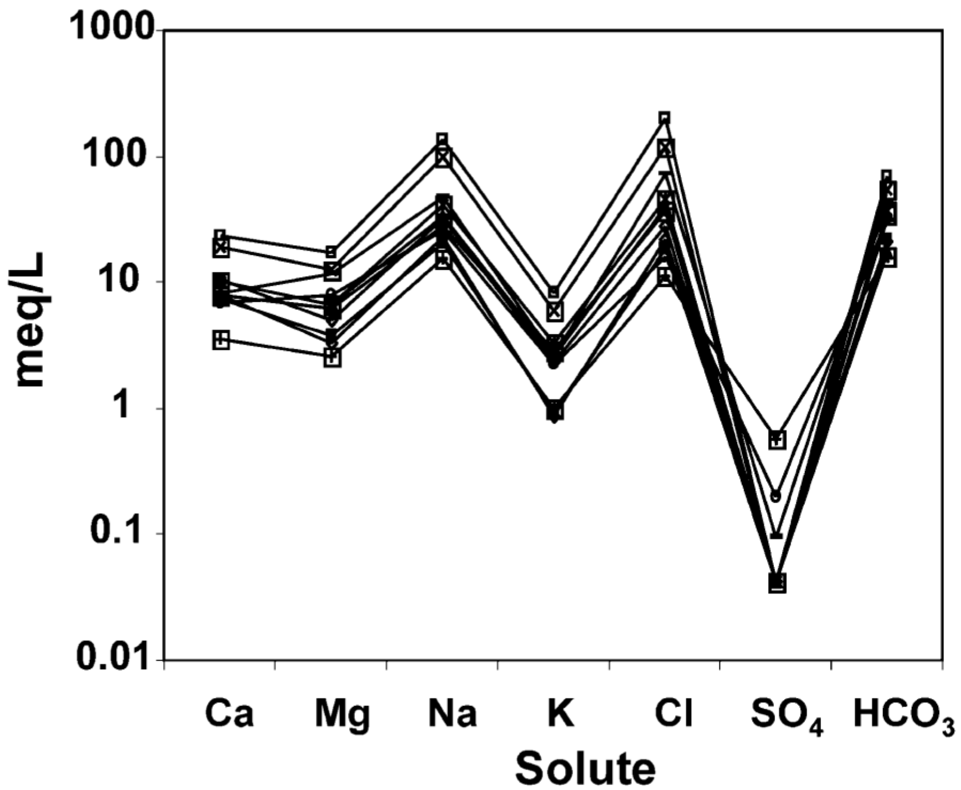

Figure 7 - Semilogarithmic plot of major solutes in different Saratoga Springs indicating that upwelling brine is being diluted by meteoric water (Data are from Putnam & Young, 1985).

This goes a long way toward explaining why Saratoga Springs water was considered medicinal, at least in the early nineteenth century, and why the water was later considered to be suitable for bottling. By 1856, more than 7 million bottles of Saratoga Springs water was being produced and sold each year, and they fetched as much as $2.00 (in modern dollars) per pint (about half a liter) (Davis & Davis, 1997). This chemistry, in turn, has greatly affected the history of Saratoga Springs and the history of the bottled water industry in America (Exercise 1↴).

4.1.4 Poland Spring

In 1797, a man named Jabez Ricker and his sons built an inn on the road linking Portland, Maine, and Montreal, Canada. The inn, located near the little town of Poland, Maine, was an instant success, providing food and accommodations for weary travelers. One of the attractions of the inn was a small spring on the side of the hill that produced unusually good drinking water. In addition to having a place to rest, tired and thirsty travelers and their horses could count on having a drink of cool, refreshing water. In deference to the nearby town, the Ricker family named the spring Poland Spring.

In 1827 Wentworth Ricker, who inherited the inn from his father Jabez, fell ill with what was described as "gravel," as kidney stones were called in those days. The doctors attending Wentworth, such as they were, despaired of his recovery. However, Wentworth, who was in his forties, remembered that his younger brother Joseph had recovered from a fever after drinking water from Poland Spring. Lacking any better medical help, Wentworth decided to try using the water as a cure. His family moved his sickbed to the spring, where he drank as much water as he could. After a few days his pains disappeared, possibly because drinking the water helped him pass a kidney stone, and he got up from his bed. The Wentworth Ricker Inn, as it came to be called, continued to be successful until Wentworth's death in 1837. Wentworth's son Hiram then took over the business.

The various accounts of cures wrought by drinking Poland Spring water caught the attention of Dr. Eliphalet Clark, a friend of Hiram Ricker. At this point in the nineteenth century, healing water was all the rage in the serious practice of medicine. Saratoga Springs had already come to prominence as a source of medicinal water. Many physicians had built lucrative practices by prescribing the water from the many Saratoga springs. Dr. Clark wondered if the water from Poland Spring might have similar properties. Dr. Clark wrote Hiram Ricker, who now was the head of the family, and asked him to send a barrel of this "elixir." Hiram obliged, and a month later the results were in. According to Dr. Clark, every patient that he gave the water to had made a remarkable recovery. Not surprisingly, Dr. Clark began to buy the water from Hiram and sell it to his patients.

Since 1845, Hiram had been selling 11-liter (3-gallon) demijohns (clay jugs) of Poland Spring water in local grocery stores for 15 cents each. Selling water to Dr. Clark was a natural extension of this new business, and soon physicians from Boston, New York, and Philadelphia were buying Poland Spring water and prescribing it to their patients. The captains of clipper ships and whaling fleets—which were major businesses in New England at that time—began to purchase barrels of Poland Spring water for use on their ships. Poland Spring water had the unusual property that it did not spoil in barrels as rapidly as other water. Hiram Ricker had begun a new and profitable business. Water from Poland Spring has been bottled and sold ever since.

4.1.5 Hydrology and Geochemistry of Poland Spring

The hydrology of Poland Spring is much simpler than that of the Saratoga Springs, and that simplicity is reflected in the chemistry of its water. Like many springs in the Northeast and Superior Uplands Region, it consists of two basic components. The first is a mantle of glacial outwash which overlies the second, which is fractured bedrock (Figure 8). Glacial outwash forms when glaciers are melting and retreating. The meltwater collects in channels, and the resulting streams and rivers often flow at relatively high velocities. This flowing meltwater washes the glacial tills, effectively removing the low-permeability clays and silts leaving the sands and gravels behind. Consequently, glacial outwash is relatively permeable and forms very productive aquifers. Rain and snowmelt that recharges the aquifer percolates downward through the glacial outwash until it encounters the underlying fractured rock, which is much less permeable. This directs the groundwater laterally, and when the water table rises to land surface, springs are formed (Figure 8). Poland Spring is one of hundreds of springs in the northeast formed in this manner.

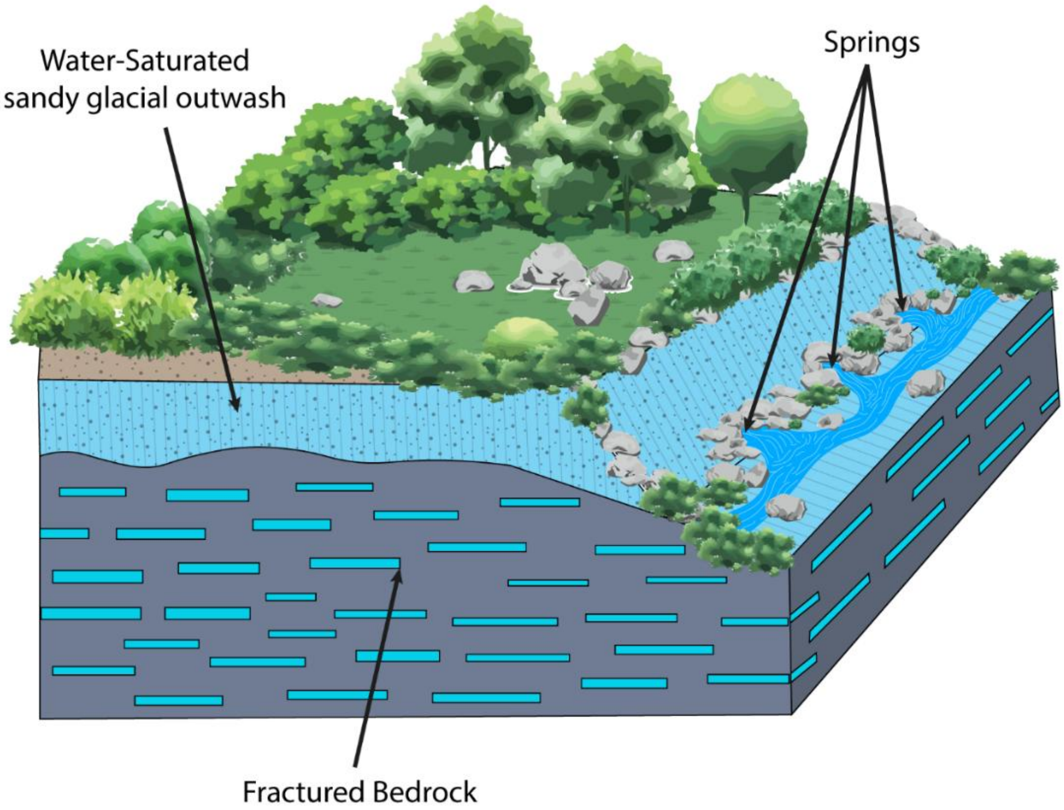

Figure 8 - Springs formed between a mantle of permeable glacial outwash and relatively impermeable fractured bedrock (modified from Chapelle, 2005. Blue indicates water bearing zones.

This relatively simple hydrology is interconnected to the chemistry of Poland Spring's water. The water is characterized by very low TDS concentrations (30–50 mg/L) and a relatively low pH (~5–6.5) for three reasons.

1. The glacial aquifer is recharged entirely by atmospheric precipitation.
2. The groundwater flow paths from recharge areas to the spring are relatively short.
3. The fine-grained material has been washed out of the glacial outwash.

Concentrations of calcium, magnesium, sodium, bicarbonate, and chloride are similarly low (Table 2).

Table 2 - Major dissolved solids in Poland Spring groundwater.

Dissolved Component	**Concentration (mg/L)**
Bicarbonate	14
Chloride	5.3
Fluoride	<0.1
Sulfate	3.2
Calcium	5.3
Magnesium	0.9
Potassium	0.7
Sodium	2.1
Total Dissolved Solids (TDS)	45
pH	5.5

Data from https://www.polandspring.com/products/spring-water↗.

This water chemistry explains some of the characteristics that made Poland Spring desirable as a bottled water. First, in the early and middle nineteenth century and before the advent of well drilling technology, all municipal water in the major American cities (New York, Philadelphia, Baltimore, New Orleans) was surface water that often had rather high TDS concentrations. The low TDS concentrations of Poland Spring water would have tasted pleasantly refreshing to people used to higher TDS drinking water. Secondly, the relatively low pH of Poland Spring water probably explains why it did not spoil as rapidly when stored in wooden barrels on ships. Low pH water is slightly inhibitory to the microorganisms that contribute to the spoiling of water in barrels. Finally, epidemics of cholera and typhoid fever, both of which are water-borne diseases, occurred regularly in large cities. From the end of the American Civil War to about the year 1920, drinking bottled spring water was widely considered a way to avoid possibly contaminated municipal water. The taste, longevity, and lack of infectious bacteria all contributed to the increasing popularity of bottled water in America in the late nineteenth century.

Poland Spring water was exhibited at the Chicago Columbian Exposition of 1893, a celebration of the four hundredth anniversary of Columbus's arrival in the New World. Poland Spring water received a medal for its purity. A few years later at the St Louis World's Fair (1904), Poland Spring won the Grand Prize as "besting all of the waters of the world." That prize was significant in that it enshrined the American taste for low TDS bottled water, a taste that endures to this day (Exercise 2↴).

4.1.6 Bottled Water Prospects in the Northeast and Superior Uplands Region

The mineral water of Saratoga Springs is produced by high TDS, carbon dioxide-charged water from deep basement rocks rising upward along the Saratoga Fault (Figure 6) and mixing with lower TDS water present in shallower aquifers. Saratoga Springs water is still bottled today by the State of New York. However, low TDS groundwater from shallow aquifers of glacial origin, such as Poland Spring, are more suited for bottling operations in the American market.

4.2 Western Mountain Ranges Region

The location of the Western Mountain Ranges Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 9.

Begin Excerpt from Heath, 1984, pages 20–23. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by mountains with thin soils over fractured rocks, alternating with narrow alluvial and, in part, glaciated valleys

The Western Mountain Ranges encompass three areas totaling 708,000 km^2. The largest area extends in an arc from the Sierra Nevada in California, north through the Coast Ranges and Cascade Mountains in Oregon and Washington, and east and south through the Rocky Mountains in Idaho and Montana into the Bighorn Mountains in Wyoming and the Wasatch and Uinta Mountains in Utah (Figure 9). The second area includes the southern Rocky Mountains, which extend from the Laramie Range in southeastern Wyoming through central Colorado into the Sangre de Cristo Range in northern New Mexico. The smallest area includes the part of the Black Hills in South Dakota in which Precambrian rocks are exposed. Summits in the Rocky Mountains and Sierra Nevada exceed 3,500 m. The general appearance of the Western Mountain Ranges—except for the Black Hills—is tall, massive mountains alternating with relatively narrow, steep-sided valleys. The summits and sides of the mountains in much of the region have been carved into distinctive shapes by mountain glaciers. The ranges that comprise the southern Rocky Mountains are separated by major lowlands that include North Park, Middle Park, South Park, and the Wet Mountain Valley. These lowlands occupy downfolded or down-faulted structural troughs as much as 70 km wide and 160 km long. The mountains in the Black Hills are lower in altitude than most of the mountains in other parts of the region.

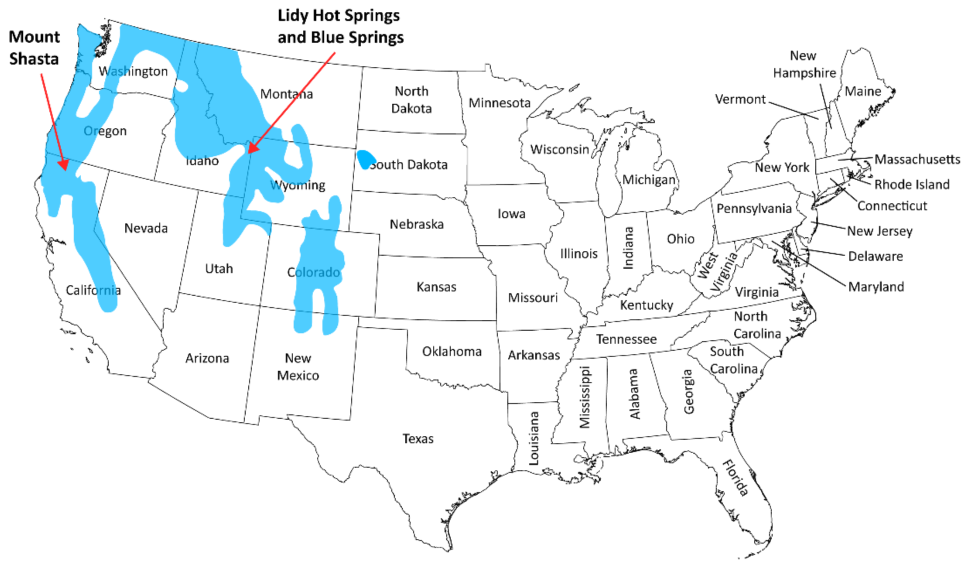

Figure 9 - The Western Mountain Ranges Groundwater Region (modified from Heath, 1984).

As would be expected in such a large region, both the origin of the mountains and the rocks that form them are complex. Most of the mountain ranges are underlain by granitic and metamorphic rocks flanked by consolidated sedimentary rocks of Paleozoic to Cenozoic age. The other ranges, including the San Juan Mountains in southwestern Colorado and the Cascade Mountains in Washington and Oregon, are underlain by lavas and other igneous rocks. The summits and slopes of most of the mountains consist of bedrock exposures or of bedrock covered by a layer of boulders and other rock fragments produced by frost action and other weathering processes acting on the bedrock. This layer is generally only a few meters thick on the upper slopes but forms a relatively thick apron along the base of the mountains. The narrow valleys are underlain by relatively thin, coarse, boulder alluvium washed from the higher slopes. The large synclinal valleys and those that occupy downfaulted structural troughs are underlain by moderately thick deposits of coarse-grained alluvium transported by streams from the adjacent mountains (Figure 10).

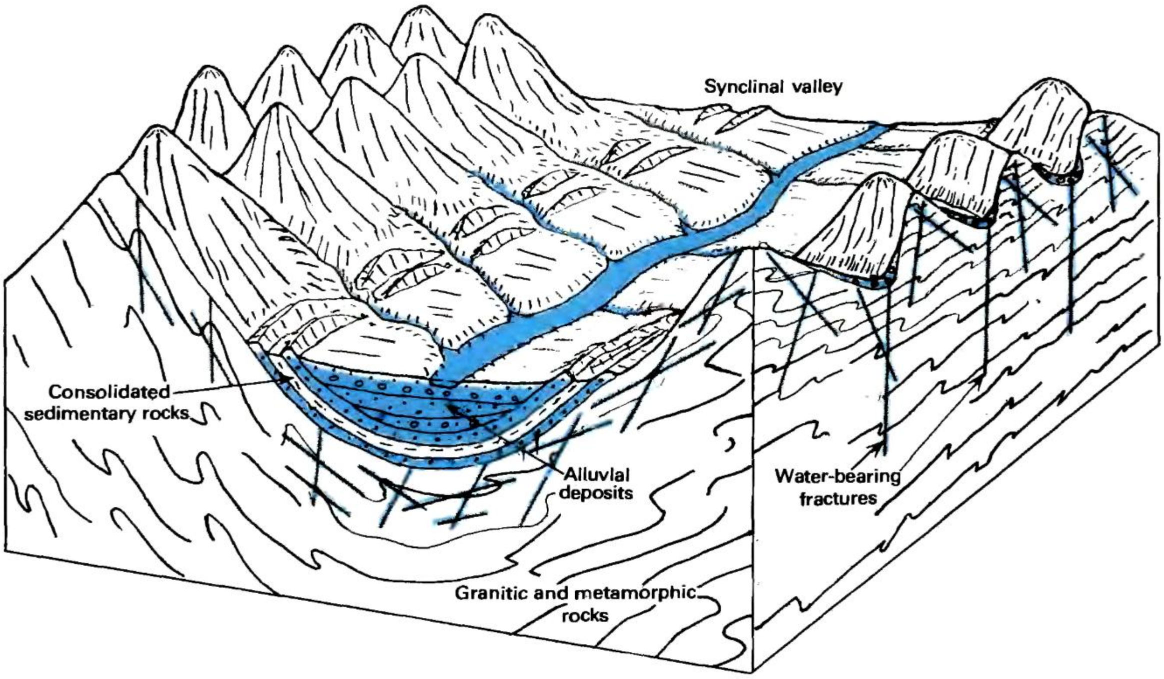

Figure 10 - Topographic and geologic features in the southern Rocky Mountains part of the Western Mountain Ranges Region (Heath, 1984). Blue indicates water bearing zones.

End Excerpt from Heath, 1984, pages 20–23.

4.2.1 Groundwater Chemistry of the Western Mountain Ranges

The chemistry of groundwater in the Western Mountain Ranges is largely a function of elevation. In general, the lowest TDS values (<500 mg/L) are found at the highest elevations (>3,000 m) where the aquifers are recharged by rainfall and snowmelt. This recharge water is primarily calcium-magnesium bicarbonate in character reflecting the dissolution of calcite, dolomite, and plagioclase feldspars. As groundwater moves to lower elevations in river valleys (~2,000 m), TDS concentrations increase to up to 3,000 mg/L, concentrations of sulfate increase reflecting dissolution of gypsum and anhydrite, and concentrations of calcium and magnesium decrease due to cation exchange reactions. Given the evolution of dissolved solids, groundwater collected at higher elevations is more suitable for the low-TDS bottled water that Americans generally prefer.

4.2.2 Groundwater Chemistry of Mount Shasta

An example of this generality is provided by Mount Shasta in California where spring water has been bottled since the late 1800s. The chemistry of Shasta spring water reflects a set of climatologic, hydrologic, and geologic conditions that are characteristic to the Western Mountain Ranges. Climatically, the prevailing westerly winds coming off the Pacific Ocean carry large amounts of moisture. As those winds are forced upward by the mountains, the air cools and moisture condenses first as rain and then as snow. The underlying volcanic rocks are recharged with rainfall and snowmelt. The dissolution of minerals making up the underlying lithology determines the chemical character of the groundwater. Many mountain peaks in the Western Mountain Ranges, including Mount Shasta, are blanketed with year-round snow (Figure 11). Mount Shasta, incidentally, holds the North American record for the deepest single-storm snowfall event ever recorded (4.8 meters). Not surprisingly, Mount Shasta has seven named glaciers as well.

Figure 11 - Mount Shasta covered with snowfall. U.S. Geological Survey File photo.

Geologically, Mount Shasta is composed of four major volcanic cones built with distinct layers of ash and lava and is classified as a compound stratovolcano. Hydrologically, due to the high permeability of young volcanic rocks, the transport of snowmelt occurs almost exclusively as groundwater. Furthermore, because the permeability of volcanic rocks tends to decrease with depth, numerous springs develop on the flanks of Mount Shasta at a variety of elevations. One famous series of springs fed by groundwater originating on Mount Shasta are in Mount Shasta City Park, forming the headwater of the Sacramento River.

The chemistry of the spring water depends on the travel time from the point of recharge to the spring outfall and the composition of the rocks (basaltic or andesitic) encountered along the flow path. Furthermore, because of the highly fractured nature of the volcanic rocks, as well as the presence of *lava tubes* this transport can be extremely rapid (Figure 12).

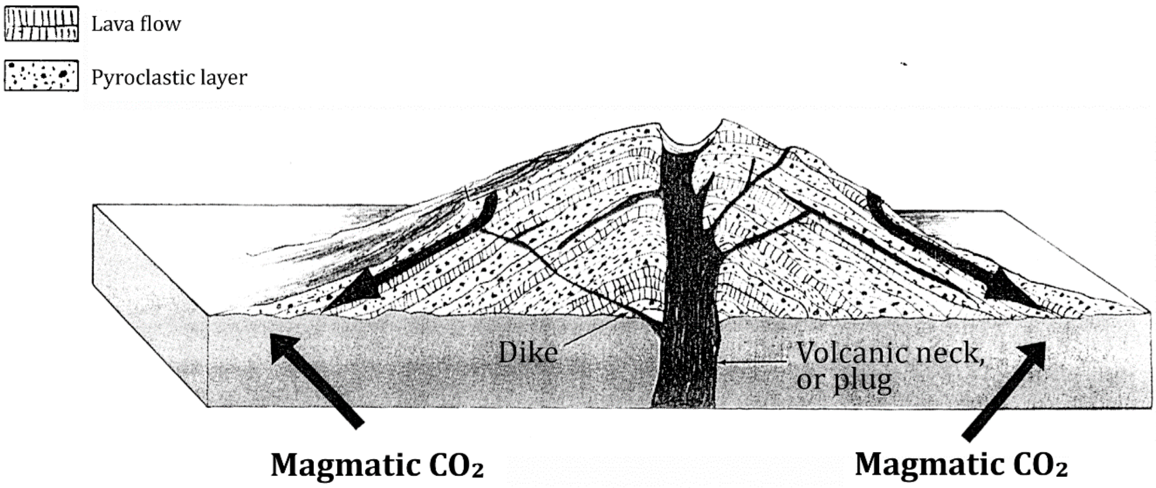

Figure 12 - Fractures and lava tubes in the interior of Mount Shasta (from Davisson and Rose, 1997).

For example, at Horse Camp Springs, located just 5.8 km (3.6 miles) southwest of Mount Shasta's summit, the spring water has a total dissolved solids (TDS) concentration of between 12.0 and 24.5 mg/L (Visser et al., 2017). Such low TDS concentrations are similar to those of unreacted snowmelt. It might be expected that springs at lower elevations would exhibit higher concentrations of TDS. That holds true at Beaughan Spring located 17.4 km (10.9 miles) due west of Mount Shasta's summit with a TDS concentration of 90.5 mg/L (Visser et al., 2017). That does not hold, however for water discharging from several springs at Big Springs in Mount Shasta City Park, located 17.6 km (11.0 miles) southwest from Mount Shasta's summit, where TDS concentrations range from 10.4 to 19.1 mg/L (Visser et al., 2017). That, in turn, suggests more rapid flow through volcanic lava tubes and less corresponding time for reaction with volcanic rocks.

The low TDS spring water that can be found at Mount Shasta is a principal reason why it is attractive for bottled-water operations. Many different companies have gone into business over the last one hundred years to bottle Mount Shasta spring water. These companies use the unique geologic and hydrologic properties of the area in their marketing, noting that "geologists tell us our spring water originates from glaciers high atop Mt. Shasta. The water flows through miles of volcanic rock to springs located on our property at the base of the mountain…" (Exercise 3↴).

4.2.3 Water Chemistry Variation in the Western Mountain Ranges Region

The low-TDS spring water found at relatively high elevations in the Western Mountain Ranges is generally preferred as a source of bottled water, whereas the higher

TDS water found at lower elevations is not. Furthermore, the geologic complexity of the mountain ranges and their associated valleys can lead to surprising differences in spring water chemistry. An example of this can be found at two springs located about a kilometer apart in the Bitterroot Range near the small town of Dubois, Idaho. One spring, known as Lidy Hot Springs, has a water temperature of 58.5 °C, a TDS of 480 mg/L, and a hardness of 290 mg/L as $CaCO_3$ (Table 3). The other spring, known as Blue Spring, is much colder (12.5 °C), has a lower TDS (295 mg/L), and a lower hardness (182 mg/L) (Table 4).

Table 3 - Groundwater Chemistry of Lidy Hot Springs, Idaho (Data from Knobel et al., 1999).

Dissolved Component	Concentration (mg/L)
Bicarbonate	235
Chloride	6.7
Nitrate	<0.1
Hardness (as $CaCO_3$)	290
Sulfate	200
Calcium	88
Magnesium	16
Potassium	15
Sodium	27
Total Dissolved Solids (TDS)	480
Dissolved Oxygen	<0.1
pH	7.1
Temperature (°C)	58.5

Table 4 - Groundwater Chemistry of Blue Springs, Idaho (Data from Chapelle, 2005).

Dissolved Component	Concentration (mg/L)
Bicarbonate	164
Chloride	16
Nitrate	0.7
Hardness (as $CaCO_3$)	182
Sulfate	21
Calcium	73
Magnesium	7.5
Potassium	2.9
Sodium	10.8
Total Dissolved Solids (TDS)	295
Dissolved Oxygen	4.0
pH	8.33
Temperature (°C)	12.5

The most obvious difference between water from the two springs is the 46-degree difference in temperature, but they also have different concentrations of TDS, hardness, sodium, and pH. Interestingly, the concentration of calcium is similar. These water chemistries reflect the different sources of the spring water. Both springs are in the foothills of the Bitterroot Range, with Blue Springs being about 75 m higher in elevation. Lidy Hot Springs, on the other hand, is located a few hundred meters closer to a broad valley known as the Snake River Plain. The eastern Snake River Plain traces the path of the North

American Plate over the Yellowstone hotspot, now centered below Yellowstone National Park. The eastern plain is a topographic depression that cuts across the mountain structures, more or less parallel to North American Plate motion. It is underlain almost entirely by basalt erupted from large shield volcanoes. Beneath the basalts are rhyolite lavas and ignimbrites that erupted as the lithosphere passed over the hotspot (Figure 13).

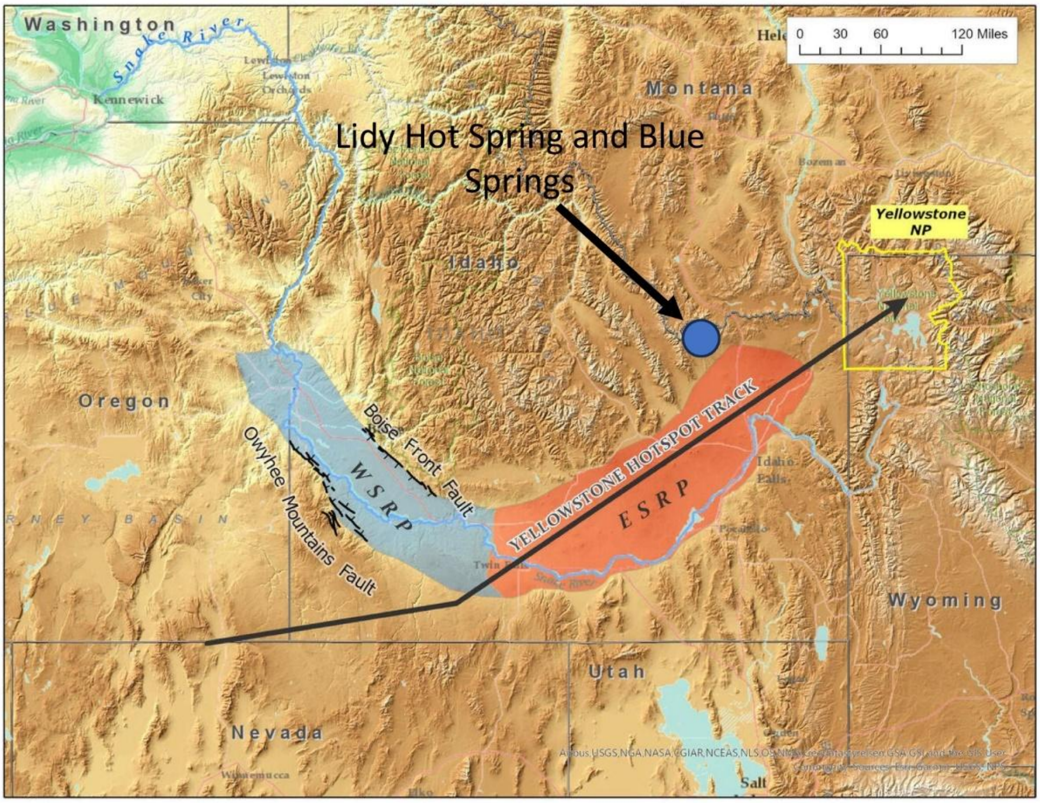

Figure 13 - The Track of the Yellowstone Hot Spot that formed the Snake River Plain (WSRP is Western Snake River Plain and ESRP is Eastern Snake River Plain) and the location of Lidy Hot Spring and Blue Springs (adapted from U.S. Geological Survey file map).

The water feeding Lidy Hot Springs, and hundreds of other hot springs found on the Snake River Plain, are heated at depth by residual volcanic activity. In contrast, the water feeding Blue Spring is recharged at higher altitude in the Bitterroot Range north of the Snake River Plain. That, in turn, explains the differences in temperature and water chemistry. Lidy Hot Springs was operated as a spa and bathing resort beginning in the 1920s. It quickly became a favorite place in Clark County for socializing, dancing, swimming, and bathing. This lasted until the 1960s. Lidy Hot Springs water was never used for bottling, at least not officially. However, many other hot springs in the Snake River Valley, with chemistries like Lidy Hot Springs have served as bottled water over the years. An example being Lava Hot Springs Inn Mineral Water of Pocatello, Idaho (https://idahopreferred.com/members/lava-hot-springs-inn-mineral-water↗). Blue Springs presently has a bottling operation that began in the late 1990s and continues to the present day.

4.2.4 Bottled Water Prospects for the Western Mountain Ranges Region

The consistent groundwater chemistry trend of spring water in the Western Mountain Ranges—with recharge occurring at high altitudes producing low-TDS water that progressively mineralize during flow to lower altitudes forming high TDS water—largely restricts bottled water operations to high-altitude spring sources. Mount Shasta in California is a good example of snowmelt recharging very permeable aquifers at high altitude—with rapid groundwater flow through lava tubes and fractures to lower altitudes—producing TDS concentrations below 100 mg/L. Blue Spring of Idaho is an example of snowmelt recharge to aquifers high in the Bitterroot Range, that traverses a longer groundwater flowpath, producing moderate TDS concentrations (~300 mg/L). In Idaho, where much of Blue Spring bottled water is consumed, the higher mineral content is considered to produce a more pleasant taste than lower TDS water. Finally, Lidy Hot Springs is a good example of groundwater heated thermally at depth and producing spring water of relatively high TDS (~500 mg/L). While Lidy Hot Springs has not been used for bottling, many similar springs in the Snake River Valley have histories of bottling operations and being marketed as mineral water.

4.3 Alluvial Basins Region

The Alluvial Basins Region was called the Alluvial Valleys region by Heath. Its location is shown with all groundwater regions of the USA in Figure 2 and it is the blue area of Figure 14.

Begin Excerpt from Heath, 1984, pages 23–27. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thick alluvial deposits in basins and valleys bordered by mountains and locally of glacial origin

The Alluvial Basins region occupies a discontinuous area of 1,025,000 km^2 extending from the Puget Sound-Willamette Valley area of Washington and Oregon to west Texas. The region consists of an irregular alternation of basins or valleys and mountain ranges. From the standpoint of topography, it is useful to contrast this region (Figure 14) with the Western Mountain Ranges (Figure 9). In the Western Mountain Ranges the high areas, the mountains, are the dominant feature. In the Alluvial Basins Region the low areas, the basins and valleys, are the dominant feature. Most of the Nevada and all the Utah parts of this region are an area of internal drainage referred to as the Great Basin. No surface or subsurface flow leaves this part of the region, and all water reaching it from adjacent areas and from precipitation is returned to the atmosphere by evaporation or by the transpiration of plants.

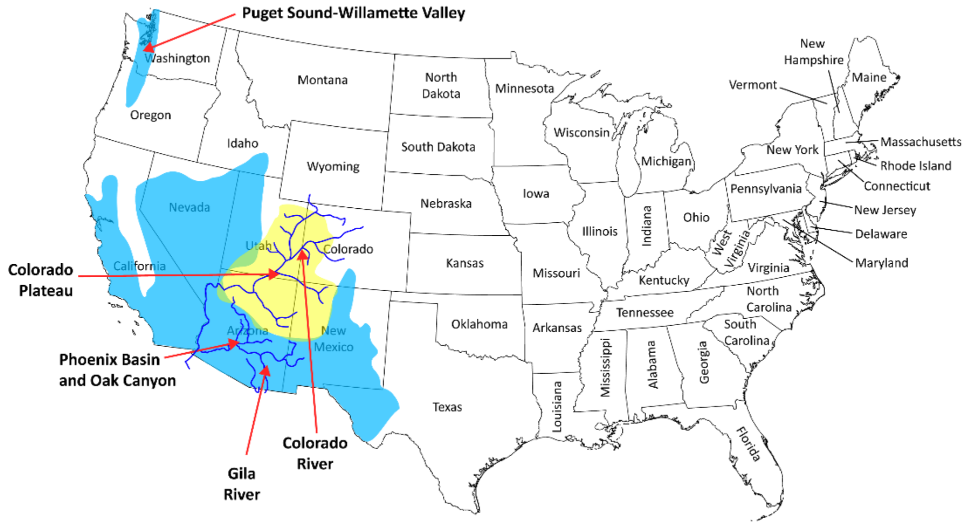

Figure 14 - The Alluvial Basins Groundwater Region (modified from Heath, 1984).

The surrounding mountains, and the bedrock beneath the basins, consist of granite and metamorphic rocks of Precambrian to Tertiary age and consolidated sedimentary rocks of Paleozoic to Cenozoic age. The rocks are broken along fractures and faults that may serve as water-bearing openings. However, the openings in the granitic and metamorphic rocks in the mountainous areas have a relatively small capacity to store and to transmit groundwater. The dominant element in the hydrology of the region is the thick—several hundred to several thousand meters—layer of generally unconsolidated alluvial material that partially fills the basins (Figure 15). Except for the part of the region in Washington and Oregon, the material was derived from erosion of the adjacent mountains and was transported down steep gradient streams into the basins, where it was deposited as alluvial fans. Generally, the coarsest material in an alluvial fan occurs at its apex, adjacent to the mountains; the material gets progressively finer toward the centers of the basins. However, in most fans there are layers of sand and gravel that extend into the central parts of the basins. In time, the fans formed by adjacent streams coalesced to form a continuous and thick deposit of alluvium that slopes gently from the mountains toward the center of the basins. These alluvial-fan deposits are overlain by or grade into fine-grained flood plain, lake, or playa deposits in the central part of most basins. The fine-grained deposits are especially suited to large-scale agriculture.

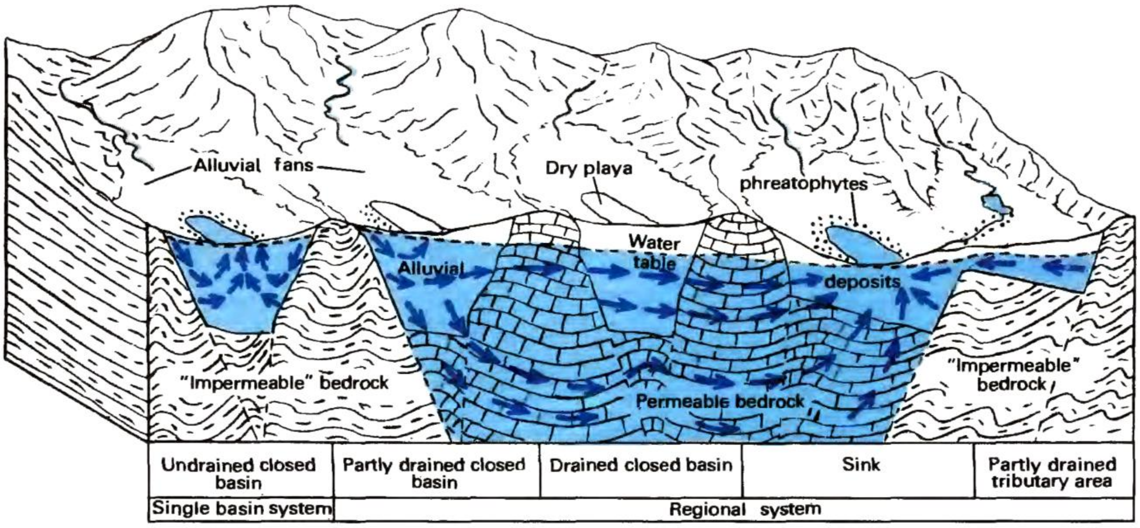

Figure 15 - Common groundwater flow systems in the Alluvial Basins region (Heath, 1984). Blue indicates water bearing zones.

End Excerpt from Heath, 1984, pages 23–27.

4.3.1 Hydrology and Geochemistry of Alluvial Basins

Groundwater is recharged to the alluvial aquifers as 1) infiltration of precipitation and runoff along mountain fronts (mountain-front recharge); 2) infiltration along streams that generally traverse the central axis of basins (basin-center recharge); and 3) underflow from adjacent basins of higher altitude. The source of most of the groundwater is precipitation that falls in the mountains surrounding the basins. Only basins along the Colorado River are recharged by water that does not originate within the Alluvial Basins Region (Robertson, 1991).

The groundwater in the Alluvial Basins Region, as indicated by dissolved-solids and trace-element content, generally is of suitable chemical quality for most purposes but is not without some problems. Total dissolved-solids (TDS) concentrations range from an average of less than 500 mg/L in eleven of the twenty-eight basins sampled by Robertson (1991) to more than 3,000 mg/L in basins along the Gila and Colorado Rivers. In addition to high TDS, the groundwater in most basins has relatively high hardness values of greater than 120 mg/L as calcium carbonate (Robertson, 1991). In several basins, groundwater contains high concentrations of the trace elements fluorine, chromium, arsenic, lead, boron, or selenium that exceed standards established for public supply or some agricultural uses. The pH values of groundwater in recharge areas of most basins generally are near neutral (pH ~7.2–7.6). In downgradient and discharge areas, however, pH values can be considerably more alkaline and can be as high as 9.5. Dissolved oxygen is near saturation in ground water in recharge areas (~8.0 mg/L) and typically decreases by half (~4.0 mg/L) near discharge areas (Anderson, 1995).

The high dissolved solids concentrations, relatively hard water, elevated pH, and the presence of trace elements reflects the composition of basin-fill sediments. These include clastic and carbonate sediments, evaporites, interbedded volcanic rocks, stream alluvium, and flood-plain deposits. Dissolution of these minerals as groundwater moves from the mountainous recharge areas to the middle of the basins explains much of the observed water chemistry (Robertson, 1991) (Exercise 4⤵).

4.3.2 Hydrology and Geochemistry of the Phoenix Basin

The high-TDS, high-hardness, high-pH character of groundwater in most of the alluvial basins in the southwest presents challenges to users of both groundwater and surface water. These challenges, and some of the technical measures employed to deal with them, can be illustrated in one of the largest basins in Arizona, the Phoenix Basin.

According to the City of Phoenix Water Services Department, about 95 percent of Phoenix's water comes from surface water (lakes and rivers) and the remaining water comes from groundwater (wells). However, given the hydrology of alluvial basins in general, and the Phoenix Basin in particular, most of the water present in lakes and rivers originates in the mountains as groundwater before discharging to surface-water bodies. As a result, the surface water collected in the Phoenix Basin mirrors the chemical composition of groundwater. In the hot summer months, the growth of algae in surface water can lead to seasonal taste and odor issues. The City of Phoenix treats the raw water with standard engineering processes including pre-sedimentation, coagulation, flocculation, sedimentation, filtration, and disinfection that produces a finished tap water that meets or exceeds all federal and state requirements for health and safety. While perfectly safe for human consumption, some residents find the high-TDS and high-hardness character of the municipal tap water unpleasant. For that reason, there is a considerable market for bottled water, as well as for water-purification systems in the Phoenix Basin and other alluvial basins in the Southwest.

Bottled-water companies face the same problems of high-TDS and hardness issues as municipal water systems if they use locally sourced water. These local bottled water companies approach those problems in two ways. The first is to source their water higher up in the mountain canyons where the water has had less time to interact with basin fill sediments. These sources generally have lower TDS values (~100 mg/L) and lower hardness values (~10 mg/L). For water sources located lower in the basins, bottled water companies use reverse osmosis technologies to lower both TDS and hardness values.

Interestingly, some bottled water companies use high-pH values as a marketing tool. One company in the Phoenix area markets their naturally occurring high-pH water claiming that, among other things, alkaline water neutralizes stomach acid, helps reduce blood pressure, is good for bone health, and hydrates better than low pH water. Many bottled water companies touting naturally high-pH water also use reverse osmosis to lower TDS and hardness.

4.3.3 Hydrology and Geochemistry of Oak Canyon

Much of the groundwater found in the Alluvial Basins Region, because of the nature of the subsurface flow systems (Figure 15) and the alluvial sediments filling the basins, is unsuitable for bottling as untreated water. The highlands that form the boundaries of the individual basins, however, are a different story. An example of this can be found in the vicinity of Sedona, and Oak Creek Canyon, Arizona.

The Sedona-Oak Creek area is situated in the transition zone between the Basin and Range Region and the Colorado Plateau and Wyoming Basin Region (Bezy, 2012). The sedimentary and volcanic rocks are beautifully exposed north of Sedona, and in ascending order consist of the Supai Group, the Coconino Sandstone, the Toroweap and Kaibab Formations of Paleozoic age, and the Neogene basalts of the San Francisco volcanic Field (Figure 16).

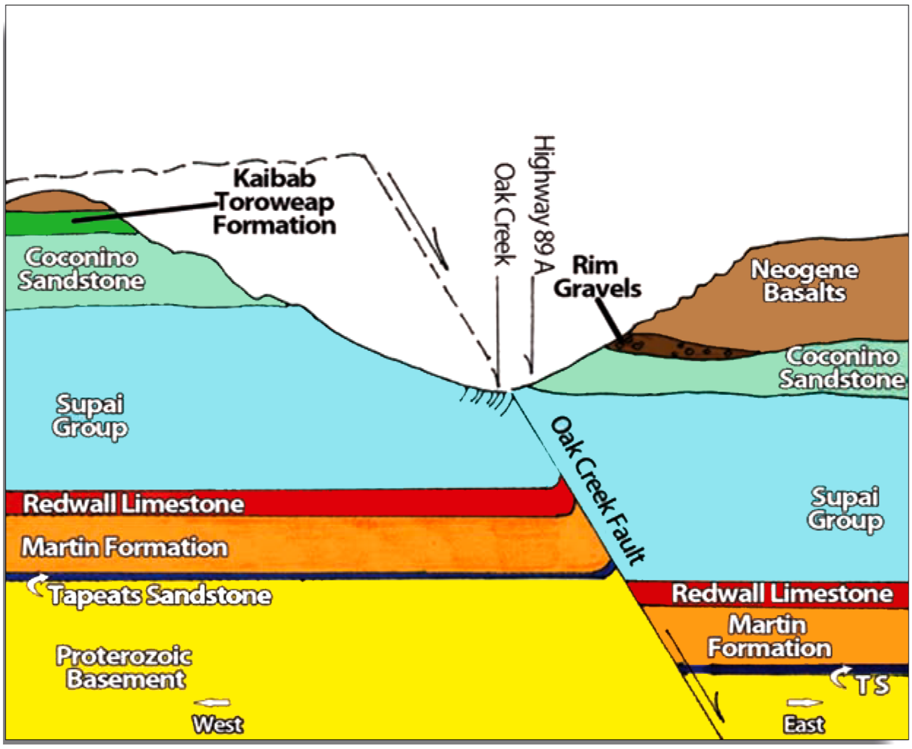

Figure 16 - East-west cross-section of Oak Creek Canyon showing the location of the Oak Creek Fault and the vertical displacement along the fault trace (Reproduced from Bezy, 2012; courtesy of P. A. Lindberg).

The structural weakness of the Oak Creek Fault resulted in extensive erosion by Oak Creek. Oak Creek, in turn, is fed by dozens of seeps and springs discharging into the canyon. Groundwater has been an active geomorphic agent in the Sedona-Oak Creek area for millions of years, resulting in the formation of some spectacular sinkholes (Lindberg, 2010). These springs are fed by snowmelt that recharges the limestone and sandstone aquifers of the Colorado Plateau. Where contact time with the surrounding sedimentary rocks is limited, the water chemistry of these springs can be suitable for bottled water operations (Table 5).

Table 5 - Groundwater Chemistry of an Oak Canyon Spring (Data from Hidell International for Sedona Bottling Company, Phoenix, Arizona).

Dissolved Component	Concentration (mg/L)
Bicarbonate	130
Chloride	2.4
Hardness (as $CaCO_3$)	68
Sulfate	5.0
Calcium	27
Magnesium	13.0
Potassium	<0.2
Sodium	5.0
Total Dissolved Solids (TDS)	160
pH	7.7

4.3.4 Bottled Water Prospects in the Alluvial Basins Groundwater Region

In general, the hydrology and geochemistry of aquifers in the Alluvial Basins Groundwater Region are not often favorable for bottled water operations. One challenge is the arid or semi-arid nature of the climate of the region which tends to raise the TDS values of both groundwater and surface water. In addition, many alluvial basins had seasonal lakes in low-lying areas during the Pleistocene (2.6 million to 11,700 years BP) and Holocene (11,700 years BP to present). This has led to the deposition of evaporites which also tends to raise TDS values. Nevertheless, using reverse osmosis technology as well as exploiting springs in the highlands surrounding alluvial basins, is the basis for bottled water in this part of the country.

4.4 Columbia Lava Plateau Region

The location of the Columbia Lava Plateau Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 17.

Begin Excerpt from Heath, 1984, pages 28–31. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thick sequences of lava flows irregularly interbedded with thin unconsolidated deposits and overlain by thin soils

The Columbia Lava Plateau occupies an area of 366,000 km^2 in northeastern California, eastern Washington and Oregon, southern Idaho, and northern Nevada (Figure 17). As its name implies, it is basically a plateau standing at an altitude generally between 500 and 1,800 m above sea level that is underlain by a great thickness of lava flows irregularly interbedded with silt, sand, and other unconsolidated deposits. The plateau is bordered on the west by the Cascade Range, on the north by the Okanogan Highlands, and on the east by the Rocky Mountains. On the south it grades into the Alluvial Basins region, as the area occupied by lava flows decreases and the typical *basin and range* topography of the Alluvial Basins region gradually prevails. Most of the plateau in Idaho is exceptionally flat over large areas, the principal relief being low cinder (volcanic) cones and lava domes. This area and much of the area in California, southeastern Oregon, and Nevada is underlain by much of the youngest lava, some of which is less than 1,000 years old. In Washington the flows are older, some dating back to the Miocene Epoch. Altitudes in a few of the mountainous areas in the plateau region exceed 3,000 m. The great sequence of lava flows, which ranges in thickness from less than 50 m adjacent to the bordering mountain ranges to more than 1,000 m in south-central Washington and southern Idaho, is the principal water-bearing unit in the region (Figure 18).

Figure 17 - The Columbia Lava Plateau Groundwater Region (modified from Heath, 1984).

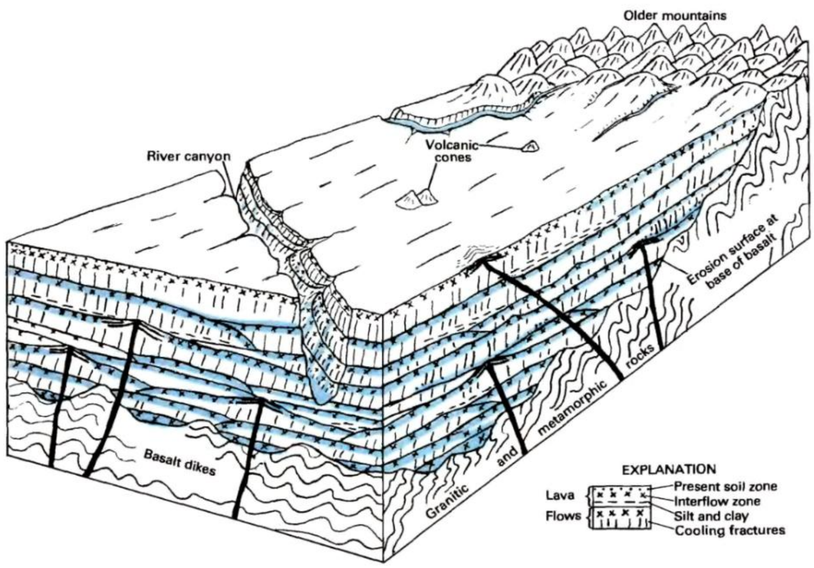

Figure 18 - Topographic and geologic features of the Columbia Lava Plateau region (Heath, 1984). Blue indicates water bearing zones.

The volcanic rocks yield water mainly from permeable zones that occur at or near the contacts between some flow layers. The origin of these flow-contact or interflow zones is complex but involves, among other causes, the relatively rapid cooling of the top of flows, which results in formation of a crust. As the molten lava beneath continues to flow, the crust may be broken into a rubble of angular fragments which in places contain numerous holes where gas bubbles formed and which give the rock the appearance of a frozen froth. The slower cooling of the central and lower parts of the thicker flows results in a dense, flint-like rock which in the lower part contains relatively widely spaced, irregular fractures and which grade upward into a zone containing relatively closely spaced vertical fractures that break the rock into a series of hexagonal columns (Figure 18).

End Excerpt from Heath, 1984, pages 28–31.

4.4.1 Groundwater Chemistry of the Columbia Lava Plateau Region

The chemical composition of groundwater in the Columbia Lava Plateau region is controlled principally by four factors. The first is the composition of the basalt flows which vary from flow to flow. The second is the composition of the clay and silt interbeds between lava flows. The third is the distance and time that the groundwater has moved through the aquifer system, and the fourth is the thickness of the overburden covering the basalt flows (Whiteman et al., 1994).

The basalt rocks consist mainly of a black plagioclase feldspar known as labradorite, a black pyroxene known as augite, and volcanic glasses typically found at the base of individual lava flows (basal vitrophyres). In addition, the most common accessory minerals include apatite, olivine, and metal sulfides such as pyrite. Dissolution of these minerals by percolating recharge water containing atmospheric and soil-derived carbon dioxide initially produces a slightly alkaline pH (~7.3) calcium bicarbonate-type water with moderate concentrations of total dissolved solids (TDS ~243 mg/L). As groundwater moves further along regional flowpaths concentrations of sodium (40 mg/L), magnesium (14 mg/L), sulfate (30 mg/L), and TDS increase (>400 mg/L), and the water becomes more alkaline (pH>8.0) (Steinkampf, 1989).

4.4.2 Bottled Water Prospects in the Columbia Lava Plateau Region

Like the Alluvial Basins region of the Southwest, the common occurrence of high TDS groundwater has a marked effect on the practice of the bottled water industry. In short, groundwater produced from the basalt aquifers is not considered suitable without prior treatment to lower TDS concentrations. In the city of Yakima, Washington, located in the northern part of the Columbia Lava Plateau, water bottlers use two treatment strategies—reverse osmosis and vapor distillation—for lowering TDS prior to bottling (Exercise 5↴).

4.5 Colorado Plateau and Wyoming Basin Region

The location of the Colorado Plateau and Wyoming Basin Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 19.

Begin Excerpt from Heath, 1984, pages 32–34. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thin soils over consolidated sedimentary rocks

The Colorado Plateau and Wyoming Basin region occupies an area of 414,000 km^2 in Arizona, Colorado, New Mexico, Utah, and Wyoming (Figure 19). It is a region of canyons and cliffs; of thin, patchy, rocky soils; and of sparse vegetation adapted to the arid and semiarid climate. The large-scale structure of the region is that of a broad plateau standing at an altitude of 2,500 to 3,500 m and underlain by essentially horizontal to gently dipping layers of consolidated sedimentary rocks. The plateau structure has been modified by an irregular alternation of basins and domes, in some of which major faults have caused significant offset of the rock layers. The region is bordered on the east, north, and west by mountain ranges that tend to obscure its plateau structure. The northern part of the region—the part occupied by the Wyoming Basin—borders the Non-glaciated Central region at the break in the Rocky Mountains between the Laramie Range and the Bighorn Mountains. The region contains small, isolated mountain ranges, the most prominent being the Henry Mountains and the La Sal Mountains in southeastern Utah. It also contains, rather widely scattered over the region, extinct volcanoes and lava fields (Figure 20), the most prominent example being the San Francisco Mountains in north-central Arizona.

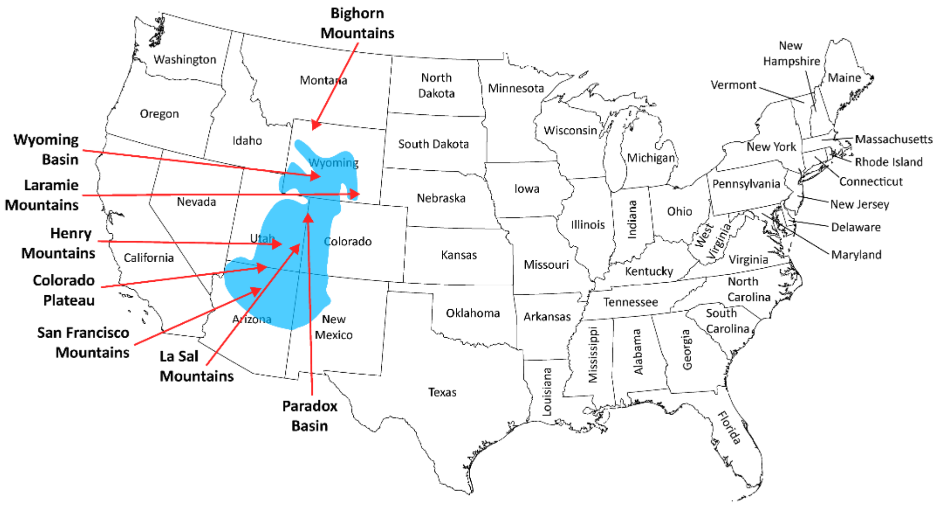

Figure 19 - The Colorado Plateau and Wyoming Basin Groundwater Region (modified from Heath, 1984).

The rocks that underlie the region consist principally of sandstone, shale, and limestone of Paleozoic to Cenozoic age (Figure 20). In parts of the region these rock units include significant amounts of gypsum (calcium sulfate). In the Paradox Basin in western Colorado the rock units include thick deposits of sodium- and potassium-bearing minerals, principally halite (sodium chloride). The sandstones and shales are most prevalent and most extensive in occurrence. The sandstones are the principal sources of ground water in the region and contain water in fractures developed both along bedding planes and across the beds and in interconnected pores. The most productive sandstones are those in which calcium carbonate or other cementing material has been deposited only around the point of contact of the sand grains. Thus, many of the sandstones are only partially cemented and retain significant primary porosity.

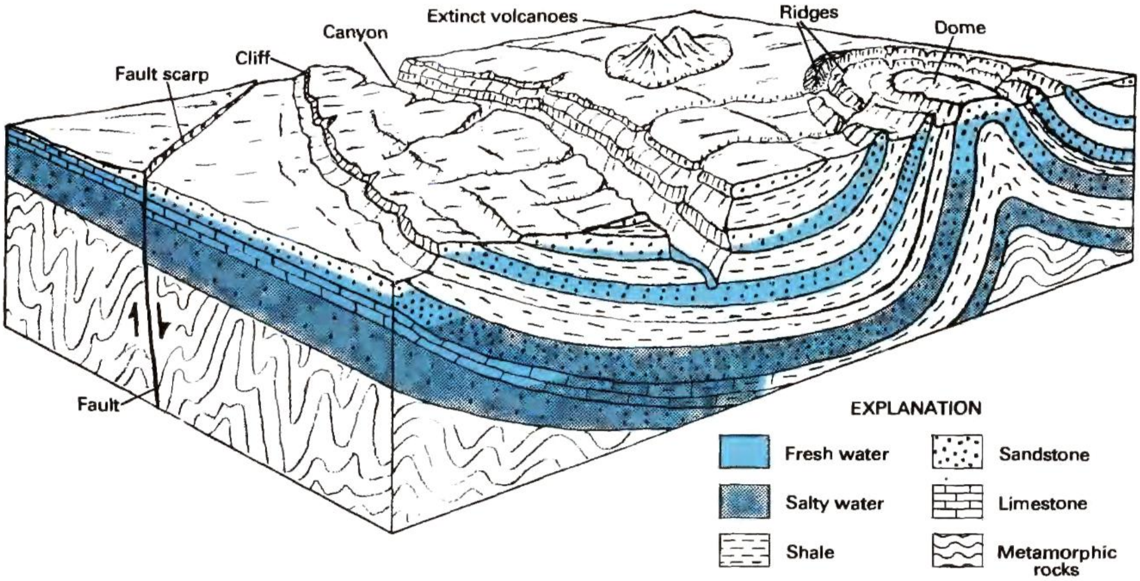

Figure 20 - Topographic and geologic features of the Colorado Plateau and Wyoming Basin region (Modified from Heath, 1984). Blue indicates water bearing zones.

Unconsolidated deposits are of relatively minor importance in this region. Thin deposits of alluvium capable of yielding small to moderate supplies of groundwater occur along parts of the valleys of major streams, especially adjacent to the mountain ranges in the northern and eastern parts of the region. These deposits are partly of glacial origin. In most of the remainder of the region there are large expanses of exposed bedrock, and the soils, where present, are thin and rocky. Erosion has produced extensive lines of prominent cliffs in the region. The tops of these cliffs are generally underlain and protected by resistant sandstones. Erosion of the domes has produced a series of concentric, steeply dipping ridges, also developed on the more resistant sandstones (Figure 20).

Recharge of the sandstone aquifers occurs where they are exposed above the cliffs and in the ridges. Average precipitation ranges from about 150 mm in the lower areas to about 1,000 mm in the higher mountains. The heaviest rainfall occurs in the summer in isolated, intense thunderstorms during which some recharge occurs where intermittent streams flow across sandstone outcrops. However, most recharge occurs in the winter during snowmelt periods. Water moves down the dip of the beds away from the recharge areas to discharge along the channels of major streams through seeps and springs and along the walls of canyons cut by the streams (Figure 20).

End Excerpt from Heath, 1984, pages 32–34.

4.5.1 Groundwater Chemistry of the Colorado Plateau and Wyoming Basin Region

Given the variety of geologic, topographic, and climatic conditions encountered in the Western Mountain Ranges Region, it is not surprising that there are also wide variations in groundwater chemistry. These variations were illustrated by Naftz (1996) in a study of selected aquifers in the Paleogene Rocky Mountains of Wyoming, Colorado, and Utah. In general, the lowest TDS values (<500 mg/L) are found at the highest elevations (>3,000 m) where the aquifers are recharged by rainfall and snowmelt. This recharge water is primarily calcium-magnesium bicarbonate in character reflecting the dissolution of calcite, dolomite, and plagioclase feldspars. As groundwater moves to lower elevations in river valleys (~2,000 m), TDS concentrations increase to up to 3,000 mg/L, concentrations of sulfate increase reflecting dissolution of anhydrite, and concentrations of calcium and magnesium decrease due to cation exchange reactions. Groundwater collected at higher elevations is more suitable for the low-TDS bottled water that Americans generally prefer.

4.5.2 Bottled Water Prospects in the Colorado Plateau and Wyoming Basin Region

The dynamics of bottled water sources from the Colorado Plateau and Wyoming Basin region, are similar to what is found in the Western Mountain Ranges region. Springs and wells that tap aquifers located at higher elevations with low to moderate TDS concentrations are generally favored.

It is common to divide the climatic conditions found in mountainous areas into three distinct zones. The first of these, corresponding to the highest elevation is called the *upper mountain zone* and includes the steepest slopes. Because of its elevation and steepness, sediments and rock fragments from weathering bedrock are washed away faster than they can be formed. Consequently, the land surface tends to be barren, devoid of well-developed soils. Hydrologically, the upper mountain zone is where snow and ice accumulate during the long cold winters. In the spring and summer, meltwater from this snow and ice fills the steep valleys and gullies with cold, clear streams. Because this water begins as snow and has so little time to react with the underlying rocks, it tends to be very cold and have very low concentrations of TDS. These would be a near perfect characteristics for a source of bottled water. The problem, however, is that this water is too transient (spring and summer) and the logistics of collecting it are formidable. For this reason, water from the upper mountain zone is not commonly used for bottling operations.

The *middle mountain zone*, on the other hand, is characterized by extensive weathering caused by freeze-thaw cycles. These rock fragments accumulate along the bases of valleys, forming thick wedges of sediment consisting of boulders and gravels. Such sediments, called colluvium or talus, are extremely porous and very permeable. They soak up water transported from the upper mountain zone and direct them into the subsurface. This groundwater moves to lower elevations, known as the *lower mountain zone,* where it often emerges as springs. It is these springs, rather than the higher-elevation streams, that are more easily utilized as sources of water for bottling (Exercise 6↴).

4.6 High Plains Region

The location of the High Plains Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 21.

Begin Excerpt from Heath, 1984, pages 34–38. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thick alluvial deposits over fractured sedimentary rocks

The High Plains Region occupies an area of 450,000 km^2 extending from South Dakota to Texas. The plains are a remnant of a great alluvial plain built in Miocene time by streams that flowed east from the Rocky Mountains. The plain originally extended from the foot of the mountains to a terminus some hundreds of kilometers east of its present edge. Erosion by streams has removed a large part of the once extensive plain, including all the part adjacent to the mountains, except in a small area in southeastern Wyoming (Figure 21).

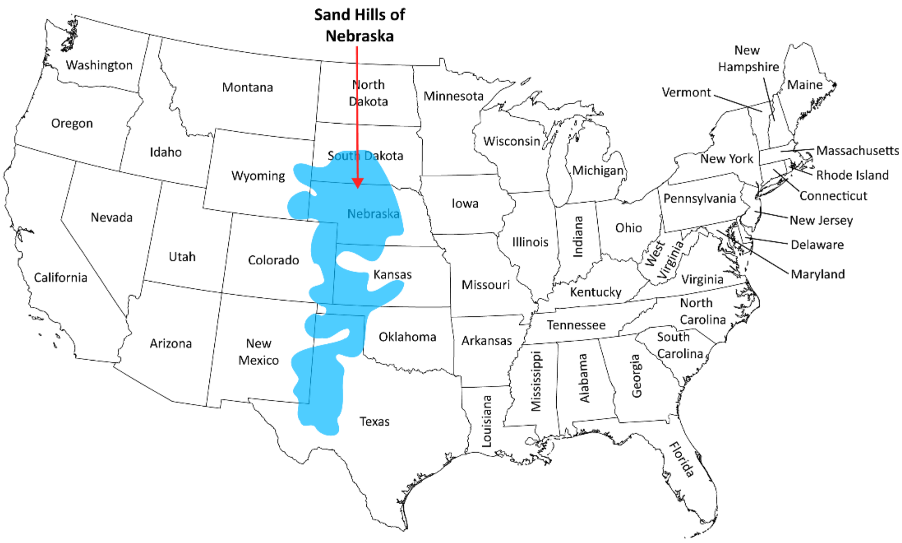

Figure 21 - The High Plains Groundwater Region (modified from Heath, 1984).

The original depositional surface of the alluvial plain is still almost unmodified in large areas, especially in Texas and New Mexico, and forms a flat, imperceptibly eastward-sloping tableland that ranges in altitude from about 2,000 m near the Rocky Mountains to about 500 m along its eastern edge. The surface of the southern High Plains contains numerous shallow circular depressions, called playas, that intermittently contain water following heavy rains. Some geologists believe these depressions are due to the dissolution of soluble materials by percolating water and accompanying compaction of the alluvium. Other significant topographic features include sand dunes, which are especially prevalent in central and northern Nebraska, and wide, down cut valleys of streams that flow eastward across the area from the Rocky Mountains (Figure 22). The High Plains region is underlain by one of the most productive and most intensively developed aquifers in the United States. The alluvial materials derived from the Rocky Mountains, which are referred to as the Ogallala Formation, are the dominant geologic unit of the High Plains aquifer. The Ogallala ranges in thickness from a few meters to more than 200 m and consists of poorly sorted and generally unconsolidated clay, silt, sand, and gravel.

Younger alluvial materials of Quaternary age overlie the Ogallala Formation of late Paleogene age in most parts of the High Plains. Where these deposits are saturated, they form a part of the High Plains aquifer; in parts of south-central Nebraska and central Kansas, where the Ogallala is absent, they comprise the entire aquifer. The Quaternary deposits are composed largely of material derived from the Ogallala and consist of alluvial deposits of gravel, sand, silt, and clay and extensive areas of sand dunes. The most extensive area of dune sand occurs in the Sand Hills area north of the Platte River in Nebraska.

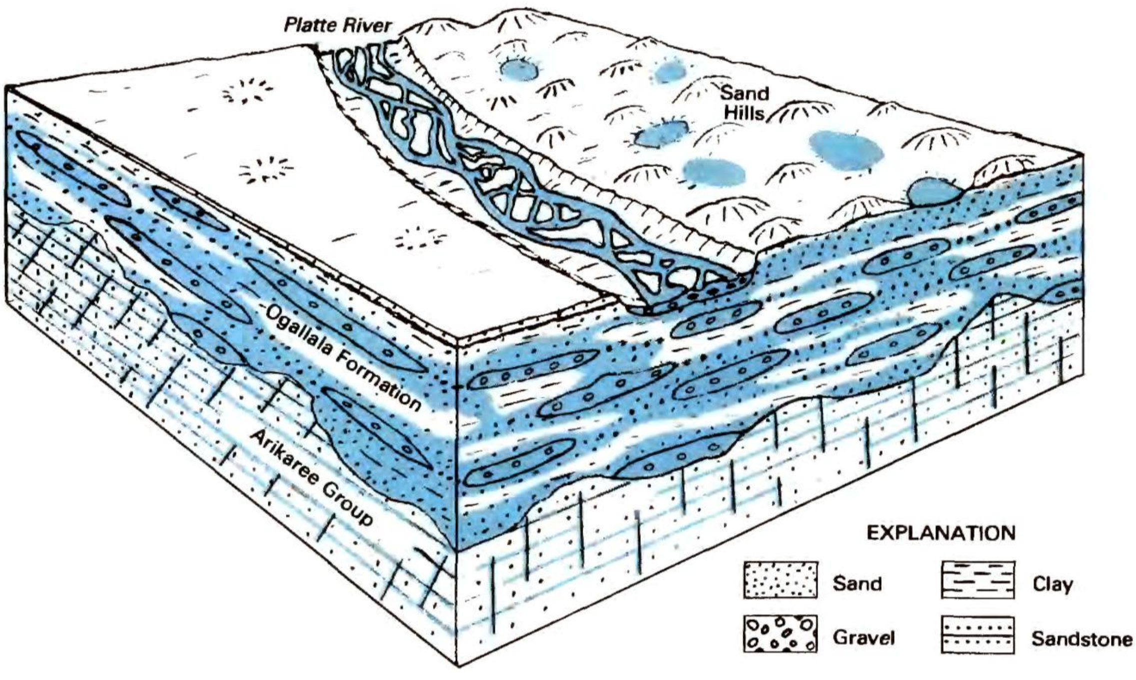

Figure 22 - Topographic and geologic features of the High Plains region (Modified from Heath, 1984). Blue indicates water bearing zones.

Prior to the erosion that removed most of the western part of the Ogallala, the High Plains aquifer was recharged by the streams that flowed onto the plain from the mountains to the west as well as by local precipitation. The only source of recharge now is local precipitation, which ranges from about 400 mm along the western boundary of the region to about 600 mm along the eastern boundary. Precipitation and ground-water recharge on the High Plains vary in an east-west direction, but recharge to the High Plains aquifer also varies in a north-south direction. The average annual rate of recharge has been determined to range from about 5 mm in Texas and New Mexico to about 100 mm in the Sand Hills in Nebraska. This large difference is explained by differences in evaporation and transpiration and by differences in the permeability of the surficial materials.

End Excerpt from Heath, 1984, pages 34–37.

4.6.1 Groundwater Chemistry of the High Plains Region

The aquifers underlying the High Plains Region consists of sands and gravels deposited by streams and rivers flowing out of the Rocky Mountains to the west. Much of the groundwater in the aquifers today was recharged at the end of the last ice age about 10,000 years ago. Groundwater ages based on radiocarbon dating show that much of the water is about 9,000 years old (Gurdak et al., 2009).

It has been estimated that the High Plains aquifers contain more water than Lake Huron and that they produce more water—about 23 trillion m^3 per year—than any other aquifer in North America (McGuire, 2011). Ninety-seven percent of that water is used for agricultural irrigation. From the air, the most striking evidence for this vast amount of irrigation is the giant polka-dot effect of green circular fields that stand out vividly from the surrounding brown plains. These circular fields are the result of the center-pivot irrigation systems that were developed specifically to utilize the High Plains aquifers to support agriculture. Originally, the idea was to drill a well in the center of a 0.16 km^2 (forty-acre) field, pump the water to irrigation lines that were equipped with wheels, and slowly rotate the lines in a huge circle. This allowed water to be spread over the rolling plains more efficiently than with conventional flood irrigation. Over the years, this technology has become increasingly complex to make the best use of available land and water. Nowadays, when flying over the High Plains you can see circular green fields for hundreds of miles in all directions (Figure 23).

Figure 23 - Center pivot irrigation fields and the surrounding brown prairies of the High Plains. U.S. Geological Survey File Photo.

But while the High Plains aquifers excel in terms of groundwater production, it is not always the most desirable drinking water. The amount of TDS in the groundwater ranges from a low of about 100 mg/L in the northern-most parts of the High Plains to more than 2,500 mg/L in areas characterized by upwelling of saline groundwater from underlying geologic units. Evaporation of irrigation groundwater applied to agricultural fields that subsequently recharges the water table also tends to increase TDS concentrations (Gurdak et al., 2009). Agricultural recharge to the underlying aquifers also increases concentrations of nitrate in groundwater, in many places nitrate concentrations are as high as 10 mg/L (Exercise 7⮧).

4.6.2 Bottled Water Prospects in High Plains Region

The relatively high TDS concentrations in groundwater from the High Plains aquifers largely precludes its use as bottled water without TDS-removal treatment. However, as is the case with the Alluvial Basins of the southwest, the high TDS groundwater produces a market for both imported spring water and treated drinking water. Consequently, most bottlers that source from the High Plains aquifers use reverse osmosis or distillation treatment for their products. However, there are several natural spring water bottling operations in the Sand Hills of Nebraska. In this area, TDS concentrations hover around 100 mg/L and provide bottled water products without resorting to TDS-lowering technologies.

4.7 Non-glaciated Central Region

The location of the Non-glaciated Central Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 24.

Begin Excerpt from Heath, 1984, pages 39–42. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thin regolith over fractured sedimentary rocks

The Non-glaciated Central region is an area of about 1,737,000 km^2 extending from the Appalachian Mountains on the east to the Rocky Mountains on the west. The part of the region in eastern Colorado and northeastern New Mexico is separated from the remainder of the region by the High Plains region. The Non-glaciated Central region also includes the Triassic Basins in Virginia and North Carolina and the "driftless" area in Wisconsin, Minnesota, Iowa, and Illinois where glacial deposits, if present, are thin and of no hydrologic importance (Figure 24). The region is a topographically complex area that ranges from the Valley and Ridge section of the Appalachian Mountains on the east westward across the Great Plains to the foot of the Rocky Mountains. It includes, among other hilly and mountainous areas, the Ozark Plateaus in Missouri and Arkansas. Altitudes range from 150 m above sea level in central Tennessee and Kentucky to 1,500 m along the western boundary of the region.

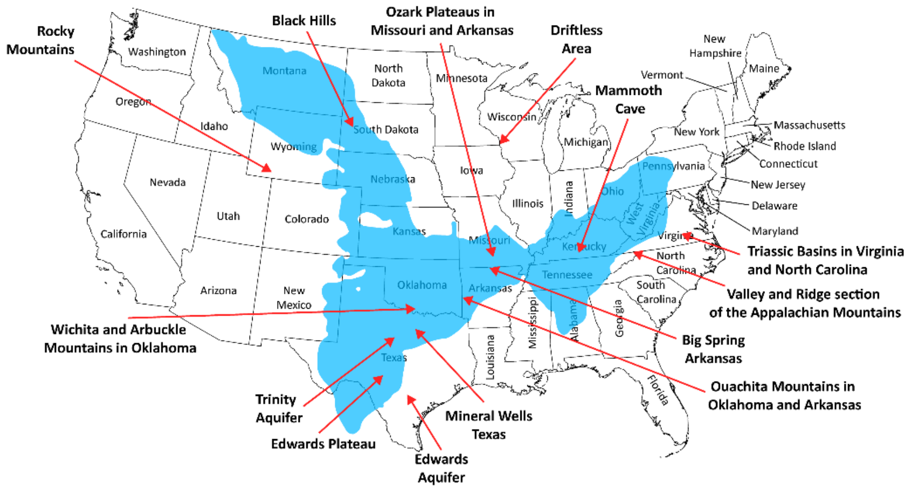

Figure 24 - The Non-glaciated Central Region (modified from Heath, 1984).

The region is also geologically complex. Most of it is underlain by consolidated sedimentary rocks that range in age from Paleozoic to Tertiary and consist largely of sandstone, shale, carbonate rocks (limestone and dolomite), and conglomerate. A small area in Texas and western Oklahoma is underlain by gypsum. Throughout most of the region the rock layers are horizontal or gently dipping (Figure 25). Principal exceptions are the Valley and Ridge section, the Wichita and Arbuckle Mountains in Oklahoma, and the Ouachita Mountains in Oklahoma and Arkansas, in all of which the rocks have been folded and extensively faulted. Around the Black Hills and along the eastern side of the Rocky Mountains the rock layers have been bent up sharply toward the mountains and truncated by erosion (Figure 26). The Triassic Basins in Virginia and North Carolina are underlain by moderate to gently dipping beds of shale and sandstone that have been extensively faulted and invaded by narrow bodies of igneous rock. These basins were formed in Triassic time when major faults in the crystalline rocks of the Piedmont resulted in the formation of structural depressions up to several thousand meters deep and more than 25 km wide and 140 km long.

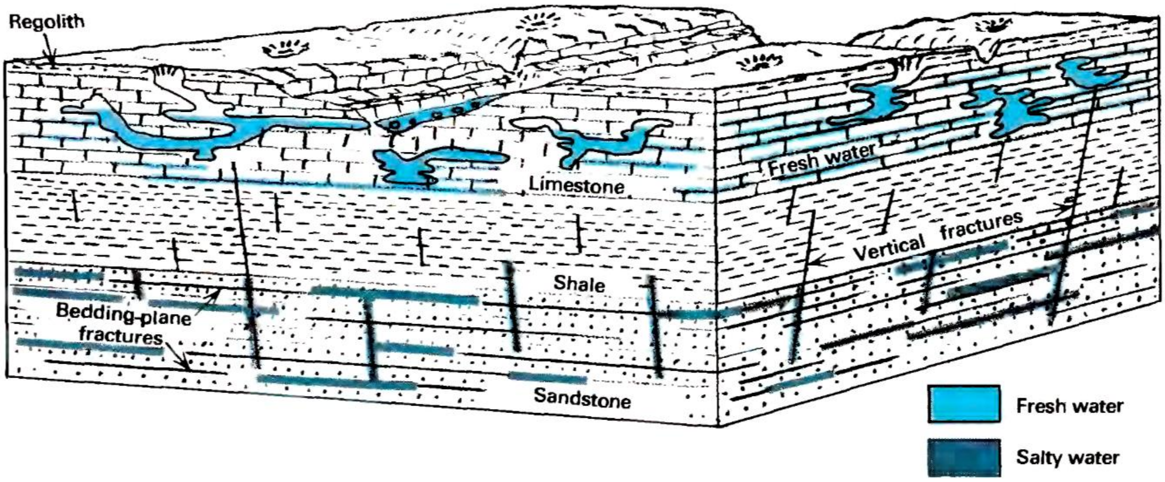

Figure 25 - The Geologic and Topographic Features of the Non-glaciated Central Region (Heath, 1984). Blue indicates water bearing zones.

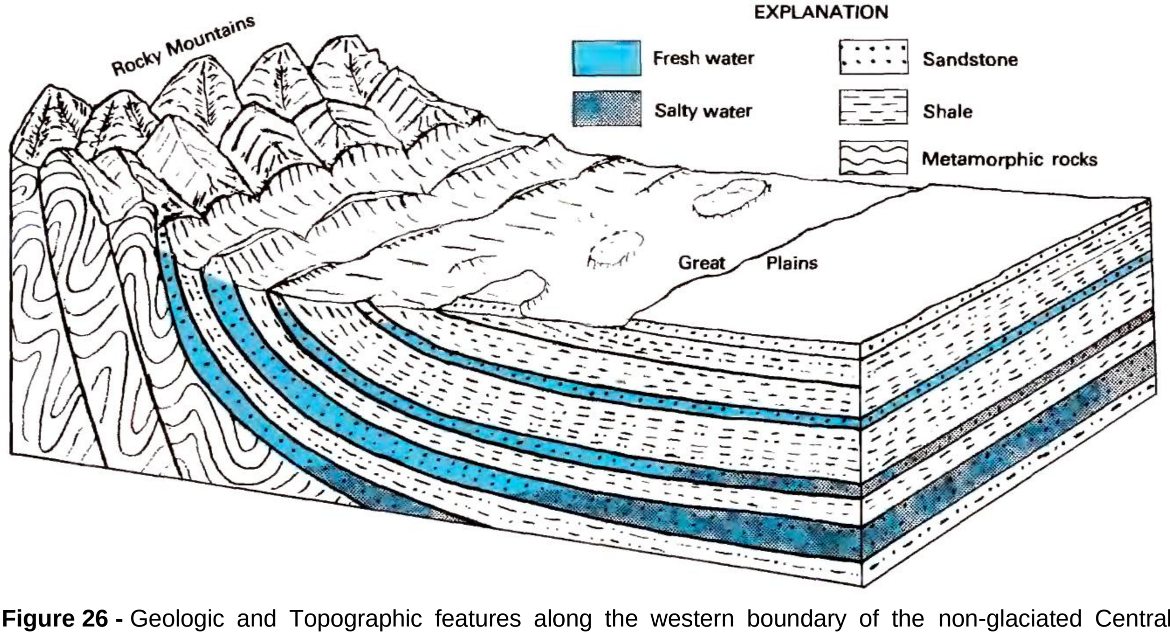

Figure 26 - Geologic and Topographic features along the western boundary of the non-glaciated Central Region (Heath, 1984). Blue indicates water bearing zones.

The land surface in most of the region is underlain by regolith formed by chemical and mechanical breakdown of the bedrock. In the western part of the Great Plains the residual soils are overlain by or intermixed with eolian (wind-laid) deposits. The thickness and composition of the regolith depend on the composition and structure of the parent rock and on the climate, land cover, and topography. In areas underlain by relatively pure limestone, the regolith consists mostly of clay and is generally only a few meters thick. Where the limestones contain chert and in areas underlain by shale and sandstone, the regolith is thicker, up to 30 m or more in some areas. The chert and sand form moderately permeable soils, whereas the soils developed on shale are finer grained and less permeable.

The principal water-bearing openings in the bedrock are fractures along which the rocks have been broken by stresses imposed on the Earth's crust at different times since the rocks were consolidated. The openings developed along most fractures are less than a millimeter wide. The principal exception occurs in limestones and dolomites, which are more soluble in water than most other rocks. Water moving through these rocks gradually enlarges the fractures to form, in time, extensive cavernous openings or cave systems. Cave systems developed in limestones, dolomites, and other carbonate rocks in the United States. Many large springs emerge from these openings; one in this region is Big Spring, in Missouri, which has an average discharge of 36.8 m^3sec^{-1}. Recharge of the groundwater system in this region occurs primarily in the outcrop areas of the bedrock aquifers in the uplands between streams. Precipitation in the region ranges from about 400 mm per year in the western part to more than 1,200 mm in the eastern part. This wide difference in precipitation is reflected in recharge rates, which range from about 5 mm per year in west Texas and New Mexico to as much as 500 mm per year in Pennsylvania and eastern Tennessee. Discharge from the groundwater system is by springs and seepage into streams and by evaporation and transpiration in areas where the water table is within a few meters of land surface. The yield of wells depends on (1) the number and size of fractures that are penetrated and the extent to which they have been enlarged by solution, (2) the rate of recharge, and (3) the storage capacity of the bedrock and regolith. Yields of wells in most of the region are small, in the range of 10 to 1,000 liters per minute (2.6 to 264 gallons per minute), making the Non-glaciated Central region one of the least productive ground-water regions in the country. Even in parts of the areas underlain by cavernous limestone, yields are moderately low because of both the absence of a thick regolith and the large water-transmitting capacity of the cavernous openings which quickly discharge the water that reaches them during periods of recharge.

The exceptions to the small well yields are the cavernous limestones of the Edwards Plateau, the Ozark Plateaus, and the Ridge and Valley section. The Edwards Plateau in Texas is bounded on the south by the Balcones Fault Zone, in which limestone and dolomite up to 150 m in thickness has been extensively faulted. The faulting has facilitated the development of solution openings which makes this zone one of the most productive aquifers in the country. Wells of the City of San Antonio are in this zone; individually, they have yields of more than 60 m^3min^{-1}. In most of the Non-glaciated Central Region, except the Ozark Plateaus, the Ouachita and Arbuckle Mountains, and the Ridge and Valley section, the water in the bedrock contains more than 1,000 mg/L of dissolved solids at depths greater than 150 m (Figure 25).

End Excerpt from Heath, 1984, pages 39–42.

4.7.1 Groundwater Chemistry of the Non-glaciated Central Region

Because of the great diversity of groundwater systems in the Non-glaciated Central Region, there is also a great diversity in the groundwater chemistry as well. However, since the focus of this book is bottled spring water, we can narrow down our consideration to the carbonate aquifers found in this region. The reason for this is that springs and wells tapping carbonate aquifers account for most of the water judged to be suitable for bottling in this region. These aquifers include the Edwards-Trinity aquifer of Texas, the Springfield Plateau and Ozark aquifers of Arkansas and Missouri, the Mississippian aquifers of Tennessee, and the Valley and Ridge aquifers of Tennessee and Virginia.

Carbonate aquifers are most commonly composed of the mineral calcite ($CaCO_3$) and/or the mineral dolomite ($CaMg(CO_3)_2$). In arid climates that lack abundant rainfall such as the southwestern United States, carbonate geologic formations are relatively resistant to chemical and mechanical erosion and often form prominent ridges and hills. In humid climates, such as the eastern portions of the Non-glaciated Central Region, however, carbonate minerals are subject to efficient chemical weathering by carbon dioxide (CO_2) driven dissolution as shown in Equations (1) and (2).

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + + 2HCO_3 \quad (1)$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3 \quad (2)$$

The principal source of the carbon dioxide is from the organic-rich soils characteristic of the humid Midwest. Rain falling on the soils dissolves carbon dioxide and transports it to the underlying carbonate rocks, driving their dissolution. That dissolution, in turn, leads to the creation of solution channels that vastly increases the hydraulic conductivity of carbonate aquifers. It also leads to the formation of vast underground cave systems such as Mammoth Cave in Kentucky (White, 1989). Mammoth Cave is the longest cave system known in the world. Due to limestone and dolomite dissolution, the chemistry of carbonate aquifers is dominated by calcium and magnesium bicarbonate-type water. In some places the presence of gypsum, pyrite, and other sulfur compounds leads to the development of calcium-magnesium-bicarbonate-sulfate type water.

The carbonate Trinity and Edwards aquifers of Texas are both predominantly calcium-magnesium-bicarbonate type water although there are some differences between the two systems. Rocks of the Edwards aquifer are lithologically and chemically more uniform than those of the Trinity aquifer and this is reflected in observed TDS concentrations. The median TDS concentration for the Trinity aquifer is 550 mg/L. In the unconfined Edwards aquifer, on the other hand, the median TDS concentration is considerably lower being about 280 mg/L. In some places the Edwards exhibits a more calcium-magnesium-chloride or calcium-magnesium sulfate character. This is usually associated with the saline-water transition zone or involves contributions from underlying aquifers (Sharp & Green, 2022). In the confined part of the Edwards aquifer (including springs) the median TDS is higher at about 300 mg/L. In the portion of the Edwards aquifer located in urban areas, the median TDS is 328 mg/L (Fahlquist & Ardis, 2004).

Rain that falls on the Springfield and Ozark Plateaus seeps into fractures and crevices of the limestones and dolomites, dissolving and enlarging them over time (Figure 25). The downward movement of this water is ultimately impeded by the underlying basement rocks, and groundwater flow is directed laterally toward the foot of the plateaus. There groundwater discharges from hundreds of springs. Some of these springs, such as Big Spring in Arkansas, have spectacularly large flows that emerge from openings enlarged by the dissolution of the limestones and dolomites (Figure 27). These springs have been used as water supply for as long as humans have been in North America.

Figure 27 - Big Spring, Arkansas (From the U.S. National Park Service).

Springs issuing from the carbonate aquifers of the Springfield and Ozark Plateaus have median TDS values of about 200 mg/L and 280 mg/L respectively. Median TDS values in water from drilled wells in those two units are 220 mg/L and 240 mg/L respectively (Berndt et al., 2005).

The groundwater chemistry in the Valley and Ridge aquifers is influenced by natural and anthropogenic factors. Natural factors, such as topographic position and mineral composition of underlying geology, influence properties such as pH, temperature, specific conductance, and alkalinity. Anthropogenic factors, such as land use and surface contamination, can contribute nutrients, pesticides, pesticide degradation products, dissolved organic carbon, volatile organic carbon compounds, and fecal-indicator bacteria to groundwater. In addition, land use can influence surface and soil properties and thus aquifer recharge. Recharge, in turn, can influence residence time, dissolved oxygen, and pH (Johnson et al., 2011).

Carbonate-rock aquifers in the Valley and Ridge section consist mainly of fractured limestone and dolomite with localized solution-enlarged conduits. Siliciclastic-rock aquifers consist primarily of fractured sandstone but some are fractured shale . The water chemistry of these two broad classes of aquifers differs substantially. The median TDS concentrations found in six different carbonate aquifers was about 400 mg/L, whereas median TDS concentrations in three siliciclastic aquifers was significantly lower at about 200 mg/L. Unsurprisingly, median hardness values of carbonate aquifers were much higher (~175 mg/L as $CaCO_3$) than in siliciclastic aquifers (~85 mg/L as $CaCO_3$) (Exercise 8↴).

4.7.2 Bottled Water Prospects in the Non-glaciated Central Region

There is a long history of bottled water production in the Non-glaciated Central Region, particularly in the springs that develop at the base of carbonate mountains in the eastern parts of the region. One such spring in Arkansas, called Eureka Springs, has a particularly interesting history. According to legend, sometime around 1800 an Osage Indian chieftain brought his daughter, who was suffering from an eye affliction, to the springs. When she bathed her eyes in the spring water her sight was miraculously restored. This story was picked up by a gentleman calling himself Dr. Jackson, who began bottling the water under the name “Dr. Jackson’s Eye Water” in the 1870s. Rumors of miraculous healings began circulating, and people flocked to Eureka Springs to partake of the water. Eureka Springs was incorporated as a city in 1880, and by 1889 it had become the second largest city in Arkansas behind Little Rock.

Another notable bottled water operation traces its beginnings in 1877 when the Lynch family moved west from Denison, Texas searching for a drier climate to help with the unpleasant symptoms they were suffering from rheumatism. They settled in a valley 80 kilometers (50 miles) west of Fort Worth, Texas, where the climate was noticeably drier than that of Denison. The valley was located about six and a half kilometers (four miles) from the Brazos River, the only nearby source of water. In 1880, tired of hauling water from the river, Lynch hired a driller to drill a well. Water was found about thirty meters (~100 feet) below land surface and the well was completed there. At first, the Lynches were suspicious of the water because it tasted strange. So, rather than drinking it immediately, they gave it to their cows and waited to see if the "strange" taste was something poisonous. The cows drank the water happily and did not show any adverse effects, and so the Lynches began drinking the water themselves. As the story goes, Mr. and Mrs. Lynch's rheumatism began to abate, and word quickly got out that this was "healing" water. Soon people began coming to the well to "take the waters." So many people came that Mr. Lynch laid out a town he called Mineral Wells in 1881, and appointed himself the town's mayor. This makes a good story, but from a scientific point of view it has the obvious flaw that Lynch's original idea was to cure their rheumatism with the drier climate in their valley. So, whether the "cures" were wrought by the water or by the drier climate or by a placebo effect, remains an open question.

By 1882, a stagecoach line began operations linking the terminus of the Texas and Pacific Railroad to Mineral Wells. Soon, thousands of people were coming to Mineral Wells seeking cures for a variety of ailments. In 1885, one Billy Wiggins drilled another well in town. An elderly woman suffering from some kind of mental issues, drank water from the well and reputedly her ailment subsided. An eyewitness account of this story was given later by a man named R. L. Yeager (Fowler, 1991):

> I was about ten years old at that time and recall very vividly the "Crazy Woman." She was my father's patient and would go to the then Uncle Billy Wiggins Well and sit around under the shade of the adjacent trees and drink the water when it was brought to her…the school children, learning that the woman wasn't exactly right in the mind, children-like, got to referring to her as the crazy woman, and because of the fact that she could always be seen by them sitting near the Wiggins well, began referring to it as the Crazy Woman Well. I remember distinctly now that in the course of weeks the woman began to get better and when she left here she was greatly improved. After she left, the Wiggins well was still referred to as the Crazy Well.

The name took hold and "The Crazy Well" is the name that the well bears to this day. Businesses such as hotels, sanitoriums, bathing houses and water-drinking establishments boomed. By 1920, there were more than four hundred wells in and around the town of Mineral Wells.

All of this history and legend aside, the groundwater produced in and near Mineral Wells is also interesting for its hydrology and geochemistry, which was first studied in the early 1930s by the U.S. Geological Survey (Turner, 1934). The sedimentary rocks underlying the town of Mineral Wells, are Pennsylvanian in age and dip steeply to the northwest. The principal water-producing bed is called the Brazos River conglomerate member of the Garner Formation. The lower portion of this member is characterized by a coarse conglomerate but further up-section, lenses of sandstones, mudstones, and limestones are encountered (Fisher, Mace, & Boghici, 1996).

Hydrologically, most of the groundwater production is from the conglomerate member, which serves as the principal aquifer. The groundwater chemistry of the aquifer is unusual. Groundwater produced from the deepest part of the conglomerate aquifer has the lowest concentrations of dissolved solids (735 mg/L) whereas groundwater from progressively shallower depths becomes more mineralized (4,200 mg/L) (Table 6). That is contrary to the usual pattern that groundwater becomes more mineralized with depth. The analyses of Table 6 are from water samples collected from wells located 800 meters apart and are roughly on strike with the dipping beds. The difference is that well 123 is drilled to a depth of 98 meters (322 feet) and that well 105 is drilled to a depth of 61 meters (202 feet) (Table 6). The shallower groundwater has higher TDS than the deeper groundwater from the Brazos River conglomerate member. This unusual pattern probably reflects the lenses of mudstone and limestones that are found in the upper parts of the Brazos River Conglomerate.

Table 6 - Groundwater chemistry of groundwater produced from two wells completed in the Brazos Conglomerate, Mineral Wells, Texas (Data from Turner, 1934).

Well number	Drilled depth (m)	Date	Ca	Mg	Na	HCO_3	SO_4	Cl	TDS
123	98	1931	37	49	169	422	190	84	735
105	61	1931	200	158	974	606	2,308	260	4,200

Groundwater from Mineral Wells was bottled and sold nationwide in the early twentieth century. However, with the flagging demand for bottled water as the twentieth century progressed, and the relative unpopularity of mineral water in the United States, most companies that bottled water from Mineral Wells went out of business in the 1930s. Today, only one bottled water company is active in Mineral Wells. Interestingly, its marketing takes advantage of the depth-dependent TDS concentrations. The deeper, lower TDS water is sold as *The Famous Mineral Water Company No. 2, Low/ Medium content* (TDS 685), whereas the shallower, higher TDS water is sold as *The Famous Mineral Water Company No. 4, High Content* (TDS 2,763) (https://visitmineralwells.org/top_ten/the-famous-mineral-water-company↗).

4.8 Glaciated Central Region

The location of the Glaciated Central Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 29.

Begin Excerpt from Heath, 1984, pages 43–46. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by glacial deposits over fractured sedimentary rocks

The Glaciated Central region occupies an area of 1,297,000 km^2 extending from the Triassic Basin in Connecticut and Massachusetts and the Catskill Mountains in New York on the east to the northern part of the Great Plains in Montana on the west (Figure 28).

Figure 28 - The Glaciated Central Region (modified from Heath, 1984).

The part of the region in New York and Pennsylvania is characterized by rolling hills and low, rounded mountains that reach altitudes of 1,500 m. Westward across Ohio to the western boundary of the region along the Missouri River, the region is flat to gently rolling. Among the more prominent topographic features in this part of the region are low, relatively continuous ridges (moraines) which were formed at the margins of ice sheets that moved southward across the area one or more times during the Pleistocene (Figure 29). The Glaciated Central Region is underlain by relatively flat-lying consolidated sedimentary rocks that range in age from Paleozoic to Tertiary. They consist primarily of sandstone, shale, limestone, and dolomite. The bedrock is overlain by glacial deposits which, in most of the area, consist chiefly of till, an unsorted mixture of rock particles deposited directly by the ice sheets. The till is interbedded with and overlain by sand and gravel deposited by meltwater streams, by silt and clay deposited in glacial lakes, and, in large parts of the North Central States, by loess, a well-sorted silt believed to have been deposited primarily by the wind (Figure 29).

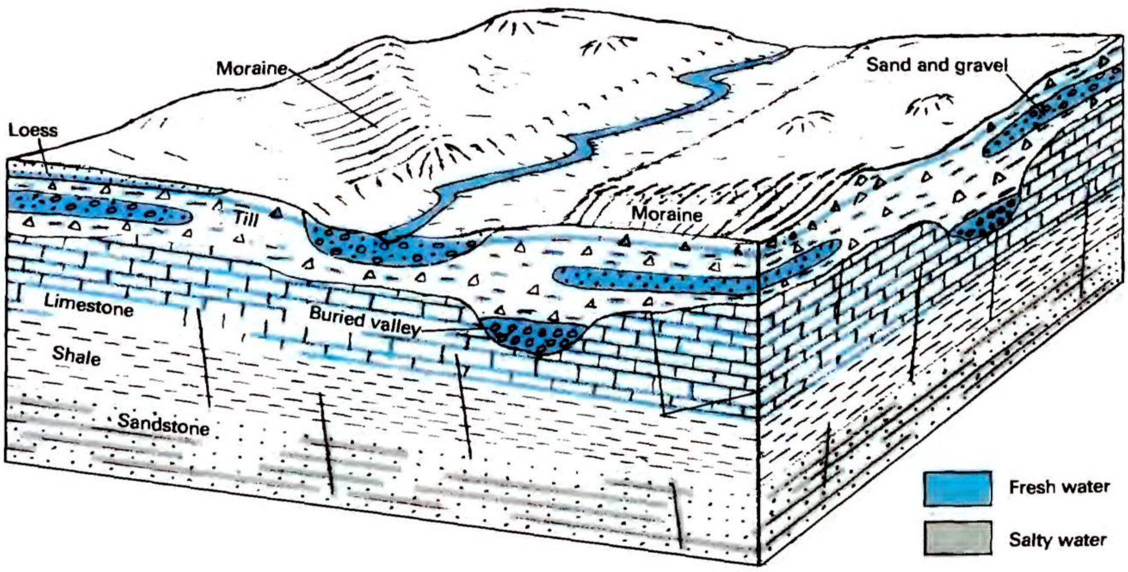

Figure 29 - Topographic and geologic features of the Glaciated Central region (Heath, 1984). *Blue indicates water bearing zones.

On the Catskill Mountains and other uplands in the eastern part of the region, the glacial deposits are typically only a few to several meters thick, but localized deposits as much as 30 m thick are common on southerly slopes. In much of the central and western parts of the region, the glacial deposits exceed 100 m in thickness. The principal exception is the “driftless” area in Wisconsin, Minnesota, Iowa, and Illinois, where the ice, if it invaded the area, was too thin to erode preexisting soils or to deposit a significant thickness of till. Thus, the bedrock in this area is overlain by thin soils derived primarily from weathering of the rock. This area, both geologically and hydrologically, resembles the Non-glaciated Central region and is, therefore, included as part of that region.

The glacial deposits are thickest in the valleys on the bedrock surface. Thicknesses of 100 to 300 m occur in the valleys of the Finger Lakes in New York. In most of the region westward from Ohio to the Dakotas, the thickness of the glacial deposits exceeds the relief on the preglacial surface, with the result that the locations of valleys and stream channels in the preglacial surface are no longer discernible from the land surface. The glacial deposits in valleys include, in addition to till and lacustrine silts and clays, substantial thicknesses of highly permeable sand and gravel (Figure 29).

Ground water occurs both in the glacial deposits and in the bedrock. Water occurs in the glacial deposits in pores between the rock particles and in the bedrock primarily along fractures. The dominant water-bearing fractures in the bedrock are along bedding planes. Water also occurs in the bedrock in steeply dipping fractures that cut across the beds and, in some sandstones and conglomerates, in primary pores that were not destroyed in the process of cementation and consolidation. Large parts of the region are underlain by limestones and dolomites in which the fractures have been enlarged by solution. Caves are relatively common in the limestones where the ice sheets were relatively thin, as near the southern boundary of the region and in the "driftless" area (Figure 25). A few caves occur in other parts of the region, notably in the Mohawk River valley in central New York, where they were apparently protected from glacial erosion by the configuration of the bedrock surface over which the ice moved. However, on the whole, caves and other large solution openings, from which large springs emerge and which yield large quantities of water to wells in parts of the Non-glaciated Central Region, are much less numerous and hydrologically much less important in the Glaciated Central Region (Figure 25).

End Excerpt from Heath, 1984, pages 43–46.

4.8.1 Groundwater Chemistry of the Glaciated Central Region

Because of the great diversity of groundwater systems in the Glaciated Central Region, there is also great diversity in the groundwater chemistry as well. Since the focus of this book is on bottled water, we can narrow our consideration to the glacial aquifers found in this region. Much of the spring water bottled in this region is sourced from glacial aquifers. Good examples of spring water bottled from glacial aquifer springs are found in Michigan, of which the northern part of the state is mantled in glacial tills (fine-grained silts and clays), sands, and gravels found in numerous lateral moraines. Examples of glacially derived springs which are presently bottled, or have been in the past, include Evart, White Pine, and Sanctuary springs located in the northwestern part of Michigan's Lower Peninsula.

Although they were not formed by wind, the moraines are sometimes referred to as dunes. An example of how the hydrology of these dune aquifer systems work was given by Shedlock and others (1994) as illustrated in Figure 30. The aquifers are recharged by rainfall at topographic highs corresponding to lateral or border moraines, and groundwater moves downward until it encounters low hydraulic conductivity glacial till sediments. Often, as groundwater moves laterally, it emerges as springs at the contact between high-hydraulic conductivity sands and low-hydraulic conductivity glacial tills. Many of those springs form marshes that are drained by streams containing clear, cold water. Those streams are important to sportsmen because they support large populations of native brook trout.

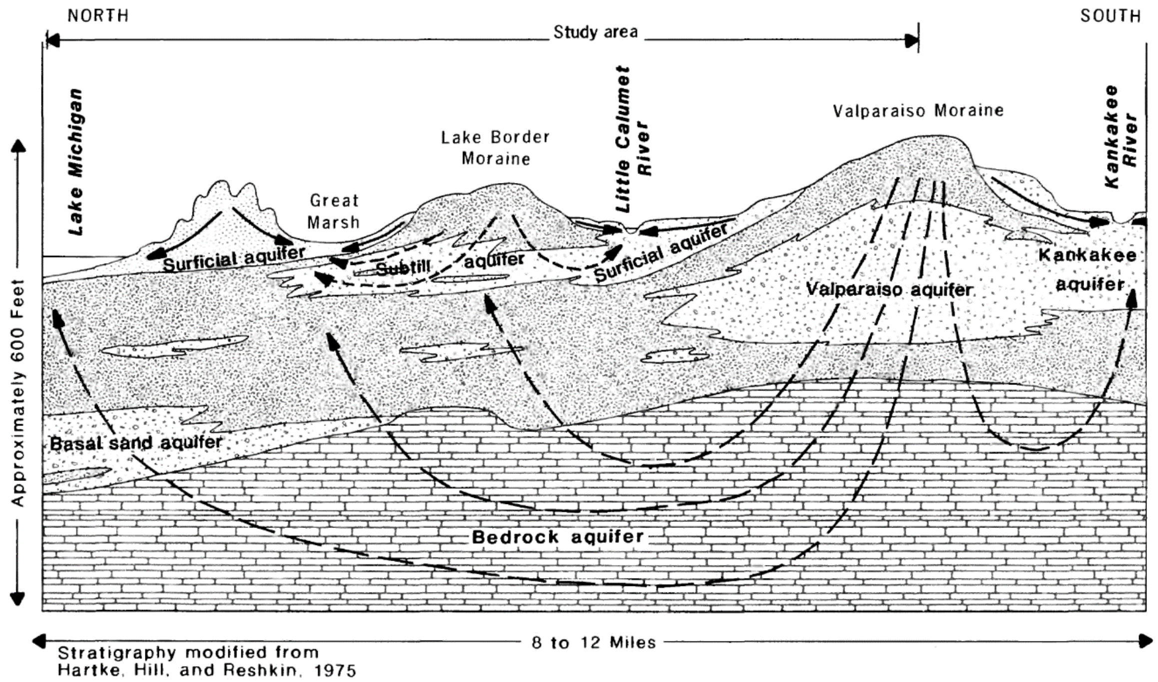

Figure 30 - Diagrammatic hydrogeologic sections showing conceptual ground-water flow in the Indiana Dunes National Lakeshore, northwestern Indiana (Adapted from Shedlock et al., 1994).

The chemical composition of groundwater in the glacial sediments depends on sediment type—clayey till, moraine sands, or gravels—and the distance that the groundwater has flowed following recharge. Because the bedrock aquifers underlying much of the Glaciated Central Region are carbonate/dolomite formations, the glaciers moving over the bedrock picked up carbonate debris and deposited it as till or moraines. The groundwater chemistry of the glacial aquifers is largely controlled by exposure to carbonate/dolomite debris in glacial sediments. In general, springs fed by groundwater flowing through moraine sands over relatively short distances (1–5 km) tend to be less mineralized (TDS~270 mg/L). Springs fed by groundwater with more contact with glacial tills and longer flow paths tend to be more mineralized (TDS~450 mg/L). Most of the groundwater is calcium magnesium bicarbonate in character with calcium concentrations in the 40–60 mg/L range, magnesium concentrations in the 30–40 mg/L range, and bicarbonate concentrations in the 340–445 mg/L range (Shedlock et al., 1994). Also, because of the relatively high concentrations of calcium and magnesium, glacial aquifer groundwater tends to be hard (180–320 mg/L as $CaCO_3$).

Not surprisingly, the chemistry of most bottled water sourced from glacial aquifers tend to be on the low end of those concentration ranges. Evart Spring in Michigan, which is one source of bottled spring water, has low calcium (46–77 mg/L), magnesium (15–31 mg/L), and bicarbonate (195–378 mg/L) concentrations (Exercise 9↴).

4.8.2 Bottled Water Prospects in the Glaciated Central Region

The unique hydrology of springs in the Glaciated Central Region, in which rainfall recharges the aquifers at topographic highs with the groundwater discharging to marshes, streams or rivers at topographic lows (Figure 30) after moving short distances (<10 km), has created controversy for some local bottled water operations. Because collecting water from natural springs at land surface introduces the possibility of bacterial or chemical contamination, the Food and Drug Administration (FDA) which regulates bottled water in America, prefers water to be sourced from finished wells rather than from spring outlets. However, withdrawing water from shallow glacial aquifers by pumping can reduce groundwater discharge to adjacent marshlands and streams with possibly adverse ecological effects. Concern about this issue has affected several bottled water operations throughout the Glaciated Central Region, particularly in the State of Michigan.

The effects of groundwater pumping on stream flows are largely a function how much rain or snow falls on a basin, and the area of that basin. Consider a hypothetical ground-water basin located in a glacial terrain with an area of one square kilometer being drained by a single small stream. In much of the Glaciated Central Region, annual precipitation (both rain and snowfall) is typically about 1,524 millimeters (60 inches). Approximately 305 mm (12 inches) of that precipitation reaches the water table and recharges the underlying glacial aquifer. Given a recharge area of one square kilometer, a total of $3x10^9$ liters of water is recharging the aquifer every year, or 100 liters per second (LPS). That recharge (100 LPS) is, on average, discharged to and carried away by the stream. In the United States, streamflow is usually expressed in units of cubic feet per second (CFS), and 100 LPS equals 3.5 CFS, which is a very small stream. If a well is drilled adjacent to the stream and pumps 10 LPS (158 gallons per minute) it would reduce the streamflow from 100 to 90 LPS and could negatively impact the ecology of that stream. So, concern about the effects of groundwater pumping on surface water bodies is warranted.

One square kilometer is a very small basin, which is why it produces such a small stream. If the area of a basin is 10 square kilometers (still a small basin), the streamflow would be more substantial (1,000 LPS) and a well pumping 10 LPS would reduce the streamflow to 990 LPS. That reduction is likely immeasurable and the pumping would not have any noticeable effect on the ecology of the stream. In much of the Glaciated Central Region, therefore, springs (or wells tapping the aquifer feeding springs) for bottling water typically tap basins that are greater than 10 square kilometers in area to avoid deleterious effects of groundwater withdrawal.

4.9 Piedmont Blue Ridge Region

The location of the Piedmont Blue Rudge Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 31.

Begin Excerpt from Heath, 1984, pages 46–48. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify

locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thick regolith over fractured crystalline and metamorphosed sedimentary rocks

The Piedmont and Blue Ridge Region is an area of about 247,000 km^2 extending from Alabama on the south to Pennsylvania on the north (Figure 31). The Piedmont part of the region consists of low, rounded hills and long, rolling, northeast-southwest trending ridges whose summits range from about a hundred meters above sea level along its eastern boundary with the Coastal Plain to 500 to 600 m along its boundary with the Blue Ridge area to the west. The Blue Ridge is mountainous and includes the highest peaks east of the Mississippi. The mountains, some of which reach altitudes of more than 2,000 m, have smooth-rounded outlines and are bordered by well-graded streams flowing in relatively narrow valleys.

Figure 31 - The Piedmont Blue Ridge Region (modified from Heath, 1984).

The Piedmont and Blue Ridge Region is underlain by bedrock of Precambrian and Paleozoic age consisting of igneous and metamorphosed igneous and sedimentary rocks. These include granite, gneiss, schist, quartzite, slate, marble, and phyllite. The land surface in the Piedmont and Blue Ridge is underlain by clay-rich, unconsolidated material derived from in situ weathering of the underlying bedrock. This material, which averages about 10 to 20 m in thickness and may be as much as 100 m thick on some ridges, is referred to as saprolite. In many valleys, especially those of larger streams, flood plains are underlain by thin, moderately well-sorted alluvium deposited by the streams. When the distinction between saprolite and alluvium is not important, the term regolith is used to refer to the layer of unconsolidated deposits.

The regolith contains water in pore spaces between rock particles. The bedrock, on the other hand, does not have any significant intergranular porosity. It contains water, instead, in sheetlike openings formed along fractures—that is, breaks in the otherwise "solid" rock (Figure 32). The hydraulic conductivities of the regolith and the bedrock are similar and range from about 0.001 to 1 m per day. The major difference in their water-bearing characteristics is their porosities, that of regolith being about 20 to 30 percent and that of the bedrock about 0.01 to 2 percent (Figure 32). Small supplies of water adequate for domestic needs can be obtained from the regolith through large-diameter bored or dug wells. However, most wells, especially those where moderate supplies of water are needed, are relatively small in diameter and are cased through the regolith and finished with open holes in the bedrock. Although, as noted, the hydraulic conductivity of the bedrock is like that of the regolith, bedrock wells generally have much larger yields than regolith wells because, being deeper, they have a much larger available drawdown.

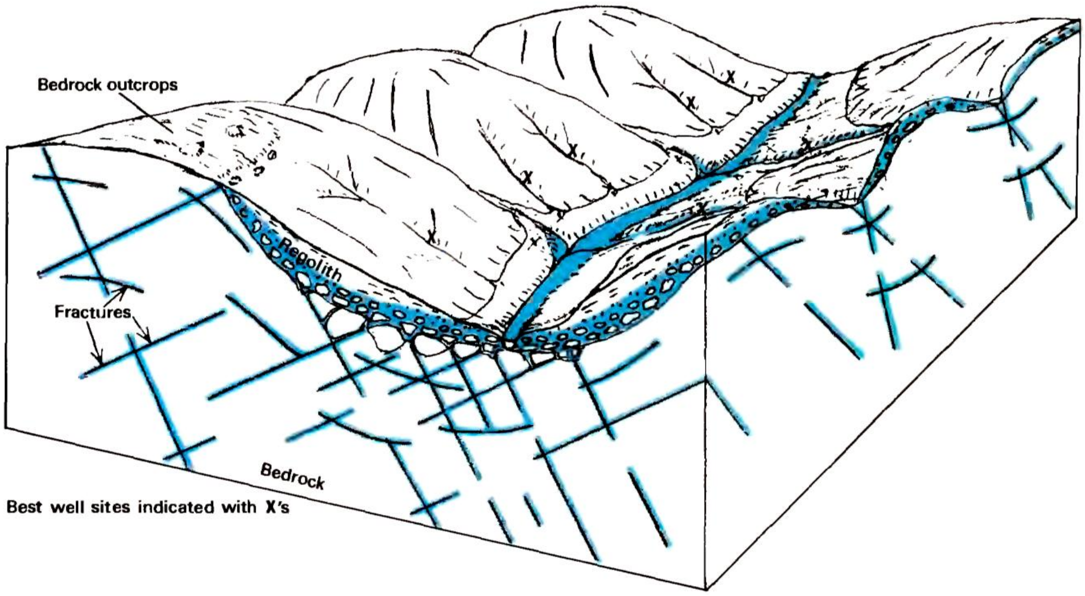

Figure 32 - Topographic and geologic features of the Piedmont and Blue Ridge Region (Heath, 1984). *Blue indicates water bearing zones.

All groundwater systems function both as reservoirs that store water and as pipelines (or conduits) that transmit water from recharge areas to discharge areas. The yield of bedrock wells in the Piedmont and Blue Ridge region depends on the number and size of fractures penetrated by the open hole and on the replenishment of the fractures by seepage into them from the overlying regolith. Thus, the ground-water system in this region can be viewed, from the standpoint of groundwater development, as a terrane in which the reservoir and pipeline functions are effectively separated. Because of its larger porosity, the regolith functions as a reservoir which slowly feeds water downward into the fractures in the bedrock. The fractures serve as an intricate interconnected network of pipelines that transmit water either to springs or streams, or to wells.

End Excerpt from Heath, 1984, pages 46–48.

4.9.1 Groundwater Chemistry of the Piedmont and Blue Ridge Region

The ancient (~550 million-year) fractured metamorphic rocks that make up much of the Piedmont and Blue Ridge Region with groundwater flow largely occurring in fractures (Figure 32) has a marked effect on the chemistry of groundwater. Because of the high temperatures of regional metamorphism over the millennia, the minerals present in the rocks have been rendered relatively unreactive to groundwater. Furthermore, the relatively high flow rates in fractures tends to minimize contact time between groundwater and rocks. For those reasons, much of the groundwater in this region tends to be relatively unmineralized. In the piedmont of South Carolina, median concentrations of TDS in groundwater are 25 mg/L, hardness of 6.4 mg/L as $CaCO_3$, and a slightly acidic pH of 5.7 (Mitchell, 2004). While more mineralized groundwater occurs, relatively unmineralized groundwater is the rule rather than the exception.

4.9.2 Bottled Water Prospects in the Piedmont and Blue Ridge Region

The abundant springs found in the Piedmont and Blue Ridge Region have a long history of use by humans, first by Native Americans and later by European settlers. Georgia is famous for its red clay which is a weathering product of the underlying metamorphic rocks. Rainwater is acidic (pH~5) and dissolves the silica out of the metamorphic rocks over time leaving behind a soft, porous, residue called saprolite that retains some of the structures of the parent metamorphic rock. This red saprolite mantles much of the Piedmont and Blue Ridge Region south of Pennsylvania (further north it was scraped off by glaciers) and acts like a gigantic sponge, storing vast quantities of groundwater. The saprolite is also an excellent filter, cleansing the groundwater of surface contaminants and microorganisms. Eventually, this saprolite-cleansed water seeps into the network of fractures present in the underlying metamorphic rocks. These fractures serve as conduits, moving groundwater rapidly through the subsurface. Springs develop where these water-bearing fractures intersect the land surface in valleys. These saprolite-filtered springs often produce water that is cool, clear, and excellent for drinking. Native Americans used these springs for thousands of years, and the Scotch-Irish settlers who arrived in the eighteenth century followed suit. One such spring, Pleasant Springs of Tiger, Georgia, has served as the source for bottled water since 1997. Pleasant Springs is located near Black Rock Mountain State Park. It is Georgia's highest elevation state park and is noted for its several waterfalls fed by springs discharging groundwater from fractures.

Spring water used for bottling in the nineteenth century almost always had reputations for healing properties. Water from the Whitestone Spring in the piedmont of South Carolina acquired its healing reputation early in the nineteenth century. Chemical analyses conducted early in the twentieth century indicated that the water had measurable concentrations of lithium, and this was used in marketing water bottled from the spring. A modern analysis of the spring water, however, indicates that lithium concentrations are below the detection level (0.02 mg/L) as measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (Table 7).

Table 7 - Chemistry of Whitestone Spring Groundwater (Data from the Author).

Dissolved Component	Concentration (mg/L)
Bicarbonate	76.4
Hardness (as CaCO3)	194
Sulfate	<0.02
Calcium	75.6
Magnesium	2.2
Lithium	<0.02
Sodium	7.3
Iron	~0.3
Total Dissolved Solids (TDS)	162
Fecal Coliform (CFU/100 ml)	<1
pH	7.5

Located near the city of Spartanburg, by the early twentieth century Whitestone Spring was attracting enough visitors that a hotel with guestrooms for 500 people was built. The hotel burned down some years later and the bottling operations ceased, but the ruins of the hotel and the building used to bottle water can still be seen in Croft State Park in South Carolina. The spring outlet and the foundations of the water-bottling plant can still be visited (Figure 33), although it is a three-mile hike from the closest trailhead. The presence of the yellowish minerals precipitating below the spring outlet, suggests dissolved iron concentrations of approximately 0.3 mg/L which may explain the "irony" taste of the raw water (Exercise 10⤵).

Figure 33 - Whitestone Spring with the discharge pipe used for bottling operations in the early 20th century (Photo by the Author).

The low concentrations of TDS, the relative softness of the water (Whitestone Spring is an exception), makes spring water from the Piedmont and Blue Ridge Region generally attractive for bottling water. Working against it is the fact that many of the springs, like many drilled wells, do not have sufficiently high flows to make bottling feasible.

4.10 The Atlantic and Gulf Coastal Plain Region

The location of the Atlantic and Gulf Coastal Plain Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 34.

Begin Excerpt from Heath, 1984, pages 52–55. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by complexly interbedded sand, silt, and clay

The Atlantic and Gulf Coastal Plain Region is an area of about 844,000 km^2 extending from Cape Cod, Massachusetts, on the north to the Rio Grande in Texas on the south. This region does not include Florida and parts of the adjacent States; although those areas are a part of the Atlantic and Gulf Coastal Plain physiographic province, they form a separate ground-water region (Figure 34).

Figure 34 - The Atlantic and Gulf Coastal Plain Region (Heath, 1984).

The Atlantic and Gulf Coastal Plain region ranges in width from a few kilometers near its northern end to nearly a thousand kilometers in the vicinity of the Mississippi River. The great width near the Mississippi reflects the effect of a major down-warped zone in the Earth's crust that extends from the Gulf of Mexico to about the confluence of the Mississippi and Ohio Rivers. This area is referred to as the Mississippi embayment.

The topography of the region ranges from extensive, flat, coastal swamps and marshes 1 to 2 m above sea level to rolling uplands, 100 to 250 m above sea level, along the inner margin of the region.

The region is underlain by unconsolidated sediments that consist principally of sand, silt, and clay transported by streams from the adjoining uplands. These sediments, which range in age from Jurassic to the present, range in thickness from less than a meter near the inner edge of the region to more than 12,000 m in southern Louisiana. The greatest thicknesses are along the seaward edge of the region and along the axis of the Mississippi embayment. The sediments were deposited on floodplains and as deltas where streams reached the coast and, during different invasions of the region by the sea, were reworked by waves and ocean currents. Thus, the sediments are complexly interbedded to the extent that most of the named geologic units into which they have been divided contain layers of the different types of sediment that underlie the region. These named geologic units (i.e., geologic formations) dip toward the coast or toward the axis of the Mississippi embayment, with the result that those that crop out at the surface form a series of bands roughly parallel to the coast or to the axis of the embayment (Figure 35). The oldest formations crop out along the inner margin of the region, and the youngest crop out in the coastal area.

Within any formation the coarsest grained materials—sand, at places interbedded with thin gravel layers—tend to be most abundant near source areas. Clay and silt layers become thicker and more numerous downdip (Figure 35).

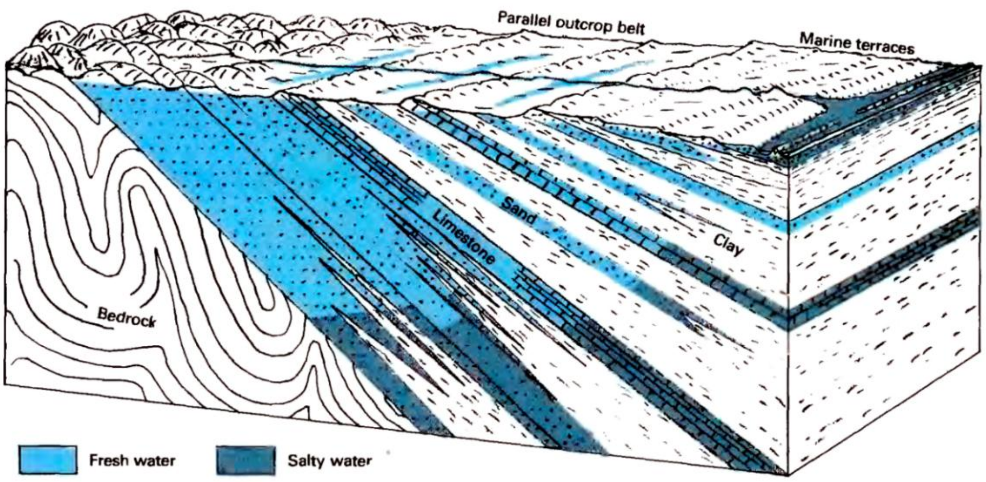

Figure 35 - Topographic and Geologic Features of the Atlantic and Gulf Coastal Plain (Heath, 1984). *Blue indicates water bearing zones.

From the standpoint of well yields and groundwater use, the Atlantic and Gulf Coastal Plain is one of the most important regions in the country. Recharge to the groundwater system occurs in the interstream areas, both where sand layers crop out and by percolation downward across the interbedded clay and silt layers. Discharge from the system occurs by seepage to streams, estuaries, and the ocean. Movement of water from recharge areas to discharge areas is controlled, as in all ground-water systems, by hydraulic gradients, but in this region the pattern of movement is complicated by downdip thickening of clay which hampers upward discharge. As a result, movement down the dip of the permeable layers becomes increasingly slow with increasing distance from the outcrop areas. This causes many flow lines to converge on the discharge areas located on major streams near the downdip part of outcrop areas.

Wells that yield moderate to large quantities of water can be constructed almost anywhere in the region. Because most of the aquifers consist of unconsolidated sand, wells require screens; where the sand is fine-grained and well sorted, the common practice is to surround the screens with a coarse sand or gravel envelope.

End Excerpt from Heath, 1984, pages 52–55.

4.10.1 Hydrology and Groundwater Chemistry of the Atlantic and Gulf Coastal Plain Region

The Atlantic and Gulf Coastal Plain Region consists of a wedge-shaped body of sediments that, from Georgia to the north, dip gently toward the Atlantic Ocean (Figure 35). The Gulf Coast sediments are also wedge-shaped that, from Louisiana westward dip to the south toward the Gulf of Mexico. Since all these sediments were originally deposited horizontally, the characteristic dip is due to tectonic uplift of the underlying basement rocks that outcrop in the Piedmont and Blue Ridge physiographic provinces. This uplift, which has been ongoing since Miocene time (~23 million years), leads to aquifer recharge occurring in outcrop areas with groundwater flow being directed downdip as in the Middendorf Aquifer shown in Figure 36.

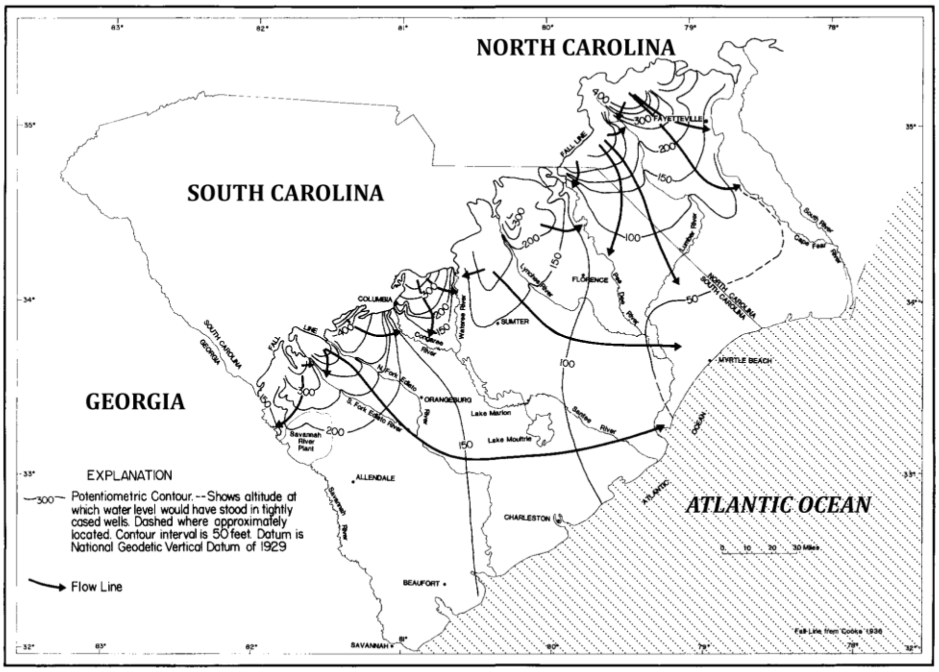

Figure 36 - Water levels in the Middendorf Aquifer of South Carolina, with the resulting groundwater flow moving generally in a downdip direction toward the Atlantic Ocean (Adapted from Aucott & Speiran, 1985).

The water chemistry changes systematically as groundwater moves downgradient. A good example of this is how water chemistry in the Aquia aquifer of southern Maryland changes from being relatively low TDS dominated by calcium bicarbonate in the outcrop area to a high TDS water dominated by sodium and bicarbonate (Figure 37) (Chapelle & Knobel, 1983).

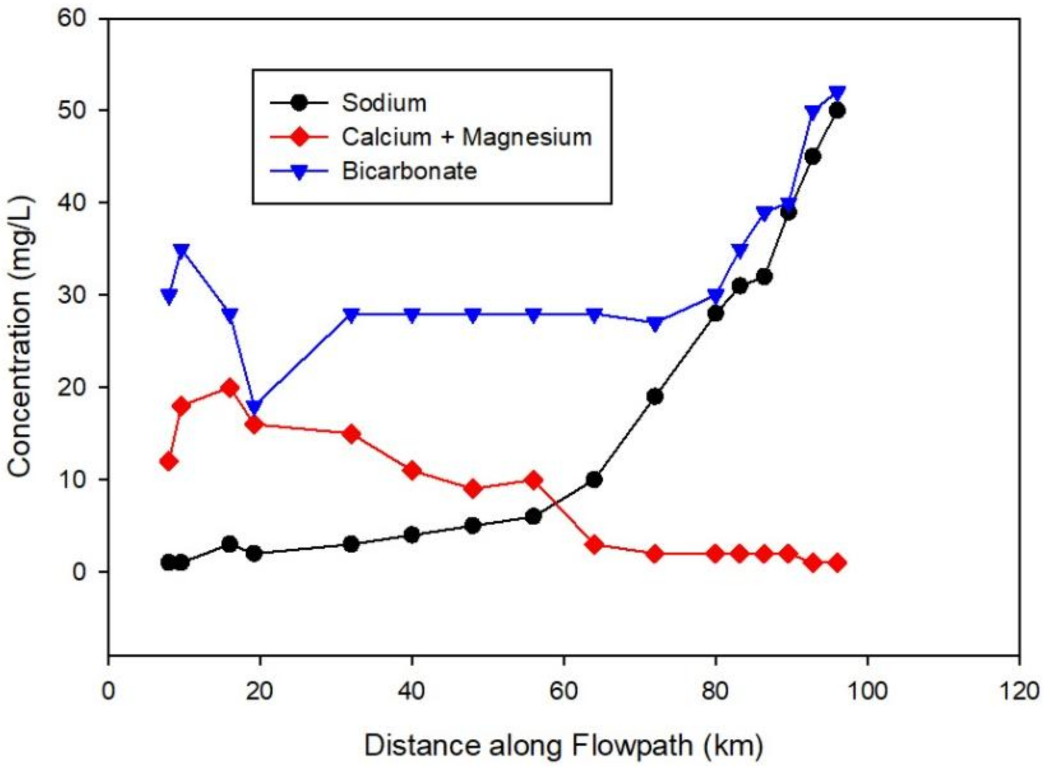

Figure 37 - Water chemistry changes along the flowpath of the Aquia aquifer in Maryland (Adapted from Chapelle & Knobel, 1983).

This pattern, which is almost ubiquitous in aquifers of the Atlantic Coastal plain, illustrates the concept of what has been termed *hydrochemical facies* in the literature (Back, 1966). These facies, or zones, begin with a calcium bicarbonate water near the recharge area due to the dissolution of carbonate or silicate minerals (zone 1, Figure 38). As groundwater flows downgradient, cation exchange reactions on clay mineral surfaces adsorb calcium ions and release sodium ions (zone 2, Figure 38). Further downgradient mineral dissolution continues, increasing TDS concentrations and leading to the precipitation of other minerals, often calcite (zone 3, Figure 38). Finally at the most downgradient zone, fresh groundwater mixes with connate seawater creating a sodium chloride brine (Exercise 11↴).

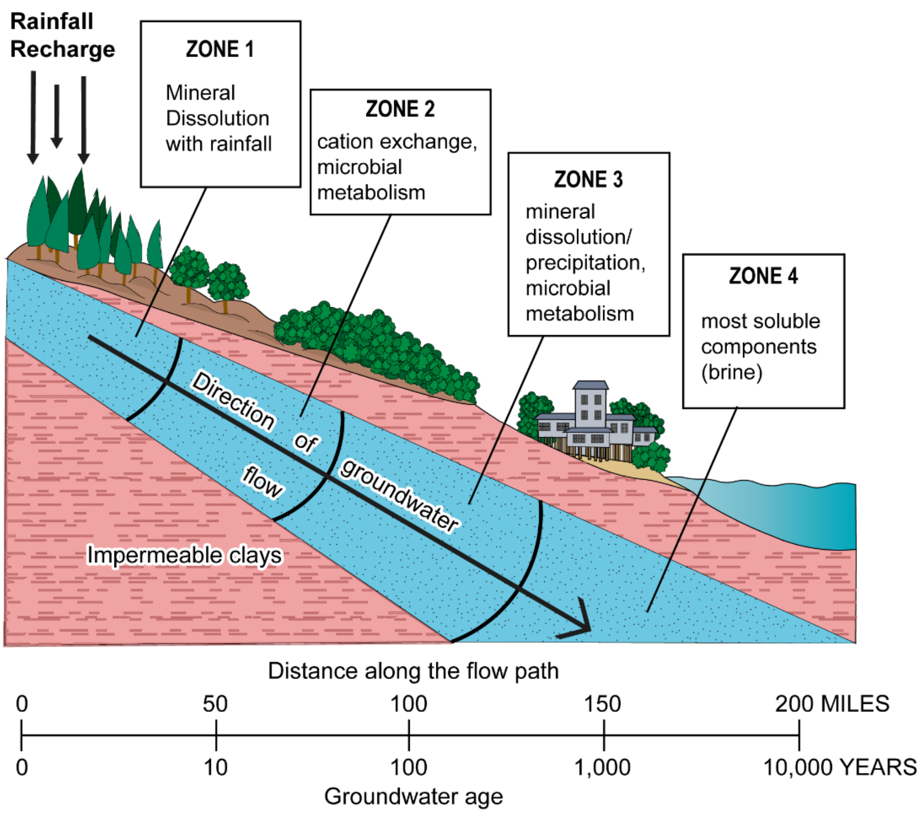

Figure 38 - Hydrochemical zonation typical of coastal plain aquifers as outlined by Back (1966).

4.10.2 Hydrology and Geochemistry of Camp Holly Springs, Virginia

The American preference for low-TDS bottled water tends to restrict bottling operations to zone 1 of Figure 38. An example of a zone 1 spring is Camp Holly Springs located just south of Richmond, Virginia. The word “camp” in Camp Holly Springs reflects the history of human use of the spring. The spring outlet is on the side of a hill, and for thousands of years was used as a campsite by Native Americans. Because of the convenience of having a source of clean water, the site was also used as a military encampment for troops during the Revolutionary War, the War of 1812, and the Civil War. Beginning in 1923, bottling operations began with the spring water being distributed mainly to Richmond. In 1954, a man named Roland Dowdy purchased the spring and began bottling operations in 1962. The spring and the bottling operation has remained in the Dowdy family to this day.

The surficial aquifer in the vicinity of Camp Holly Spring consists of Pliocene and Pleistocene (~5 million years ago) sediments that were deposited as a series of marine terraces. These deposits were laid down in nearshore, fluvial-estuarine environments and consist of pebble gravels, sands, and sandy clays. The terraces were formed during periods of high sea-level stands during interglacial periods in Pleistocene time. The sands and gravels form a productive aquifer that is recharged directly by precipitation and thus corresponds to zone 1 of a typical coastal plain aquifer (Figure 38). The terrace surfaces range in altitude from 3 to 55 meters above sea level, and much of the recharge occurs at the higher elevations. The groundwater flows downgradient from topographic highs, discharging to seeps, streams, and springs of which Camp Holly Spring is one. It is possible that the discharge of water to Camp Holly Spring, which is visibly larger than most of the seeps and small springs in the area, is structurally influenced by an underlying high-angle reverse fault known as the Dutch Gap Fault (Dischinger, 1987).

The water chemistry of Camp Holly Springs shows a low-TDS, low-hardness, sodium chloride-type water (Table 8). That, in turn, reflects the fluvial-marine nature of the Plio-Pleistocene sediments that make up the shallow aquifer. That also reflects the humid, subtropical climate of Virginia with an average rainfall of 1,100 mm per year that has flushed much of the sodium and chloride out of the sediments since the deposition of the last marine terrace approximately 80,000 years ago. The resulting low TDS groundwater ideally suits the American taste for low-TDS bottled water.

Table 8 - Chemistry of Camp Holly Springs Groundwater

(data from http://www.campghollysprings.com/water-quality-report↗).

Dissolved Component	Concentration (mg/L)
Bicarbonate	<1
Chloride	11
Hardness (as $CaCO_3$)	4.5
Sulfate	1.1
Calcium	1.8
Magnesium	3.2
Potassium	1.7
Sodium	5.8
Total Dissolved Solids (TDS)	36
pH	5.5

4.10.3 History of Healing Spring, South Carolina

Just after daybreak, an old-model car with a beat-up finish pulled into the dirt parking lot and stopped next to a small headstone. At first glance, the headstone appeared to mark a grave. The driver, a woman who looked to be about 50 years old, stepped out of the car, walked around to the back, and opened her trunk. In the trunk were ten or twelve empty milk jugs. One by one, she carried the jugs down to the spring, which was hidden by the early morning mists. She filled them with bubbling spring water and returned them to the car. In a few minutes the water jugs were filled and neatly arranged in her trunk. She got back into the car, started it, and pulled away from the headstone, which, as it happens, did not mark a grave. The headstone reads:

God's Acre
Healing Springs
Deeded to Almighty God,
To be used by the sick and afflicted
by
L.P. "Lute" Boylston
July 21, 1944

Anywhere from a dozen to more than 200 people a day—depending on the weather and season—visit Healing Springs, located near the little town of Blackville, South Carolina. Most of these people bring an assortment of jugs and bottles to be filled with water for use at home (Figure 39). Some wade or even bathe in the shallow pools that surround the springs. These springs, like hundreds of others throughout the United States, are the stuff of local legend and history.

Figure 39 - The spigots Lute Boylston installed at Healing Springs of South Carolina to collect bottled water between 1907 and 1910 (Photo by the author).

In 1781, during the American Revolutionary War, British soldiers made a raid on some suspected patriots near Blackville. The skirmish that followed, called the Battle of Slaughter Field, left sixteen patriots killed and seven British soldiers badly wounded as documented by the Barnwell County, South Carolina, Virtual Museum↗. The British soldiers were so badly wounded that they could not be taken back to Charleston. The British commander left the wounded men at Healing Springs, along with two uninjured soldiers who had orders to bury them when they died. Instead, the wounded soldiers drank the spring water, bathed, and rested. In a few weeks, all seven walked into Charleston and returned to duty, their wounds healed.

The legend grew over the years, and in 1907 a gentlemen named Lute Boylston, the owner of the springs, tried to capitalize on the water's fame by bottling and selling it to local merchants. There was ample precedent for this. Saratoga Springs, Poland Spring, and water from countless other springs had been bottled and sold for much of the nineteenth century as healing water. However, by 1907 demand for curative bottled water in the United States was waning. It seems that by then, medical science had advanced to the point that there was less of a demand for miraculous water cures. The spigots that Boylston installed at depth to collect the spring water hygienically can still be seen today (Figure 39) and visitors still use them to fill their bottles with spring water. However, after three hard years of work collecting the water in green glass bottles—which are collector's items today—and hauling them to Charleston and other towns, the Healing Springs Bottling Company went out of business.

Nonetheless the renown of the Healing Springs water in the countryside around Blackville continued to grow, so much so that Boylston began to worry what would happen to the springs when he died. Convinced that the water was a gift from God, Boylston had the novel idea of giving it back to the Almighty. In his will, which was executed in 1944, one acre of land surrounding the springs was left to God. The deed in the county courthouse lists the owner of the property as "God Almighty."

4.10.4 Hydrology and Geochemistry of Healing Springs, South Carolina

The Healing Springs are in the Upper Coastal Plain physiographic province, and their hydrogeologic setting is much different than that of Camp Holly Springs in Virginia. The sediments immediately underlying the springs are Eocene in age (60 to 34 million years ago) and consist of sand, silt, and clay sediments of fluvial deltaic origin. Underlying the fluvial deltaic sediments are limestones, also of Eocene age. Groundwater produced from fluvial deltaic sediments are characterized by maximum calcium concentrations of 8.7 mg/L, magnesium concentrations 4.2 mg/L, and bicarbonate concentrations of 17 mg/L. In contrast, groundwater produced from the Eocene limestones is more mineralized with maximum calcium concentrations of 47 mg/L, magnesium concentrations of 9.4 mg/L and bicarbonate concentrations of 171 mg/L (Siple, 1967).

Groundwater issuing from the Healing Springs exhibits calcium concentrations of 32.2 mg/L, magnesium concentrations of 0.628 mg/, and bicarbonate concentrations of ~200 mg/L (Table 9). It seems unlikely, therefore that Healing Springs groundwater originates in the fluvial Eocene sands. Rather, it seems more likely it originates, at least in part, from the underlying Eocene limestones. That is supported by groundwater age dates (time since recharge) based on carbon 14 and carbon 13 analyses (Table 9) of between 4,000 and 3,000 years before present (Peter Stone, South Carolina Department of Health and Environmental Control (SCDHEC) written communication, 2024).

Table 9 - Chemistry of Healing Springs Groundwater (Data from author).

Dissolved Component	Concentration (mg/L)
Bicarbonate	101
Chloride	<5
Hardness (as $CaCO_3$)	100
Calcium	32.2
Magnesium	0.628
Sodium	1.4
Total Dissolved Solids (TDS)	146
pH	7.35
^{14}C (percent modern carbon)	41.2
$\delta\ ^{13}C$ (per mil)	-13.7

Somewhat understandably, SCDHEC is uncomfortable with people filling bottles with water for drinking purposes, and regularly monitors the springs for a variety of chemical and microbial contaminants. To date, the groundwater has always tested negative for fecal microorganisms. That, in turn, is also consistent with the notion that the spring water comes from a deeper source than the fluvial Eocene sands present at land surface.

It is possible that high-angle compressional reverse faults, which developed in the vicinity of Healing Springs during Cretaceous and Paleogene time (Faye & Prowell, 1982), may provide a conduit for upward groundwater flow from the deeper Eocene calcareous sediments to the Healing Springs. If so, it would provide an explanation for the relatively ancient, higher pH, calcium, and bicarbonate concentrations free of fecal microorganisms. Yarborough (2010) sampled Healing Springs groundwater and constructed slurries of distilled water with Eocene sediments collected near the Springs. A statistical comparison of calcium and magnesium concentrations in spring water and slurry water concluded that it was unlikely that Healing Springs groundwater could have originated solely in the fluvial Eocene sediments.

The mystic stories surrounding the Healing Springs of South Carolina, as well as the hydrologic uncertainty as to the source of the water, are typical of many springs that were once used as sources for bottled water in the United States.

4.11 The Southeast Coastal Plain Region

The location of the Southeast Coastal Plain Region is shown with all groundwater regions of the USA in Figure 2 and is the blue area of Figure 40.

Begin Excerpt from Heath, 1984, pages 55–58. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by thick layers of sand and clay over semi-consolidated carbonate rocks

The Southeast Coastal Plain is an area of about 212,000 km^2 in Alabama, Florida, Georgia, and South Carolina (Figure 40). It is a relatively flat, low-lying area in which altitudes range from sea level at the coast to about 100 m down the center of the Florida peninsula and as much as 200 m on hills in Georgia near the interior boundary of the region. Much of the area, including the Everglades in southern Florida, is a nearly flat plain less than 10 m above sea level.

Figure 40 - The Southeast Coastal Plain Region (Heath, 1984).

The land surface of the Southeast Coastal Plain is underlain by unconsolidated deposits of Pleistocene age consisting of sand, gravel, clay, and shell beds and, in southeastern Florida, by semi-consolidated limestone. From the coast up to altitudes of nearly 100 m, the surficial deposits are associated with marine terraces formed when the Coastal Plain was inundated at different times by the sea. In most of the region the surficial deposits rest on formations, primarily of middle to late Miocene age, composed of interbedded clay, sand, and limestone. The most extensive Miocene deposit is the Hawthorn Formation (Figure 41). The formation is of middle to late Miocene age and, where those formations are absent, the surficial deposits overlie semi-consolidated limestones and dolomites that are as much as 1,500 m thick. These carbonate rocks range in age from Paleocene to early Miocene and are generally referred to collectively as Tertiary limestones.

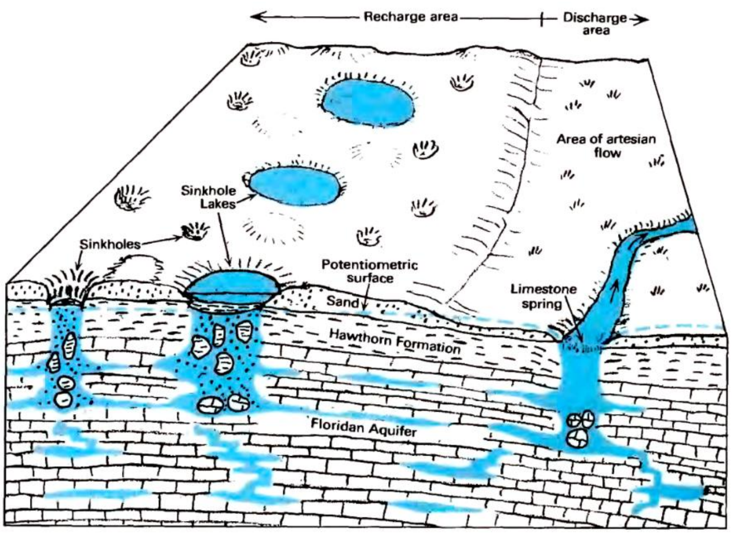

Figure 41 - Topographic and geologic features of the Southeast Coastal Plain Region (Heath, 1984). *Blue indicates water bearing zones.

The Tertiary limestone that underlies the Southeast Coastal Plain constitutes one of the most productive aquifers in the United States and is the feature that justifies treatment of the region separately from the remainder of the Atlantic and Gulf Coastal Plain. The aquifer, which is known as the Floridan aquifer, underlies all of Florida and southeast Georgia and small areas in Alabama and South Carolina. The Floridan aquifer consists of layers several meters thick composed largely of loose aggregations of shells of foraminifera and fragments of echinoids and other marine organisms interbedded with much thinner layers of cemented and cherty limestone. The Floridan, one of the most productive aquifers in the world, is the principal source of groundwater supplies in the Southeast Coastal Plain Region.

End Excerpt from Heath, 1984, pages 55–58.

4.11.1 Hydrology and Groundwater Chemistry of the Southeast Coastal Plain Region

Florida, which encompasses much of the Southeast Coastal Plain Region, has a geologic history that favors the development of springs, some of which produce water that is particularly desirable as drinking water. What is now Florida has been on the trailing edge of North America as the continent has drifted north and west over geologic time. Because of this, tectonic forces have not produced mountain-building activity near Florida for a long time. Beginning in Cretaceous time (130 to 65 million years ago), a large shallow sea covered all of what is now Florida. Because there were no mountains nearby to produce sand, silt, or clay, the seafloor was covered mostly with the shells of marine organisms. These included corals, foraminifera, clams, and snails, all of which have shells made of calcium carbonate. Over millions of years, this shell material accumulated into thick beds of limestone, the weight of which depressed the underlying crust, forming several basin structures. This, in turn, allowed carbonate material to accumulate to as much as 3,000 meters in thickness.

These basins tend to be warped and bent, with some areas subsiding more others, and some areas being pushed upward. One of these upward-bending structures known as the *Peninsular Arch*, now extends down the center of the Florida Peninsula (Miller, 1986). Over the last 20 million years, the Peninsular Arch has subsided less than the Georgia Embayment to the west, Southeast Georgia embayment to the north, and the South Florida Basin to the south. In more recent times, the Peninsular Arch has been pushed upward slightly, raising it about 30 meters above sea level and forming the Florida that we see today.

Florida has a tropical climate with abundant rainfall averaging 1,790 millimeters per year. In many parts of the world, much of this water would collect into surface streams and rivers and be carried off to the ocean. But not in Florida. Because the underlying limestones are so porous and permeable, and because slightly acidic rainfall actively dissolves limestone creating cavernous flow, most of the rainwater seeps directly into the ground through sinkholes (Figure 41). In effect, the Peninsular Arch acts as a large recharge area for the underlying Floridan aquifer. Once in the ground, the water is carried off to the ocean beneath the land surface, not over it. How this groundwater is discharged is affected by how confined the Floridan aquifer is. In the southern part of Florida, much of the aquifer occurs under confined conditions (Figure 42). Where the overlying confining bed is thin or absent, a significant amount of discharge occurs as springs. These springs, in turn, have been an important source of bottled water in Florida.

Figure 42 - The areal extent of the Floridan Aquifer, the confined and unconfined parts of the aquifer, and the location of the flow path from Avon Park to Fort Ogden (Base map adapted from the U.S. Geological Survey).

Calcite, the most abundant mineral in the Floridan aquifer system, ranges in composition from stoichiometric calcite ($CaCO_3$) to magnesian calcite ($Ca\ 0.96Mg\ 0.04\ CO_3$). Dolomite ($CaMg(CO_3))_2$ is also present in some horizons, along with gypsum ($CaSO_4$). Given this mineralogy, it is not surprising that much of Floridan groundwater is calcium-magnesium-bicarbonate-sulfate in character. The geochemical evolution from Avon Park, located on the Peninsular Arch in the recharge area, to Fort Ogden (Figure 42) located near the discharge area on the Gulf Coast is shown in Figure 43.

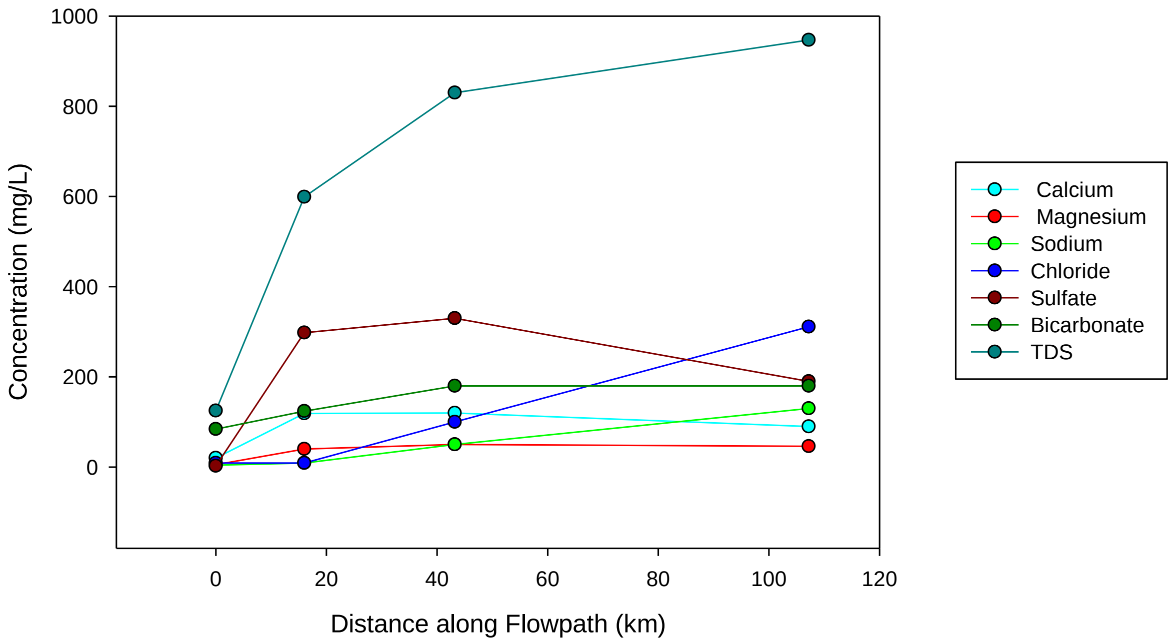

Figure 43 - Concentration changes of major solutes in Floridan Aquifer groundwater from Avon Park on the Peninsular Arch to Fort Ogden on the Gulf Coast (Data from Sprinkle, 1989).

In the recharge area (Avon Park), the groundwater has relatively low TDS concentrations of between 100 to 200 mg/L, comprised mostly of calcium and bicarbonate. As groundwater flows 17 kilometers downgradient to the next well along the flowpath in the town of Crewville, the TDS increases to about 600 mg/L. Concentrations of calcium and magnesium (120 and 50 mg/L respectively) and sulfate and bicarbonate (300 and 125 mg/L respectively) increase, largely due to the dissolution of calcite, dolomite, and gypsum (Sprinkle, 1989). From the perspective of water suitable for bottling much of Floridan aquifer groundwater is unsuitable because TDS concentrations are much too high. The exception to this rule is groundwater that is in or near recharge areas associated with the Peninsular Arch (Exercise 12↴).

4.11.2 History of Ginnie Springs

The American preference for low-TDS bottled water tends to restrict bottling operations in Florida to springs located near the Peninsular Arch recharge area. An example of this kind of spring is Ginnie Springs, located about sixteen kilometers north of Gainesville, Florida (Figure 40). People who are familiar with the sport of cave diving, diving into underwater caverns using SCUBA (Self-Contained Underwater Breathing Apparatus) gear, will recognize the name Ginnie Springs. It was one of the first springs in Florida to develop as a resort for people wanting to swim, snorkel, and SCUBA dive in the warm (22 °C or 72 °F) spring water. Ginnie Springs discharges about 1,444 liters per second (LPS) or 50 cubic feet per second (CFS). It has been used as a source of bottled water since the early 1990s.

4.11.3 Hydrology and Geochemistry of Ginnie Spring, Florida

From the perspective of a potential source for bottled water, Ginnie Springs has several advantages. First, it is close to the Peninsular Arch and thus is relatively close to the recharge area. Second, is the well-developed network of solution cavities and caverns characteristic of the unconfined parts of the Floridan aquifer (Figure 41). These caverns facilitate the rapid transport of groundwater from recharge areas to Ginnie Springs, minimizing the contact time between the limestone and the groundwater. Consequently, the TDS of Ginnie Springs water is relatively low for Floridan aquifer groundwater (~270 mg/L) with comparably low concentrations of calcium, magnesium, and bicarbonate (Table 10).

Table 10 - Chemistry of Ginnie Springs Groundwater (Data from Katz et al., 1999).

Dissolved Component	Concentration (mg/L)
Bicarbonate	175
Chloride	5.1
Nitrate	1.2
Hardness (as $CaCO_3$)	135
Sulfate	7.8
Calcium	54
Magnesium	4.7
Potassium	0.23
Sodium	2.4
Total Dissolved Solids (TDS)	270
pH	7.5

Because Ginnie Springs is used for swimming and SCUBA diving, water taken directly from the springs cannot be used for bottling because of the possibility of fecal contamination. To obtain groundwater for bottling, it was necessary to drill a borehole upgradient of the spring to withdraw water. Also, to label the bottled product as spring water, it was necessary for the borehole to tap the same caverns or fractures feeding Ginnie Springs. Accordingly, in the early 1990s, sophisticated geophysical tools were used to locate subsurface caverns leading to Ginnie Springs so as to drill into one. That borehole has been the source of Ginnie Spring bottled water ever since.

The hydrology and geochemistry of the springs feeding the Suwannee and Santa Fe rivers in northern Florida have been well-studied over the years because of their economic importance. One question that people visiting Ginnie Springs often ask is, "How long does it take for recharging groundwater to reach the springs?" One way to answer that question is to measure concentrations of chlorofluorocarbons (CFCs) in the groundwater (Katz et al., 1999). CFCs have been used as coolants in refrigerators and air conditioners since the 1930s. However, because of their volatility they accumulate in the atmosphere where they interfere with the natural production of ozone. Ozone in the stratosphere is important because it helps shield earth's surface from harmful radiation. As a result, production of CFCs has been highly regulated since the early 1990s. Nevertheless, because CFC concentrations in the atmosphere—and thus in rainfall recharging aquifers—is known over time, they make a useful tracer for estimating how long groundwater that has been isolated from the atmosphere has been in the earth.

One of the springs that Katz and others (1999) sampled in 1998 was Ginnie Springs. Based on measured concentrations of three different CFCs (CFC-11, CFC-12, and CFC-113) Katz's team estimated that Ginnie Spring water had been recharged anywhere from 7 to 3 years before 1998. Considering that most Floridan aquifer water, particularly where the aquifer is confined, has ages of hundreds or thousands of years (Plummer et al., 1977), Ginnie Springs water is young indeed. That is good for the water's suitability for bottling, but there is a downside. Because the water is so young, it is vulnerable to contamination by human activities. Florida has an important agricultural industry and nitrogen fertilizers are widely applied. While concentrations of nitrate at Ginnie Springs remain low (1.2 mg/L), nitrate concentrations at some other springs feeding the Santa Fe and Suwannee rivers exceed the drinking water standard of 10 mg/L (Katz et al., 1999).

4.12 The Hawaiian Islands Region

The location of the Hawaiian Islands Region is shown with all groundwater regions of the USA in Figure 2. One of the islands, the Big Island of Hawaii, is shown as Figure 44.

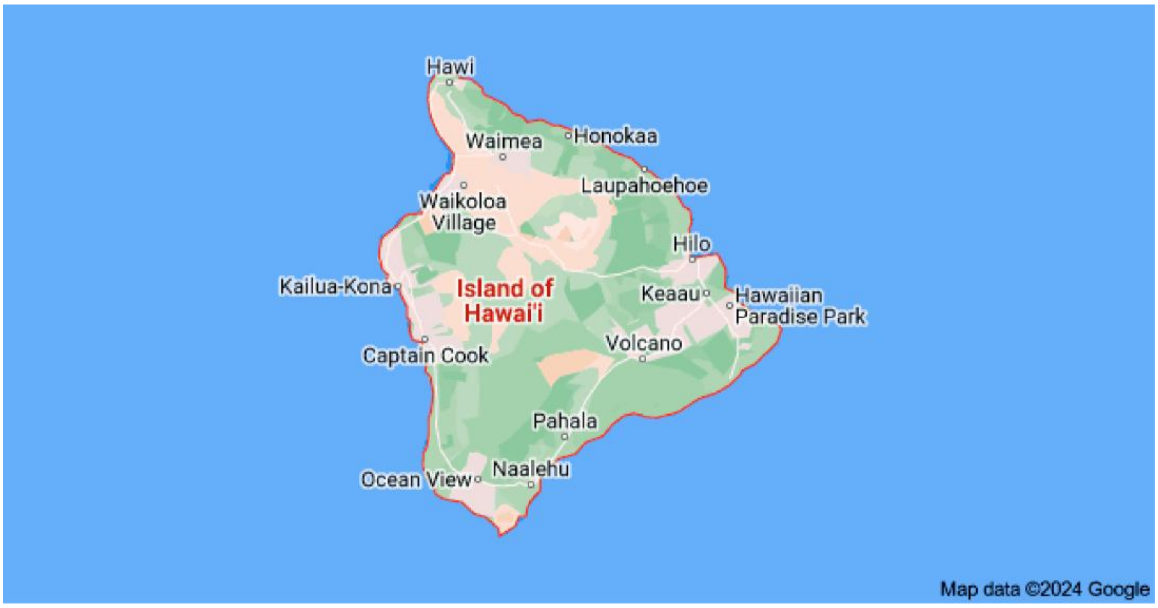

Figure 44 - Map of the Big Island of Hawaii. Source: Google Maps, 2024.

Begin Excerpt from Heath, 1984, pages 61–65. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by lava flows segmented in part by dikes, interbedded with ash deposits, and partly overlain by alluvium

The Hawaiian Islands Region encompasses the State of Hawaii and consists of eight major islands occupying an area of 16,706 km^2 in the Pacific Ocean 3,700 km southeast of California. The islands are the tops of volcanoes that rise from the ocean floor and stand at altitudes ranging from a few meters to more than 4,000 m above sea level. Each island, such as the Big Island of Hawaii (Figure 44), was formed by lava that issued from one or more eruption centers. The islands have a hilly to mountainous appearance resulting from erosion that has carved valleys into the volcanoes and built relatively narrow plains along parts of the coastal areas (Figure 45).

Each of the Hawaiian Islands is underlain by hundreds of distinct and separate lava flows, most of which are composed of basalt. The lavas issued in repeated outpourings from narrow zones of fissures, first below sea level, then above it. The lavas that extruded below the sea are relatively impermeable. Those formed above sea level tend to be highly permeable, with interconnected openings that formed as the lava cooled, cavities and openings that were not filled by the overlying flow, and lava tubes (tunnels). The central parts of the thicker flows tend to be more massive and less permeable; the most common water-bearing openings are joints and faults that formed after the lava solidified. Thin layers of ash and weathered volcanic rock occur irregularly between some of the flows that formed above sea level. The lava flows in valleys and parts of the coastal plains are covered by a thin layer of alluvium consisting of coral (limestone) fragments, sand-size fragments of basalt, and clay (Figure 45).

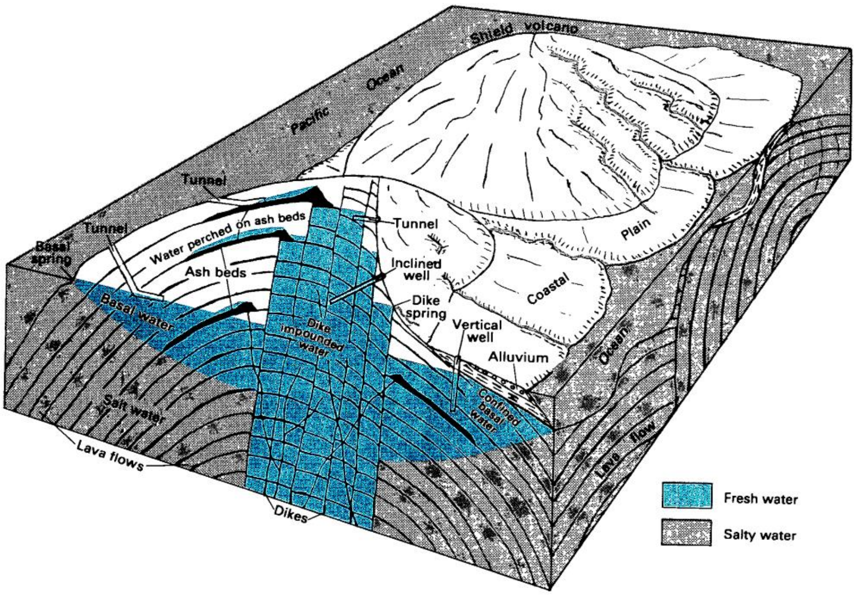

Figure 45 - Topographic and geologic features of a Hawaiian island (Heath, 1984). *Blue indicates openings bearing fresh water.

The fissures through which the lava erupted tend to cluster near eruption centers. Flows from the fissures moved down depressions on the adjacent slopes to form layers of lava that dip at angles of 4 to 10 degrees toward the margins of the volcanoes. The result, prior to modification by erosion, is a broad, roughly circular, gently convex mountain similar in shape to a warrior's shield. Thus, volcanoes of the Hawaiian type are referred to as shield volcanoes. When eruption along a fissure ceases, the lava remaining in the fissure solidifies to form a dike (Figure 45).

All the islands have sunk, to some extent, as a result of a downward flexing of the Earth's crust caused by the weight of the volcanoes. This has resulted in flows that formed above sea level being depressed below sea level. The upper parts of these flows contain freshwater that serves as an important source of water.

In mineral composition and nature of the water-bearing openings, the lavas that form the Hawaiian Islands are very similar to those in the Columbia Plateau Region. Thus, from these two standpoints, these regions could be combined into one. There is, however, one important difference that justifies their treatment as separate regions. This difference relates to the presence of seawater around and beneath the islands, which significantly affects the occurrence and development of water supplies.

From the standpoint both of description and of development, it is useful to divide the groundwater of the Hawaiian Islands into three parts. The first part consists of the higher areas of the islands in the vicinity of the eruption centers. The rocks in these areas are formed into a complex series of vertical compartments surrounded by dikes developed along eruption fissures. The ground water in these compartments is referred to as *dike-impounded groundwater* (Figure 45). The second, and by far the more important, part of the system consists of the lava flows that flank the eruption centers and that contain fresh ground water floating on saline ground water. These flank flows are partially isolated hydraulically from the vertical compartments developed by the dikes that surround the eruption centers (Figure 45). The fresh ground water in these flows is referred to as *basal groundwater*. In parts of the coastal areas the basal water is confined by the overlying alluvium. The third part of the system consists of *perched groundwater*, primarily in lava flows, on soils, ash, or thick impermeable lava flows above basal ground water (Figure 45).

The groundwater system is recharged by precipitation which ranges annually from about 160 mm to more than 11,000 mm. This wide range in precipitation reflects the effect of the islands on the moist northeast trade winds. As the moisture-laden winds are deflected upward by the mountains, precipitation falls on the higher elevations. Precipitation is heaviest on mountains below 1,000 m and lightest in the coastal areas on the leeward side of the islands and at elevations above 1,000 m on the islands of Maui and Hawaii. The average annual precipitation on the islands is estimated to be about 1,800 mm. Because of the highly permeable nature of the volcanic soils, it is estimated that about 30 percent of the precipitation recharges the ground-water system.

End Excerpt from Heath, 1984, pages 61–65.

4.12.1 Hydrology and Groundwater Chemistry of the Hawaiian Island Region

The groundwater hydrology of the Hawaiian Islands, and of most other Pacific Islands, is unlike the hydrology of any continental environment. This is largely due to hydraulic characteristics of basaltic aquifers as well as the fact that the islands are surrounded by seawater. Because of the high hydraulic conductivity of basalt flows, filled as they are with vesicles and fractures, most of the atmospheric precipitation that falls percolates quickly into the ground. Surface water streams can be found in some locations that receive large amounts of rainfall, but they are not common and are generally short-lived before disappearing into the underlying basalt. Mark Twain, who visited the island of Hawaii in the 1860s, noticed some of these oddities. In his book *Roughing It*, published in 1872, Mark Twain had this to say about the hydraulic properties of basalt:

> The lava is the accumulation of ages; one torrent of fire after another has rolled down here in old times, and built up the island structure higher and higher. Underneath, it is honey-combed with eaves: it would be of no use to dig wells in such a place; they would not hold water—you would not find any (water) for them to hold, for that matter. Consequently, the planters depend upon cisterns (for water supply).

As Mark Twain noted, conventional water wells in much of Hawaii's rugged interior are simply not practical. That, in turn, makes it difficult to describe the complex hydrology of the Hawaiian Islands. Over the years, however, hydrologists have developed a number of methods to address that problem. Some of the most interesting are the use of environmental isotopes and age-dating techniques to provide hydrologic insight.

Because of their volcanic origin, there are vast altitude and climatic differences on islands like Hawaii. Elevations on Hawaii range from sea level on the coasts to as high as 4,170 meters (13,680 ft) above sea level at the summit of Mona Loa. That, in turn, produces significant differences in the isotopic composition of snow and rain that falls on the island. Scholl and others (1996) used stable oxygen isotopes to track the sources and movements of groundwater on the island (Figure 46). Because O^{18} is heavier than O^{16} in atmospheric moisture, it is preferentially removed by precipitation, enriching the remaining moisture in O^{16}. Thus, the ratio of O^{18} to O^{16} in snow and rain (expressed as volume-weighted average (vwa) $\delta^{18}O$) reflects the preferential removal of O^{18}. Unprecipitated trade winds blowing east and west of the island have a similar O^{18} to O^{16} ratio (Figure 46). However, trade winds subjected to the rain shadow created by Mona Loa and Haulālai are more depleted in O^{18} (Figure 46). In addition, precipitation falling at higher elevations is also more depleted in O^{18}. All of this makes it possible to trace the source of recharge (trade wind versus rain shadow) as well as the elevation at which recharge occurred.

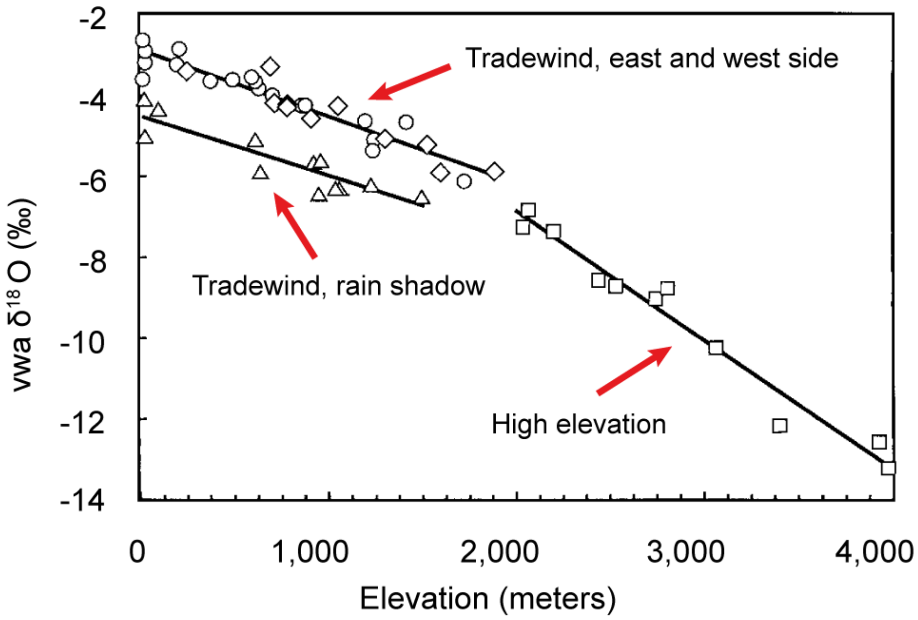

Figure 46 - Relation between volume-weighted average (vwa) $\delta^{18}O$ values and elevation on the east side of Hawaii near the Helo district (Adapted from Scholl et al., 1996).

Scholl and others (1996) used these differences to deduce the sources of precipitation (trade winds versus rain shadow) and the elevations that the precipitation fell. Then, by documenting the isotopic composition of groundwater samples collected from wells along the coast on the eastern side of the island near Hilo (Figure 44), they could postulate flowpaths that groundwater had followed from points of recharge to points of discharge.

More recently, Fackrell and others (2020) used a similar approach to postulate flowpath directions on the western side of the island (Figure 47) from the summit of Mauna Loa west toward Kaʻūpūlehu in the Kona District (Figure 44).

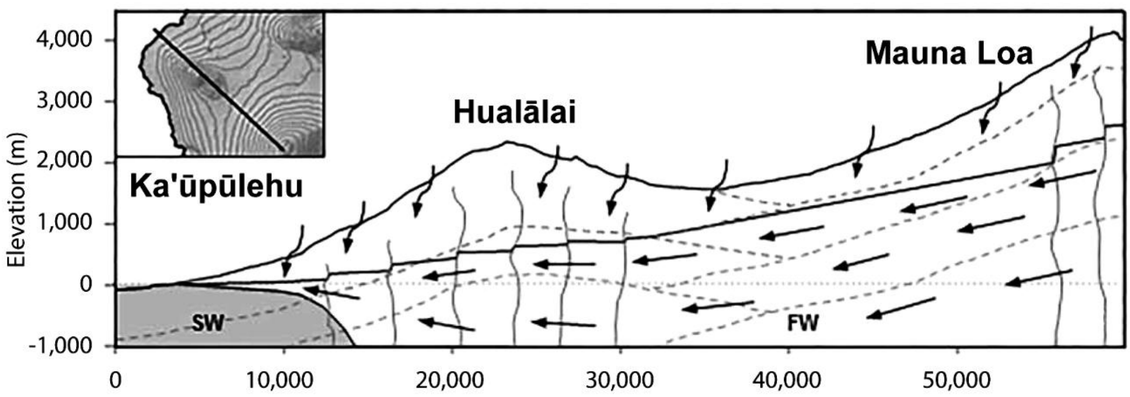

Figure 47 - Postulated flowpath from the summit of Mauna Loa, beneath the summit of Hualālai, before discharging to the sea near Kaʻūpūlehu (Adapted from Fackrell et al., 2020).

Age-dating techniques, such as measuring and modeling tritium concentrations in groundwater can also provide insight to the geologic complexities that affect the flow systems. Scholl and others (1996) also measured concentrations of radioactive tritium in groundwater, and analyzed the results using well-mixed reservoir and piston-flow models (Yurtsever, 1983). These models, which make assumptions of radioactive decay and the presence or absence of mixing with other water sources, allow estimates of groundwater age (time since recharge) to be made. Because large amounts of tritium were injected in the atmosphere before atmospheric testing of atomic weapons were banned in 1963, and because of radioactive tritium's short half-life (12.3 years), tritium concentrations are useful for estimating ages for relatively young (<45 years in 1996) groundwater.

The groundwater dating results of Scholl and others (1996) on the eastern side of the island are shown in Figure 48. They show relatively young (18 to 25 years since recharge) groundwater is present southwest and north of the Kilauea Rift Zone, whereas older (>35 years since recharge) groundwater is clustered due south of the Kilauea Volcano (Figure 48). This suggests that dike intrusions within the rift zone, such as those shown schematically in Figure 45, divert younger groundwater flow to the east and west leaving older groundwater to discharge directly south of the Kilauea volcano.

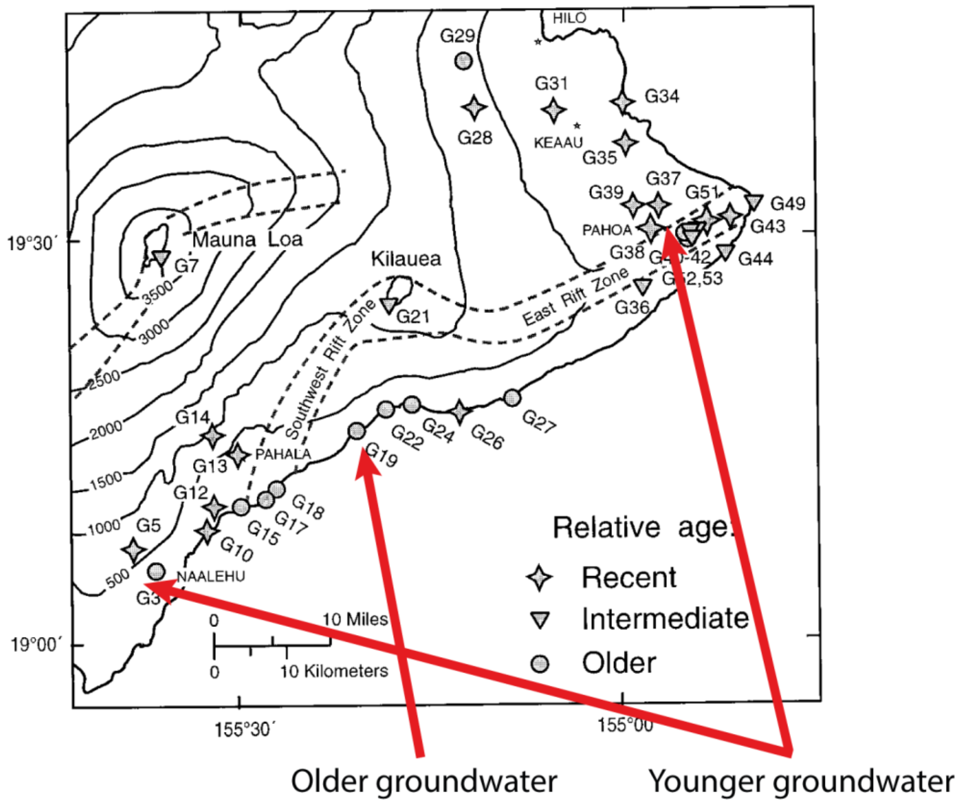

Figure 48 - Distribution of older (>35 years) and younger (18–25 years) groundwater suggesting diversion of groundwater flow by the Kilauea Rift Zone (Adapted from Scholl et al., 1996).

The geochemistry of potable groundwater in the Hawaiian Island Region is predominantly controlled by (1) structural entrapment of rainwater at higher altitudes by lateral dikes forming *dike-impounded groundwater*, (2) the presence of seawater at depth beneath each island with a freshwater lens of variable thickness known as *basal groundwater* that is continuously being replenished by atmospheric precipitation, and (3) rock-water interactions between fresh groundwater and the largely basaltic rocks that form the islands (Swain, 1973).

The major ion chemistry of groundwater sampled from dike-impounded and basal sites in the Kona and Hilo Districts of Hawaii are shown in Table 11. The climate of these two districts is very different. Hilo is located on the eastern side of the island exposed to the trade winds and receives about 3300 millimeters of rainfall (130 inches) whereas Kona in located on the western side of the island in the rain shadow of Mt. Hualālai and receives about 760 millimeters of rainfall (30 inches). The chemical contrast between the dike-impounded (low chloride) and basal groundwater (higher chloride) is evident and reflects the impact of seawater on basal groundwater. The higher sodium and bicarbonate concentrations in Kona dike-impounded groundwater relative to Hilo groundwater suggests a greater influence of basalt rock-water interactions that could reflect longer flowpaths (Figure 47) (Exercise 13↴).

Table 11 - Groundwater Chemistry of Dike Impounded and Basal Groundwater from two Districts on the Island of Hawaii (Data from Swain, 1973). Concentration units are mg/L.

Kona District	Well number	Date	Ca	Mg	Na	HCO_3	SO_4	Cl	TDS	pH
Dike	3557-2	1967	5.5	4.8	20	74	8.0	15	120	7.2
Basal	3758-1	1958	15	37	236	44	76	440	1160	7.1
Hilo District										
Dike	4203-22	1964	8.0	4.4	10	1.0	2.5	11	128	7.0
Basal	4202-1	1953	38	15	80	34	32	180	440	7.4

4.12.2 Bottled Water Prospects of the Hawaiian Island Region

Bottled water of all kinds is widely consumed in the Hawaiian Island Region. Spring water, however, is not an important source of commercially available bottled water. Springs do occur in convenient places for collecting water for bottling, particularly at the base of volcanic mountains. Springs discharging near the coasts occur widely, but most are not suitable for commercial bottling operations. Groundwater that is bottled on the island of Hawaii is derived from either deep wells, or is ocean water treated using reverse osmosis to remove dissolved solids.

As basal groundwater generally has elevated concentrations of chloride due to interaction with the underlying seawater (Table 11), it is not suitable for commercial bottled water operations. Water produced from dike-impounded aquifers, on the other hand, can be suitable. A deep well tapping a dike-impounded aquifer is one source of bottled water on the island of Hawaii. The well is located on the eastern flank of Mouna Loa and produces a low TDS water that is slightly alkaline (pH 7.8–8.2) with low concentrations of calcium (4.8 mg/L), magnesium (2.6 mg/L), and potassium (1.9 mg/L), but fairly high concentrations of silica (39 mg/L) as indicted by the Hawaii Volcanic Beverages website↗. This chemistry clearly reflects rock-water interaction with basalt flows that make up the aquifer.

Another deep well used as a source of bottled water also probably also taps a dike-impounded aquifer. This well, located near the town of Kea'au (Figure 44), produces water with a low TDS (84 mg/L), calcium (6 mg/L), magnesium (3 mg/L), potassium (2 mg/L), and silica (37 mg/L) as indicted by the Hawaiian Springs Water website. This chemistry also reflects basaltic rock-water interactions. However, its location just south of Hilo suggests an additional source. Hilo is located in a classic rainforest and receives anywhere from 3,300 to 5,500 millimeters (130 to 215 inches) of rainfall per year. Due to the permeability of the basaltic rocks, there are no surface streams in the area dispite the large amouns of rainfall. The low TDS of the Kea'au groundwater probably also reflects the influence of relatively young (<20 years) water delivered directly from precipitation. That would be consistant with the relatively young groundwater documented by Scholl and others (1996) in that general area (Figure 48).

The Kona District currently does not have bottling operations for its groundwater. However, it is interesting that it bottles water derived from the ocean. This particular operation draws ocean water from a deep current off the coast of Kona and subjects it to a reverse osmosis treatment that reduces the TDS to about 250 mg/L as indictaed by the Kona Deep website↗. The finished product is marketed throughout the Hawaiian Islands.

4.13 The Alaska Region

The location of the Alaska Region is shown with all groundwater regions of the USA in Figure 2 and is shown in Figure 49).

Begin Excerpt from Heath, 1984, pages 65–69. Figure numbers have been changed from those of Heath so as to be sequential in this book, some labels have been added to identify locations of features that are mentioned in Heath's text, and asterisks indicate words added to captions for the purpose of this book.

Characterized by glacial and alluvial deposits, occupied in part by permafrost, and overlying crystalline, metamorphic, and sedimentary rocks

The Alaska region encompasses the State of Alaska, which occupies an area of 1,519,000 km^2 at the northwest corner of North America. Physiographically, Alaska can be divided into four divisions—from south to north, the Pacific Mountain System, the Intermontane Plateaus, the Rocky Mountain System, and the Arctic Coastal Plain (Figure 49). The Pacific Mountain System is the Alaskan equivalent of the Coast Range, Puget Sound Lowland, and Cascade provinces of the Washington-Oregon area. The Intermontane Plateaus is a lowland area of plains, plateaus, and low mountains comparable to the area between the Cascades–Sierra Nevada and the Rocky Mountains. The Rocky Mountain System is a continuation of the Rocky Mountains of the contiguous United States and Canada, and the Arctic Coastal Plain is the geologic equivalent of the Great Plains of the

United States and Canada. The coastal areas and lowlands range in altitude from sea level to about 300 m, and the higher mountains reach altitudes of 1,500 to 3,000 m. Denali in the Pacific Mountain System is the highest peak in North America, with an altitude of about 6,200 m.

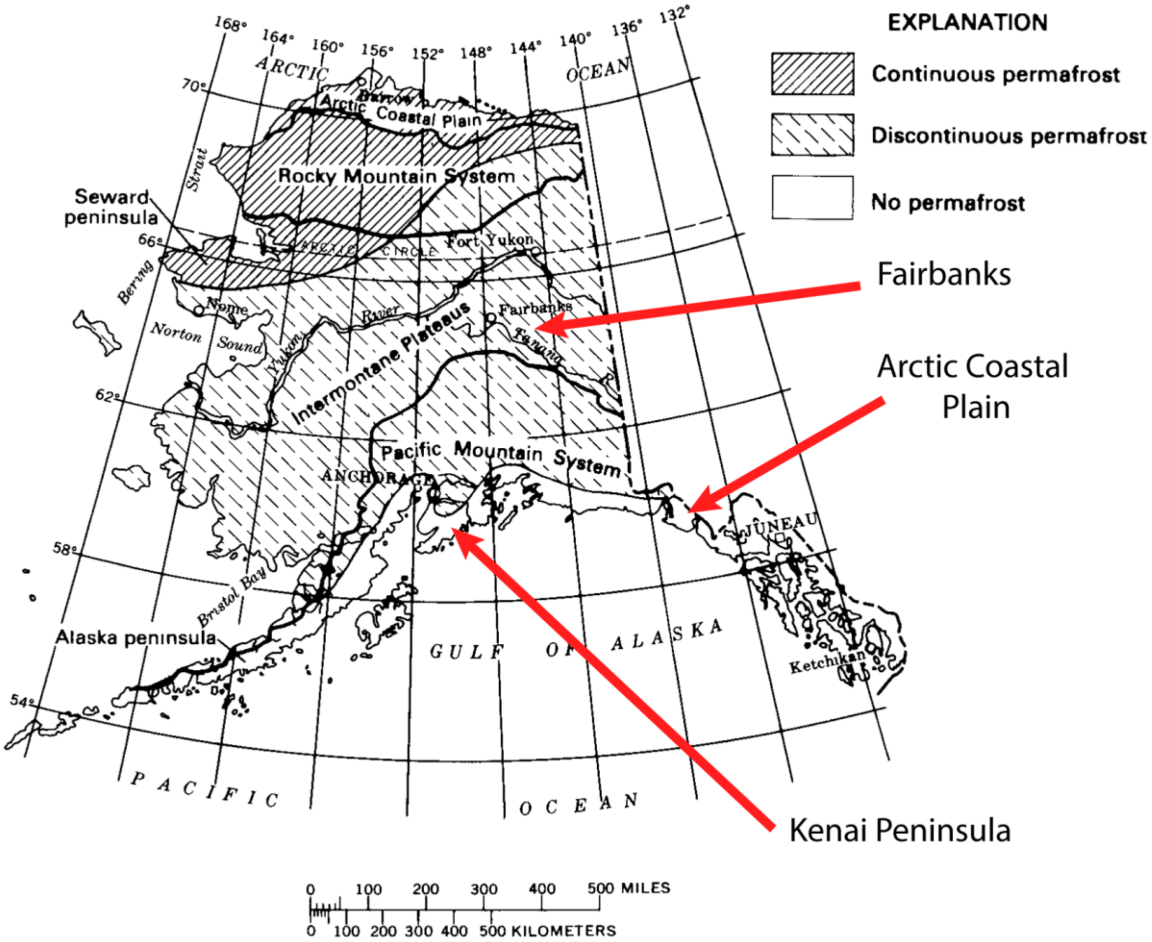

Figure 49 - Physiographic divisions and permafrost zones of Alaska.

As would be expected of any area its size, Alaska is underlain by a diverse assemblage of rocks. The principal mountain ranges have cores of igneous and metamorphic rocks ranging in age from Precambriam to Mesozoic. These are overlain and flanked by younger sedimentary and volcanic rocks. The sedimentary rocks include carbonates, sandstones, and shales. In much of the region the bedrock is overlain by unconsolidated deposits of gravel, sand, silt, clay, and glacial till (Figure 50).

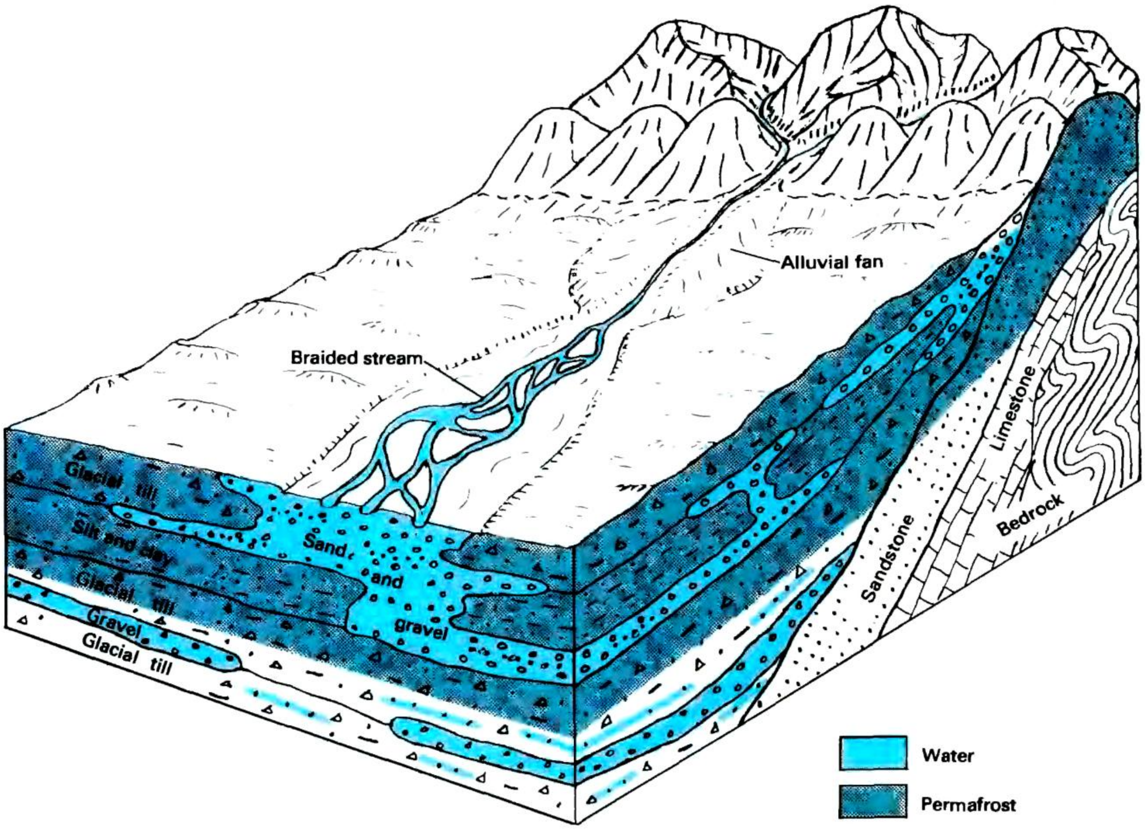

Figure 50 - Topographic and geologic features of parts of Alaska (Heath, 1984). *Blue indicates water bearing zones.

Climate has a dominant effect on hydrologic conditions in Alaska. Mean annual air temperatures range from −12 °C in the Rocky Mountain System and the Arctic Coastal Plain to about 5 °C in the coastal zone adjacent to the Gulf of Alaska. The present climate and the colder climates that existed intermittently in the past have resulted in the formation of permafrost, which is perennially frozen ground. Permafrost is present throughout the State except in a narrow strip along the southern and southeastern coasts. In the northern part of the Seward Peninsula, in the western and northern parts of the Rocky Mountain System, and in the Arctic Coastal Plain, the permafrost extends to depths as great as 600 m and is continuous except beneath deep lakes and in the alluvium beneath the deeper parts of the channels of streams. South of this area and north of the coastal strip, the permafrost is discontinuous and depends on exposure, slope, vegetation, and other factors. The permafrost is highly variable in thickness in this zone but is generally less than 100 m thick.

Much of the water in Alaska is frozen for at least a part of each year: that on the surface as ice in streams and lakes or as snow or glacier ice and that below the surface as winter frost and permafrost. Approximately half of Alaska, including the mountain ranges and adjacent parts of the lowlands, was covered by glaciers during the Pleistocene. About 73,000 km^2, or one-twentieth of the region, is still occupied by glaciers, most of which are in the mountain ranges that border the Gulf of Alaska. Precipitation, which ranges from about 130 mm/yr in the Rocky Mountain System and the Arctic Coastal Plain to about

7,600 mm/yr along the southeast coast, falls as snow for 6 to 9 months of the year and even year-round in the high mountain regions. The snow remains on the surface until thawing conditions begin, in May in southern and central Alaska and in June in the arctic zone. During the period of subfreezing temperatures, there is no overland runoff, and many streams and shallow lakes not receiving substantial ground-water discharge are frozen solid.

From the standpoint of ground-water availability and well yields, Alaska is divided into three zones. In the zone of continuous permafrost, ground water occurs beneath the permafrost and also in small, isolated, thawed zones that penetrate the permafrost beneath large lakes and deep holes in the channels of streams (Figure 50). In the zone of discontinuous permafrost, ground water occurs below the permafrost and in sand and gravel deposits that underlie the channels and floodplains of major streams. In the zone of discontinuous permafrost, water contained in silt, clay, glacial till, and other fine-grained deposits usually is frozen. Thus, in this zone the occurrence of ground water is largely controlled by hydraulic conductivity. In the zone not affected by permafrost, which includes the Aleutian Islands, the western part of the Alaska Peninsula, and the southern and southeastern coastal areas, ground water occurs both in the bedrock and in the relatively continuous layer of unconsolidated deposits that mantle the bedrock.

Recharge of the aquifers in the Alaska region occurs when the ground is thawed in the areas not underlain by permafrost. This period generally lasts only from June through September. Because the ground, even in nonpermafrost areas, is still frozen when most snowmelt runoff occurs, relatively little recharge occurs in interstream areas by infiltration of water across the unsaturated zone. Instead, most recharge occurs through the channels of streams where they flow across the alluvial fans that fringe the mountainous areas and in alluvial deposits for some distance downstream. Because of the large hydraulic conductivity of the sand and gravel in these areas, the rate of infiltration is large. Seepage investigations along Ship Creek near Anchorage indicate channel losses of 0.07 $m^3 sec^{-1} km^{-1}$, which gives an infiltration rate through the wetted perimeter of about 0.4 m day^{-1}.

End Excerpt from Heath, 1984, pages 65–69.

4.13.1 Hydrogeology and Groundwater Chemistry of the Alaskan Region

The chief hydrologic distinction of the Alaskan Region from the rest of the United States is the presence of permafrost (Figure 49). Permafrost, particularly in the far north where it is present year-round and in thicknesses that can approach several hundred meters, makes characterizing groundwater systems and chemistry virtually impossible. Not that people haven't tried. One particularly interesting attempt revolved around the observation that deep fresh-water lakes, which are fairly common on Alaska's North Slope, do not freeze all the way to the lake's bottom even in the coldest winters. In other words, the lakes provide a "window" to the underlying groundwater system that may allow characterization of groundwater chemistry (Hinkel et al., 2017). This study could document significant chemical differences between twenty deep lakes that did not freeze completely during the winter, but could not detect a hydrochemical signiture distinct from nearby lakes that froze completely during the winter. It is possible that the groundwater contribution to the lakes that freeze completely is too small relative to surface-water contributions to reliably characterize groundwater chemisty.

Characterizatizing groundwater systems and chemistry in the zone of discontinuous permafrost in the Intermontane Plateaus, the Pacific Mountain System, and the Arctic Coastal Plain (Figure 49), is somewhat easier. The city of Fairbanks, Alaska's second largest population center, is located in the Intermontane Plateau. The rocks underlying Fairbanks and the surrounding area are all part of the Yukon-Tanana terrane, a displaced pericratonic block of late Paleozoic and older age that has undergone multiple episodes of deformation and metamorphism (Foster et al., 1994). The major-element composition (Mg, Ca, K, Na, and SiO_2) of groundwater in the vicinity of Fairbanks varies over a wide range, particularly Ca (2.6 to 140 ppm) and Mg (0.8 to 70 ppm) (Table 12).

Table 12 - Groundwater chemistry from two wells in the vicinity of Fairfield, Alaska (Adapted from Farmer et al., 1998). Concentration units are mg/L.

Well number	Temp ^0C	Ca	Mg	Na	K	SO_4	HCO_3	As	TDS	pH
98-06	7.2	140	28	9.6	0.7	330	317	0.0054	826	7.3
98-17	7.2	2.6	0.8	1.2	0.2	2.3	18	<0.003	25	6.1

In addition, the TDS ranges from nearly rainwater (25 mg/L) to well above the drinking water standard of 500 mg/L (826 mg/L). In addition, some of the groundwater has concentrations of arsenic (0.0054 mg/L) that are above the drinking water standard set for arsencic (0.001 mg/L). These characteristics will have an impact on the suitability of groundwater in the vicinity of Fairbanks for bottled water operations.

The city of Juneau, the capital of Alaska, is located in the Mendenhall Valley of the Arctic Coastal Plain. The valley is underlain by outwash and moraine glacial deposits as well as glaciomarine sediments and alluvium from the surrounding mountains. The Mendenhall Valley has two aquifers, an upper unconfined and a lower confined aquifer. The confined aquifer has brackish groundwater and is not used for water supply. The unconfined aquifer, which is used for water supply, consists of a downward-fining sequence of glaciofluvial and alluvial sediments (Alcorn & Hogan, 1995). The groundwater chemisty of the unconfined aquifer is calcium-magnesium bicarbonate in character with relatively low concentrations of TDS (Table 13). These coastal plain sediments are bounded on the east by metamorphosed volcanic and sedimentary rocks of the Pacific Mountain System (Figure 49). Drilled wells tapping these rocks are also calcium-magnesium bicarbonate-chloride in character with somewhat higher TDS concentrations (Table 13).

Table 13 - Groundwater chemistry from two wells in the vicinity of Juneau, Alaska (Adapted from Barnwell & Boning, 1968). Concentration units are mg/L.

Well number	Geologic Setting	Ca	Mg	Na	K	SO_4	HCO_3	Cl	As	TDS	pH
31	**Coastal Plain**	21	3.8	7.8	2.0	4.8	97	3.5	<0.003	108	7.0
8	**Bedrock**	34	12.0	45	4.3	3.3	264	45	<0.003	329	7.7

The Arctic Coastal Plain on the western part of the Kenai Peninsula in southcentral Alaska (Figure 49) is bounded by the Cook Inlet and the Kenai Mountains. Groundwater is the predominant source of water for commercial, industrial, and domestic uses on the Peninsula. Unconsolidated sediments of glacial and fluvial origin are the most productive aquifers. In the northwestern peninsula, almost all groundwater is withdrawn from sediments which may be as thick as 250 meters. The chemical quality of groundwater ranges excellent to marginal (Glass, 1996). Wells drilled near Cook inlet exhibit higher TDS concentrations dominated by sodium and chloride indicating saltwater intrusion (well BBBD1, Table 14). Further inland away from Cook Inlet groundwater has a calcium-magnesium-bicarbonate character sith relatively low TDS concentrations. Concentrations of arsenic are problematic on the Peninsula, often exceeding the EPA maximum concentration level of 0.001 mg/L (wells ACBA1 and ABBB1, Table 14) (Exercise 14⤵).

Table 14 - Groundwater chemistry from three wells on the Kenai Peninsula, Alaska (Adapted from Glass, 1996). Concentration units are mg/L. NM = not measured.

Well number	Geologic Setting	Ca	Mg	Na	K	SO_4	HCO_3	Cl	As	TDS	pH
SB0050112 3ACBA1	**Coastal Plain**	31	6.6	5.4	2.7	0.2	146	3.0	0.0019	176	8.1
SB0060121 1BBBD1	**Coastal Plain**	3.4	4.4	201	8.9	42	NM	94	0.0071	520	7.9
SB0070121 1ABBB1	**Coastal Plain**	20	3.2	5.2	2.2	1.6	89	5.6	0.007	111	8.4

4.13.2 Prospects for Bottled Spring Water in the Alaskan Region

Springs are common in the Alaskan Region, but spring water suitable for bottling operations are uncommon. This has more to do with climate rather than hydrology. Springs are present in the the Rocky Mountain System, but the fact that much of that system is above the Arctic circle (Figure 49) means that the springs are frozen for much of the year. That makes bottling operations impossible. Springs are also present in the Intermontane Plateau System (Figure 49), but they tap surficial aquifers that produce water of relatively poor water quality that includes high TDS and arsenic concentrations (Table 12). Reverse osmosis would be needed to render the water suitable for bottling.

Water sourced from a mountain spring located in the Pacific Mountains System (Figure 49) provides one example of Alaskan spring water that is used for bottling operations. The spring is located near the city of Juneau at the base of Thunder Mountain. The water is collected by a catch system (very unusual in the bottled water industry), and subjected to filtration and UV treatment prior to bottling in accordance with Federal Food and Drug Administration best pratices guidence.

In short, spring water suitable for bottling is available in Alaska, but the combination of climate, hydrology, and geochemistry necessarily are limitations on such operations.

5 Wrap-up

Heath's (1984) survey of the different Groundwater Regions of the United States shows a great deal of hydrologic diversity. Part of that diversity is due to the differing climates of each region. The frigid mountain peaks of the Rocky Mountains, the baking hot dry deserts of the southwestern alluvial basins, and the equally hot, but humid southeastern coastal plain illustrate that climatic diversity. In addition, there are many differences in the underlying rocks and sediments of each region. There are the thick and not quite homogeneous beds of basaltic lava in the Columbia Plateau, the carbonate hills and caves of the Ozark Mountains, and the flat-lying sediments of the Gulf Coast and Southeast Coastal Plain. This diversity produces a vast variety in the chemical composition of groundwater.

Given that the focus of this book is on the suitability of groundwater for bottling operations, much of the geologic and hydrologic variety disappears from consideration. The reason for this has to do with American perceptions of what constitutes high quality drinking water. There are several historical reasons for American perceptions, chiefly that the beginnings of America's bottled water industry in the nineteenth century focused on providing drinking water for people in cities as an alternative to often-polluted (pre-chlorination) municipal water supplies. However, their perceptions reflect the impact of marketing as well. When Poland Spring water, characterized by very low concentrations of total dissolved solids (~40 mg/L) was awarded the Grand Prize as "besting all of the waters of the world" at the 1904 Louisiana Purchase Exposition in St. Louis, low TDS bottled water became fashionable and that fashion that persists in America to this day.

6 Exercises

Exercise 1

Explain why the groundwater chemistry of the twenty or so Saratoga Springs differ so much?

Solution to Exercise 1⤵

Return to where text linked to Exercise 1⤴

Exercise 2

Explain the climatic, geologic, and hydrologic reasons for the very low Total Dissolved Solids concentrations in Poland Spring groundwater.

Solution to Exercise 2⤵

Return to where text linked to Exercise 2⤴

Exercise 3

Explain the climatic, geologic, and hydrologic reasons for the very low Total Dissolved Solids concentrations in Mt. Shasta spring water.

Solution to Exercise 3⤵

Return to where text linked to Exercise 3⤴

Exercise 4

Explain the high concentrations of TDS that are characteristic of most groundwater in the Alluvial Basins Groundwater Region.

Solution to Exercise 4⤵

Return to were text linked to Exercise 4⤴

Exercise 5

Groundwater in the Columbia Lava Plateau Groundwater Region is characterized by slightly alkaline pH (~7.3) calcium bicarbonate-type water with moderate concentrations of total dissolved solids (TDS ~243 mg/L). As groundwater moves further along regional flowpaths concentrations of sodium (40 mg/L), magnesium (14 mg/L), sulfate (30 mg/L), and TDS increase (> 400 mg/L), and the water becomes more alkaline (pH> 8.0). What two water treatment technologies are used in this region to lower TDS concentrations to a level suitable for spring water bottling operations?

Solution to Exercise 5⤵

Return to where text linked to Exercise 5⤴

Exercise 6

It is common to divide the climatic conditions found in mountainous areas into three distinct zones. Name these three zones. Which of these zones is most efficient at producing springs?

Solution to Exercise 6⤵

Return to where text linked to Exercise 6⤴

Exercise 7

What are two hydrologic processes that lead to high TDS concentrations in in the High Plains Aquifer?

Solution to Exercise 7⤵

Return to where text linked to Exercise 7⤴

Exercise 8

What climatic condition leads to extensive cave formation in carbonate aquifers in the eastern parts of the Non-Glaciated Central Region that are lacking in the western parts of the same region?

Solution to Exercise 8⤵

Return to where text linked to Exercise 8⤴

Exercise 9

What two hydraulic properties of the glacial aquifers in the Glaciated Central Region affects the total dissolved solids (TDS) of groundwater?

Solution to Exercise 9⤵

Return to where text linked to Exercise 9⤴

Exercise 10

What role does the weathering product called saprolite overlying the fractured metamorphic rocks of the Glaciated Central Region play in the water quality of groundwater and its suitability for bottling operations?

Solution to Exercise 10⤵

Return to where text linked to Exercise 10⤴

Exercise 11

Of the four hydrochemical zones characteristic of coastal plain aquifers (Figure 38), which zone is most suited to be sources of bottled water? What chemical characteristics of this zone explains its desirability?

Solution to Exercise 11⤵

Return to where text linked to Exercise 11⤴

Exercise 12

What geographic feature in Florida leads to the production of low TDS spring water from the Floridan aquifer that is suitable for bottling operations in the Southeast Coastal Plain Region?

Solution to Exercise 12⤵

Return to where text linked to Exercise 12⤴

Exercise 13

Because of the great depth to the water table for most of the island of Hawaii, drilling wells is not a practical for characterizing groundwater hydrology. What two other geochemical methods have been used to delineate sources of recharge and directions of groundwater flowpaths on the island?

Solution to Exercise 13⤵

Return to where text linked to Exercise 13⤴

Exercise 14

What two chemical constituents commonly found in Alsakan groundwater (Table 13 and Table 14) limit its suitability for bottled water operations?

Solution to Exercise 14⤵

Return to where text linked to Exercise 14⤴

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8 Exercise Solutions

Exercise Solution 1

Brines upwelling along faults from the deeply buried Appalachian Basin and Canadian Shield mix with shallower phreatic groundwater present in Cambrian sandstones and dolomites. Because the proportion of deep and shallow groundwater mixing together differs between springs, the chemical composition of the spring water is different as well.

Return to Exercise 1↑

Return to where text linked to Exercise 1↑

Exercise Solution 2

Poland Spring groundwater is characterized by very low TDS concentrations (30-50 mg/L) because the glacial aquifer is recharged entirely by atmospheric precipitation, the flow paths from recharge areas to the spring are relatively short, and the glacial outwash sediments are coarse-grained.

Return to Exercise 2↑

Return to where text linked to Exercise 2↑

Exercise Solution 3

The climate of Mt. Shasta produces large amounts of snowmelt that has naturally low TDS concentrations (<10 mg/L). The chemistry of the spring water at the base of the mountain depends on the travel time from the point of recharge to the spring outfall and the composition of the rocks (basaltic or andesitic) encountered along the flow path. Furthermore, because of the highly fractured nature of the volcanic rocks, as well as the presence of "lava tubes", flow can be extremely rapid resulting in very low TDS concentrations (12-30 mg/L) in spring water because there is not much time for the water to dissolve minerals.

Return to Exercise 3↑

Return to where text linked to Exercise 3↑

Exercise Solution 4

Total dissolved-solids (TDS) concentrations range from an average of less than 500 mg/L in 11 of the 28 basins sampled by Fredrickson (1991) to more than 3,000 mg/L in basins along the Gila and Colorado Rivers. In addition to high TDS, the groundwater in most basins has relatively high hardness values of greater than 120 mg/L as calcium carbonate. The high TDS and hardness reflects the presence of carbonate material as well as evaporite deposits present in alluvium that fills the down-faulted basins.

Return to Exercise 4↑

Return to were text linked to Exercise 4↑

Exercise Solution 5

Reverse osmosis and vapor distillation.

Return to Exercise 5↥

Return to where text linked to Exercise 5↥

Exercise Solution 6

The first of these, corresponding to the highest elevation is called the upper mountain zone and includes the steepest slopes. The middle mountain zone, is characterized by extensive weathering caused by freeze-thaw cycles. This generates coarse-grained sediments that are transported to lower altitudes where they accumulate in the lower mountain zone. These sediments are extremely porous and very permeable. They soak up water transported from the upper and middle mountain zones and that water often emerges as springs, some of which are suitable for water bottling operations.

Return to Exercise 6↥

Return to where text linked to Exercise 6↥

Exercise Solution 7

Upwelling of brines from deeper geological formations and evaporation of irrigation groundwater applied to agricultural fields that subsequently recharges the water table.

Return to Exercise 7↥

Return to where text linked to Exercise 7↥

Exercise Solution 8

Abundant rainfall.

Return to Exercise 8↥

Return to where text linked to Exercise 8↥

Exercise Solution 9

Hydraulic conductivity and length of groundwater flow paths.

Return to Exercise 9↥

Return to where text linked to Exercise 9↥

Exercise Solution 10

The soft, porous saprolite serves as a filter, cleansing percolating recharge water from surface contaminants and microorganisms.

Return to Exercise 10

Return to where text linked to Exercise 10

Exercise Solution 11

Zone 1, because of its calcium bicarbonate character and its relatively low TDS.

Return to Exercise 11

Return to where text linked to Exercise 11

Exercise Solution 12

The Peninsular Arch.

Return to Exercise 12

Return to where text linked to Exercise 12

Exercise Solution 13

Ratios of stable oxygen isotopes ^{18}O and ^{16}O, and concentrations of radioactive tritium ^{3}H.

Return to Exercise 13

Return to where text linked to Exercise 13

Exercise Solution 14

Total Dissolved Solids (TDS) and arsenic (As).

Return to Exercise 14

Return to where text linked to Exercise 14

9 About the Author

Francis H. Chapelle retired from a forty-year career with the U.S. Geological Survey in 2020. He has authored more than 130 peer-reviewed scientific papers and textbooks, work that won him the O. E. Meinzer Award in Hydrogeology given by The Geological Society of America and the U.S. Geological Survey Distinguished Service Award. In addition, he has written two books for the general reader about competing mystical and scientific explanations of groundwater (The Hidden Sea) and a natural history of bottled spring water (Wellsprings).

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