



Photograph by David Stannard, U.S. Geological Survey

Groundwater discharge from a basaltic rock aquifer adjacent to Metolius River, Deschutes river Basin, Oregon

A BASIC STUDY IN GROUNDWATER AND THE HYDROGEOLOGIC CHARACTERISTICS OF PRINCIPAL AQUIFERS IN THE UNITED STATES

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Introduction

Groundwater has been a significant fresh water supply source for the United States (US), being withdrawn as needed, with minimal government oversight or regulation (Joshi, 2005). Groundwater has also been expected to be a major future source of fresh water for our nation (Alley et al, 2013). However, groundwater has been and will continue to be under stress from intensive long-term pumping (Konikow, 2015), anthropogenic contaminants (USGS, 2015), climate change (Kumar, 2012), and ecosystem degradation (ESA, 2015), (Knapp, 2001) (River Network, 2015).

As a critical natural resource groundwater has provided fresh water to millions of people across the US over the past century (USGS, 2014). The primary use of fresh groundwater in the US has been for irrigation, followed by public and domestic supply, livestock and aquaculture, industrial, mining and thermoelectric power generation purposes. In 2010 for example, an estimated 76 billion gallons per day (bgd) of fresh groundwater was withdrawn, with about 65% of the total (~ 49.5 bgd) being used for irrigation. Public supply and domestic supply consumed about 25% (~19.2 bgd) (NGWA, 2015), providing approximately 268 million people with potable water, including 43 million people who pump groundwater from private wells (i.e. domestic supply) (USGS, 2015). Livestock and aquaculture utilized about 4% (~ 3 bgd) of 2010 fresh groundwater withdrawals, while industrial manufacturing of products such as metal, wood, and paper products, chemicals, gasoline, and oils used about 4% (~2.9 bgd). Mining activities such as extraction of minerals, coal, iron, sand, crude oil, and natural gas used about 1% (~1.1 bgd) (USGS-Perlman, 2014), thermoelectric power generation utilized less than 1% (~ 0.6 mgd) of 2010 fresh groundwater withdrawals (NGWA, 2015).

Consequently, intensive long-term pumping of groundwater has outpaced recharge rates in some regions of the country, leading to depletion of groundwater supplies (US Geological Survey, 2014). Between 1900 and 2008 overall groundwater depletion across the US was estimated to be about 264 trillion gallons (1000 km^3) (Konikow, 2013). For comparison, the volume of water contained in Lake Erie is about 128 trillion gallons (483 km^3) (Lake Erie Waterkeeper, 2015). The groundwater storage volume depleted in the US over the past century is roughly equivalent to emptying Lake Erie twice.

Between 1945 and 1960 average US groundwater storage depletion rates averaged $13.6 \text{ km}^3/\text{year}$, or 3.6 billion gallons per year (bgy). From 1960 and after 2000 groundwater depletion rates increased to about $24 \text{ km}^3/\text{year}$ (6.3 bgy) (Konikow, 2015). The aquifer systems with the three largest storage volume depletions in the US include, the High Plains aquifer underlying the Great Plains Physiographic Province in the central US, with annual depletions of 10.2 km^3 (2.7 bgy), the Mississippi River Alluvial Valley aquifer with annual depletions of 8 km^3 (2 bgy), and California's Central Valley aquifer with annual depletion rates of 3.9 km^3 (1 bgy) (Konikow, 2015) (Figure 1). All three of these aquifer systems have had irrigation as the greatest consumer (NOAA, 2014).

A previously unforeseen factor that will potentially impact groundwater storage volumes in the U.S. is the changing climate of Earth (Famiglietti, et al., 2011). Over the past 134 years mean global temperatures have been rising, with ten of warmest years on record occurring since 1998. The year 2014 was ranked as the warmest year on record, with a global average temperature of 0.68°C (33.2°F) (NASA, 2015). Climate change may also impact groundwater resources by modifying the renewable portion of groundwater storage through changes in recharge (Crosbie, et al., 2013). For example, while global climate models for California project increased

temperatures by as much as 5°C (9°F) during the 21st century, less groundwater recharge is projected as a result of reduced Sierra Nevada snowpack (Faunt, 2009).

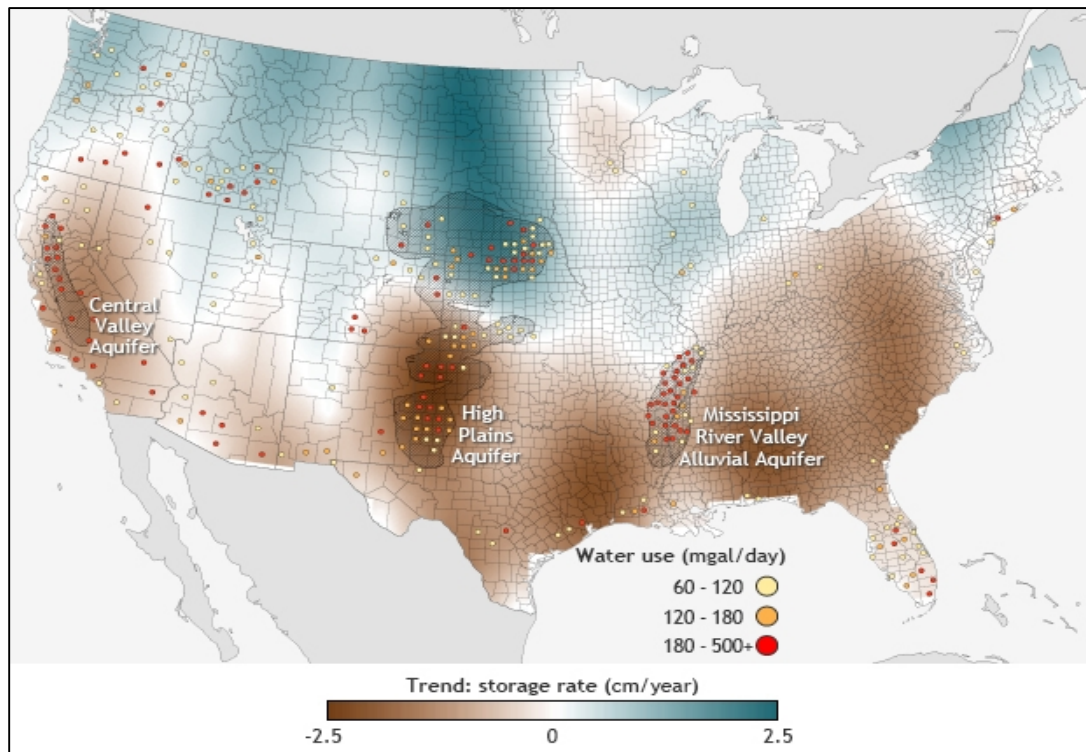


Figure1. Satellite based estimates of changes in groundwater storage levels across the US from 2003 to 2012. Storage increases are in blue, and brown areas indicate decreases in storage. Dots indicate locations where water use exceeded 60 million gallons per day or more as of 2005 (NOAA, 2014).

For the High Plains region climate models project increased recharge in the Northern High Plains (+8%), and a slight decrease in the Central High Plains (-3%), but a larger decrease in groundwater recharge in the Southern High Plains (-10%) is projected, magnifying the current spatial trend in recharge from north to south (Crosbie, et al., 2013). In the Mississippi River Embayment Region, which encompasses the Mississippi River Alluvial Valley aquifer, climate change scenarios indicate groundwater depletion ranges from 14.6 to 13.9 percent of the region having greater than 100 feet of groundwater decline, 14.5 to 13.8 percent having between 75 and 100 feet of groundwater decline, and 15.8 to 15.7 percent having 51 to 75 feet of decline in the alluvial aquifer (Clark, et al., 2011).

Intensive groundwater pumping is not sustainable when extraction rates exceed recharge rates over the long term, as this practice may lead to irreversible groundwater depletion (Faunt, 2009). Some deleterious consequences of permanent groundwater depletion include permanent land subsidence and fissures in the Earth (Borchers, et al., 2014), lower water tables, permanent reduction in total storage capacity of some aquifers (USGS, 2014), seawater intrusion of aquifers along coastal areas, water quality degradation (Barlow, et al., 2012), lower dry season stream baseflows (USGS, 2014), increased summer stream temperatures, and decreased perennial stream habitats (Jackson, et al., 2001), (Barlow, et al., 2012).

In addition to groundwater depletion from excessive pumping, there are many potential groundwater contamination sources (US EPA, 2014), including but not limited to microorganisms, xenobiotic compounds such as disinfectants, disinfection byproducts, inorganic chemicals, organic chemicals, and radionuclides, injection wells, pesticides, herbicides, nitrogen and phosphate rich fertilizers, factory farm animal wastes, mining activities, and hydraulic fracturing products and byproducts (Dubrovsky, et al., 2010), (Fitts, 2013) (Reddy, et al., 2008), (Allen, et al., 2013). Injection wells are conduits through which liquid contaminants are forced into subsurface geologic formations for disposal (Fitts, 2013). Liquid contaminants may include brines and water from oil fields containing hydrogen residues, heavy metals, hydrogen sulfide, and boron (Allen, et al., 2013). Fluids from mining of coal, copper, lead, zinc, and uranium contain deleterious contaminants (Fitts, 2013) such as heavy metals, sulfurous compounds (Allen, et al., 2013), and radioisotopes (leachate from uranium mines). Contemporary commercial farming practices such as spraying liquid pesticides and herbicides, and applying fertilizers with high nitrogen and phosphate content may contribute to high concentrations of these substances in groundwater (Fitts, 2013). Factory farm feedlots for cattle and swine and

other animals generate enormous amounts of animal wastes containing nitrates, pharmaceuticals, and steroid hormones that may contaminate recharge to underlying groundwater (Fitts, 2013). Contaminants found in groundwater and drinking water wells near hydraulic fracturing sites include methane and benzene, (Allen, et al., 2013), methanol, ethanol, and heavy metals such as arsenic, selenium, and strontium (Fontenot, et al., 2013). Organic contaminants such as petroleum based products, fossil fuels, and organic solvents have contributed to the contamination and degradation of groundwater resources across the U.S. (Fitts, 2013), (Reddy, et al., 2008). Between 1990 and 2010 increasingly greater concentrations of dissolved solids, chloride, and nitrates were found in two thirds of U.S. groundwater well networks tested. Concentrations of nitrates and synthetic organic compounds such as pesticides and volatile organic compounds (VOCs) were detected in shallow aquifers underlying agricultural and urban lands. Fifty-five VOCs were detected in analyses of samples collected at well heads from about 2,400 domestic wells and about 1,00 public wells (Zogorski, et al., 2006). Contaminants such as these could percolate down to deeper aquifers that supply much of our drinking water (DeSimone, et al., 2014). Moreover, many natural ecosystems such as forests, grasslands, wetlands, and marshes that inherently provide water purification services to groundwater recharge have been greatly reduced in area and degraded as the US population has grown, resulting in the expansion of urban areas and agricultural lands (ESA, 2015). The U.S. Forest Service estimates that old growth forests in the U.S. have been reduced by 97% since the early 1600's (Mane, 2013). Up to 99% of tall prairie grasslands in the Central Plains have been plowed up and converted primarily for agricultural and to lesser extent, urban development (Knapp, 2001). More than 50% of the 220 million acres of wetlands have been destroyed since the

1600's, with current estimates of wetland destruction between 58,000 and 60,000 acres annually (River Network, 2015).

Purpose and Scope

The objective of this report was to investigate the hydrogeologic materials and processes associated with groundwater flow and storage systems and anthropogenic influences effecting groundwater supplies. An overview of principal aquifers of the US is given with particular emphasis given to aquifer systems that have been in decline consequently from long-term, intensive pumping. Current groundwater flow modeling methods are included, as well as techniques for assessing groundwater vulnerability to contamination. In addition, natural water purification processes and groundwater conservation and protection practices for sustainable groundwater management are discussed.

General Overview of Groundwater and Aquifers

Groundwater occurs almost everywhere beneath Earth's surface (Reilly, et al., 2008), being contained within and flowing through porous sediments and fissured rocks or geologic formations known as aquifers (Custodia, 2013). Aquifers absorb, store, and yield significant quantities of groundwater to wells and springs (U.S. Geological Survey, 2014). Aquifers also discharge water to rivers, lakes, coastal areas, and wetlands (Custodia, 2013). Aquifers may be located at any depth below Earth's surface, from a few meters or less, to hundreds or thousands of meters deep (Kaufman, et al., 2011). Some fresh water bearing rocks are buried as deep as 6000 feet below Earth's surface (USGS, 2014). However, potable water is typically pumped from aquifers at depths ranging between 300 and 1200 feet (Clark, et al., 2013).

Aquifers are categorized as either unconfined or confined. An unconfined aquifer, also referred to as a water table aquifer, is below the unsaturated zone (i.e. vadose zone) and

relatively close to the land surface, existing under atmospheric pressure, and extending from the surface of the water table down to an impermeable boundary known as an aquitard (EPFL, 2015). Unconfined aquifers have no impermeable barriers to the land surface; consequently they are susceptible to contamination from the surface. In contrast, confined aquifers are overlain by aquitards (Figure 2) and exist under hydrostatic pressure which increases with depth (Indiana DNR, 2015). Aquitards have little or no permeability and low hydraulic conductivity, and thus, inhibit groundwater movement. Aquitards consist of unconsolidated, very fine grained sediments such as clay or unfractured metamorphic or igneous rock units such as shale, or basalt (Fitts, 2013). Aquitards isolate groundwater from Earth's surface, thereby inhibiting recharge, yet serving to protect confined aquifers from surface contamination (Indiana DNR, 2015).

Groundwater recharge and discharge

Natural groundwater recharge occurs as water from precipitation and snowmelt soaks into the ground, percolates down through the unsaturated zone, and enters saturated areas of the subsurface (Focazio, et al., 2002). Leakage from surface water bodies such as streams, wetlands, marshes, and lakes (Kresic, 2007) also contribute to groundwater recharge. Anthropogenic sources of recharge include return flow from irrigated agriculture (Faunt, 2009) and runoff from impervious surfaces. Factors affecting groundwater recharge quality and quantity include land cover, land use, permeability and hydraulic conductivity of soils and geologic strata, locations of surface water bodies, and depths to water tables (Jackson, et al., 2001), (Kellner, et al., 2015). Soils and sediments of vegetated ecosystems such as grasslands, forests, and wetlands have greater capacities to intercept and absorb recharge water, naturally filtering and buffering potential pollutants via soil minerals and microorganisms (Firth, 2015), (USDA NRCS, 2015).

Groundwater naturally discharges in low lying areas to streams, lakes, wetlands, saltwater bodies (bays, estuaries, or oceans), and springs (Fitts, 2013). Groundwater discharge is a significant contributor to the baseflow of many streams, both seasonal and perennial, especially in arid regions of the southwest and during times of drought (U.S. EPA, 2013). For groundwater to discharge into a surface waterbody such as a stream channel, the altitude of the water table near the stream must be higher than the stream water surface (Healy, et al., 2007). The hydraulic properties of aquifers and confining layers that make up an aquifer system may impact the timing, locations, and rates of streamflow as well (Barlow, et al., 2012) (Table 2). As shown in Table 1 the percentage of groundwater providing stream baseflow is wide ranging, due to the contrasting geology of various catchments across the U.S. (Younger, 2007). For some perennial streams such as the Dismal River and Sturgeon River, groundwater contributes to at least 90 percent of the total stream baseflow (Healy, et al., 2007) (Table 1). Seepage meters placed at various locations along the reach of a stream are used to measure exchange rates between surface waters and groundwater. The difference in discharge between any two points along a stream will be equal to net stream loss or gain from an aquifer along that reach (Healy, et al., 2007).

Table 1. Percentage of groundwater contribution as base flow to total streamflow for selected streams across the United States (Healy, et al., 2007).

Stream	State	Percentage of ground-water contribution
Dismal River	Nebraska	94
Forest River	North Dakota	13
Sturgeon River	Michigan	90
Ammonoosuc River	New Hampshire	61
Brushy Creek	Georgia	68
Homochitto River	Mississippi	36
Dry Frio River	Texas	58
Santa Cruz River	Arizona	35
Orestimba Creek	California	23
Duckabush River	Washington	65

Potentiometric surface and groundwater monitoring wells

The potentiometric or piezometric surface is a hypothetical or imaginary line representing the water table of an unconfined aquifer or the level to which groundwater will rise in a well from a confined aquifer (EPFL, 2015) (Figure2). Potentiometric surface mapping (i.e. contour mapping) of local or regional aquifers primarily provide groundwater flow directions, yet with additional data, calculations can be made of hydraulic gradients, flow velocities and flow rate estimates, particle travel times, hydraulic conductivity and transmissivity, and locations of recharge and discharge areas (Indiana DNR, 2015), (Kresic, 2007).

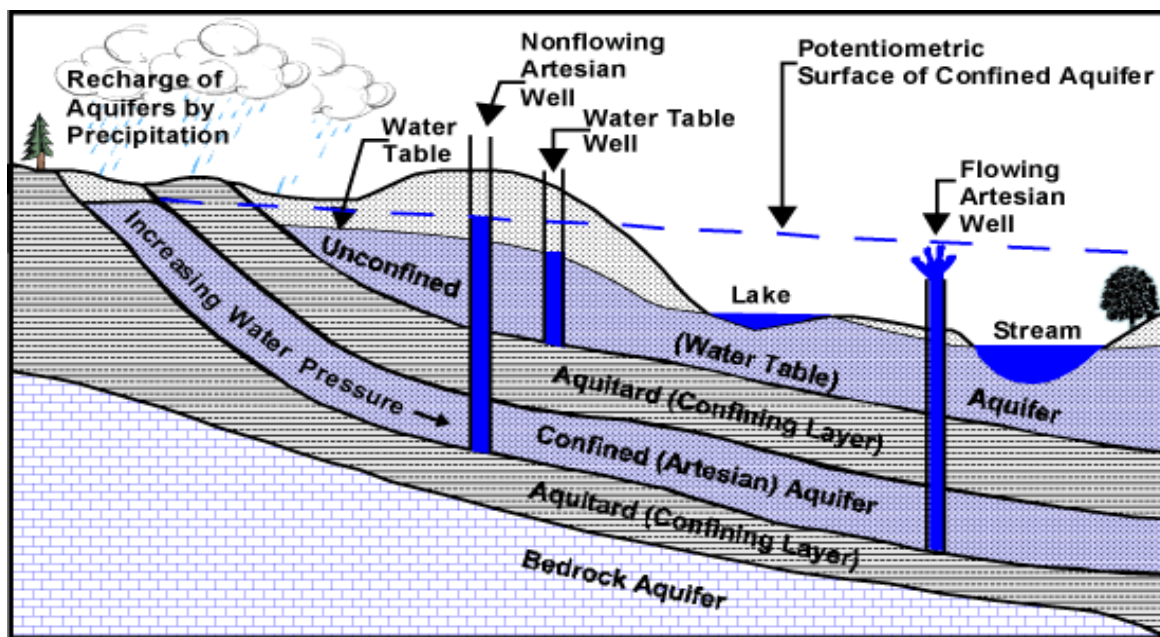


Figure2. Representation of aquifer types and groundwater movement (Indiana DNR, 2015).

Potentiometric surface maps (i.e. contour maps) are created by plotting elevations of static water levels in wells not being pumped, under confined or unconfined conditions, then generating contour lines of equal elevation (EPFL, 2015). Natural groundwater flow is generally from recharge areas at higher elevations to discharge areas at lower elevations in the landscape, and perpendicular to the potentiometric and land surface contour lines (Indiana DNR, 2015) (Figure 3).

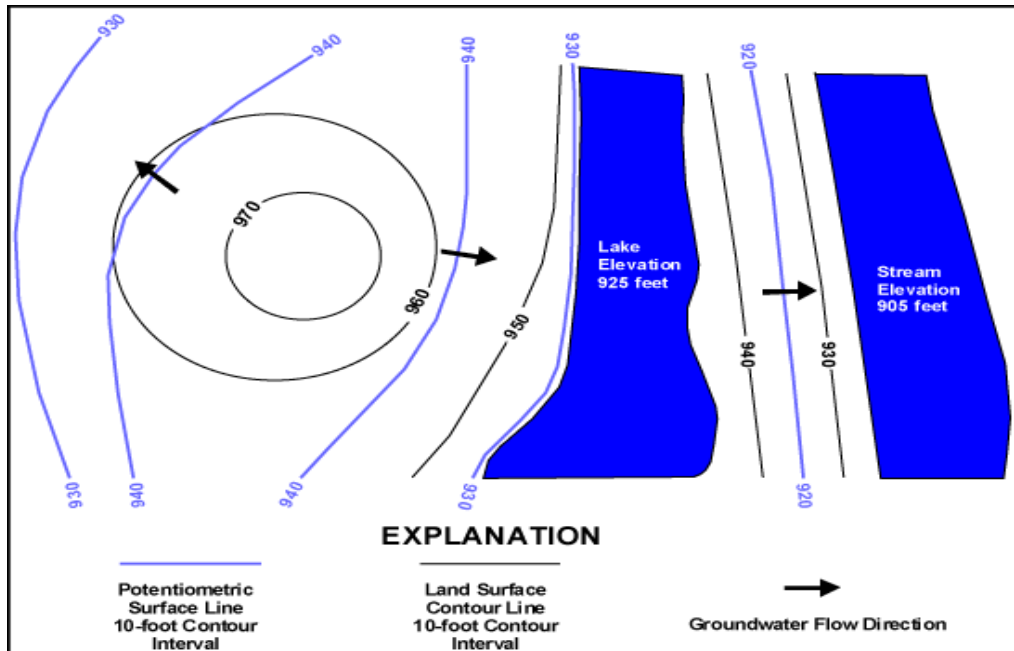


Figure 3. Schematic showing groundwater flow direction perpendicular to potentiometric surface lines (Indiana DNR, 2015).

However, contour maps are two-dimensional representations of three-dimensional flow areas. For aquifers having known significant vertical gradients, two contour maps are created, one for shallower depths and one for deeper depths of the aquifers. Cross-sectional maps are also created, depicting the cross-sectional flow net of an aquifer or aquifer system (Kresic, 2007) (Figure 4).

Groundwater monitoring wells are installed at various points along the landscape from recharge areas to discharge areas to measure groundwater levels and to collect water samples in order to test for potential contaminants (USACE, 2000). Monitoring wells have wide range screens, from 20 feet below the water table to 10 feet above the water table, in order to allow for groundwater table fluctuations. Perforations in monitoring wells extend from just below the ground surface to the bottom of the pipe (USACE, 2000). As well, any petroleum products floating at the water table level may enter the well (Adini, 2011).

Piezometers are wells that are narrower in diameter than monitoring wells, and are used to measure groundwater levels, the pressure of the groundwater at various locations and depths (Adini, 2011), and to determine groundwater flow directions (Barlow, et al., 2012).

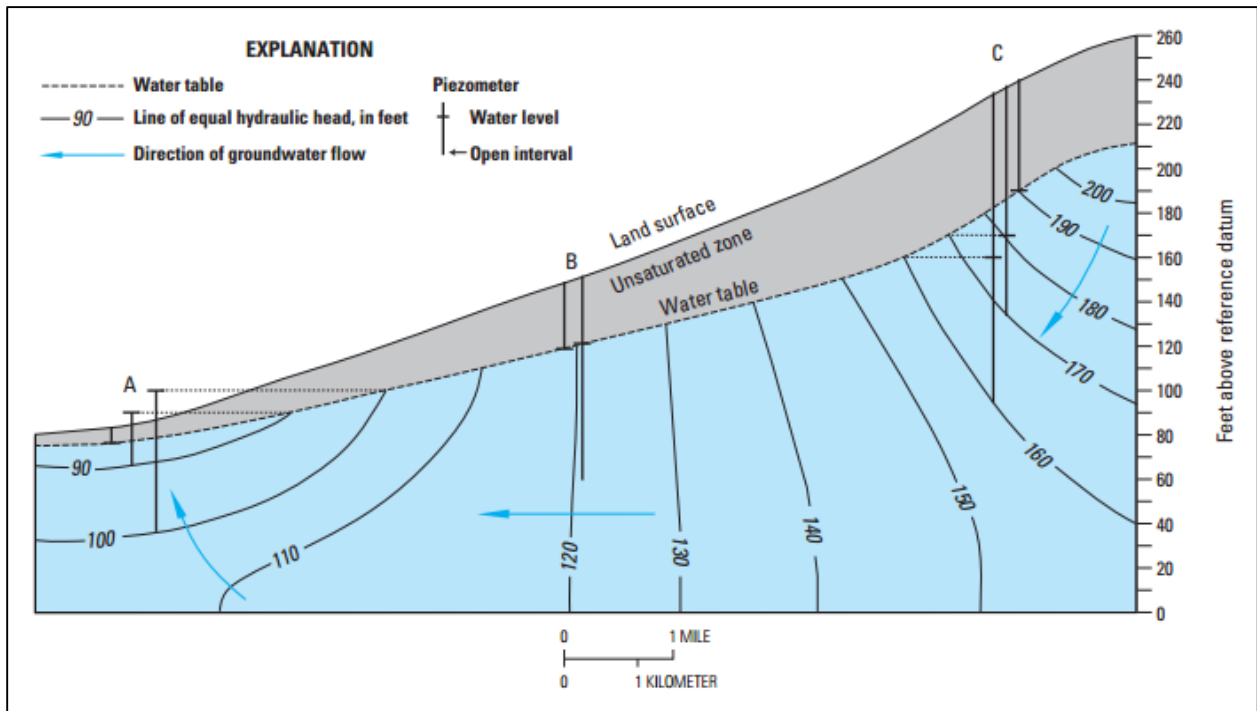


Figure 4. Vertical section of hypothetical water-table aquifer with distribution of hydraulic head contours (groundwater levels). The head measurements at piezometers A, B, and C were made at various depths. Downward groundwater flow is indicated at location C, whereas head measurements at piezometer B show lateral flow, and upward flow at piezometer A (Barlow, et al., 2012).

Groundwater flow paths are determined from water level altitudes within the piezometers which are calculated relative to a common datum plane, such as the National Geodetic Vertical Datum of 1929, which is at sea level (Barlow, et al., 2012). Piezometers generally consist of a pipe installed in the subsurface with the upper end open to the atmosphere so that the water surface in the pipe is at atmospheric pressure ($P = 0$). At or near the bottom of the pipe holes or slots allow water to move into the pipe from the surrounding saturated soil or rock. The level to which the water rises in the pipe is the hydraulic head, also referred to as pressure head (Fitts, 2013). Sets of piezometers are placed at varying depths both up and down gradient along

suspected groundwater flow paths to determine the direction of water flow. The exact depths of piezometers will depend on the topographic position in the landscape and the stratigraphy of the subsurface (USACE, 2000).

Figure 5 is a schematic diagram comparing a groundwater monitoring well with a piezometer.

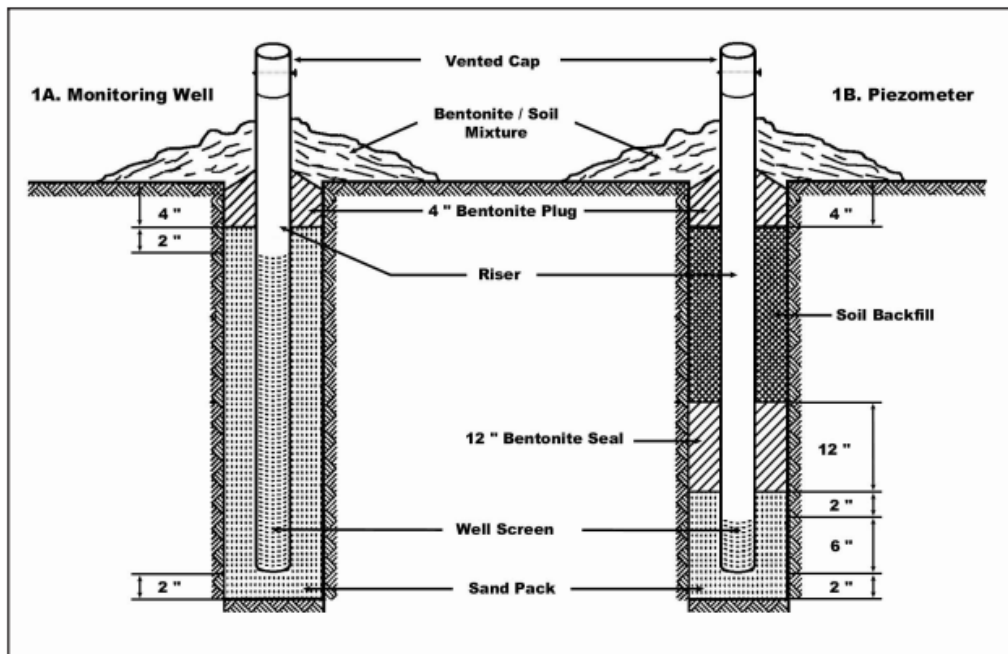


Figure 5. Schematic diagram of installed monitoring well and piezometer
 1A. Shallow monitoring well 1B. Piezometer (USACE, 2000).

Groundwater flow and the hydrogeologic properties of aquifers

Groundwater flow occurs either by seepage through granular pore spaces of unconsolidated materials or, between bedding planes, or through fractures, joints, faults, or karst openings of consolidated materials (Kresic, 2007), (USGS, 2015) (Focazio, et al., 2002). Groundwater flow volume and velocity within a groundwater system are highly dependent on the hydrogeologic properties of the aquifers and confining layers of the system (Barlow, et al., 2012), specifically the effective porosity and hydraulic conductivity of geologic materials, as well as the hydraulic gradient (Kresic, 2007).

There are several categorical terms for porosity. Porosity, sometimes referred to as primary porosity, (Focazio, et al., 2002) is the volume of voids within the total volume of geologic material. It is a function only of the rocks or sediments of the aquifer, and may or may not be available for transmission of groundwater (Focazio, et al., 2002). Porosity is dimensionless and is usually expressed as a percentage (Fitts, 2013) (Equation 1).

$$n = \left(\frac{V_v}{V_t} \right) \times 100 \quad \text{Equation 1}$$

n is the total porosity, V_v is the volume of voids (L^3); V_t is the total volume of voids and aquifer material (L^3).

Effective porosity (n_e), also called the kinematic porosity, or residual water content (Argonne EVS, 2015), is the volume of interconnected pore spaces, fractures, or other voids that transmit groundwater (Fitts, 2013) (Equation 2), thus making it the most significant type of porosity.

$$n_e = \frac{V_{vi}}{V_t} \quad \text{Equation 2}$$

Effective porosity of the aquifer, n_e , is dimensionless, V_{vi} is the volume of interconnected voids that are available for fluid transmission (L^3), V_t is the total volume of voids and aquifer material (L^3). Effective porosity is always less than total porosity (Argonne EVS, 2015).

Primary porosity of a rock is developed as the rock is formed. For example, the primary porosity of an extrusive volcanic rock such as basalt occurs as gas bubbles (vesicles) form near the surface of the rock as it cools (Chernicoff, et al., 2007). Secondary porosity occurs after a rock has formed as a result of physical processes such as tectonic events, freeze-thaw cycles, or from chemical processes such as dissolution and leaching of minerals (US EPA, 2007), thereby creating fractures, faults, fissures, or porous openings (Kresic, 2007). Porosity of unconsolidated sediments is termed intergranular porosity, while porosity of consolidated rocks is termed matrix porosity. As depth increases matrix porosity and the number of fractures decreases (Kresic,

2007), due to the weight of overlying rocks and water (Fitts, 2013). Some unconsolidated and consolidated rock porosity ranges and averages are given in Figure 6; igneous and metamorphic rock porosities are shown in Figure 7.

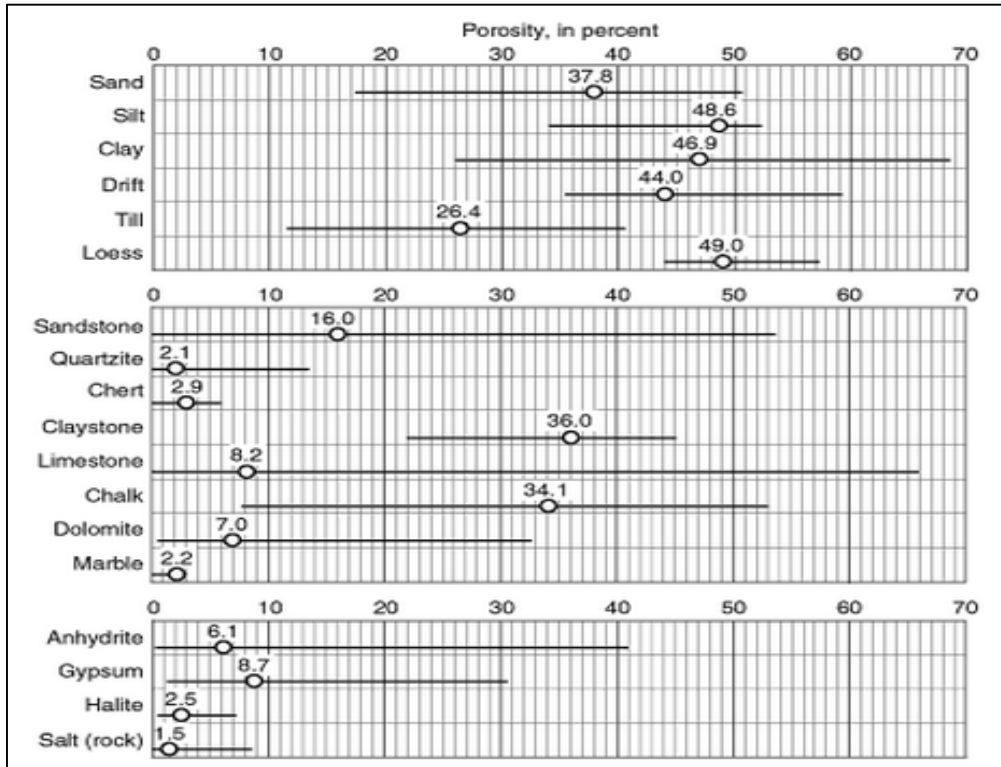


Figure 6. Porosity range (horizontal bars) and average porosities (circles) of unconsolidated and consolidated sedimentary rocks (Kresic, 2007).

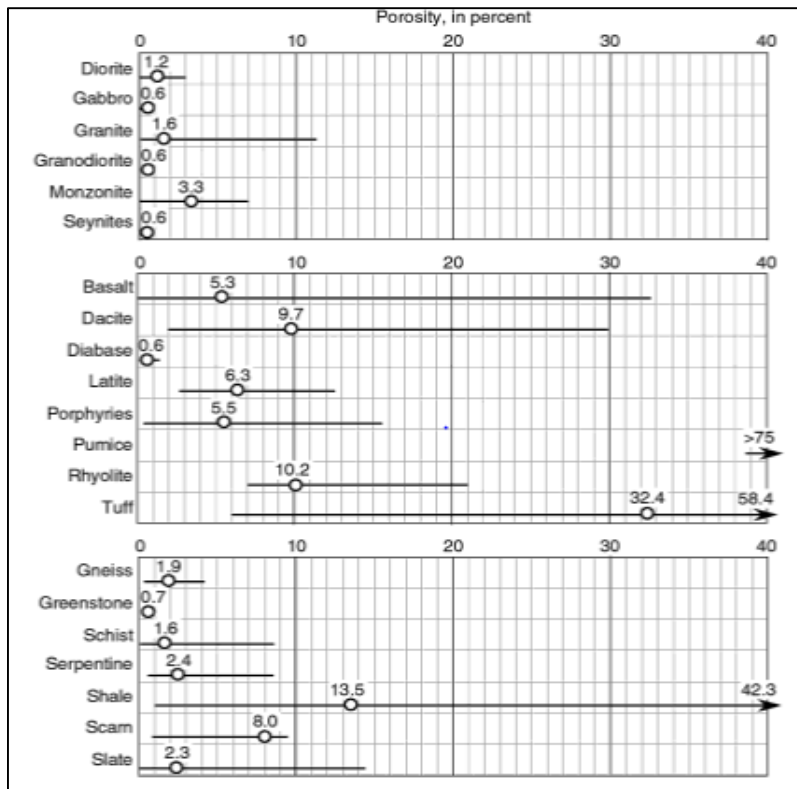


Figure 7. Porosity range (horizontal bars) and average porosities (circles) of magmatic and metamorphic rocks (Kresic, 2007).

Unconsolidated coarse sand and gravels are generally found at shallower depths than consolidated rocks, and are some of the most porous and permeable geologic materials (Fitts, 2013). Coarse sand and gravels constitute aquifers with significant specific yields, and low specific retentions (Kresic, 2007), (Fitts, 2013) (Figure 8). Glacial till is the exception to unconsolidated sediments, as it consists of poorly sorted large rock fragments surrounded by a fine grained matrix of sand, silt, and clay (Chernicoff, et al., 2007). Clays have the highest total porosities of unconsolidated sediments, yet they have the lowest specific yields (Kresic, 2007) (Figure 8). This is due to several factors; clay minerals are sheet silicates with high electrostatic attractions (e.g. negatively charged faces and positively charged edges), and clays have the smallest grain sizes, less than 0.002 mm, allowing for greater compaction (Fitts, 2013).

Igneous rocks such as granite, diorite, and gabbro have very low porosity, as they were formed through slow crystallization of magma beneath Earth's surface (Chernicoff, et al., 2007). Metamorphic rocks such as gneiss, greenstone, and others have very low porosities, as they were subjected to high pressures and temperatures that fused the individual grains of rock together as they underwent metamorphism (Chernicoff, et al., 2007). Although the porosity of most igneous and metamorphic rocks is less than one percent, most of the porosity of these rocks is in the interconnected fractures. (Fitts, 2013).

Limestone, a sedimentary rock composed primarily of calcium carbonate, has the highest variability in total porosity, ranging from about 66% down to less than 1 % (Figure 6). As young limestones undergo dissolution by percolation of water along fractures and bedding planes, karst terranes form with porosities of up to 66% (Kresic, 2007). As limestone ages it becomes compacted and under extreme heat or pressure, it may recrystallize, resulting in its having reduced porosities, down to less than 1% (Kresic, 2007).

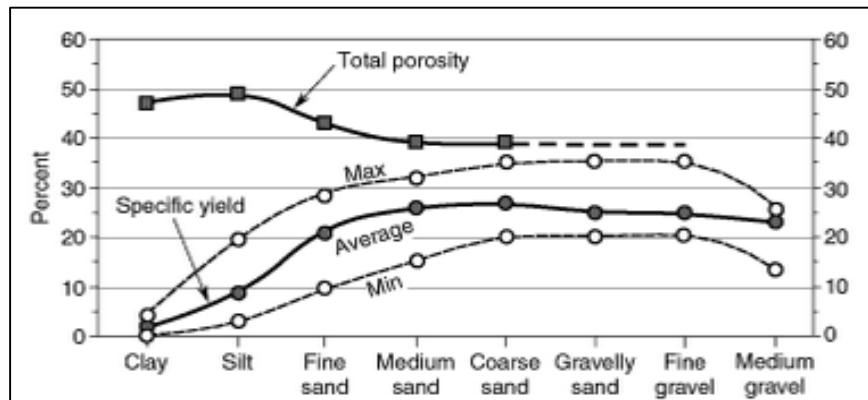


Figure 8. Approximated total porosity (squares) versus specific yield (circles) of unconsolidated sediments (Kresic, 2007).

Specific yield (S_y) of an aquifer is the volume of groundwater that can freely drain by gravity and is equal to the storativity (S) of the aquifer (Fitts, 2013). Specific yield represents the amount of water available for supply and consumption (Kasenow, 2001). The distinction

between effective porosity and specific yield is that specific yield is the volume of groundwater that is freely extracted from an aquifer, while effective porosity relates to groundwater flow and velocity through the interconnected pore spaces (Kresic, 2007).

Specific retention, also termed field capacity for soils (Argonne EVS, 2015), is the volume of water left in porous media which cannot be drained by gravity (Kresic, et al., 2013). The relationship between effective porosity (ϕ), specific yield (SY), and specific retention (SR) is shown in Equation 1, whereby effective porosity can be expressed as the sum of specific yield and specific retention of geologic materials (Kasenow, 2001) (Equation 3).

$$\phi = SY + SR \qquad \text{Equation 3}$$

Permeability and Hydraulic Conductivity

The permeability of various geologic materials such as soils, sediments, and rocks is the extent to which groundwater is able to move through each, and is a function of the sizes and numbers of interconnected pore spaces, fissures, or fractures. For example, the pore spaces between grains of sand can be greater than 1000 times larger than the pore spaces between clay particles; thus, sand is more permeable than clay. Rocks such as basalt have low porosity, yet fracture as they cool, resulting in many connected fractures, allowing them to be more permeable (Chernicoff, et al., 2007).

Hydraulic conductivity describes the rate of flow of a volume of water through a unit area of aquifer under a unit gradient of hydraulic head (Barlow, et al., 2012), is a way to quantify permeability (Chernicoff, et al., 2007). Hydraulic conductivity depends on the size and distribution of pore spaces, or the intergranular porosity in unconsolidated materials, and primary and secondary porosities in consolidated materials (Kresic, 2007). When variation of hydraulic conductivity values occur from one location to another within an aquifer, the aquifer is referred

to as heterogeneous. In contrast, an aquifer with hydraulic conductivity the same everywhere is referred to as homogeneous (Barlow, et al., 2012). Many times average hydraulic conductivity within the same hydrogeologic terrain can vary by orders of magnitude (Healy, et al., 2007) (Figure 9). Hydraulic conductivity, K, is measured as the distance groundwater travels over a given period of time (e.g. cm/s or m/d) (Chernicoff, et al., 2007). Gravel, cavernous carbonate rocks, and lava flow basalt may have very high hydraulic conductivities, and potentially allow groundwater movement of between 1000 and 10,000 meters per day (Healy, et al., 2007). Unfractured basalt, crystalline igneous, and metamorphic rocks, including shale can have some of the lowest hydraulic conductivities, down to 10^{-8} meters per day, as they have extremely low porosities (Kresic, 2007) (Figures 7 and 9).

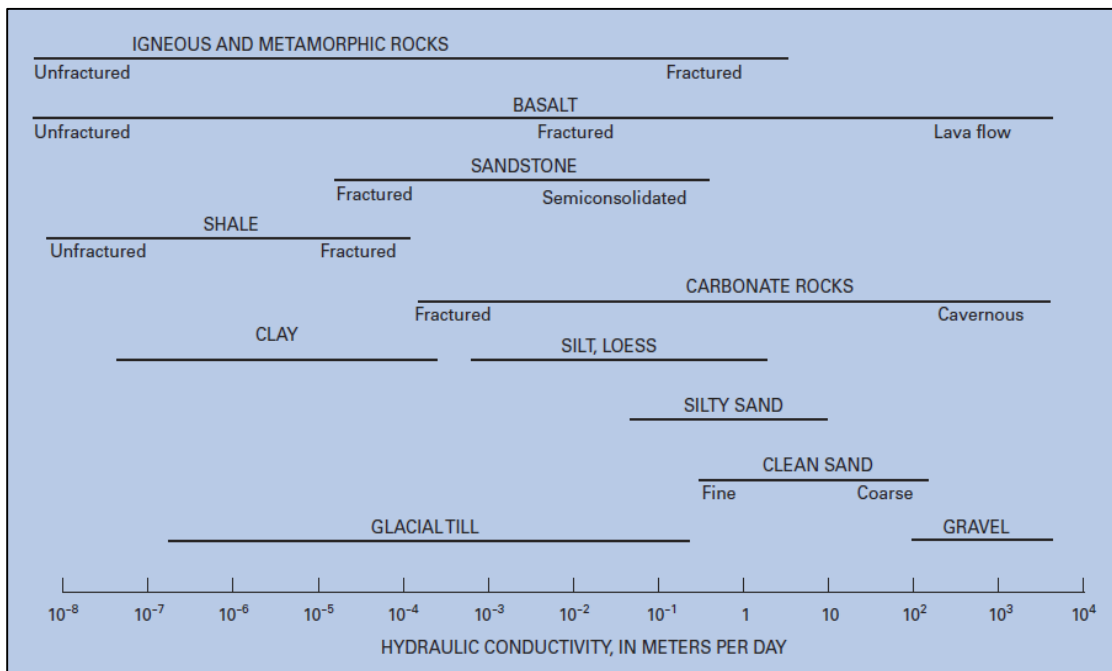


Figure 9. Approximate ranges of hydraulic conductivity for selected geologic materials (Healy, et al., 2007).

Transmissivity is a measure of the rate at which water moves through one unit width of an aquifer under one unit of hydraulic gradient, and is a function of the density and viscosity of the fluid, and hydraulic conductivity and thickness of the porous layer within an aquifer. As shown

in Equation 4 transmissivity (T) is equal to the hydraulic conductivity of the porous material of the aquifer (K_t) multiplied by the thickness of the porous layer (b). Transmissivity is measured in units of $\frac{L^2}{t}$, where L is length and t is time (Fitts, 2013).

$$T = K_t b \quad \text{Equation 4}$$

If an aquifer layer is composed of n number of strata of thicknesses, b_i , and having hydraulic conductivity $(K_t)_i$, then the total transmissivity of the layer is equal to the sum of the transmissivities of each stratum (Fitts, 2013) (Equations 5 and 6):

$$T = \sum_{i=1}^n T_i \quad \text{Equation 5} \quad = \quad \sum_{i=1}^n (K_t)_i b_i \quad \text{Equation 6}$$

Specific storage (S_s) is the amount of water expelled from one unit of volume of saturated material when the pore water is subject to a unit decline in hydraulic head (Fitts, 2013)

(Equation 7).

$$S_s = - \frac{dV_w}{V_t} \frac{1}{dh} \quad \text{Equation 7}$$

The volume of water expelled, dV_w , from an aquifer of volume V_t as the hydraulic head changes, dh , is equal to the specific storage S_s of the aquifer. The negative sign is there because S_s is a positive constant, and when the hydraulic head declines dh is negative and the volume of water expelled, dV_w , is positive. So for a unit volume $V_t = 1$, and a unit decline in head equals $dh = -1$, the specific storage is equal to the change in the volume of water expelled (Fitts, 2013) (Equation 8).

$$S_s = dV_w \quad \text{Equation 8}$$

Water Budget for an Aquifer

One of the most basic ways to quantitatively evaluate the movement of groundwater through an aquifer system is through developing a water budget for the system (Lundmark, et al., 2007). The creation of a water budget enables water resource managers to evaluate the availability and sustainability of a water supply within a system (Healy, et al., 2007). Beginning with the simple but necessary water balance equation, the change in storage is equal to the sum of inflows minus the sum of outflows (Equation 9).

$$\sum \text{inflows} - \sum \text{outflows} = \Delta \text{ storage} \quad \text{Equation 9}$$

During predevelopment of groundwater, water inflows were equal outflows and a steady state, or long-term equilibrium occurred in which there was no net change in storage (Fitts, 2013) (Equation 10).

$$R - Q^{\text{bf}} - \text{ET} - Q^{\text{gw}} - Q^{\text{w}} = 0 \quad \text{Equation 10}$$

R is recharge, Q^{bf} is discharge to the surface as baseflow, Q^{gw} is groundwater flow out of the system, and ET is evapotranspiration from the saturated zone. Q^{w} is well discharge, which during predevelopment times was equal to zero. As well, the zero on the right side of Equation 9 means that no change in groundwater storage occurred; the system was in long-term equilibrium.

However, when pumping of wells began, Q^{w} threw the system out of equilibrium, as outflows became greater than inflows and a change in storage occurred (Fitts, 2013). A post-development water budget equation shows that the change in the volume of water stored in an aquifer is balanced by the rate at which water flows into and out of the aquifer (Healy, et al., 2007). A contemporary mass balance equation for a groundwater budget for a particular aquifer or aquifer system is shown in Equation 11.

$$S + R - Q^{\text{bf}} - \text{ET} - Q^{\text{gw}} - Q^{\text{w}} = \Delta S^{\text{gw}} \quad \text{Equation 11}$$

S is the groundwater storage volume. ΔS^{gw} is the change in groundwater storage. Minimizing groundwater storage reductions is accomplished when recharge and discharge are in equilibrium. Accurately calculated water budgets can be important tools used by groundwater managers can use to reach this equilibrium. Actions taken that improve accuracy in creating water budgets include monitoring groundwater levels and measuring stream flow on a regular basis, obtain accurate and reliable information about pumping and irrigation rates within the watershed, and improve estimate rates of natural recharge and irrigation return flow (Healy, et al., 2007).

Groundwater Flow

Groundwater movement or flow occurs between any two points with differing elevation and pressure; that is, groundwater flow is driven by gravity and the differences in pressure on groundwater due to the weight of overlying water or rocks (Chernicoff, et al., 2007). Flow of groundwater generally happens by slow seepage through pore spaces of unconsolidated materials such as sand and gravel or between bedding planes, networks of fissures, and fractures, or karst openings of consolidated rocks (Kresic, 2007). Flow velocities vary with the permeability of geologic materials, hydraulic gradients, and fluid properties (e.g. fresh water vs salt water) (Kaufman, et al., 2011). Groundwater flow is always from the higher hydraulic head or pressure head (h) towards a lower hydraulic head. As groundwater flows it loses energy due friction between the groundwater molecules and the porous geologic media (Kresic, 2007). Figure 10 is a schematic representation of groundwater flow from well #1 (h_1) to well #2 (h_2) in an unconfined aquifer. Well #1 has a higher pressure head than well #2, as it is at a higher elevation. Taking the difference between the two pressure heads will show the loss of energy, or the change in pressure head (Δh) (Kresic, 2007) (Equation 12).

$$\Delta h = h_1 - h_2$$

Equation 12

Darcy's law and equations related to groundwater flow

Darcy's law describes the flow of groundwater within a porous media. Darcy's equation is a simple quantification of linear flow of groundwater discharged through a cross-sectional area of an aquifer (Kresic, 2007) (Equation 13).

$$Q_s = - K \left(\frac{dh}{dL} \right) A \quad \text{Equation 13}$$

where the discharge flow volume, Q_s , in the s direction, is directly proportional to the hydraulic conductivity constant, K , of the geologic material, and the change in hydraulic head (labeled as dh in Equation 5 or as Δh in Figure 10), and the cross-sectional area through which groundwater flows, A . Discharge flow volume is inversely proportional to the distance between the two wells (dL) (Kresic, 2007). The minus sign on the right side of the equation represents the fact that hydraulic head decreases in the direction of the flow (Fitts, 2013).

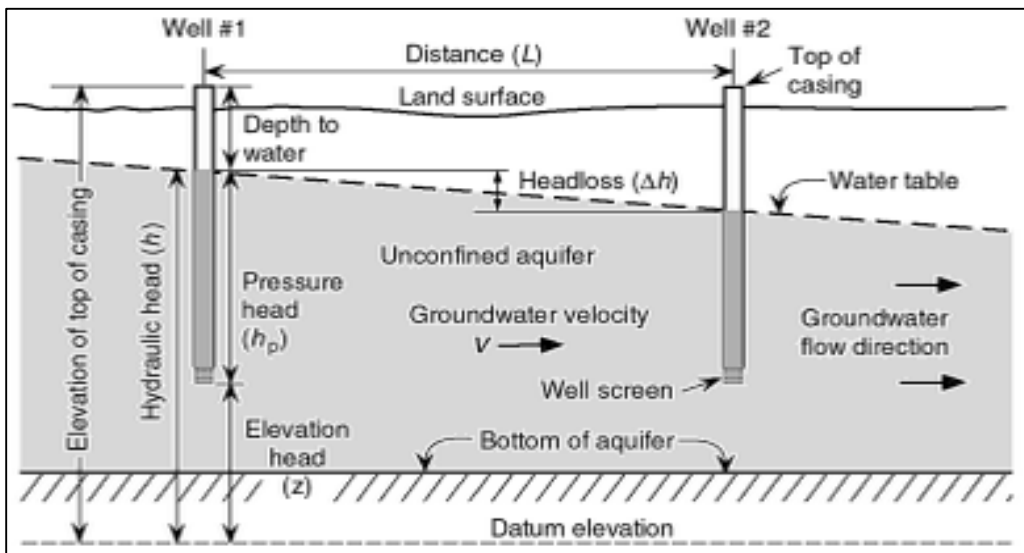


Figure 10. Schematic of key elements for determining hydraulic head and hydraulic gradient in an unconfined aquifer (Kresic, et al., 2013).

The average linear velocity is equal to the average velocity of groundwater flowing through the pore spaces of a groundwater flow system (Focazio, et al., 2002) (Equation 14).

$$v = \left(\frac{Ki}{n_e} \right) \quad \text{Equation 14}$$

v is the average linear velocity $\left(\frac{L}{T}\right)$, K is the hydraulic conductivity $\left(\frac{L}{T}\right)$, I is the hydraulic gradient (difference in hydraulic head / distance) which is dimensionless, and n_e is the effective porosity (dimensionless) (Focazio, et al., 2002).

Thus, the specific discharge, q , also known as Darcy velocity, is the discharge rate per unit cross-sectional area in the L direction (Fitts, 2013) (Equation 15).

$$q = Q/A = - K \left(\frac{dh}{dL} \right) \quad \text{Equation 15}$$

Groundwater movement may occur as two-dimensional flow in the horizontal plane, which may be the case in some confined aquifers that have horizontal dimensions that are hundreds or thousands of times greater than their vertical thicknesses (Fitts, 2013), (Czarnecki, et al., 2003). Equation 16 shows the partial differential equation for two-dimensional flow in the x, y plane, for an aquifer allowing for anisotropy and spatial variations over time. The transmissivities in the x and y directions are given as T_x and T_y respectively. The x and y components of the hydraulic gradient are given as $\frac{\delta h}{\delta x}$ and $\frac{\delta h}{\delta y}$ respectively. The net specific discharge coming in from the top and bottom are shown as N , with dimensions of volume/time/area ($L^3/T/L^2$). The rate of change in the volume of water stored in the element (volume/time) is $S \frac{\delta h}{\delta t}$ (Fitts, 2013).

$$\frac{\delta}{\delta x} \left(T_x \frac{\delta h}{\delta x} \right) + \frac{\delta}{\delta y} \left(T_y \frac{\delta h}{\delta y} \right) + N = S \frac{\delta h}{\delta t} \quad \text{Equation 16}$$

Non-linear flow occurs generally in unconfined aquifers, as vertical movement of hydraulic head occurs more readily and groundwater movement is in the three-dimensional direction.

In calculating the velocity of water movement through an unconfined aquifer the Cartesian x, y, z coordinate system is used to describe groundwater flow in each of the three directions (Fitts, 2013), (Igboekwe, et al., 2011). Equation 17 is the most universal form of saturated groundwater flow equation, allowing flow in all three directions.

$$\frac{\delta}{\delta x} \left(K_x \frac{\delta h}{\delta x} \right) + \frac{\delta}{\delta y} \left(K_y \frac{\delta h}{\delta y} \right) + \frac{\delta}{\delta z} \left(K_z \frac{\delta h}{\delta z} \right) = S_s \frac{\delta h}{\delta t} \quad \text{Equation 17}$$

K_x , K_y , and K_z is hydraulic conductivity of geologic materials in the x, y, and z directions, respectively. Change in hydraulic head, δh , is a function of δx , δy , and δz , and at time period δt .

The rate of change in the volume of water stored in the element (volume/time) is $S \frac{\delta h}{\delta t}$ (Fitts, 2013).

Groundwater systems may be either in a steady state or a transient state. A steady state system occurs when the groundwater levels (i.e. hydraulic head) and flow rates within and along the boundaries of the system are constant with time, and the rate of storage change within the flow system is zero (Barlow, et al., 2012). As well, the direction of flow is constant throughout the steady state system (GroundwaterSoftware.com, 2015). A transient groundwater system occurs when groundwater levels and flow rates change with time along with changes in storage (Barlow, et al., 2012). A transient system may occur in response to changes in flow rates along the boundaries of a groundwater system resulting from fluctuations in recharge rates, or fluctuations in pumping rates (Barlow, et al., 2012). Transient groundwater flow is calculated using Equation 18 (GroundwaterSoftware.com, 2015).

$$\frac{\delta(\rho w q w)}{\delta x} + \frac{\delta(\rho w q w)}{\delta y} + \frac{\delta(\rho w q w)}{\delta z} = \frac{\delta(\rho w \phi S w)}{\delta t} \quad \text{Equation 18}$$

In Equation 16 above, ρ_w is the density of water, q_w is the Darcy flux of water, ϕ is porosity, and S_w is saturation.

During steady state, groundwater flow time is not an independent variable, and there is no change in the amount of water stored, no change in hydraulic head, and saturation remains the same (GroundwaterSoftware.com, 2015) (Equation 19).

$$\frac{\delta(\rho_w q_w)}{\delta x} + \frac{\delta(\rho_w q_w)}{\delta y} + \frac{\delta(\rho_w q_w)}{\delta z} = 0 \quad \text{Equation 19}$$

ρ_w is the density of water and q_w is the Darcy flux of water (GroundwaterSoftware.com, 2015).

Determining Residence time and Flow Paths

The measure of time between recharge and discharge of groundwater from an aquifer flow system is known as residence time or groundwater age (Loaiciga, 2004). Residence time is variable, ranging from days to years in unconfined aquifers and from centuries to tens of thousands of years in deeper, confined aquifers (National GeoEnvironmental Laboratories, 2014) (Figure 11). Average residence times, including very deep and saline waters, are approximately 20,000 years (Fitts, 2013).

Residence time (T_r) of groundwater is calculated as the volume (V) of the reservoir (L^3) divided by the total flux (Q) in or out of the reservoir, (L^3/ T) (Fitts, 2013) (Equation 20).

$$T_r = V/Q \quad \text{Equation 20}$$

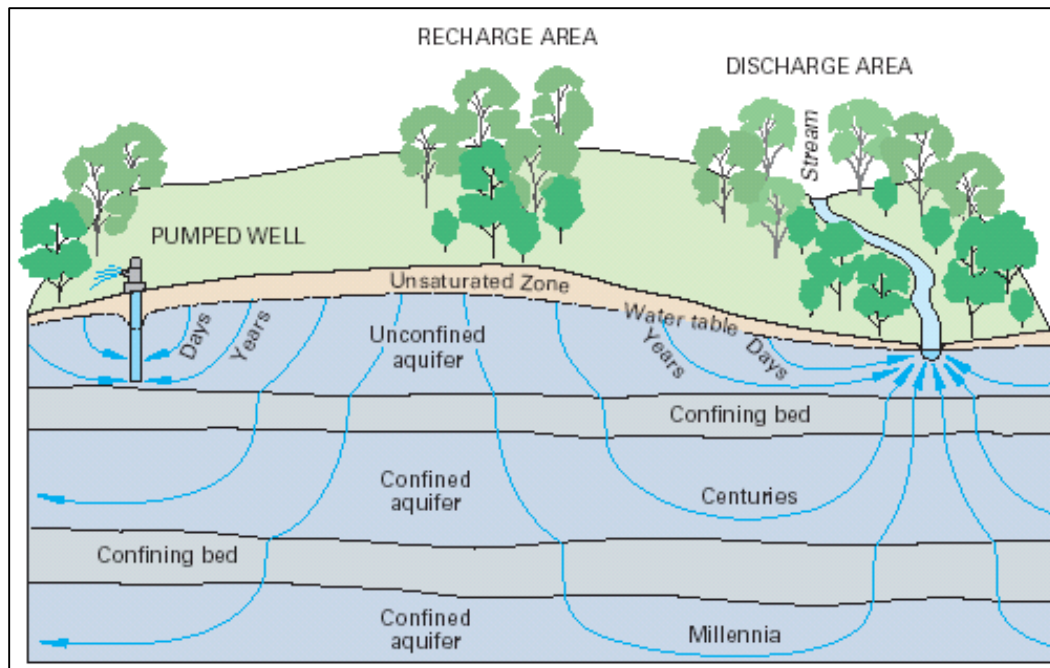


Figure 11. Depiction of groundwater flow paths in a multi-aquifer groundwater system. Groundwater flows from recharge areas at the water table to discharge locations at the stream and well. The residence time of groundwater can range from days to millennia. (Focazio, et al., 2013), (Barlow, et al., 2012).

Residence time can be determined using various methods such as tracers, water-budgets, ground water flow modeling, stream flow hydrograph analysis, and water table fluctuation measurements (Resources, 2013). Tracers are chemicals or isotopes that are transported by water, that can not only be used to determine groundwater age, but also groundwater velocities, travel times, and travel paths (Healy, et al., 2007). Examples of tracers used in groundwater studies are given in Table 2. Isotopic tracers and chemical tracers are categorized as environmental, historical, or applied. Oxygen, carbon, chloride, sulfate, and nitrate isotopes are also environmental tracers. Measuring fractions of the isotopes of oxygen ($\delta^{18}\text{O}$) and hydrogen-deuterium (^2H , δD) in groundwater, as well as in precipitation and surface water bodies interacting with groundwater, can be helpful in determining the residence time of groundwater, the source of the groundwater, and seasonal variations in groundwater recharge (Yeh, et al., 2014).

Table 2. Examples of tracers used in groundwater budget studies (Healy, et al., 2007).

Use	Naturally occurring in the environment	Historical-Added to the environment from human activity in the past	Applied-Added to the environment in the present	Example study
Groundwater age-- Time since recharge water became isolated from the atmosphere	³⁵ S, ¹⁴ C, ³ H/ ³ He, ³⁹ Ar, ³⁶ Cl, ³² Si	³ H, ³⁶ Cl, ⁸⁵ K, Chlorofluorocarbons, herbicides, caffeine, pharmaceuticals		(Plummer, et al., 2001)
Temperature of recharge	N ² /Ar solubility			(Plummer, 1993)
Tracing groundwater flow paths	¹⁸ O, ² H, ¹³ C, ⁸⁷ Sr		Cl, Br, dyes	(Renken, et al., 2005)
Exchange of surface water and ground water	¹⁸ O, ² H, ³ H, ¹⁴ C, ²²² Rn		Cl, Br, dyes	(Katz, et al., 1997)
Surface water discharge and travel time			Cl, Br, dyes	(Kimball, et al., 2004)

Historical tracers are compounds that have been released into the environment continuously or at specific times in the past. Historic tracers include radionuclides such as tritium (³H) and chlorine-36 (³⁶Cl), which were released during nuclear bomb testing in the 1950s and 1960s. Chlorofluorocarbons (CFCs), introduced in the early 1930s, were used as solvents in refrigeration, foam production, and as propellants in aerosols, while sulfur hexafluoride (SF₆), introduced in the late 1970s, was used in the electrical industry and for glazing. Applied tracers such as chlorine (Cl), bromine (Br), and dyes are utilized to measure velocities and flow paths of groundwater movement, and to quantify exchange rates between surface and groundwaters (Healy, et al., 2007).

Groundwater flow modeling and groundwater vulnerability assessment methods

In general the subsurface geologic strata can vary from simple, homogeneous layers of sand to a more complex heterogeneous strata, anisotropic in nature, in which the hydraulic conductivity may vary in all directions (Fitts, 2013), due to variability in sedimentation and

distributions of bedding planes, fractures, folds and faults, particularly where past tectonic events occurred. Thus, it is generally difficult to completely and accurately characterize groundwater flow paths (Fitts, 2013). Computer simulated groundwater flow and storage models are mathematically based programs (Fitts, 2013), designed to aid water resource managers in determining groundwater flow volumes and paths, and predicting how water levels in aquifers will be affected by changes in groundwater withdrawals and recharge rates (Healy, et al., 2007).

One contemporary computer flow modeling program is MODFLOW, originally written by the USGS in 1984 as a groundwater flow simulation code. MODFLOW-2005 uses the Finite Difference Model that solves the groundwater flow equation using linear and nonlinear numerical solution methods. MODFLOW uses a block centered grid system which simulates three-dimensional groundwater flow (USGS, 2015) (Figure 12).

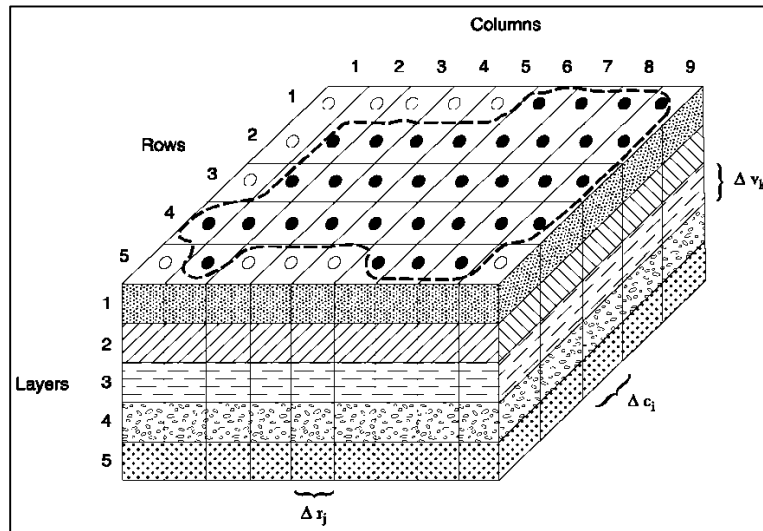


Figure 12. Schematic representation of MODFLOW block-centered grid (USGS, 2015).

MODFLOW programs have the capability to simulate coupled groundwater/surface water systems, transient groundwater flow in surficial, intermediate, and deeper aquifer systems (Sepulveda, et al., 2013), solute transport, variable-density flow (including saltwater), aquifer system compaction and land subsidence, parameter estimation, and groundwater management

(USGS, 2014). MODFLOW-2005 simulates steady and nonsteady flow in irregularly shaped flow systems for confined, unconfined, or a combination of both groundwater systems, and incorporates external stresses such as pumping wells, areal recharge, evapotranspiration, and flow through riverbeds. Other variables calculated using MODFLOW-2005 include hydraulic conductivities and transmissivities for various aquifer layers, including anisotropic (i.e. having different properties in all directions) and heterogenic (e.g. variability in geologic material, such as sediment textures, stratification, and bedding planes). Hydraulic head and flux boundaries can also be simulated, as well as head-dependent flux along the model's outer boundary (USGS, 2015).

Another program which is primarily used for estimating water storage on Earth is the Gravity Recovery and Climate Experiment (i.e. GRACE), a gravity based satellite imagery program. GRACE maps changes in Earth's gravity field that result from the movement of water over the planet. GRACE maps regions of Earth that gain or lose water storage on monthly to decadal time scales. The development of GRACE was based on studies that correlated variations in total water storage in a region (i.e. snow, ice, surface water, soil water, and groundwater) to Earth's gravity field. With additional hydrological datasets, GRACE provides estimates in groundwater storage change (NASA, 2014).

In order to calculate storage variation estimates, GRACE measures and integrates changes in total water storage, impacts of natural climate fluctuations, global change, and human water use, including groundwater extraction. GRACE has the ability to calculate changes in the volume of water stored in an entire basin, including water lost through evapotranspiration (Famiglietti, et al., 2013). Since its launch into orbit in 2002, GRACE has mapped monthly changes in Earth's gravity field with extreme accuracy (Famiglietti, et al., 2011). Figure 13 shows a map of the

contiguous U.S. generated with data gathered from the GRACE mission showing increases and decreases in U.S. groundwater storage between 2003 and 2012.

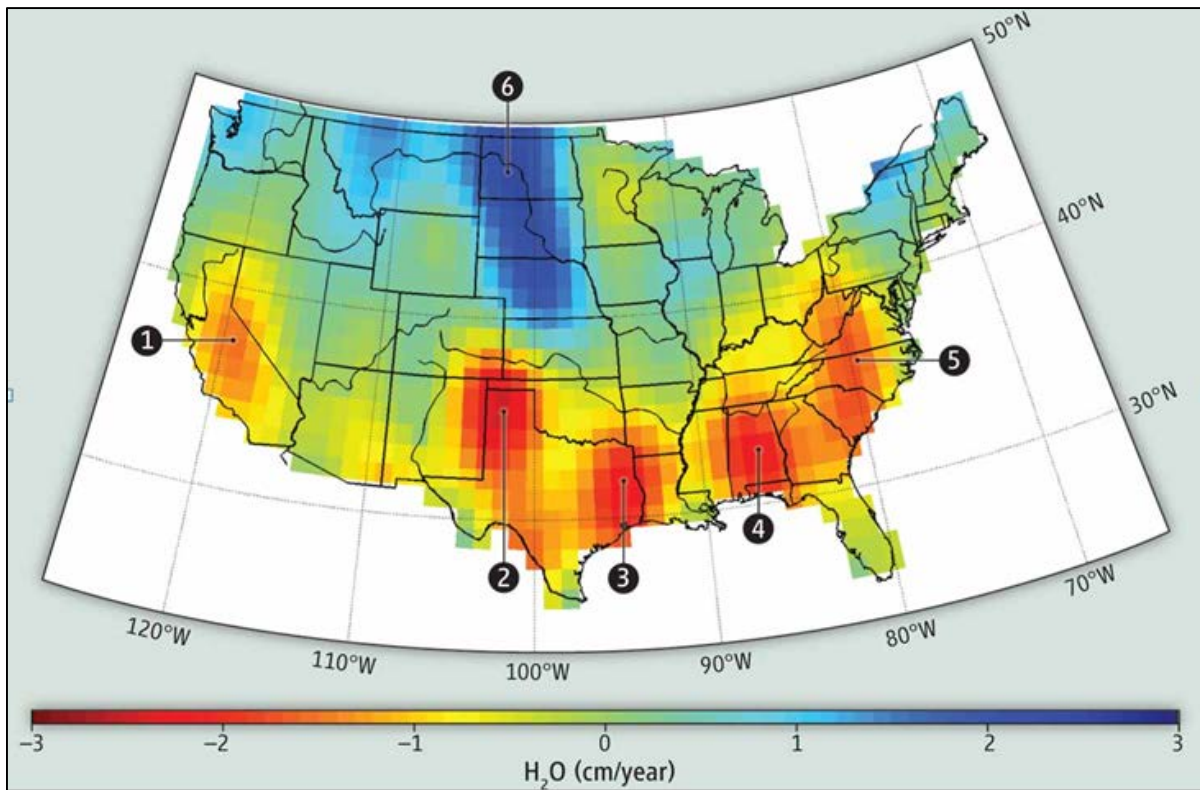


Figure13. GRACE data show water losses in agricultural regions such as California's Central Valley (1) (-1.5 ± 0.1 cm/yr) and the Southern High Plains Aquifer (2) (-2.5 ± 0.2 cm/yr), caused by overreliance on groundwater to supply irrigation water. Regions where groundwater is being depleted as a result of prolonged drought include Houston (3) (-2.3 ± 0.6 cm/yr), Alabama (4) (-2.1 ± 0.8 cm/yr), and the Mid-Atlantic states (5) (-1.8 ± 0.6 cm/yr). Water storage is increasing in flood-prone Upper Missouri River basin (6) (2.5 ± 0.2 cm/yr) (Famiglietti, et al., 2013).

Between 2003 and 2012 the greatest increases in groundwater storage occurred in the Upper Missouri River Basin, western Washington State, and in the northern reaches of Montana, New York, Vermont, and Maine. The greatest declines in groundwater storage occurred in Texas, Louisiana, Alabama, inland areas of South and North Carolina, Virginia, and California.

Generally, the northern latitudes from 40°N to 50°N, ranged from about 0 to +3 cm in groundwater storage, while the southern latitudes, from about 25°N to about 40°N had ranges of 0 to -3 cm, with some variability (Famiglietti, et al., 2013).

Groundwater Vulnerability Assessment

Groundwater vulnerability to contamination depends on the natural hydrogeologic processes such as hydraulic conductivity and porosity of the geologic deposits, hydraulic gradients, and interactions with surface waters, as well as the physical and chemical nature of the contaminant, its source and proximity to recharge areas (Focazio, et al., 2013). Groundwater vulnerability assessment studies have been developed for assessing the vulnerability of groundwater to potential contamination (Beaujen, et al., 2014). Groundwater vulnerability studies use parameters that include physical characteristics and thickness of the unsaturated zone, stratigraphic lithology, hydraulic conductivity and transmissivity, recharge rates, confined or unconfined nature of the underlying aquifer, ground-water travel time (i.e. age of groundwater within the aquifers), and the proximity of the aquifer to potential contaminant sources. Other parameters include the characteristics of contaminant sources, and whether contaminants are from natural sources or anthropogenic sources. Natural sources of contaminants would include the mineralogy or geochemical composition of the aquifer stratum. Anthropogenic contaminant sources may include land use, including urban, industrial, and agricultural (USGS, 2014).

Two major groups of methods for determining vulnerability of aquifers to contaminants are subjective rating methods, and statistical and process-based methods. Subjective rating methods are developed by, and for water resource decision makers whose focus is on policy or management objectives. Statistical and process based methods are created by scientists and focus on science objectives, which do not produce subjective categories, yet are used by decision makers to defend their decisions.

Subjective rating methods for assessing groundwater vulnerability range from index methods to subjective hybrid methods, with each categorizing the vulnerability of groundwater. Index

based mapping methods were designed to represent the physical attributes and protective effects of layers overlying an aquifer. The physical attributes are then weighted to generate a vulnerability index from which vulnerability maps can be generated. DRASTIC, EPIK, and GOD are typical index-based methods used to predict potential vulnerability to groundwater contamination (i.e. intrinsic vulnerability, I_v) (Beaujen, et al., 2014), (Polemio, et al., 2009).

DRASTIC, developed by the U.S. Environmental Protection Agency (USEPA) and the National Water Well Association is an acronym for seven parameters, including **D**epth to water, **R**echarge, **A**quifer media, **S**oil media, **T**opographic slope, **I**mpact of vadose zone media, and **C**onductivity, each of which is numerically weighted and ranked from one to ten, to describe the potential for groundwater contamination (Aller, et al., 1987). The DRASTIC INDEX is the numerical value which prioritizes areas with the greatest potential for groundwater contamination, with one having the least potential and ten having the greatest potential (Aller, et al., 1987). DRASTIC is relatively inexpensive, simple, and uses limited data that are generally available or estimated, and an end product is produced that is easily interpreted for decision making (Focazio, et al., 2002), (Beaujen, et al., 2014). One disadvantage of DRASTIC is that it has some limitations with karstic aquifers (Polemio, et al., 2009).

EPIK is another parameter weighting and rating method, similar to DRASTIC, having parameter weights that express the contribution of each parameter to vulnerability. The EPIK method was designed to be applied in karstic or carbonate aquifers, as it is able to discriminate the potentially most dangerous locations for pollution sources (Polemio, et al., 2009).

GOD, an acronym for **G**roundwater hydraulic confinement/**O**verlying strata /**D**epth to groundwater table, is a vulnerability assessment method developed in Great Britain where most groundwater resources are in hard rock aquifers, primarily sandstone and limestone. GOD

considers the soil and unsaturated zone without taking the transport processes in the saturated zone (Beaujen, et al., 2014). The GOD method works well in mapping large areas with high vulnerability contrasts (Polemio, et al., 2009).

DPSIR, a groundwater vulnerability or sensitivity assessment method developed by the European community is an example of a statistical and process based approach. DPSIR was developed to quantitatively describe the interactions between society and the environment. The DPSIR framework defines a chain of **D**rivers (e.g. anthropogenic activities such as industrial or agricultural) that exert **P**ressure (e.g. land use change or pumping of groundwater) on the **S**tate of the environment (i.e. a combination of physical, chemical, and biological conditions changed and degraded by the pressures), which then generates an **I**mpact (i.e. a consequence of the changed state of the environment) that will require an appropriate **R**esponse (required that society improve the state of the environment) (Beaujen, et al., 2014). This is a systematic and physically based approach that combines the DPSIR framework with numerical groundwater flow and/or pumping data, and uses sensitivity coefficients that reflect the inherent ease with which the groundwater state transmits pressures into impacts. Upstream factors (UF) are the pressures which have direct effects on downstream factors (DF), which are the impacts. Groundwater resource vulnerability (GRV) is the vulnerability of an entire aquifer or aquifer system to a given pressure, such as contamination. Groundwater source vulnerability (GSV) is the vulnerability of specific components of the groundwater system, such as the vulnerability of a pumping well to changes in groundwater recharge. The groundwater state vulnerability, S , that relates impacts, I , to pressures, P is quantitatively defined by equation 21 (Beaujen, et al., 2014).

$$S \equiv S_{ij} = \frac{\delta I_j}{\delta P_i} \quad i=1, n_P \quad j=1, n_I \quad \text{Equation 21}$$

The number of impacts, n_i , and the number of pressures, n_p are considered. As well, the “system vulnerability,” V , which is defined here as how far the current state of the groundwater resource/source is from a critical damage state, can be quantified by a ratio that reflects the distance between the current state of the groundwater system and the damaged state (Beaujen, et al., 2014) (Equations 22 and 23).

$$V = \text{sensitivity/ state relative to threshold} \quad \text{Equation 22}$$

$$V = \frac{|S_{ij}|}{W/W_0} \quad \text{Equation 23}$$

$|S_{ij}|$ is the absolute value of the groundwater state vulnerability, W is the current state and W_0 is the threshold above which the system is assumed to be damaged. The vulnerability coefficient is normalized by the maximum calculated sensitivity coefficient (Equation 24).

$$V' = \frac{V}{S_{max}} \quad \text{Equation 24}$$

Consequently a value of 1 indicates the groundwater system is damaged and its sensitivity is the largest. A lower value would mean that the groundwater system, whether source or resource, is either damaged or its current state is being degraded, but its sensitivity would less than or equal to the maximum sensitivity.

Two main approaches of DPSIR include the sensitivity equation method, also known as the differential approach, and the adjoint operator method. The differential approach is best used to determine groundwater resource vulnerability (GRV), for example, in assessing the sensitivity of hydraulic heads of an aquifer to a change in the pumping rate of a well, or the changes in recharge rates at the ground surface. The adjoint operator approach would be beneficial in determining groundwater source vulnerability (GSV), such as the sensitivity of the hydraulic

head in an observation well to a change in pumping rate at multiple pumping wells in an aquifer (Beaujen, et al., 2014). Illustrations are given in Figure 14 of these two concepts for real world applications.

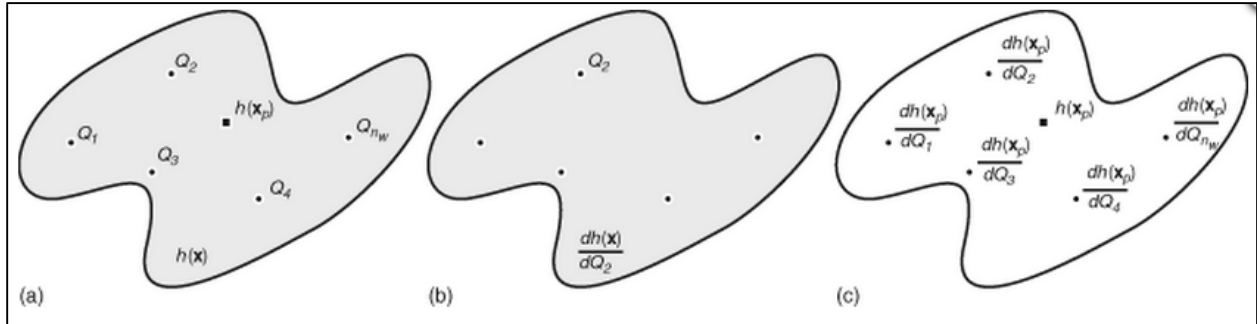


Figure 14. Illustration of the two main approaches to calculate the sensitivity coefficients. (a) Theoretical aquifer with hydraulic heads given by $h(x)$ in which there are n_w pumping wells and an observation point $h(x_p)$. The aquifer is shaded to show the hydraulic head is a continuous variable. (b) Differential approach where the sensitivity of the aquifer water levels $dh(x)/dQ_2$ are given with respect to a change in pumping rate at well Q_2 (resource sensitivity). The aquifer is shaded to show that sensitivity coefficients are continuous over the aquifer. (c) Adjoint operator approach where the sensitivity of the water level $dh(x_p)/dQ_i$ at point $h(x_p)$ is calculated with respect to a change in every pumping well Q_i (source sensitivity). The aquifer is not shaded because the sensitivity coefficients are not continuous over the aquifer, but calculated at discrete points (Beaujen, et al., 2014).

Figure 15a shows a theoretical aquifer with hydraulic heads given by $h(x)$ in which there are n_w pumping wells and an observation well at point $h(x_p)$. Shading of the area indicates the hydraulic head is a continuous variable. Figure 15b shows the differential approach where the resource sensitivity (e.g. hydraulic heads in entire aquifer) to a change, dQ_2 , in pumping rate at pumping well 2 is given by equation 25.

$$S(x)_2 = \frac{dh(x)}{dQ_2} \quad \text{Equation 25}$$

Consequently, there is a spatial and continuous distribution of sensitivity coefficients as indicated by the shaded area in Figure 15b. The general solution for the differential approach is

a sensitivity field, $S(x)$ with respect to any pumping well, Q_i given by Equation 26 (Beaujen, et al., 2014).

$$S(x)_i = \frac{dh(x)}{dQ_i} \quad \text{for } i = 1, n_w \quad \text{Equation 26}$$

There is a different sensitivity for every pumping well. The change in hydraulic head is given by $dh(x)$ and there are n_w pumping wells. Q_i is the change in every pumping well (i.e. source sensitivity) (Beaujen, et al., 2014).

The adjoint operator method is shown in Figure 15c, in which there is source sensitivity, where the sensitivity of the hydraulic heads $h(x)_p$ at observation point x_p with respect to a change dQ_i in pumping rate at well i is given in Equation 27 (Beaujen, et al., 2014).

$$S(x_p)_i = \frac{dh(x_p)}{dQ_i} \quad \text{for } i = 1, n_w \quad \text{Equation 27}$$

Consequently, the solution is a sensitivity coefficient for each discrete location i . In this situation each of the five pumping wells are the point sensitivity coefficients, as shown in Figure 15c.

Sensitivity coefficients can be computed for any user-defined model parameter. The model parameters can link external pressures with upstream factors (UF) such as change in hydraulic conductivity resulting from dissolution of minerals due to a change in water chemistry, or change in groundwater recharge resulting from changes in climate (e.g. external pressures such as change in precipitation or change in atmospheric temperatures). In this concept, all model parameters can be linked to pressures. And an array of parameters can be used in the sensitivity analysis equations. The sensitivity equation is more efficient to calculate groundwater resource vulnerability (GRV), while the adjoint operator method is most efficient for groundwater source vulnerability (GCV) (Beaujen, et al., 2014).

Principal Aquifers of the United States

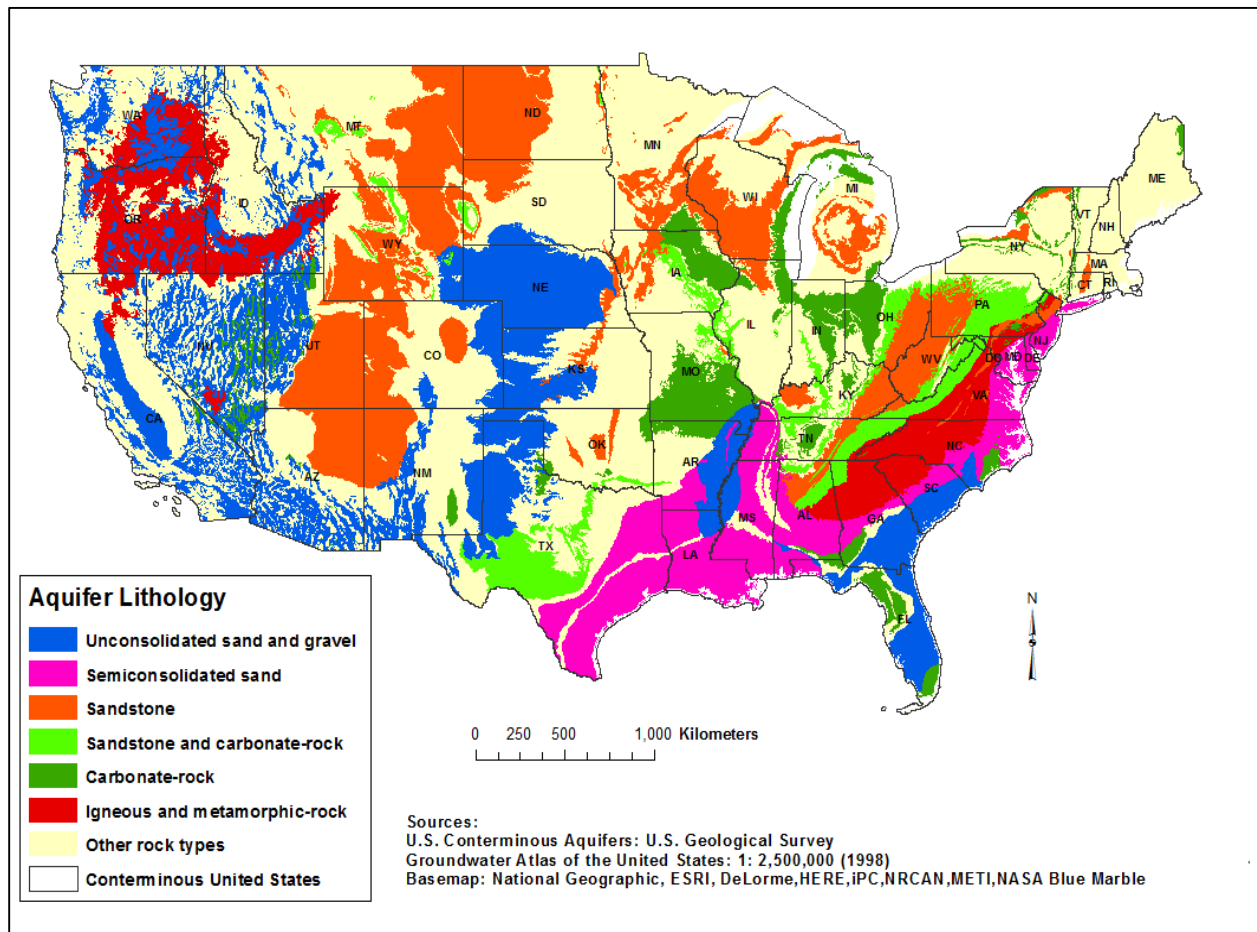


Figure 15. U.S. Principal Aquifer rock types created using ArcGIS (USGS, 2009).

Regionally extensive aquifers or aquifer systems within the United States having the potential to be sources of potable water are termed principal aquifers, and are categorized according to their primary lithologies. Sixty-two principal aquifers have been identified within the United States with lithologies such as unconsolidated sand and gravel, semiconsolidated sand, sandstone, interbedded sandstone and carbonate-rock, carbonate-rock (limestone), or igneous and metamorphic rock (USGS, 2013) (Figure 15). Approximately 80% of the groundwater pumped from U.S. aquifers comes from unconsolidated and semiconsolidated sand and gravel aquifers, while eight percent is abstracted from carbonate rock aquifers, six percent from igneous and

metamorphic-rock aquifers, two percent from sandstone aquifers, two percent from sandstone and carbonate rock aquifers, and two percent from “other” aquifers (Maupin, et al., 2013).

Unconsolidated sand and gravel aquifers

Unconsolidated sand and gravel aquifers contain groundwater at unconfined, water-table conditions, with inter-granular porosity and generally high hydraulic conductivity (USGS, 2004). These hydrogeologic features allow unconsolidated as well as semiconsolidated sand and gravel aquifers to yield the greatest volumes of groundwater (Maupin, et al., 2013). Yet these same features also make them particularly susceptible to contamination from anthropogenic sources such as wastewater systems, chemical spills, urban runoff and agricultural runoff (Thangarajan, 2007). Locations of US unconsolidated sand and gravel aquifers are shown in Figure 16. Unconsolidated sand and gravel aquifers are subcategorized according to their geologic morphology such as basin / valley-fill aquifers, blanket sand and gravel aquifers, stream-valley aquifers, and glacial- deposit aquifers (USGS, 2013).

Basin / valley-fill aquifers are generally located between mountains (Kresic, et al., 2013) and are formed either by erosion, faulting or both. Basin / valley-fill aquifers contain unconsolidated and semiconsolidated sand and gravel and have locally confining units mainly of silt and clay that become increasingly compact, and less permeable at increasing depths (USGS, 2013).

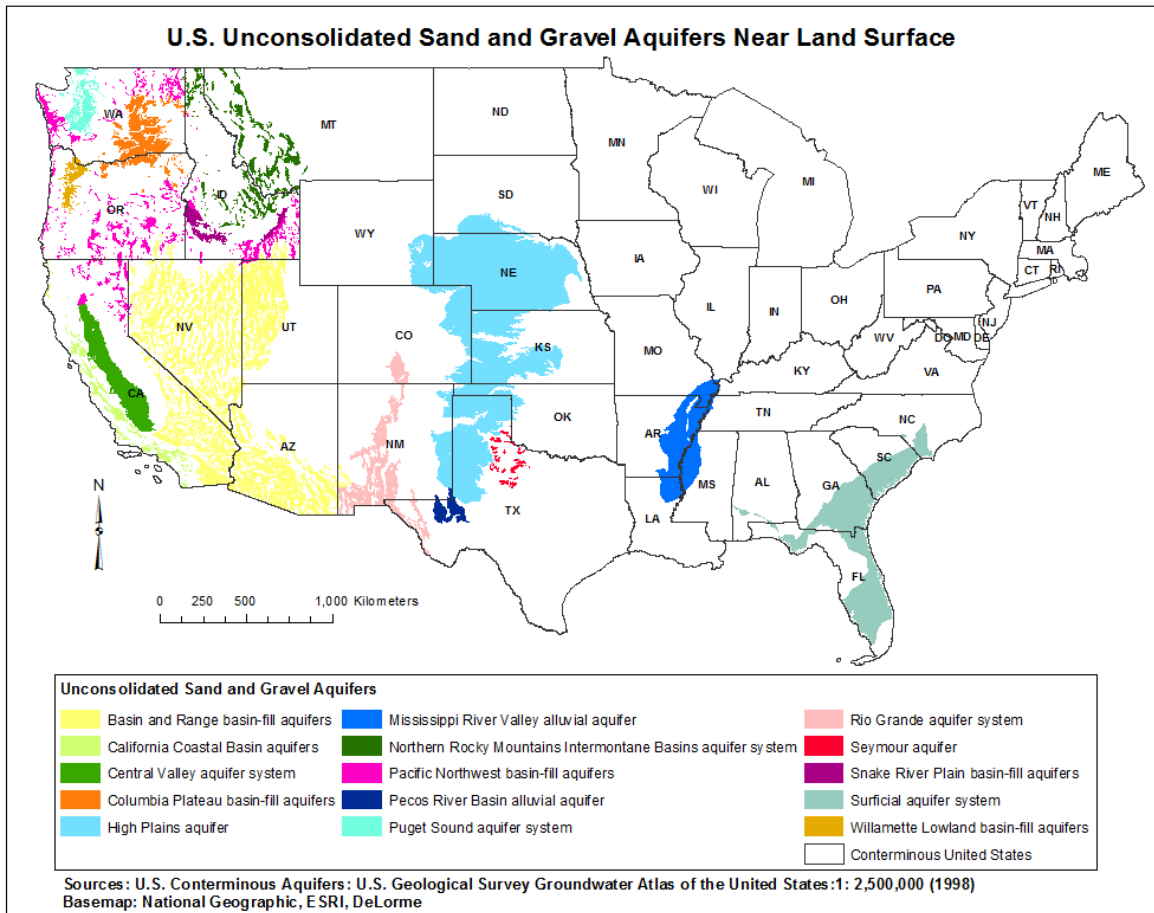


Figure 16. Principal unconsolidated sand and gravel aquifers of conterminous US. (USGS, 2009).

The thickness of basin fill deposits can exceed several thousand meters due to tectonic lowering and deposition of sediments by mountain streams (Kresic, et al., 2013). Coarse sediments such as boulders, gravel, and sand are found at basin margins while finer sediments such as silt and clay are found in central basin areas; this is due to finer sediments staying in suspension within streams longer (Kresic, et al., 2013). Basin-fill aquifers in the U.S. pumped intensively for potable water supplies and irrigation include the Pacific Northwest basin-fill aquifers, the Northern Rocky Mountains Intermontane Basins aquifer system, and California’s Central Valley aquifer system (Kresic, et al., 2013).

California Central Valley Aquifer System

The California Central Valley aquifer system is the largest water reservoir in California and the second most intensely pumped aquifer system in the U.S., with 89% of its groundwater abstracted for agricultural crop irrigation (USGS, 2009). The Central Valley covers about 20,000 mi² and is bounded by the Cascade Range to the north, the Sierra Nevada to the east, the Tehachapi Mountains to the south, and the Coast Ranges and San Francisco Bay to the west. The Central Valley is a huge agricultural region drained by the Sacramento and San Joaquin Rivers (Faunt, 2009). Geologic materials within the Central Valley consist of erosional marine and continental sediments deposited during past geologic events such as volcanic mountain building, faulting, erosion, and inundation by seawater from the Pacific Ocean more than once (Figure 17) (USGS, 2009).

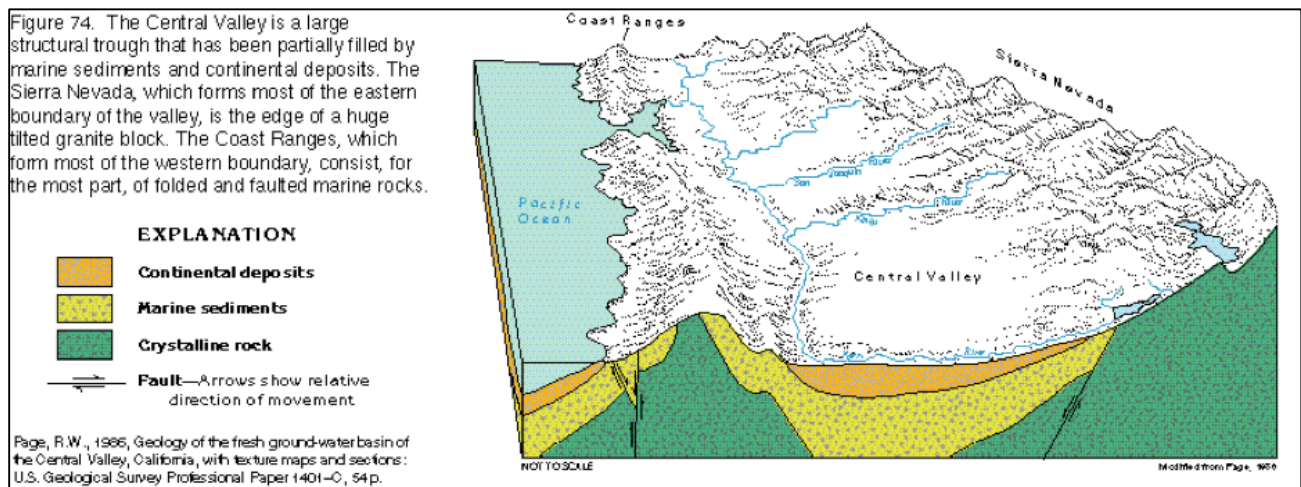


Figure 17. Depiction of California Central Valley topography and geologic strata (USGS, 2009).

The Central Valley aquifer system is composed mainly of sand and gravel, with vertically and horizontally scattered lenses of fine-grained materials such as silt and clay providing increasing confinement with depth (USGS, 2009). Underlying the California Central Valley aquifer system are nearly impermeable volcanic and crystalline metamorphic rocks (USGS, 2009). Prior to

development of surface water and groundwater resources the Central Valley aquifer system was in steady state and unstressed. The Central Valley aquifer system has historically been recharged by precipitation and snowmelt flowing down from the uplands and mountainous regions to the lower elevations (USGS, 2009). Predevelopment aquifer recharge and discharge volumes were approximately equal at about 1.5 million acre-ft per year (1.8 billion m³ per year), with the volume of water in storage generally constant, except during climate fluctuations (Faunt, 2009). However, since the mid 1920's groundwater withdrawals have generally outpaced natural recharge to the aquifer system, leading to dropping water levels, irreversible aquifer compaction, and land subsidence. In 1986 it was estimated that approximately 800 million acre-ft (about 260 trillion gallons) of fresh water was stored in the upper 1000 feet of sediments in the Central Valley. However, extraction of much of this water was determined to have potentially serious consequences (Faunt, 2009).

Drought in California is primarily a result of the absence of winter precipitation in the Sierra Nevada Mountains. Lack of winter precipitation in California occurs when an atmospheric high pressure ridge blocks storms from reaching the state. There have been five significant historical droughts (i.e. longest in duration or driest hydrology) in California within the past century preceding the current drought (Jones, 2015). However, during the current drought the water years of 2012 to 2014 were California's driest three consecutive years on record in terms of statewide precipitation (Jones, 2015) (Figure 18), with 2014 being California's driest year on record dating back to the 1800's (California DWR, 2015). Climatologists at California's Department of Water Resources (DWR) estimated that 150 % of average precipitation for all of Water Year 2015 would be needed to exit the current drought (California DWR, 2015).

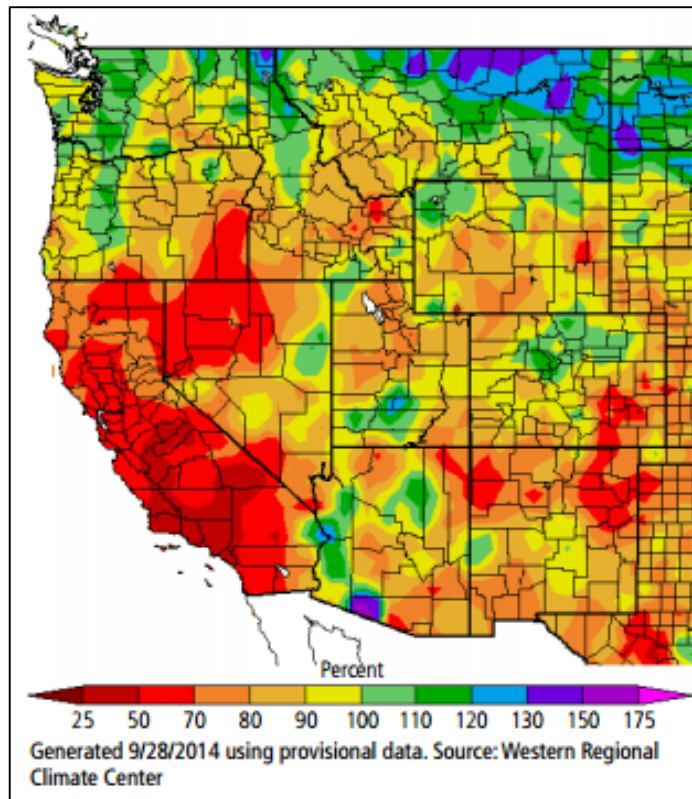


Figure 18. Three year precipitation for Septembers 2011 through 2014 as a percentage of average precipitation rates (California DWR, 2015).

According to analysis of NASA’s GRACE satellite data collection for the years between Septembers 2011 and 2014 it will take about 11 trillion gallons of water (42km^3), about 1.5 times the maximum volume of the largest U.S. reservoir, to recover from California’s continuing drought (NASA, 2014). As well, the Sacramento and San Joaquin River basins in California decreased in volume by four trillion gallons ($\sim 15\text{ km}^2$) of water each year. Figure 19 shows the severity of California’s drought affecting water resources across the state between Septembers 2011 and 2014. About two-thirds of the supply loss has been due to the depletion of groundwater from the Central Valley aquifer system (NASA, 2014).

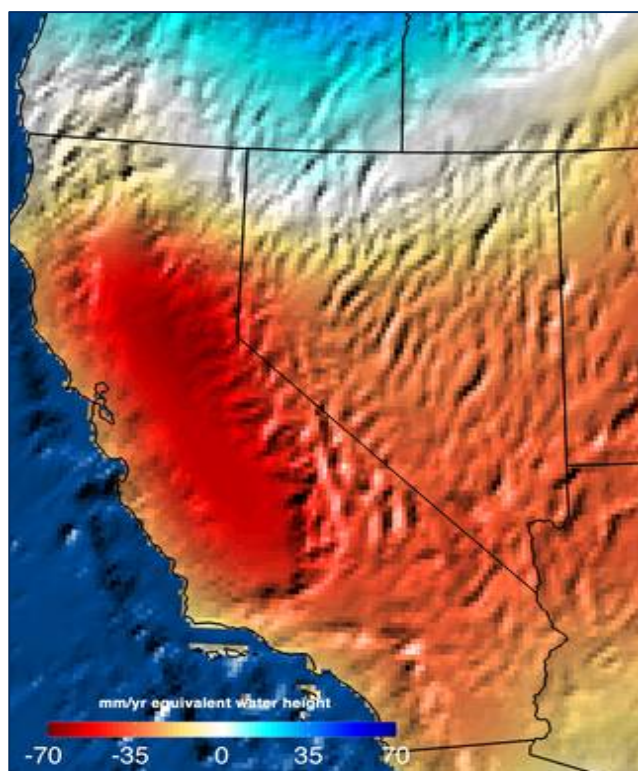


Figure 19. NASA GRACE Satellite data shows the trend in water storage between Septembers 2011 and 2014 (NASA, 2014).

Figure 20 shows California with locations of groundwater monitoring well locations and groundwater level changes from 2005 to spring 2015. Of the 2141 groundwater monitoring wells in California 1,001 (46.8%) had greater than 10 ft. decreases in water levels, 570 (26.6%) had decreases of between 2.5 and 10 ft., 427 (19.9%) had decreases of about 2.5 ft., while 100 (4.7%) had increases between 2.5 and 10 ft., and 43 (2%) had increases of greater than 10 ft. (California DWR, 2015). Due to the historic drought conditions, California's State Water Project, which provides water to about 25 million people, has estimated that it may only have the capacity to provide 20% of the water supplies needed by its customers for the year 2015 (California DWR, 2015).

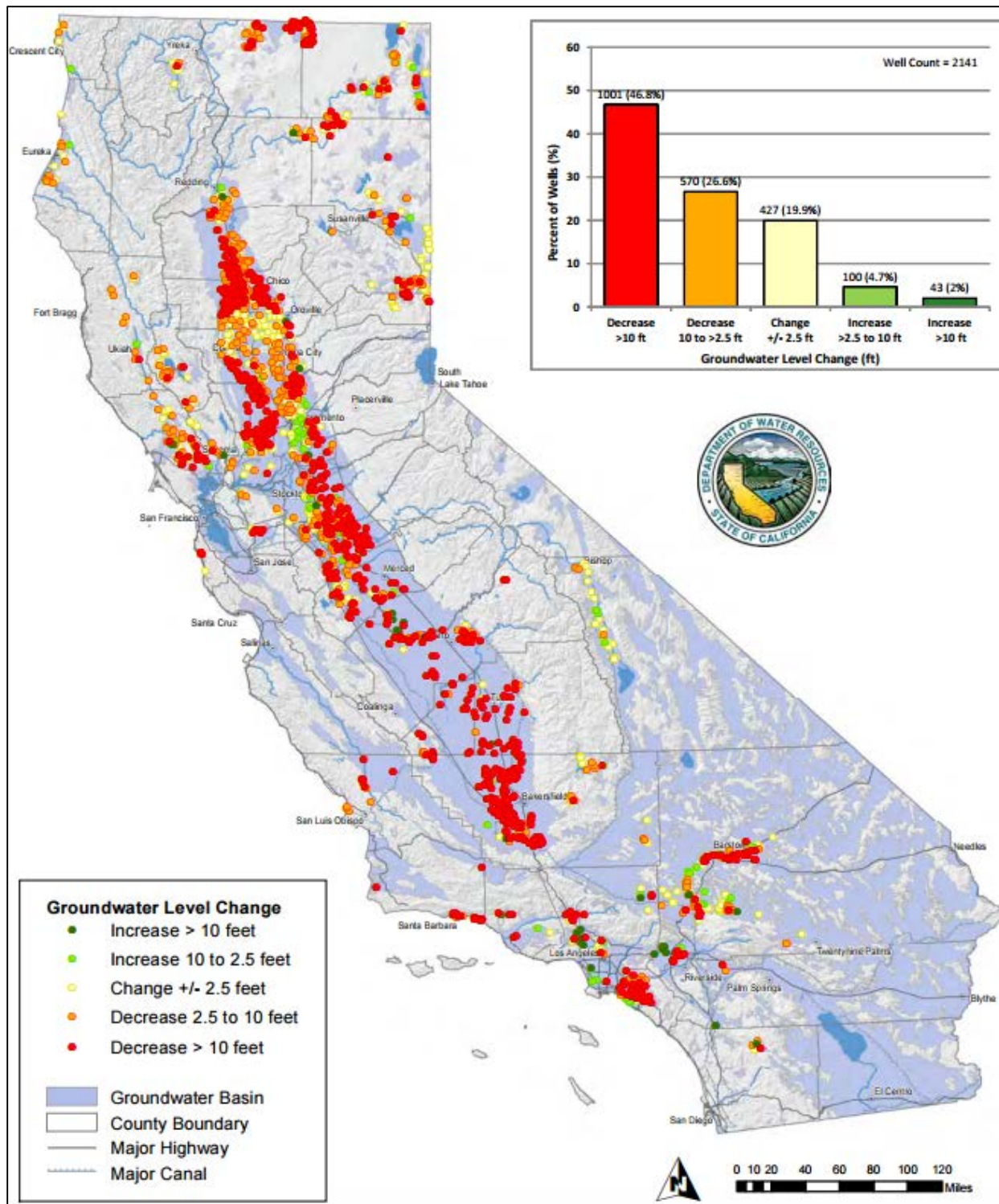


Figure 20. California groundwater level change Springs 2005 to 2015 (California DWR, 2015).

Mississippi River Valley Alluvial Aquifer

The Mississippi River Valley alluvial aquifer system underlies the Mississippi River, extending from the head of the Mississippi Embayment southward, and ultimately merging with the coastal lowlands aquifer system parallel to the Gulf Coast (USGS, 2015)(Figure 21). The Mississippi River Valley alluvial aquifer system has alluvial and terrace deposits of the Quaternary Period (2.4 Ma to present), comprised of gravel and coarse sand in the lower sections and grading to silt and clay in the upper sections which serve as a thin, confining unit above much of the aquifer. The thickness of the Mississippi Embayment alluvial aquifer system



Figure 21. Mississippi River Valley alluvial aquifer (USGS, 2015).

generally ranges in depths of between 25 ft to greater than 150 ft (USGS, 2015). Sedimentary rocks and unconsolidated sediments of Tertiary Period (65.5 Ma to 2.4 Ma) or older underlie the aquifer, creating a less permeable confining unit below (Ausbrooks, 2013).

The Mississippi River Valley alluvial aquifer system is part of the larger Mississippi Embayment aquifer system. The Mississippi Embayment aquifer system comprises six aquifers that thicken to more than 6000 feet in southern Mississippi and Louisiana, with sediments deposited by streams that flowed into the ancestral Gulf of Mexico (USGS, 2015) (Figure 22).

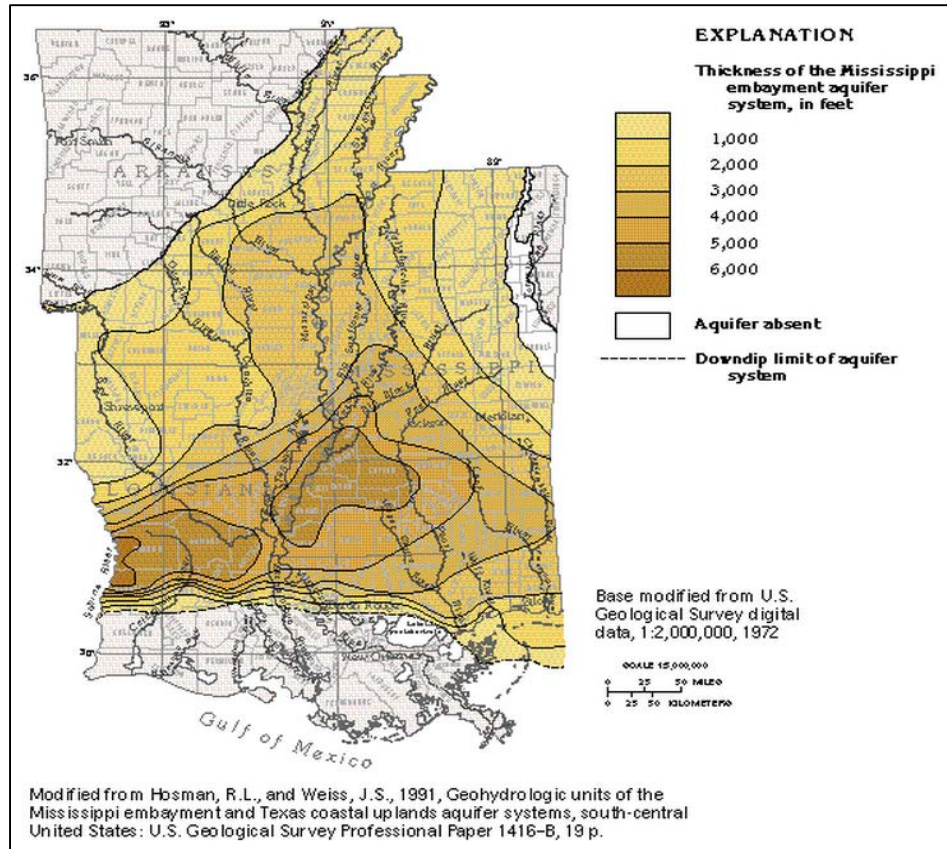


Figure 22. Range of thicknesses within the Mississippi embayment aquifer system (USGS, 1998)

Driven primarily by gravity, regional groundwater movement flows from recharge areas at 100 to 400 feet higher in elevation to the lower flat terrain within the Mississippi Alluvial Plain, where the groundwater is discharged (USGS, 2015).

The climate within the Mississippi embayment ranges from humid, temperate in the northern part to subtropical in the southern areas. Precipitation is generally greatest in the southern region of the Mississippi Embayment, which receive about 56 inches per year, while the northern part receives about 48 inches (USGS, 2015).

Cumulative groundwater pumpage from 1870 through 2007 from the Mississippi River Valley alluvial aquifer system was estimated to be over 280 million acre-feet (about 91 trillion gallons) (Peterson, et al., 2011). Between 1870 and 2007 water level declines had occurred

across the Mississippi embayment area due to groundwater pumping, with declines of more than 100 feet in an area of about 216 square miles along the Mississippi River alluvial aquifer system (USGS, 2015) (Figure 23).

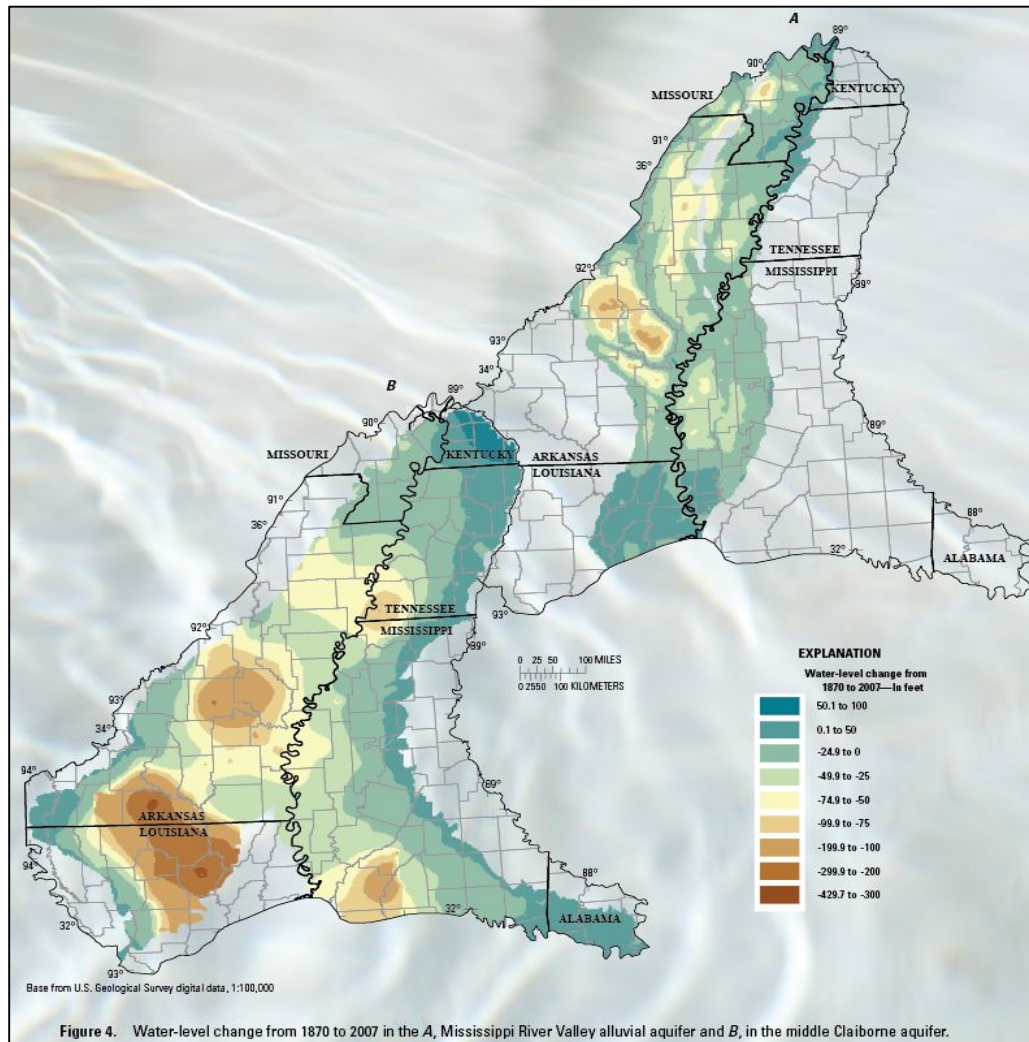


Figure 23. Water level change from 1870 to 2007 in the A, Mississippi River Valley alluvial aquifer and B, in the middle Claiborne aquifer (USGS, 2015).

In 2005 an estimated 11 billion gallons per day of groundwater was pumped from aquifers in the Mississippi embayment, with irrigation use estimated at about 10 billion gallons per day. In 2007 the volume of water stored in the Mississippi River Valley alluvial aquifer system, made by calculating the simulated thickness of the saturated zone and multiplying by the specific yield, was estimated to be about 536 million acre-feet (~ 175 trillion gallons) (USGS, 2015).

Blanket sand and gravel aquifers

Blanket sand and gravel aquifers, subcategorized under the unconsolidated sand and gravel aquifers, generally form in basins as sheets of coarse alluvial deposits from surrounding mountains or as layers of windblown sand, and commonly contain unconfined water at water-table conditions (Kresic, et al., 2013). There are some confined conditions where the blanket sand and gravel aquifers have low-permeability due to silt, clay, or marl depositions. All blanket sand and gravel aquifers in the United States except the Seymour aquifer in north Texas, overlie, or are hydraulically connected to other aquifers, and may store water that recharges deeper aquifers (USGS, 2009). Blanket sand and gravel aquifers underlie the lowlands of Alaska, the lava plateaus in Washington, the coastal plains of the Atlantic and Gulf Coasts, and the High Plains physiographic region of the Midwest (USGS, 2009).

High Plains Aquifer System

The High Plains aquifer system underlies about 174,000 mi² (~450,000 km²), within the High Plains physiographic region of the Midwest in eight states, including Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming (Gurdak, et.al, 2012), (McGuire, 2014) (Figure 24). As land elevations decline eastward from the Rocky Mountains groundwater within the High Plains aquifer system moves in a general eastward direction (USGS, 2013).

The geologic units of the High Plains aquifer system are primarily sedimentary deposits ranging in age from Oligocene to Quaternary, (~ 34 Ma to Present) (USGS, 2013), (USGS, 2014), consisting primarily of unconsolidated, poorly sorted, gravel, sand, clay, and silt, deposited by streams and wind. These deposits also include very fine to fine-grained sandstone, and siltstone containing sandstone and have interconnected fractures (USGS, 2014).

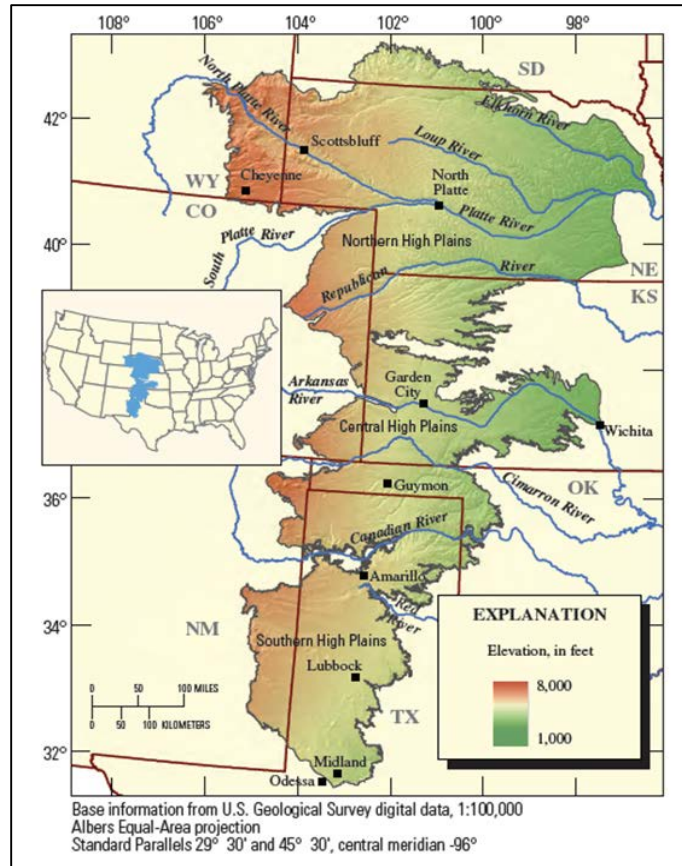


Figure 24. Location of High-Plains aquifer system and land elevations (USGS, 2013).

The Ogallala aquifer is the primary water bearing formation of the High Plains aquifer system, ranging in thickness from 0 to 700 feet, (USGS, 2014) and consisting of unconsolidated sand and gravel of alluvial and glacial origin, deposited during advances and retreats of continental glaciers during the Miocene Epoch (23 Ma to 5.3 Ma) (USGS, 2009). Groundwater age within the High Plains aquifer system ranges from less than 10 years to greater than 10,000 years. Saturated thickness from the water table to the base of the aquifer system ranges from less than 50 feet to greater than 1,100 feet (McGuire, 2014) (Figure 25). The groundwater is generally under unconfined water table conditions (USGS, 2014).

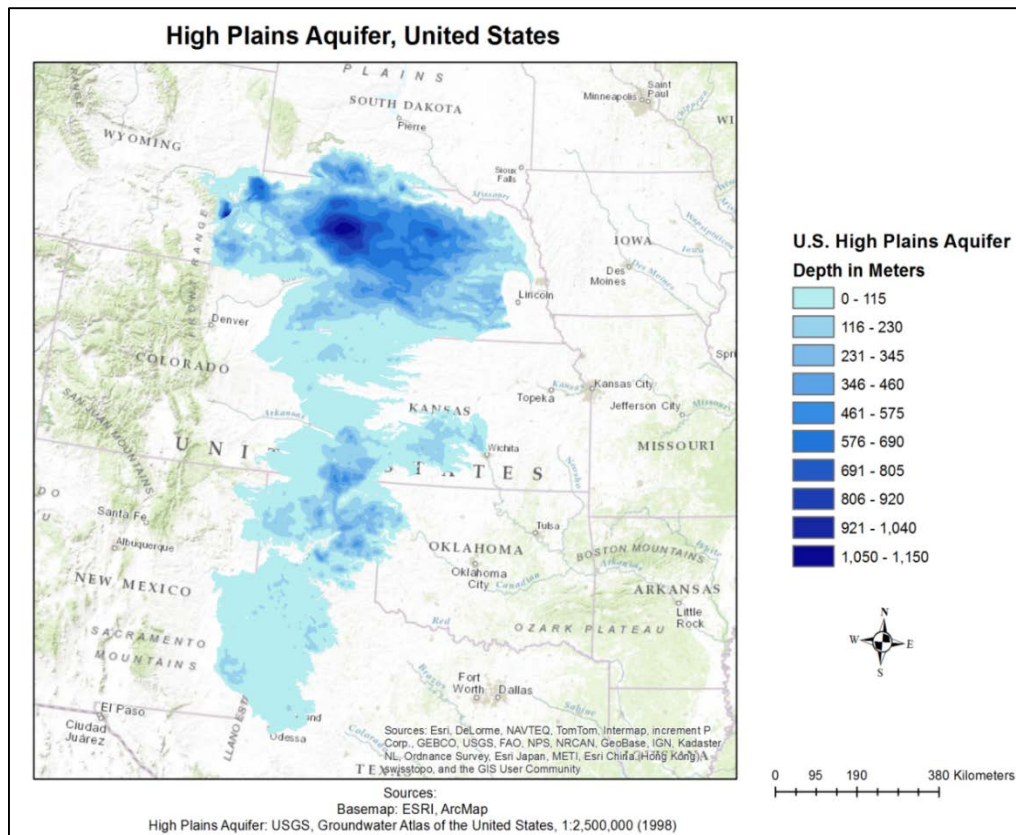


Figure 25. Variation of depth within the High Plains aquifer created using ArcGIS (USGS, 2013).

The High Plains aquifer system is the most intensely pumped aquifer system in the US (Maupin, et al., 2013), accounting for about 20% of the total groundwater withdrawn in the US (G@GPS, 2012). About 97% of the High Plains aquifer is utilized for irrigation. Other uses include public supply, domestic supply, and self-supplied industry (Gurdak, 2014).

In 2013 total groundwater storage in the High Plains aquifer system was estimated to be about 2.92 billion acre-feet (~ 952 quadrillion gallons), a decline of about 266.7 million acre-feet (~ 8.7 quadrillion gallons) since predevelopment, or about an 8% decline (USGS, 2014).

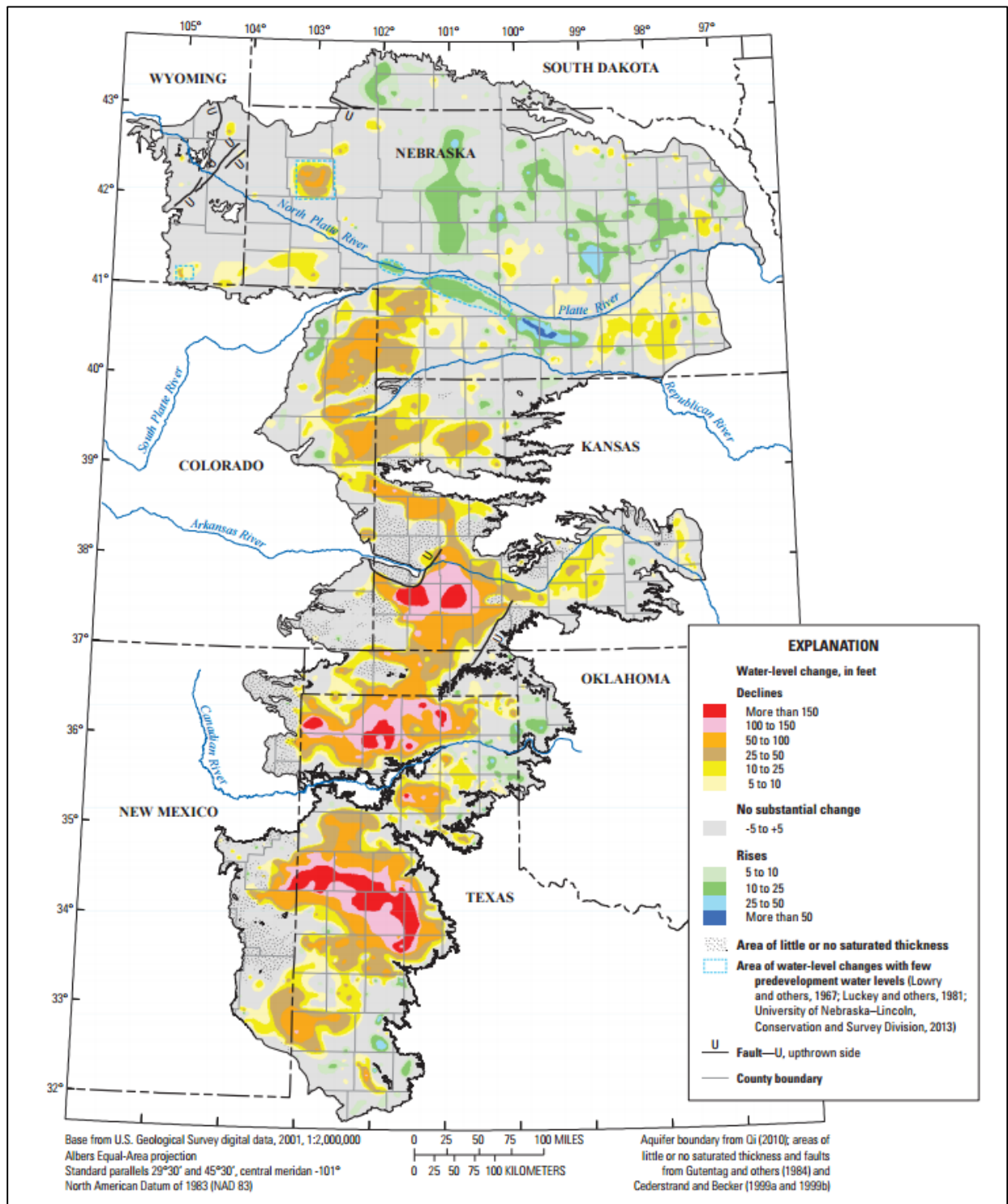


Figure 26. High Plains aquifer system water level declines from predevelopment (about 1950) to 2013 (USGS, 2014).

Water level changes from predevelopment to 2013 range from an increase of 85 feet in Nebraska to a decline of greater than 150 feet in Texas. Water level changes are based on water levels of 3,349 wells (USGS, 2014) (Figure 26). About 15 % of the aquifer area had a decrease in saturated thickness of more than 25% from predevelopment saturated thickness; 5% of the aquifer area had a decrease in saturated thickness (USGS, 2014).

Semiconsolidated sand aquifers

Semiconsolidated rock aquifers underlie the coastal plains of the Eastern and Southern United States (Figure 27), and include the Coastal lowlands aquifer system, Texas coastal uplands aquifer system, Mississippi embayment aquifer system, Southeastern Coastal Plain aquifer system, and the Northern Atlantic Coastal Plain aquifer system (USGS, 2015).

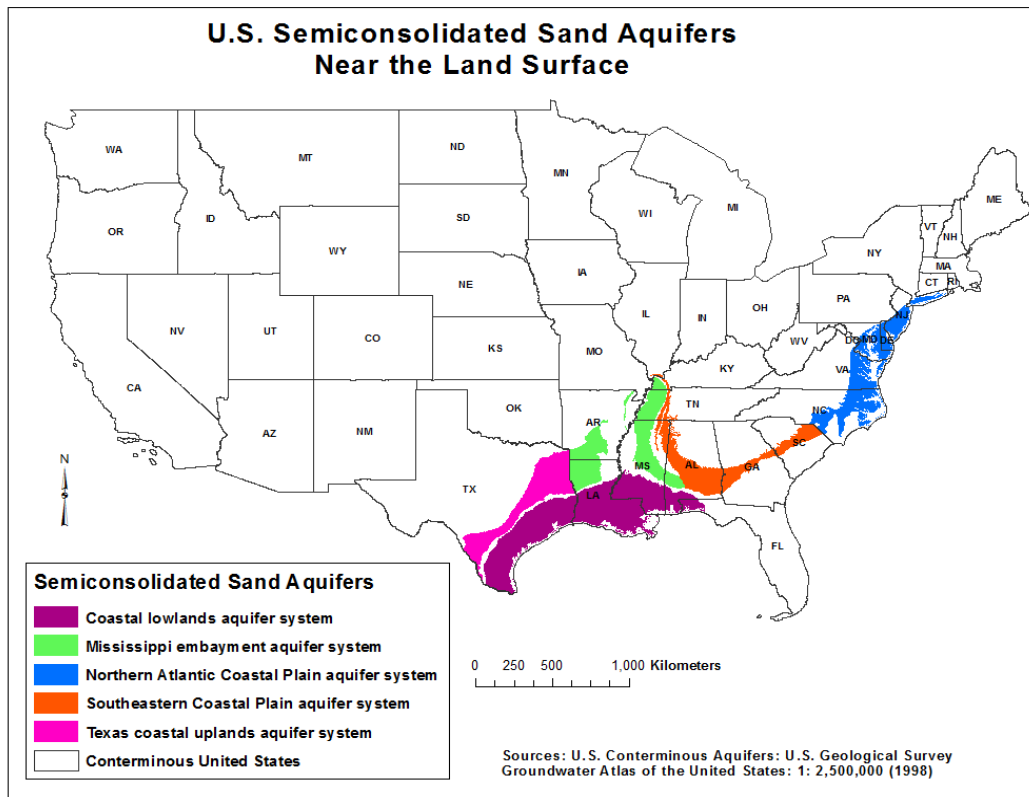


Figure 27. Principal semiconsolidated sand aquifers of the conterminous US (USGS, 2015).

Semiconsolidated sand aquifers consist of complex interbedding of fluvial, deltaic, and shallow marine origin, generally consisting of sand interbedded with silt, clay, and minor amounts of carbonate rocks (USGS, 2015). There are numerous local aquifers that spread into regional systems that are over hundreds of square kilometers. Porosity of semiconsolidated sand aquifers is intergranular, with hydraulic conductivity moderate to high (USGS, 2015).

Sandstone Aquifers

Sandstone aquifers cover large areas and provide considerable amounts of water. Figure 28 shows the locations of the shallowest principal sandstone aquifers in the US. Other sandstone aquifers exist deeper below the surface that are either covered by confining units or are overlain by other aquifers (USGS, 2015). Sandstone aquifers of Cambrian and Ordovician age (542 to 423 Ma) located in Wisconsin and adjacent states join to form an aquifer system that is as much as 650 meters thick.

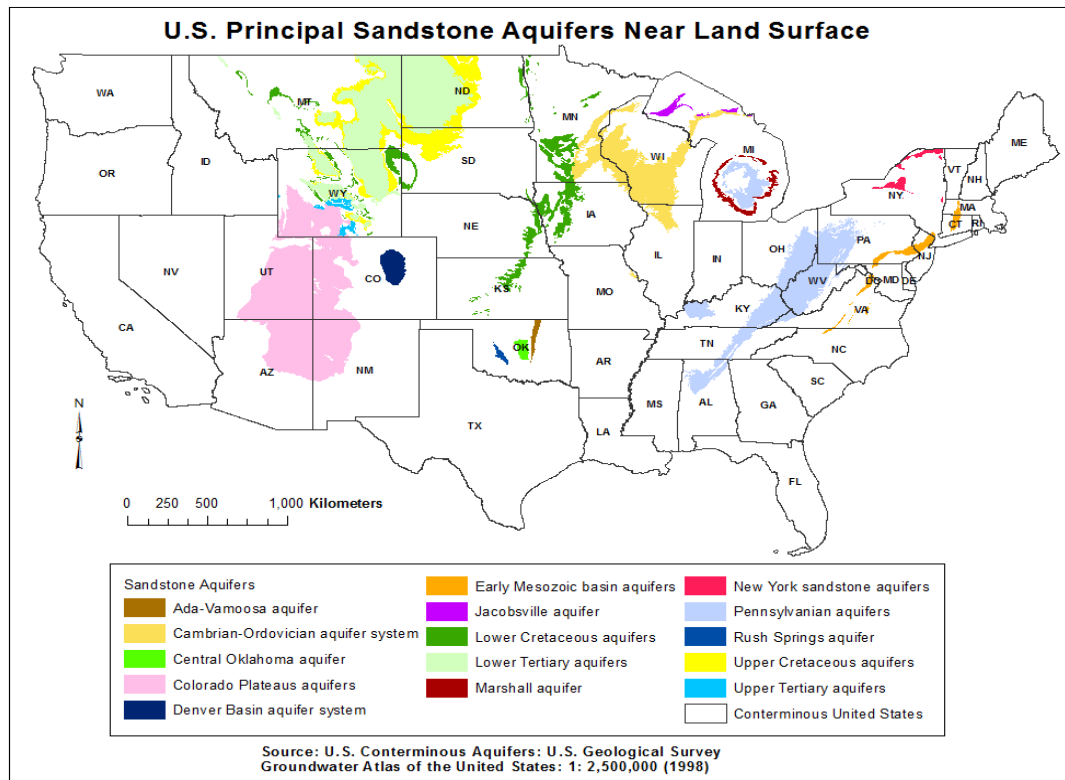


Figure28. Principal sandstone aquifers of the conterminous US (USGS, 2014).

Sandstones of the Paleozoic through Cenozoic Eras (542 Ma through present) form the Northern Great Plains aquifer system extending northeastward from Wyoming, with some permeable areas greater than 2000 meters thick. Yet, not all of this aquifer system contains fresh water (USGS, 2015).

Sandstone aquifers are composed of lithified sand-sized grains of mineral, rock, and organic material. The minerals are mainly quartz (up to 90%), and feldspar (Chernicoff, et al., 2007). Sandstone aquifers are generally less permeable with lower natural recharge rates, less than surficial unconsolidated sand and gravel aquifers (Kresic, 2007). Sandstone aquifers are frequently interbedded with siltstone or shale, with water under confined conditions. Most of the groundwater transmitted in sandstone aquifers is usually horizontally along the bedding planes, and vertically through joints and fractures (USGS, 2015).

Carbonate Rock Aquifers

Carbonate rock aquifers are extensive in the eastern United States, and are found in parts of the mid-western and southwestern states (USGS, 2014) (Figure 29). Folded and faulted carbonate rock aquifers occur in the Appalachian and Rocky Mountains (USGS, 2014). Carbonate rock aquifers are composed primarily of sedimentary limestone originating in warm shallow marine environments (Geology.com, 2014) from calcareous algae or the skeletal remains of marine organisms that range from foraminifera to mollusks dating from the Precambrian to Miocene (2.5 B to 5.3 My) (USGS, 2013). Some dolomite and marble contribute to local sources of groundwater. Limestone is composed of calcite or aragonite; dolomite is composed of calcium and magnesium ($\text{CaMg}(\text{CO}_2)_3$), while marble is metamorphosed or recrystallized calcite or dolomite (USGS, 2014).

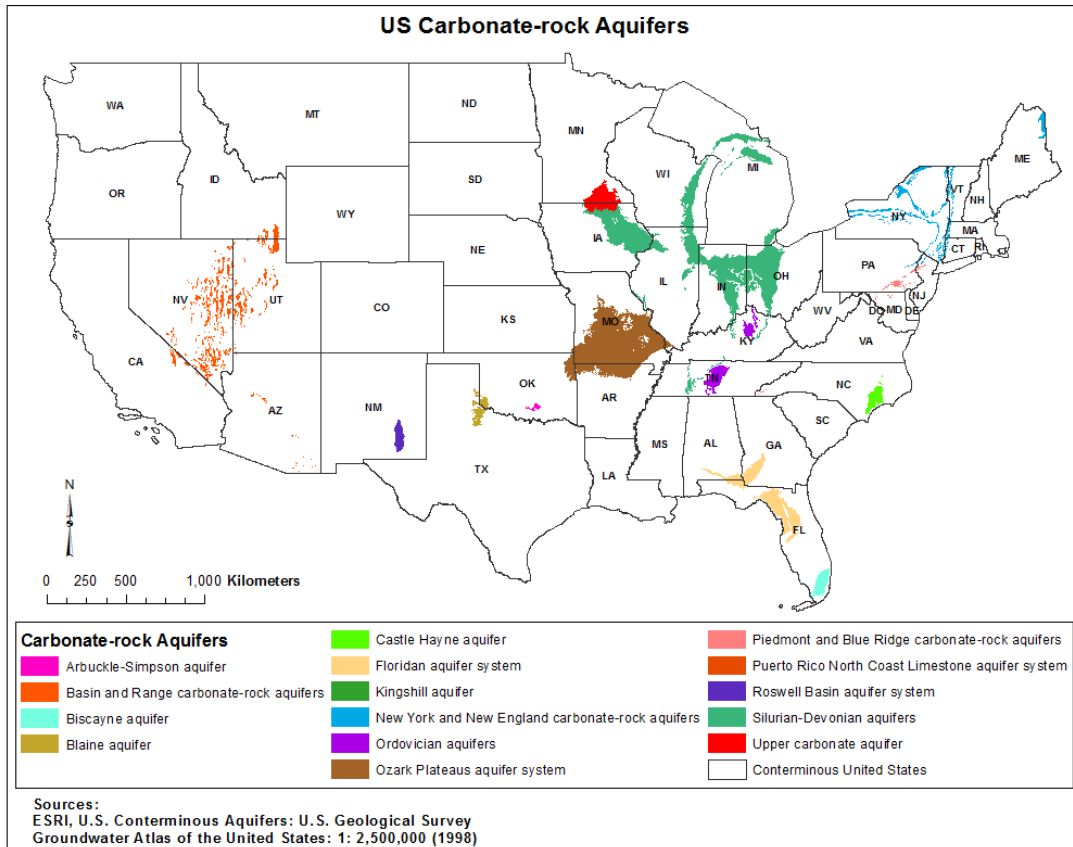


Figure 29. Principal carbonate aquifers of the U.S. (USGS, 2014).

Carbonate rock aquifers, many of which are karstified, are important resources of drinking water. Yet, karstic aquifers and environments are highly vulnerable to contamination and to anthropogenic modifications, generally due to population increases and associated demand for land (Polemio, et al., 2009). Karstic aquifers are characteristically overlain by thin soils. As well, the uppermost layer of karst aquifers, the epikarst, is frequently quite fractured and karstified (Polemio, et al., 2009), (Goldscheider, 2005). Shallow holes in the karstified layer typically exist and are often connected to karst conduits which transmit groundwater over large distances. Any contaminants in recharge water that flow into the shallow holes most assuredly will enter groundwater and be quickly transported through the conduits. Residence times of contaminants within conduits may be short, thus, inhibiting processes of contaminant attenuation (Goldscheider, 2005).

Floridan aquifer

The Floridan aquifer system is a principal carbonate rock aquifer underlying an area roughly 100,000 square miles throughout Florida and into the southern regions of Alabama, Georgia, and South Carolina (Figure 30). In southern Florida the Floridan aquifer system is confined (USGS, 2015). More than 10 million people depend on the Floridan aquifer system for drinking water. The Floridan aquifer system is also pumped for agriculture, phosphate and limestone mining, pulp and paper manufacturing (Marella, 2010). An estimated 4,111 mgd of fresh water was withdrawn from the Floridan aquifer system in 2000.

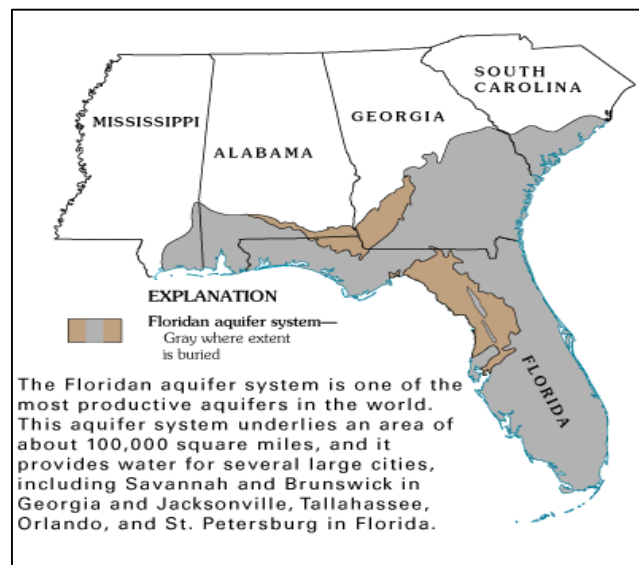


Figure30. Floridan aquifer system (USGS, 2013).

Igneous and Metamorphic-Rock Aquifer

Igneous and metamorphic rock aquifers are grouped into two categories: crystalline-rock aquifers and volcanic-rock aquifers. The principal crystalline rock aquifers include the Piedmont and Blue Ridge crystalline rock aquifers, while the volcanic rock aquifers include the Columbia Plateau basaltic rock, the Pacific Northwest basaltic rock, the Snake river Plain basaltic rock, and the Southern Nevada volcanic rock aquifers (USGS, 2013) (Figure 31).

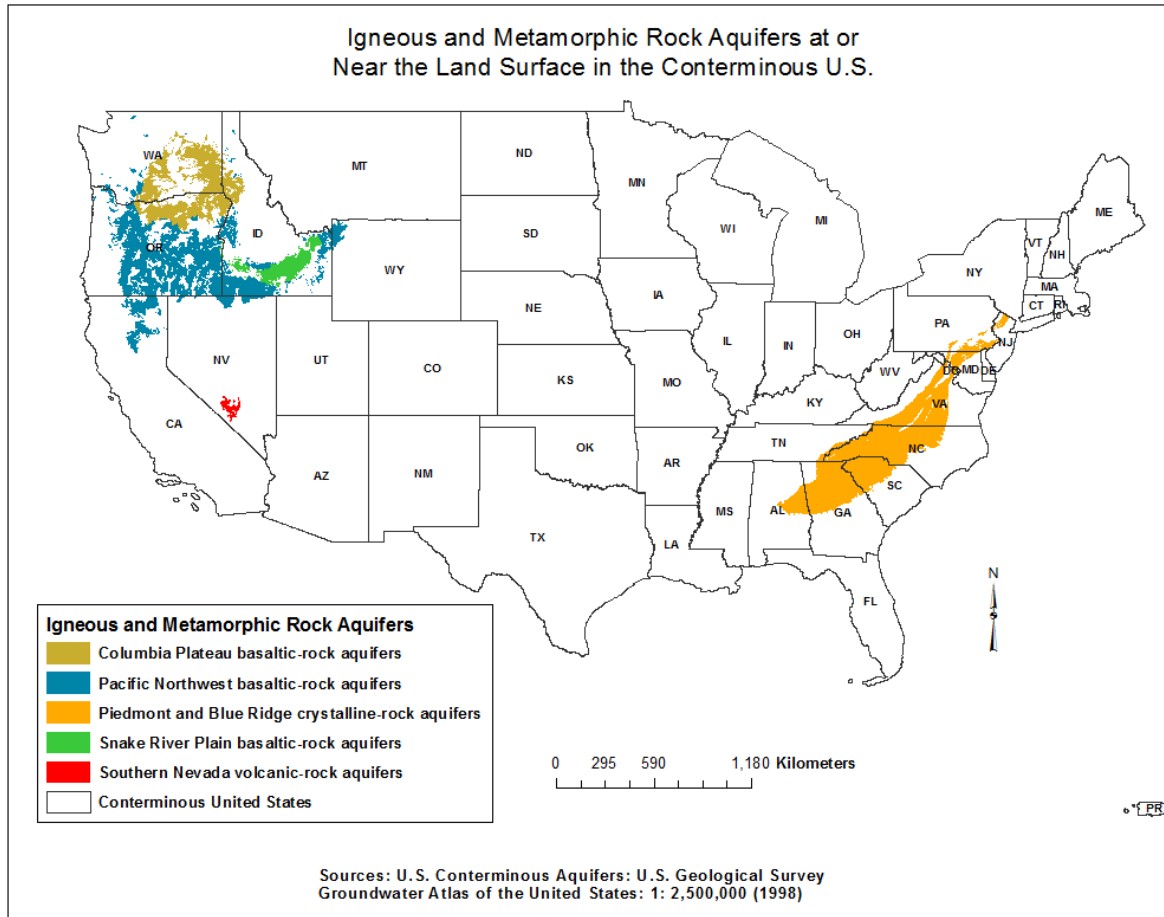


Figure31. Principal igneous and metamorphic rock aquifers in conterminous US (USGS, 2015).

Crystalline-rock and undifferentiated sedimentary-rock aquifers are the primary bedrock aquifers of the Piedmont and Blue Ridge Provinces extending from east-central Alabama up through northwestern Georgia, western South Carolina, central and western North Carolina, western Virginia, western Maryland, into eastern Pennsylvania and New Jersey (Office of Groundwater, 2009). Crystalline rocks form under intense heat and pressure, resulting in their microscopic porosity and zero permeability. Flow of groundwater within crystalline rock aquifers is restricted to fractures and overlying regolith. The main crystalline rocks consist of

coarse-grained gneisses and schists and fine grained rocks such as phyllite and metamorphosed volcanic rocks (USGS, 2015).

Volcanic rock aquifers have a wide range of permeabilities due to their varying rock types. Unaltered pyroclastic rocks may be porous, while hot pyroclastic material may have become impermeable as it settled and cooled. Silicic lavas have low permeability, while basaltic lavas are quite porous at the tops and bottoms of the flows. Basaltic flows also develop columnar joints which allow water to move vertically. Basaltic rock aquifers are highly productive (USGS, 2015).

Water Purification within the Natural Environment

Healthy natural environments provide water purification services that cannot be obtained through any other means (USDA Forest Service, 2011). As water cycles through soils, sediments, and waterbodies of natural ecosystems such as grasslands, forests, wetlands, and marshes various types of biogeochemical filtering processes occur (Firth, 2015). Soil minerals, humus, and microorganisms are mainly responsible for abiotic and biotic processes that serve to filter, buffer, degrade, decompose, transform, immobilize, and/or detoxify organic and inorganic contaminants, excess nutrients, and wastes, including industrial and municipal by-products and atmospheric deposits (Burger, et al., 2003), (USDA NRCS, 2015) (Sylvia, 2005). Grasslands act as sponges, absorbing water from precipitation and slowing its movement through the soil (Firth, 2015), allowing time for biological processes of soil organisms to interact with the soil water as it percolates down the soil profile to aquifers (Fitts, 2013). Riverine and lacustrine forests provide vital buffering functions as water moves downslope from adjacent lands to the surface water reservoirs which may contribute to groundwater recharge. The roots of forested riparian zones stabilize the soil and act as natural sponges that absorb and filter stormwater, preventing

excess nutrients and contaminants from reaching surface water reservoirs and groundwater (Maryland Forest Service, 2015).

Wetlands and marshes, which may interact with groundwater, characteristically have high plant productivity, large adsorptive buffering capacities and high rates of oxidation by microorganisms in association with wetland plants that serve to biochemically transform nutrients and pollutants (Wastewater Gardens, 2015). Toxic organic compounds such as pesticides, herbicides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pentachlorophenols (PCPs), and others are subjected to the biological and abiotic processes in wetlands, with microbial metabolism having a significant impact on their transformation and degradation (Reddy, et al., 2008). Wetland sediments also have enhanced conditions for denitrifying microorganisms such as heterotrophic anaerobic bacteria to remove excess nitrates. Denitrification is a primary pathway for removal of nitrates from wetland soils and sediments (Reddy, et al., 2008). Denitrification is most effective in the root zones, as carbon sources are available for the denitrifying bacteria (NCSU Soil Science Dept., 2015). Phosphorus in the flow through water of wetlands may also attach to soil particles and become trapped in wetland sediments. If aluminum, iron, or calcium is present the binding capacity of phosphorus increases (Reddy, et al., 2008).

Healthy soils are living ecosystems containing billions of bacteria, fungi, micro and macro organisms as well as organic matter from decaying plants and animals (Burger, et al., 2003). Microorganisms most involved in biochemical activities related to soil and water purification include bacteria and archaea which are capable of reducing or oxidizing organic and inorganic matter, including metals, and transforming or consuming them (Burger, et al., 2003), (Gomez, 2011). Archaea, ammonia-oxidizing bacterial prokaryotes (de la Torre Lab, 2010) are utilized to

treat groundwater and drinking water distribution systems (Van der Wielen, et al., 2009), Actinobacteria, fungi-like bacteria with filaments that stretch through the soil are involved in nitrogen fixation, biodegradation, and bioremediation of soils (Burger, et al., 2003).

Mycorrhizal fungi play an extremely important role in detoxification of soil water contaminated with heavy metals. Mycorrhizae produce compounds that bind soil particles and chelate significant amounts of heavy metals such as zinc and lead. A chelate is an organic chemical that forms a ring compound in which a metal is strongly held between two or more atoms enough to diminish the rate at which it is fixed by the soil, thereby making it more available for plant and microbial uptake (Burger, et al., 2003). With their net of hyphae (i.e. long branched tubular filaments), collectively called mycelium, fungi can bioaccumulate heavy metals from metal ore wastes through their metabolic activities or sorb metals through other processes. The fungal cell walls have free amino, hydroxyl, carboxyl, and other biochemical molecules that are efficient in binding heavy metals (Turnau, et al., 2006). Fungi contain various types of decomposing enzymes such as laccases that have the capacity to attack environmental pollutants such as bisphenol A (i.e., an industrial chemical used primarily to make polycarbonate plastic) and epoxy resins, as well as phthalates (i.e., a group of chemicals used to increase the flexibility of plastic and vinyl), and softening agents in sewage water (Schmidt, 2012).

Groundwater Sustainability

Sustainable use of groundwater occurs as the rate of groundwater extraction is equal to or less than the natural rate of groundwater replenishment for any level of aquifer storage (Loaiciga, et al., 2001). Knowledge, planning, implementation, and follow through are critical for sustainable groundwater management. Having fundamental knowledge of groundwater systems, including flows, storage, and their interactions with surface water (McPhee, et al., 2004), as well as

knowledge of the physical and chemical properties of soils and geologic strata, all are necessary in order to sustain groundwater levels and protect groundwater from contamination.

Sustainable management of groundwater resources includes monitoring groundwater levels and determining safe yields, monitoring and limiting water use, particularly in semiarid and arid regions, (California DWR, 2015), and monitoring and regulating industrial and agricultural practices in regions where groundwater levels have been in decline, or where groundwater is vulnerable to contamination.

Some practical water management and conservation practices include the development and use of constructed wetlands, designing cropping systems and implementing irrigation practices that minimize potential groundwater contamination while maximizing the use of water, and artificially recharging aquifers during wet seasons. Constructed wetlands are manmade ecosystems consisting of organic soils, microorganisms, algae, and vascular aquatic plants in areas where the water table is at or near the surface at least part of the year (US EPA, 2004). In the treatment effluents of constructed wetlands soil filtration, ion exchange, adsorption, and precipitation all work to treat domestic, agricultural, and industrial waste water (Wastewater Gardens, 2015).

Some conservation goals set forth by the Natural Resources Conservation Service (NRSC) for use in agricultural ecosystems include converting irrigated land to dry land, planting non-irrigated permanent vegetation, implementing nutrient and pest management, adjusting cropping systems and perennial vegetation for haying, grazing, and wildlife habitat, and replacing inefficient, flood-irrigated systems to more efficient center pivot and Sub-surface Drip Irrigation (SDI) systems (USGS, 2013).

A water conservation measure being developed and utilized in South Florida is the use of Aquifer Storage and Recovery systems (ASR) (Reese, et al., 2004). The ASR system artificially recharges parts of the Floridan aquifer with excess freshwater during the wet season while recovering the water during the dry season to supplement the drinking water supply (Figure 32).

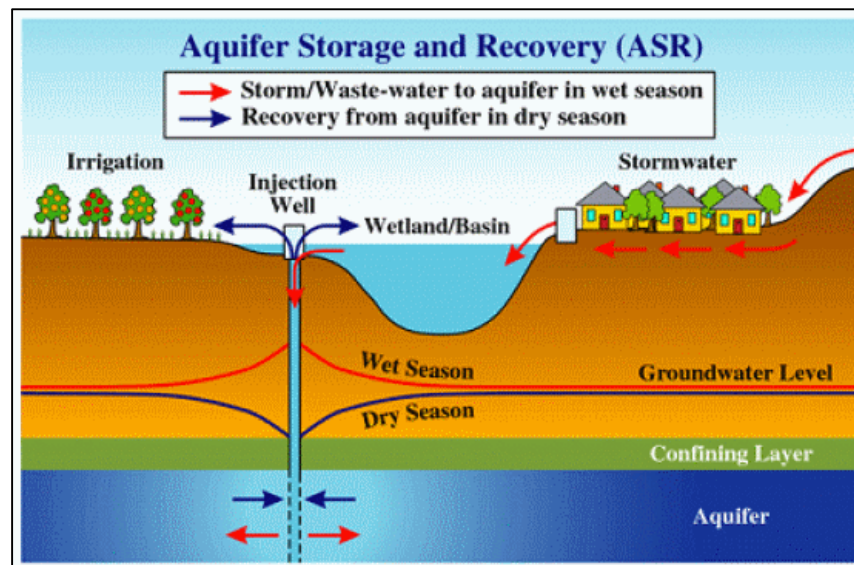


Figure32. Aquifer Storage and Recovery System (Reese, et al., 2004).

By using infiltration basins or by drilling injection wells into the aquifer at various locations, data is obtained about the hydrogeologic characteristics and performance of the aquifer and adjustments are made prior to and during the aquifer storage and recovery process. Factors that may affect fresh water recovery include the quality of water allowed for recharge into the aquifer, the potential release of naturally occurring contaminants due to the interaction between the injected fresh water and the aquifer matrix, and poor recovery due to mixing of brackish, saline, and freshwater within the aquifer (Reese, et al., 2004).

Conclusion

Access to clean potable drinking water is essential for humans to maintain biological health and survival. As climate change affects regional weather patterns potable water is becoming

scarcer in geographic areas where it once seemed abundant. As the US population continues to expand from its current population of about 321million people (US Census, 2015), we as a nation must direct our collective knowledge and efforts to remediate, restore, and sustain surface and groundwater supplies for present and future generations. We must reduce our dependence on xenobiotic chemicals and be conservative in our daily water usage.

Appendix 1

Table of Drinking Water Contaminants, Sources, and Potential Health Effects (U.S. EPA, 2014)

Organic Chemicals				
Contaminant	MCLG (MG/L)	MCL or TT (MG/L)	Potential Health Effects from Long-Term Exposure Above the MCL	Sources of Contaminant in Drinking Water
Acrylamide	zero	TT	Nervous system or blood problems; increased risk of cancer	Added to water during sewage/wastewater treatment
Alachlor	zero	0.002	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer	Runoff from herbicide used on row crops
Atrazine	0.003	0.003	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops
Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Benzo(a)pyrene (PAHs)	zero	0.0002	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines
Carbofuran	0.04	0.04	Problems with blood, nervous system, or reproductive system	Leaching of soil fumigant used on rice and alfalfa
Carbon tetrachloride	zero	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Chlordane	zero	0.002	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide
Chlorobenzene	0.1	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
2,4-D	0.07	0.07	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops

Dalapon	0.2	0.2	Minor kidney changes	Runoff from herbicide used on rights of way
1,2-Dibromo-3-chloropropane (DBCP)	zero	0.0002	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards
o-Dichlorobenzene	0.6	0.6	Liver, kidney, or circulatory system problems	Discharge from industrial chemical factories
p-Dichlorobenzene	0.075	0.075	Anemia; liver, kidney or spleen damage; changes in blood	Discharge from industrial chemical factories
1,2-Dichloroethane	zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
1,1-Dichloroethylene	0.007	0.007	Liver problems	Discharge from industrial chemical factories
cis-1,2-Dichloroethylene	0.07	0.07	Liver problems	Discharge from industrial chemical factories
trans-1,2-Dichloroethylene	0.1	0.1	Liver problems	Discharge from industrial chemical factories
Dichloromethane	zero	0.005	Liver problems; increased risk of cancer	Discharge from drug and chemical factories
1,2-Dichloropropane	zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
Di(2-ethylhexyl) adipate	0.4	0.4	Weight loss, liver problems, or possible reproductive difficulties.	Discharge from chemical factories
Di(2-ethylhexyl) phthalate	zero	0.006	Reproductive difficulties; liver problems; increased risk of cancer	Discharge from rubber and chemical factories
Dinoseb	0.007	0.007	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables
Dioxin (2,3,7,8-TCDD)	zero	0.00000003	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion; discharge from chemical factories
Diquat	0.02	0.02	Cataracts	Runoff from herbicide use
Endothall	0.1	0.1	Stomach and intestinal problems	Runoff from herbicide use
Endrin	0.002	0.002	Liver problems	Residue of banned insecticide

Epichlorohydrin	zero	TT ^a	Increased cancer risk, and over a long period of time, stomach problems	Discharge from industrial chemical factories; an impurity of some water treatment chemicals
Ethylbenzene	0.7	0.7	Liver or kidneys problems	Discharge from petroleum refineries
Ethylene dibromide	zero	0.00005	Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer	Discharge from petroleum refineries
Glyphosate	0.7	0.7	Kidney problems; reproductive difficulties	Runoff from herbicide use
Heptachlor	zero	0.0004	Liver damage; increased risk of cancer	Residue of banned termiticide
Heptachlor epoxide	zero	0.0002	Liver damage; increased risk of cancer	Breakdown of heptachlor
Hexachlorobenzene	zero	0.001	Liver or kidney problems; reproductive difficulties; increased risk of cancer	Discharge from metal refineries and agricultural chemical factories
Hexachlorocyclopentadiene	0.05	0.05	Kidney or stomach problems	Discharge from chemical factories
Lindane	0.0002	0.0002	Liver or kidney problems	Runoff/leaching from insecticide used on cattle, lumber, gardens
Methoxychlor	0.04	0.04	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock
Oxamyl (Vydate)	0.2	0.2	Slight nervous system effects	Runoff/leaching from insecticide used on apples, potatoes, and tomatoes
Polychlorinated biphenyls (PCBs)	zero	0.0005	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer	Runoff from landfills; discharge of waste chemicals
Pentachlorophenol	zero	0.001	Liver or kidney problems; increased cancer risk	Discharge from wood preserving factories

Picloram	0.5	0.5	Liver problems	Herbicide runoff
Simazine	0.004	0.004	Problems with blood	Herbicide runoff
Styrene	0.1	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories; leaching from landfills
Tetrachloroethylene	zero	0.005	Liver problems; increased risk of cancer	Discharge from factories and dry cleaners
Toluene	1	1	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Toxaphene	zero	0.003	Kidney, liver, or thyroid problems; increased risk of cancer	Runoff/leaching from insecticide used on cotton and cattle
2,4,5-TP (Silvex)	0.05	0.05	Liver problems	Residue of banned herbicide
1,2,4-Trichlorobenzene	0.07	0.07	Changes in adrenal glands	Discharge from textile finishing factories
1,1,1-Trichloroethane	0.20	0.2	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories
1,1,2-Trichloroethane	0.003	0.005	Liver, kidney, or immune system problems	Discharge from industrial chemical factories
Trichloroethylene	zero	0.005	Liver problems; increased risk of cancer	Discharge from metal degreasing sites and other factories
Vinyl chloride	zero	0.002	Increased risk of cancer	Leaching from PVC pipes; discharge from plastic factories
Xylenes (total)	10	10	Nervous system damage	Discharge from petroleum factories; discharge from chemical factories

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