Best practices to manage nitrate contamination of groundwater in agricultural zones: A comparative analysis of farming impacts on areas of Central Valley and High Plains aquifers

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This Master's Project

Best practices to manage nitrate contamination of groundwater in agricultural zones: A comparative analysis of farming impacts on areas of Central Valley and High Plains aquifers

by

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Abstract

Nitrate is one of the most common contaminants in groundwater and causes multiple health impacts when consumed. Contamination is most significant in agricultural areas and has increased steadily since the 1950s with the introduction of nitrogen fertilizers. The depth of an aquifer, sediment type, hydrogeology, redox conditions, microbe activity, fertilizer application, natural nitrogen deposits, and well construction influence the degree of nitrate contamination of an aquifer. The sources of nitrate pollution are fertilizer, manure, concentrated feeding lots, natural nitrogen deposits, atmospheric deposition, septic systems, wastewater treatment plants, and industrial activities. Nitrogen compounds applied on the surface are stored in the soil, leach into groundwater, runoff from the surface or taken up by plants. Nitrate leaches into groundwater when it dissolves in infiltrating water and percolates through the subsurface. Water infiltrates the surface during precipitation events or when irrigation water is applied. Shallow aquifers are more contaminated than deep aquifers; deeper aquifers get contaminated over a longer timeframe. This paper studies two locations in the Central Valley, California aquifer, and two locations of the High Plains aquifer in Nebraska and Texas, US. The locations have different aquifer depths, sediment types, nitrogen depositions, hydrogeology, climate, redox conditions, fertilizer application rates, and crops. These differences influence the degree of contamination of underlying aquifers. Remediation and removal of contaminants in aquifers is cost-prohibitive, and it is more effective to minimize nitrate leaching so that aquifers retain good water quality. The best practices to reduce the contamination rate are optimizing fertilizer/manure application to meet plant needs, refining irrigation timing, no-till farming, winter crops, and crop cover. Long-term studies and active monitoring can determine the effectiveness of each approach.
Definitions

Aquifer: Rock or sediment that contains water
EPA: Environmental Protection Agency
FAO: Food and Agriculture Organization of the United Nations
GRACE: Gravity Recovery and Climate Experiment
MAR: Managed Aquifer Recharge
MCL: Maximum Contaminant Level
SJV: San Joaquin Valley
SOM: Soil Organic Matter
SWRCB: California State Water Resources Control Board
1 Introduction

Water covers over 71% of the Earth's surface and has a volume of 1.386 billion cubic kilometers. It is part of oceans, rivers, lakes, groundwater, flora, fauna, glacier icecaps, and the atmosphere. The total volume of water on Earth has been constant since the beginning of time; its form changes as it moves between the environmental compartments. Of the total amount of water on Earth, only 2.5% is freshwater, of which 68.7% is found in permafrost and snow, 0.26% in rivers and lakes, and the remainder in groundwater (Gleick et al., 1993). Subsurface water or groundwater is the largest source of accessible freshwater available for humankind.

Freshwater is used in almost every aspect of our lives - from agriculture to industry to energy generation and human consumption. Communities worldwide use groundwater when surface water is insufficient or when droughts deplete other sources. California uses 40-60% groundwater yearly to meet the demands of communities, agriculture, and industries. The volume of groundwater used increases when demands increase or during extensive droughts (SWRCB, 2023). The rate of groundwater use is greater than the rate at which it gets replenished, leading to depleting resources (Lall et al., 2020).

Gravity Recovery and Climate Experiment (GRACE) satellite data shows that water resources are severely depleted in many areas globally. Data from Central Valley, California, a major agricultural hub, shows significant depletion of local surface and subsurface water resources (Lall et al., 2020). As extraction rates exceed replenishment rates, there is a high risk of groundwater contamination (Smith et al., 2018), soil compaction, and saltwater intrusion (Amanambu et al., 2020; Befus et al., 2020).

Groundwater dependence is higher in arid and semi-arid areas. Between 1.5 to 3 million people worldwide depend on groundwater for drinking water (López-Morales and Mesa-Jurado, 2017). Additionally, groundwater irrigates over 38% of global agriculture (Siebert et al., 2010). Of the groundwater extracted in a year, 60 -70% goes towards agricultural irrigation. The dependence increases as climate variability reduces surface freshwater replenishment;
population growth also pushes communities to expand agricultural lands and crop outputs. Expanded crop irrigation stresses limited freshwater supplies, pushing more communities towards groundwater extraction (Zingaro et al., 2017).

In addition to population growth, climate change impacts groundwater recharge rates and increases dependence on groundwater. Rising temperatures and extreme weather events - droughts and storms are becoming more common, and groundwater buffers against uncertainty and meets deficits (Scanlon et al., 2023). In California, up to 20% more water is sourced from groundwater during droughts to meet demands (SWRCB, 2023). Increasing temperatures correlate with higher evaporation rates from soil and lower snowpack. (Scanlon et al., 2023). Maintaining groundwater resources and water quality standards is critical to meet human and ecosystem needs.

Surface and groundwater contamination has increased since industrial activities started in the 18th century. Groundwater meets over 50% of drinking water and 40% of irrigation needs. Using contaminated water raises the risk of severe illness and negatively impacts the ecosystem's health, economy, development, and agricultural activities. The World Health Organization (WHO) and the Food and Agriculture Organization of the United Nations have set maximum limits on drinking and agricultural water pollutants. The limits guide organizations in controlling pollutants and help limit adverse outcomes from consumption (Abascal et al. 2022).

Nitrate is a ubiquitous environmental contaminant used in agricultural and industrial processes and is found in fertilizers, animal waste, wastewater effluent, and industrial waste products (Sahoo et al. 2016). It is water soluble and leaches into groundwater. Globally, 60% of areas with nitrate contamination are near croplands. As demand for cereals and animal feed increases, fertilizer consumption increases proportionally, raising the risk of surface and groundwater nitrate contamination. Climate, soil, surface-groundwater interactions, and current nitrate soil stores influence nitrate leaching into groundwater (Bijay-Singh and Craswell 2021).
Aquifer nitrate contamination is a significant concern worldwide. The contamination causes mortality in aquatic ecosystems, supports invasive species growth, and raises the risk of thyroid cancer, high blood pressure, goiter, congenital disabilities, and methemoglobinemia in humans (Sahoo et al. 2016; Abascal et al. 2022). Other studies have shown that it inhibits iodine and Vitamin D metabolism in domestic animals and poultry (Rowe and Stinnett, 1975). Nitrates are easily dissolvable and percolate into groundwater from the surface (Abascal et al. 2022) during recharge events such as precipitation, snowpack, mountain recharge systems, artificial recharge, flood irrigation, and through interactions at the stream bed (Scanlon et al., 2023; Costantini et al., 2023). A contaminated aquifer can have high nitrate concentrations if the recharge is minimal or slow (Bijay-Singh and Craswell 2021).

Groundwater recharge or infiltration is slow, as movement within the subsurface is slower than on the surface. Depending on location, subsurface water can be hours or thousands of years old (Heath 1983). Younger water is accessible closer to the surface and more likely to be contaminated than older water in deeper aquifers, assuming groundwater pumping does not affect the system (Thaw et al., 2022). The recharge rate is typically lower than extraction rates, especially in agriculture-centric basins such as the Central Valley region in California (Liu et al., 2022).

The potential for nitrate contamination in agriculture-rich areas is significant due to high nitrogen loadings and groundwater recharge processes. As surface water supplies reduce and climate change causes unpredictable precipitation behavior, more people are dependent on high-quality groundwater, and there is a need to develop effective practices to manage the problem. Research suggests there is a need to develop standardized methods for reducing and mitigating nitrate contamination of groundwater. My main research question is: what are the most effective practices for reducing groundwater and aquifer nitrate contamination, considering local land use, soil types, and conditions?
This paper reviews groundwater hydrological processes and nitrate contamination of groundwater. A case study approach uses examples from agricultural areas with high nitrate contamination and mitigation steps to reduce further contamination. Best practices and recommendations are synthesized from case studies and subsurface nitrate movement data. Finally, I propose a framework for environmental managers to follow to reduce further contamination of aquifers.

2 Research Questions

The primary research question is: What are the best practices to reduce nitrate contamination of aquifers, given soil types, local land use, and conditions? In order to answer this question, I will address the following sub-questions 1) How does groundwater recharge work? 2) What factors influence groundwater recharge and contamination? 3) What options are available to reduce nitrate contamination in the long term? 4) Given local geology, weather, and land use, what management actions will decrease groundwater contamination?

3 Methodology

My research examines groundwater contamination through literature analysis of infiltration processes, the nitrogen cycle, and contaminant transport processes and studies the link between subsurface permeability, soil composition, and contamination. I further review factors that increase or decrease subsurface nitrate contamination. Finally, I create a framework for environmental managers to select suitable mitigation options for a particular location. As stated above, I use a case study approach and comparative analysis to examine what factors increase aquifers' nitrate contamination and the recommended measures that show promise in reducing and mitigating nitrate contamination.

4 Background
Groundwater nitrate contamination occurs when infiltrating water dissolves nitrate compounds and transports them to underlying aquifers. Nitrate movement within the subsurface is influenced by subsurface flows and underlying hydrogeology, among other factors. Hydrological processes such as infiltration/recharge and exfiltration/discharge, evapotranspiration - transpiration, and water evaporation form a cycle that describes water movement between the environmental compartments (Heath, 1983). Nitrate moves along the same path as subsurface water flows; the contaminant dissolves in water and moves between surface and groundwater systems as discharge or recharge (Taylor and Alley, 2001).

The hydrological cycle depicted in Figure 1 shows groundwater recharge, discharge, and evapotranspiration processes. In the cycle, water evaporates from the ocean or water bodies and returns to liquid form as precipitation. Water infiltrating the ground contributes to groundwater recharge and transports contaminants like nitrates into aquifers. The water may flow laterally or percolate downwards and get stored when it reaches an impermeable layer. Moisture is released into the atmosphere through evapotranspiration and other processes. The hydrological cycle has water moving between the air, water, and solid form (ice/snow) environmental compartments (Heath, 1983).
The water traveling laterally or vertically in the ground is known as groundwater. The subsurface layers and the unsaturated and saturated zones are shown in Figure 2, along with the relative position of the water table and groundwater. Air and water fill the inter-soil spaces in the unsaturated or vadose zone. It comprises an upper soil layer, an intermediate layer, and the upper portion of the capillary fringe zone. The soil zone is 1-2 meters deep and contains live, decaying roots, hollows from old plant networks, and animal burrows. The following intermediate zone is less porous and is of variable thickness. The capillary fringe layer forms the bottom of the unsaturated zone and the top of the saturated zone (Heath, 1983).

The water table lies within the saturated zone; water fills all inter-soil gaps here. Springs and wells get their groundwater supply from the saturated zone; water travels to/away from the saturated zone through the unsaturated zone to the surface. The hydraulic pressure in the intermediate and capillary fringe zone is under negative hydraulic pressure, meaning it is less...
than the atmospheric pressure. The hydraulic pressure increases as the depth increases and is equal to the atmospheric pressure at the water table level. Water is discharged in springs when the hydraulic pressure exceeds the atmospheric pressure. Hydraulic gradient, atmospheric pressure, and composition of the subsurface influence subsurface water movement (Heath 1983). The layers and composition of the subsurface influence water movement, and it is crucial to have a clear understanding of the movement to shed light on contaminant paths and progress.

![Diagram of groundwater layers](image)

*Figure 2: Layers, Zones between surface and groundwater. Adapted from USGS publication of Basic Hydrology (Heath, 1983)*

The subsurface comprises consolidated and disintegrated rocks, which direct water flow paths; sediment permeability directs flow and velocity. Flows that move downwards eventually pool in permeable water-bearing rocks called aquifers. The chemical composition, hydraulic gradient, soil porosity, rock fractures, and caverns influence the infiltration rate and water flow. Fractures and caverns provide a fast path for water to bypass infiltration through soil layers; this water undergoes minimal purification and can increase groundwater contamination. In contrast to fast paths, aquitards with low permeability restrict water movement and slow down infiltration (Heath, 1983). In Figure 3, the clay bed or confining layer acts as an aquitard and restricts water movement from the upper and lower aquifers.
The permeability of soils and rocks around an aquifer restricts water movement to or from it. Aquifers with restricted upward movement are confined, while unconfined aquifers allow water to move freely upwards and downwards in the saturated zone. Water movement is curtailed in confined aquifers by a semipervious aquitard layer, which restricts upward movement in the saturated zone. Intermediate aquifers have a mix of unconfined and confined sections (Taylor and Alley, 2001); many aquifers fall into this category. Figure 3 portrays unconfined, confined aquifers, extraction wells, and a clay layer acting as an aquitard (Heath, 1983). The type of aquifer and extract wells determine contaminant movement upwards/downwards in a single aquifer or between aquifers.

![Diagram of aquifer types and well placement](image)

*Figure 3: The diagram shows the difference between unconfined and confined aquifers and how the water can be accessed. Adapted from USGS publication Basic Hydrology (Heath, 1983).*

Water infiltration into aquifers depends on the depth of the water table and whether the aquifer is shallow or deep. Water age may be hours old in shallow aquifers and thousands of years old in deeper ones (USGS, 2023). The age of the water, surface conditions, soil characteristics, and surface water quality influence the water quality of underground water.
Older water is usually less contaminated, and there is a risk of contamination when newer water percolates into the aquifers. Water movement through permeable rocks and unconsolidated material can dissolve minerals or carry pollutants, ultimately contaminating aquifers. This risk depends on the geology and land use of surface areas. Subsurface water flows control groundwater recharge rates and volumes, and an aquifer's position and water flow direction influence when it gets recharged or its degree of contamination (Taylor and Alley, 2001).

5 Movement of Water and Nitrates through the Subsurface

Infiltrating water composition, quality, and physiochemical and biological processes determine groundwater quality. It is critical to understand the processes and natural and anthropogenic factors that reduce water quality before crafting management plans to address nitrate contamination of groundwater. The knowledge will guide the creation of sustainable urban, agricultural, and industrial practices (Gurdak et al. 2009). The degree of nitrate contamination of groundwater depends on groundwater recharge, soil decontamination potential, and nitrate transport. The following sections cover these topics and provide general information on groundwater contaminant movement.

5.1 How does natural groundwater recharge work?

Natural groundwater recharge happens through the process of infiltration. The Soil Science Society of America, 1956 defined infiltration as "the downward entry of water into the soil" and the infiltration rate as the "maximum rate at which soil will absorb impounded surface water at a shallow depth." Local soil characteristics, hydraulic conductivity of the soil/rocks, hydraulic head, soil moisture, duration of application of water, depth to the water table, water composition, turbidity, temperature of water and sediments, depth of water, microbes, atmospheric pressure, and air trapped within sediments influence recharge rates (Johnson, 1963). As these factors change seasonally or over time, the infiltration rate is variable and changes over time (Free et al., 1940). A high recharge rate could mobilize high amounts of
contaminants into aquifers, or it may dilute contaminants and reduce contamination. The exact outcome for an aquifer depends on the multiple soil characteristics mentioned above.

The water infiltration rate is highest at first and drops as the unsaturated zone of soil gets saturated, and the rate holds steady. Surface runoff is significant when infiltration rates are low, and the terrain has a high gradient (Free et al., 1940). This rate is controlled by the least permeable layer of the sediment (Johnson, 1963), proving that soil composition influences infiltration rates (Free et al., 1940). Water infiltration into an aquifer is constant in a homogeneous aquifer and variable in a heterogeneous one (Hartmann et al., 2017). The potential of groundwater nitrate contamination is higher when water infiltration is high; in contrast, surface contamination is high when there is more runoff and less infiltration (Nolan and Ruddy 2016). High infiltration could introduce significant contamination or dilute contamination depending on local conditions.

Infiltration rates drop when water turbidity increases as airspaces get clogged, reducing the permeability of the surface. Microbes in the top 2 -3 meters of soil can reduce infiltration (Johnson, 1963). Invasive plant species that use more groundwater can impact stores and infiltration rates. Temperature increases of sediment and water increase the infiltration rate as viscosity decreases (Free et al., 1940). The airspaces created by vegetation, roots, and animal burrows increase recharge rates.

Groundwater infiltration happens through diffuse, focused, mountain systems and irrigation recharge processes. At a high level, diffuse recharge is recharge due to precipitation events, focused recharge is infiltration due to surface stream and ground interactions, and flood irrigation recharges groundwater under croplands. This water percolates down into underlying aquifers. Finally, mountain system recharge comprises recharge from streams at mountain bases and subsurface water transfer from mountain blocks to neighboring alluvial aquifers (mountain block recharge) (Scanlon et al. 2023). The quality of groundwater depends on the quality of infiltrating water and the layers through which it percolates. Nitrates contaminate many aquifers
worldwide; contamination is highest in agricultural zones with irrigation (Bijay-Singh and Craswell 2021). The sediment type influences the degree of contamination.

5.2 Soil Decontamination Potential

Soil is an integral part of the ecosystem, and it supports microorganisms, provides nutrients for plants, and is a habitat for earthworms and burrowing animals. It plays a significant role in filtering and removing contaminants in water as it travels from the surface to aquifers. Contaminants are removed through chemical and physical processes and degradation by microorganisms (Sarkar et al. 2021). Soil is formed from the disintegration of rocks and consists of soil minerals, organic matter and living organisms, water, and air (Queensland, 2023).

Soil minerals and organic matter influence contaminant movement, remediation, and storage through physiochemical interactions of pH, particle charge, moisture, and redox potential. Soil minerals such as clay minerals remove contaminants through adsorption. Adding inorganic salts, mineral salts, and surfactants can improve their adsorption potential. Surface charge helps minerals and organic matter retain contaminants on their surface through electrostatic attraction, ion, ligand exchange, complexation, or precipitation (Sarkar et al. 2021).

Soil organic matter (SOM), like humic acid and fulvic acid, plays an essential role in contaminant mobility, availability, and transformation. Contaminants cleave to SOM through redox reactions, adsorption, and by forming complexes. Organic and inorganic metal contaminants form complexes with SOM, minimizing their mobility and leaching capacity. The organic matter in soil can be increased by adding compost, crop remnants, and sludge from municipal wastewater treatment plants (Sarkar et al. 2021).

Microorganisms such as fungi, actinomycetes, and bacteria are essential in decontaminating organic and inorganic pollutants in soil. They are effective in smaller areas with low contamination. They decrease contamination through biodegradation, biotransformation, biomineralization, and biosorption through biotic processes. The transformation depends on the
concentration of contaminants and the physical and chemical characteristics of the soil (Sarkar et al. 2021).

The physical and chemical composition of clay soils bar pollutants from moving into other locales due to their low infiltration rate. The redox potential controls aerobic and anaerobic interactions, transforming contaminants into less toxic forms or making them bioavailable to living organisms. Similarly, soil microorganisms can increase/decrease the harmful effects of contaminants and reduce leaching (Sarkar et al. 2021). Hydrophobic soils tend to retain more organic pollutants than hydrophilic soils. The distribution of contaminants and underground contamination depends on the pollution source location, transportation mechanism, and destination (Sarkar et al. 2021).

Soil pH influences metal sorption of metals on soil particles. Metal ions are retained in the soil in insoluble forms under high pH conditions. In contrast, low pH makes metal ions bioavailable for plant uptake. Similarly, soil organic matter with humic and fulvic acids can make insoluble complexes with some metals and make complexes with other metals, amplifying toxic properties. Low amounts of natural organic matter can reduce contaminant removal or sorption. Natural organic matter and inorganic minerals manage the sorption, removal, or release of contaminants from soil (Sarkar et al. 2021).

Soil with greater filtration capacity reduces the quantity of contaminants leaching into groundwater. The capacity depends on the soil's organic matter, clay, pH, microorganisms, and ionic composition. Filtration happens chemically, as contaminants are held and unavailable in mobile or bioavailable forms. Redox reactions convert contaminants to less or more toxic forms (Sarkar et al. 2021). The transformation potential is specific to the contaminant, and some chemicals like atrazine degrade faster under anaerobic conditions (Crawford et al. 2000). Redox reactions drive the conversion of subsurface nitrates into bioavailable forms or back to nitrogen (Abascal et al. 2022).
Contaminants are less toxic when they precipitate into solids - a chemical process by which a dissolved substance precipitates into solid form by forming sorption complexes (Crawford et al. 2000). The process depends on the soil’s pH, microorganisms, enzymes, and particle charge. Contaminant precipitation reduces mobility and minimizes leaching into groundwater. The physical mobility of contaminants is restricted when pores are blocked or constricted in any way (Sarkar et al. 2021). Remediation of clogged soils is necessary to allow adequate recharge and filtration processes; this is especially critical in managed aquifer recharge projects, which are used to recharge aquifers and maintain water quality (Niswonger et al. 2017). Further research on nitrate transport in the environment is needed to understand and control the increasing groundwater nitrate contamination.

5.3 Nitrate Transport

Nitrate contamination of aquifers is a significant concern globally since its water-soluble property makes it very mobile and not easily fixed in soil (DeSimone and Howes 1998). It travels through sediment layers and contaminates underground aquifers. As nitrate concentrations increase in surface and groundwater, there is an increased risk to humans and the environment. Consumption of contaminated water raises the risk of blue baby syndrome, headaches, cancer, thyroid problems, and fatigue (Abascal et al. 2022; Sahoo et al. 2016).

Pollution of aquifers has increased since the middle of the industrial age, as the use of fertilizer and pesticides increased. Significant sources of nitrate contamination are shown in Figure 4 and include wastewater effluent, agricultural fertilizers, animal husbandry, industrial effluents, groundwater inputs, urban runoff, and atmospheric deposition. Additionally, sewage, septic tanks, and natural nitrogen deposits contribute to nitrate leaching. Local land use, the quality of wastewater effluent, and septic and sewage systems influence the degree of aquifer contamination.
In Asia, contamination is most significant due to inadequate sewage septic systems; in contrast, fertilizer use in the USA has caused nitrate contamination of aquifers (Abascal et al. 2022). Figure 5 (A) shows the risk of nitrate contamination in shallow aquifers in the United States calculated by a USGS model using nitrogen inputs and a Geographical Information System (GIS), and Figure 5(B) shows the predicted concentrations of nitrate in deeper drinking water wells. The model results indicate contamination is higher in shallow aquifers, especially in agriculture-rich areas.
Figure 5: (A) Risk of nitrate contamination of shallow groundwater in USA (B) Risk of nitrate contamination of deep drinking water from groundwater in USA. Adapted from (USGS, 2015)

The nitrogen concentration in groundwater determines the degree of contamination; any groundwater with a concentration greater than 10mg/L N is unsuitable for human consumption.
by US EPA guidelines. WHO has set a standard of 50mg/L of nitrates or 11.3mg/L nitrate-nitrogen (Sahoo et al. 2016) in drinking and irrigation water, while the FAO sets a limit of 22mg/L, and the US EPA sets the nitrate-nitrogen Maximum Contaminant Level (MCL) to 10mg/L (Abascal et al. 2022; US EPA, 2023). A study measuring nitrate concentrations in groundwater found that over 40% of shallow aquifers in agricultural areas and 3% in urban areas have concentrations higher than the US EPA MCL (Dubrovsky et al. 2010).

Plants and vegetation have different tolerances towards nitrate concentrations in water, and it is vital to control nitrate concentrations in irrigation water to protect and support plants. Maize is unaffected by nitrate-rich irrigation water, up to 132 mg/L nitrate; in contrast, sugar beets or grapes can tolerate 22 mg/L or less of nitrate-contaminated water. Excessive nitrate use raises the risk of leaching of nitrates into soil, overstimulating, or causing poor growth of plants (Abascal et al. 2022). Management of nitrates requires understanding the nitrogen cycle and movement in the subsurface.

The movement of nitrogen compounds in the environment is shown in the nitrogen cycle in Figure 6. Nitrogen fixation converts gaseous nitrogen into ammonia/ammonium; some microbes and industrial processes do the conversion. The ammonia/ammonium then gets converted to nitrites/nitrates by nitrification bacteria. Plants can use ammonia, nitrates, and nitrites as they are all bioavailable forms of nitrogen. Denitrification bacteria act on nitrates and convert them back to gaseous nitrogen. As fertilizer application increases globally, denitrification bacteria cannot keep up, and nitrate compounds leach into underground aquifers and contaminate them (Abascal et al. 2022). Nitrate leaching into soils and aquifers decreases when denitrification is higher. Vystavna et al., 2017 found that denitrification happens when the ratio of nitrate to chloride decreases. Water infiltration mobilizes nitrates in the subsurface.
Nitrate concentrations in aquifers can increase during the rainy season due to increased infiltration by contaminated rainwater, or it may decrease due to the dilution of nitrate ions by infiltrating water. Shallow groundwater under agricultural areas and areas with well-draining soils tend to be more contaminated than deeper, older groundwater. The deeper water remains clear of recent anthropogenic contaminants (Abascal et al. 2022) when groundwater pumping is absent (Thaw et al. 2022). Studies on the High Plains aquifer in the USA implicate agricultural practices and groundwater pumping as the source of nitrate contamination (Gurdak et al. 2009).

Nitrogen moves through the subsurface in gaseous form as particles in water and dissolved in water. Mineralized or inorganic compounds containing nitrogen are moved by microorganisms or as suspended particles in water. The soil's chemical, physical, and biological properties determine how much nitrogen moves in the subsurface. The local geology, climate, land characteristics, and vegetation determine these properties, which are unique to a location (Rowe and Stinnett, 1975).
The form of nitrogen determines its ease of movement in the subsurface and its contamination potential. Over 90% of soil nitrogen is biologically unavailable organic nitrogen. Microorganisms convert this nitrogen into ammonium through ammonification under optimal soil temperature and pH conditions. The negative charge of clay and the organic matter causes the suspension of ions and prevents them from percolating deeper. Under oxygenated, optimal temperature and pH conditions, nitrogen-fixing bacteria convert the ammonium to nitrites or nitrates. The nitrogen in dead microorganisms returns to the soil as organic nitrogen (Rowe and Stinnett, 1975).

Under anoxic conditions, nitrates are converted to gaseous nitrogen and released into the atmosphere through denitrification. Clay soils reduce leaching by holding more water and nitrates due to their water-soluble nature and anoxic conditions. In contrast, gravel or sandy soils allow nitrate solutes to percolate quickly and contaminate lower layers. Well-drained soils typically have high infiltration, nitrification rates, and low denitrification rates (Rowe and Stinnett, 1975). Denitrification works best in waterlogged fine soil with high organic material under anaerobic conditions (Almasri 2007).

Groundwater infiltration pushes air out of pores and creates anoxic conditions suitable for denitrification or release of nitrogen in gaseous form. Microorganisms convert the inorganic and organic nutrients in the soil. The rate of nitrogen leaching depends on soil texture, porosity, moisture, depth, infiltration rates, precipitation rates, frequency, evapotranspiration rates, temperature, vegetation, microorganisms, organic matter, land use, and the type of nitrogen applied or present in the soil (Rowe and Stinnett, 1975). The interdependent properties control the form of nitrogen in the soil and whether it leaches. The area of contamination or impact changes based on subsurface flow paths; these paths change due to precipitation or groundwater pumping (Almasri 2007).

The rate of leaching increases during precipitation due to high infiltration and low evapotranspiration rates; the negative charge of nitrogen encourages leaching. Leaching occurs
during or immediately after precipitation when the water percolates past the root system of plants. The leaching rates drop during periods of intense plant growth as bioavailable nitrogen is used (Bijay-Singh and Craswell 2021).

Figure 7 shows the processes that convert nitrogen to various forms in the subsurface and the sources of nitrogen inputs on the surface. In the subsurface, mineralization and immobilization processes reduce nitrogen mobility and leaching into groundwater. Nitrogen compounds in the ground can be part of the soil stores, transform into nitrogen, or leach into groundwater. Plants use a small portion of the applied nitrogen compounds; the rest is stored as organic nitrogen, lost in runoff, or leaches into aquifers. Any nitrogen not immobilized or taken by a plant can be released back into the atmosphere or leach into groundwater. Nitrate movement depends on fertilizer, manure applications, local water, and weather conditions (Almasri, 2007).

Figure 7: A diagram describing the surface nitrogen inputs and subsurface nitrogen forms and the processes that act on them. Adapted from (Almasri 2007)
Contaminant transport to aquifers can happen quickly or slowly, depending on the infiltration path. Figure 8 shows a contaminant’s fast and slow paths to the water table. Preferential paths or fast flow paths lie under depressions where irrigation water, precipitation, and stormwater collect or when there are burrows, fissures, or other breaks in the soil structure. In these cases, contaminants can reach the water table in months to decades. On the other hand, slow paths are typically through fine soils or beneath flat surfaces. Contaminants that percolate into the ground can take centuries or longer to reach aquifers. Shallow aquifers are closer to the surface, and contaminants reach them faster; this explains why many shallow aquifers have MCLs that exceed EPA guidelines. Water travels through more sediment layers and undergoes extra filtration before reaching deep aquifers, explaining why they have lower, slower contamination (Gurdak et al. 2009).

Figure 8: Water and contaminant fast and slow paths through the subsurface. Adapted from (Gurdak et al. 2009).

Surface nitrogen application, water input, evapotranspiration, physiochemical, biological, vadose zone thickness, well construction and depth, subsurface flow paths, natural nitrogen deposits, soil composition, and hydrogeology of the sediment above the water table,
denitrification rate, redox conditions, travel time to the aquifer, and historical nitrogen inputs influence groundwater nitrate contamination. These characteristics vary from area to area, and care should be taken to tailor solutions to local conditions (Castaldo et al. 2021). The contamination potential of a region needs to be quantified to test the effectiveness of management practices. The following section describes how environmental nitrate contamination and movement are measured or studied.

5.4 Nitrate measurements

Sediment heterogeneity, local conditions, and limited monitoring complicate the study of contaminant movement in the subsurface. Models are used with site studies to envision nitrate movement, better understand processes, and manage contamination. The Soil-crop model (STICS), Root Zone Water Quality Model (RZWQM), Soil Water Balance Model, and Soil Water Assessment Tool (SWAT) are popular models used in the last 20 years. The models are simplistic, assume homogeneous soils, and do not represent natural environments (Bijay-Singh and Craswell 2021).

Despite these shortcomings, they provide valuable information on optimal fertilizer application given precipitation, irrigation, and soil types (Bijay-Singh and Craswell 2021). The effectiveness of management practices can be assessed using the nitrate fate and transport model (NFTM) and soil nitrogen models. The complicated soil and water interactions, land use, recharge, nitrogen dynamics, physical and chemical characteristics, and soil depth complicate models and make it hard to quantify nitrate leaching or movement (Almasri 2007).

Nitrate contamination assessments change based on the area. Specifically, contamination in a riparian zone can be measured by the amount of groundwater entering the zone per unit of downstream length of the zone, also known as the groundwater flux. Nitrate concentrations in upland locations are measured against concentrations at the stream to calculate the efficiency of nitrate removal of the riparian zone. Measurements are done by installing underground pipes
and measuring nitrate concentration differences. These results can be inconclusive since they do not account for clean water inputs from other areas that are diluting nitrate concentrations (Hill 2019). Further studies and comprehensive models can provide more clarity on this topic.

Nitrate movement in the subsurface can be measured using isotopes; the pollutant source can be identified based on the concentration and type of isotope. Alternatively, remote sensing technologies can gather data on groundwater nitrate contamination (Bijay-Singh and Craswell 2021). Monitoring wells in the watershed can be used to identify long-term trends in nitrate pollution.

The drawback of many nitrate transport and contamination studies is their short duration and limited scope. It is crucial to incorporate long-term studies that track an area’s land use, geological, hydrological characteristics, and weather patterns to assess the efficacy of management plans (Hill 2019). Meals et al., (2010) found that long-term studies are needed to monitor remediation efforts and nitrate reduction rates, as it can take up to a decade to see impacts. These results are limited since they do not reveal the underlying nitrate removal mechanisms (Hill 2019).

6 What factors impact the quality of groundwater?

Soil characteristics, water quality of recharge water, nitrate contamination in the area, and local land use regulate groundwater quality. The soil’s filtration capacity determines contaminant removal and nitrate leaching. Similarly, the historical contamination and current contaminant inputs can be too high for remediation by soil filtration processes (Almasri 2007). Finally, portions of today’s agricultural land were originally rangeland, wetlands, or forests with natural nitrate deposits or high nitrate concentrations. The conversion to irrigated cropland has increased nitrate leaching into groundwater (Gurdak et al. 2009). Development activities in cities have drained marshes and wetlands, increasing pollution as water in those areas is high in nitrogen. Draining these areas increases nitrogen concentrations and leaching, and the oxic
conditions promote nitrification and ammonification processes. (Rowe and Stinnett, 1975). The following sections describe how local characteristics influence groundwater quality.

6.1 Land Use

Land use can drive nitrate contamination of surface and groundwater systems. Farming areas have the highest groundwater contamination (Mittelstet et al. 2019). The area above the High Plains aquifer was historically rangeland with natural nitrate deposits; it is now known as the “breadbasket of the world” since it is one of the world’s largest and most productive agricultural regions. The conversion of rangeland to irrigated agriculture increases nitrate leaching from fertilizer and natural nitrate deposits into groundwater (Gurdak et al. 2009). As world populations grow, more people migrate to coastal cities or urban areas, converting natural areas into urban centers.

Urban areas have higher populations, contributing to the environmental nitrate problem (UN fact sheet, 2017). They contribute to higher loads in wastewater treatment plants and increases in effluent nitrate. Additionally, these areas have more industrial activities, producing nitrate contaminants that are released into the environment (WHO 2016). The concentrated populations and industrial activities in an area can overwhelm local ecosystem services, which can no longer remediate nitrate pollution, and contamination in the areas increases alongside pollution of surface and groundwater systems (Gurdak et al. 2009). Different sediments have varying filtration capacities, determining how much nitrate is stored and how much leaches into aquifers. The following section describes soil characteristics that determine the degree of filtration.

6.2 Soil Characteristics

Sediment characteristics like particle size, space between particles, physical changes when exposed to water, and existing nitrate stores all determine its nitrate filtration efficiency (Free et
al. 1940; Yang and Zhang, 2011; Nolan and Ruddy 2016). Studies by the USGS found that excessively draining soils are coarse soils with high hydraulic gradients, high nitrate leaching rates, and low nitrate runoff. In contrast, poorly drained soils lose more nitrates to runoff and less to leaching. In Figure 9, the results of the USGS study showed that the maximum number of wells with nitrate contamination exceeding the MCL of 10mg/L N were in areas with well-drained soil with high nitrogen input; poorly drained soil with high nitrogen input has the subsequent highest contamination, followed by well-drained soil with low nitrogen input, and poorly drained soil with low nitrogen input has the least number of contaminated wells (Nolan and Ruddy 2016). The results indicate that the type of soil and nitrogen input determine the contamination outcome.

![Figure 9: Median number of wells in agricultural areas where the nitrate concentration exceeds 10mg/L N based on the soil and nitrogen inputs. Adapted from (Nolan and Ruddy 2016).](image)

Silt and clay are fine sediments with a particle size smaller than 0.05mm; they are prone to expanding/shrinking and cementing when water is applied. Free et al., 1940 found that
infiltration rates are agnostic of whether surface soil comprises silt and clay; however, rates drop when subsurface soil is silt clay mix. Conversely, infiltration rates drop when water percolates through clay with particles smaller than 0.002 mm (Free et al. 1940), irrespective of whether it is in top or subsurface soil; this is true if the clay is already wet; otherwise, the infiltration rate will be initially high as water passes through cracks in the clay. The rate will drop after the initial moisture application to clay and fine-grained sediments since the particles swell, clogging/filling air spaces (Free et al., 1940). These fine-grained sediments have greater filtration capacity, as seen in Figure 9.

The infiltration rate determines the quantity of nitrate transported in the ground; if little water infiltrates, there is less contaminant movement. Soil can upgrade or degrade water quality as it percolates through the ground. Water infiltration is higher through coarse-grained soils; however, contaminant removal is higher in finer soils (Ground Water Recharge Using Waters of Impaired Quality, 1994). When the infiltration rate is high, more water and contaminants are transported into aquifers; the lower infiltration in fine sediments transports limited water and contaminants into groundwater. Additional studies are needed to quantify whether high infiltration rates reduce contamination due to dilution or if finer soils are more efficient in removing contaminants and improving water quality.

The vadose layer can improve water quality through the adsorption or contaminant precipitation of phosphorus trace metals, reduction of nitrogen, biological and chemical compounds, and filtering out more prominent pathogens. Water quality improvements are variable and insufficient to maintain aquifer quality (Ground Water Recharge Using Waters of Impaired Quality, 1994). Soil contaminants can interact with percolating water and get transported into groundwater storage.

The vadose layer has successfully reduced heavy metals, some hydrocarbons, and organic halogen pollutants from stormwater in two areas in Northwestern Switzerland. The studies found that Cu, Co, Ni, Zn, Ni, Cr, Cd, Pb, organic bound halogens (AOX), and polyaromatic hydrocarbon
concentrations were similar in upper surface soil as in the stormwater runoff. Contamination decreased as depth increased, and water quality was purer than the stormwater effluent. An unfortunate side effect is contaminated top and upper subsurface sediments; pollutants in these layers must be remediated. Additionally, upper layers can get clogged and reduce infiltration. The results of these case studies are relevant in alkaline conditions and may vary from results from other areas. Soil and sediments can filter and remove some contaminants and become contaminated in the process (Mikkelsen et al., 1997), and the same sediment can be compacted and exhibit different filtration properties.

Soil compaction increases the density, decreases the sediments' porosity, and can lead to land subsidence. In Central Valley, CA, there is a high correlation between excessive groundwater pumping and soil compaction. Studies by Smith et al., 2018 found that contaminants like arsenic were released from a clay impermeable layer when water is over-pumped from an aquifer. In a normal situation, water is released first from the permeable layer; during over-pumping, water is released from the impermeable clay layer, leading to arsenic release and land subsidence as pore spaces get compacted (Smith et al. 2018). Further research is needed on whether nitrate concentrations would similarly increase in pumped groundwater. In addition to sediment characteristics, the groundwater recharge water itself may contribute to the nitrate problem.

6.3 Source of Recharge Water

The quality of percolating water impacts the quality of groundwater recharge. When the recharge water is from nitrate-rich stormwater runoff, processed municipal wastewater, and flows from irrigation, it contributes additional nitrate into the groundwater system (Dewandel et al., 2008). Return flows in irrigated croplands are categorized as a non-point source and are not regulated by the Clean Water Act. Contaminants in the water include nutrients, organic compounds, suspended solids, pesticides, trace metals, and salt; flows contain potentially high nitrate concentrations due to fertilizer usage. The aquifer contamination risk increases when this water percolates into the surface as it is not treated or regulated. Irrigation return flow has
inconsistent quality compared to stormwater and municipal wastewater (Ground Water Recharge Using Waters of Impaired Quality, 1994).

The infiltrating water’s biological oxygen demand, sodium adsorption ratio (affects permeability), and concentration of dissolved gases, suspended solids, nutrients, toxic compounds, and microorganisms influence the quality of water reaching the aquifer. Organic, inorganic toxic compounds, nutrients, and pathogens in water are of great concern, primarily if the water from the aquifer is used for potable uses (Ground Water Recharge Using Waters of Impaired Quality, 1994). The study area and local characteristics like industries, urban or rural location, and climate determine the runoff quality, precipitation patterns, and annual precipitation. These factors can increase or decrease the contaminants transported to underground systems. The following section describes the major sources of groundwater nitrate contamination.

6.4 Nitrate Contamination Sources

Nitrogen compounds in soil and groundwater can be deposited through natural processes, through fertilizer and manure application to cropland, from runoff from livestock facilities, inadequately treated wastewater effluent, septic systems, industrial wastes, vegetation decomposition, leaching from natural nitrogen-rich deposits such as shale, limestone, dust, precipitation, and microorganism nitrogen-fixation (Sahoo et al. 2016; Rowe and Stinnett, 1975). Nitrate-nitrogen contamination is diffuse pollution caused by many minor releases that create watershed-wide impacts (Bijay-Singh and Craswell 2021). Contamination is not static; leaching into aquifers can change as water cycles and precipitation patterns change (Bijay-Singh and Craswell 2021).

The source of contamination can be identified based on the ratio of nitrates and chlorides. A higher ratio of nitrates/chlorides implicates fertilizer and rainwater-based pollution, while a lower ratio implicates manure pollution. Similarly, a high nitrate/chloride ratio and high chloride
concentration can be attributed to sewage (Su et al., 2020). Another indicator of sewage or septic contamination is the presence of coliform Enterococcus bacteria (Abascal et al. 2022).

Soil contains a large pool of organic nitrogen from past fertilizer, manure application, and natural processes. This pool gets larger with repetitious fertilizer and manure applications, as plant uptake does not utilize all the fertilizer applied. A portion of the used nitrogen in the fertilizer gets stored in the soil-bound organic nitrogen pool, and the rest leaches into groundwater or is released into the atmosphere. The organic nitrogen stores can be mineralized and used by plants or leach into groundwater. Currently, nitrate contamination of groundwater is caused by legacy fertilizer applications from decades back (Bijay-Singh and Craswell 2021).

6.4.1 Fertilizer

Food requirements are increasing as the world population increases. In Figure 10, we see that the global use of fertilizers has been increasing since the 1960s and is plateauing or decreasing as countries recognize the impacts of nitrate contamination and take corrective actions to address the issue (Bijay-Singh and Craswell 2021). Fertilizer application is a significant source of surface and groundwater nitrate contamination and nitrous oxide greenhouse gas release to the atmosphere. Agriculture products consumed by humans and animals become another source of nitrate contamination when the biowaste is released into the environment (Sarkar et al. 2021). Nitrogen, phosphorus, and potassium compounds are key ingredients in fertilizers that improve plant growth. The first two compounds are limiting factors for plant growth in a natural system. Commercial fertilizers contain nitrogen in the form of nitrates, ammonia, ammonium, and urea (Abascal et al. 2022).

Numerous interdependent factors make it hard to assess how much nitrogen fertilizer plants use. Liu et al., (2010) estimated that the global nitrogen input to croplands was 136.6 Tg (trillion grams) N in 2000, of which over 50% is from mineral fertilizers; the output was 146.8 Tg N, of which 55% is plant uptake and related byproducts. Their assessment showed that only 59% of fertilizer is recovered or used, and up to 2/5 is lost to the environment. The same agriculture
processes in different locations can have different contamination outcomes (Bijay-Singh and Craswell 2021).

![Figure 10: Global Fertilizer Usage from 1961 to 2020. Adapted from (Bijay-Singh and Craswell 2021)](image)

As the world population increases, agriculture output becomes more and more critical. Farmers are applying more and more fertilizer to increase crop yield. In 1970, over 36 million tons of fertilizer was used (Rowe and Stinnett, 1975). Usage increased to 185.1 million tons in 2022, according to The International Fertilizer Association (IFA). The most significant contamination is uncurbed fertilizer application on very permeable soils, spills, and leaching at fertilizer plants (Rowe and Stinnett, 1975).

Agricultural processes like fertilizer application, irrigation, and tillage change soil structure and lead to increased recharge. The fertilizer introduces nitrate contaminants, and the irrigation aids nitrate movement past plant roots and into groundwater (Stanton and Fahlquist 2006). The nitrate concentration in aquifers and the number of contaminated aquifers have been increasing
worldwide, irrespective of land use. Between 1993 and 2003, the percentage of wells with nitrates that exceeded MCL increased from 16% to 21%, and the median nitrate concentration went up from 3.2mg/L to 3.4mg/L nitrogen (Dubrovsky et al. 2010). Although most deep aquifers and drinking water wells have nitrate concentrations below the MCL, pollutants continue to percolate deeper and will contaminate these aquifers. Nitrate groundwater cleanup is costly, and we need to act immediately to reduce further contamination or aquifer remediation will become a necessity.

Excess soil nitrates are not always available to plants. Zhou et al., (2016) found that nitrate accumulated in the vadose layer, out of reach of plant roots in semi-humid areas in Chinese croplands. The location of the nitrate store makes it unavailable to surface crops; oxic conditions and inadequate carbon stores prevent its conversion and release as nitrogen gas. These nitrate stores can leach into groundwater in irrigated conditions or with infiltrating water from precipitation. A study of sites from around the world indicated that at most sites, nitrate leaching increased exponentially on repeated fertilizer applications (Wang et al. 2019).

Organic manure leaches less nitrogen compounds than mineral fertilizers. Repetitious application of organic manure over time can leach the same amount of nitrate into groundwater as the organic matter stored in the soil increases (Bijay-Singh and Craswell 2021). A study by Di and Cameron., (2002) deduced that nitrate leaching is most significant in vegetable cropland, followed by plowed pastures, grazed pastures, cut grassland, and is lowest in forests. Optimal fertilizer usage based on crop needs minimizes fertilizer losses (Goulding 2000).

Oxygen isotope studies on water at 2m below roots measured nitrate seepage and indicated that nitrate was mineralized from the organic nitrogen pool; this is expected to continue for the next five decades. Crops use nitrogen from fertilizer and the soil storage pool; reducing fertilizers can help decrease nitrate groundwater infiltration (Bijay-Singh and Craswell 2021). Studies from the Mississippi River Basin predict that 25 – 70 Kg N ha⁻¹ gets added to the soil pool annually. Modeling of this data indicates that it would take 35 years for the nitrate pool
to return to historic levels, assuming 30 years of nitrogen loading in the basin (Van Meter et al. 2016). Another contributor to nitrate contamination is manure from livestock yards, which will be described further in the next section.

6.4.2 Livestock

Livestock manure is another major contributor to nitrate contamination of groundwater (Bijay-Singh and Craswell 2021). The degree of contamination depends on the location of the livestock facility, distance from drinking water wells, groundwater flows, and manure application in croplands. Livestock farming establishments contain many animals, such as pigs, chickens, and cows, in small spaces. Animal waste products from the yards, manure lagoons, and cropland manure applications contain organic and inorganic nitrogen compounds. The organic nitrogen compounds get converted to ammonia and then nitrites and nitrates by microbes.

Livestock contributions to nitrate contamination are increasing as herd sizes and the number of facilities increase to meet global meat demand (Sahoo et al. 2016). Handling the waste by spreading lagoons raises the leaching potential (Rowe and Stinnett, 1975). Additionally, improperly stored waste can infiltrate soil, become surface runoff, and contaminate surface and groundwater systems. Excess manure application in cropland makes it easy for nitrates to migrate under plant roots, become inaccessible to plants, and, over time, leach into groundwater (Sahoo et al. 2016). The following section explores other sources of nitrate contamination in urban systems.

6.4.3 Wastewater, Septic Systems, and Urban Contamination Sources

City sewage and septic systems are a source of surface and groundwater nitrate contamination. In areas with inadequate processing capabilities, nitrogen-rich water is released into surface water and can infiltrate into groundwater. Other sources are leaks from septic tanks, breaks in sewage lines, and nitrogen-rich byproducts of wastewater processing. These
byproducts introduce contaminants when applied to the land or incorrectly disposed of (Bijay-Singh and Craswell 2021). Disposal of wastewater in deep wells, pits, basins, and leaks in landfills can increase nitrogen inputs in an area (Rowe and Stinnett, 1975). Urban industrial activities like petroleum refining, meat, and dairy processing create nitrogen byproducts that must be disposed of carefully to avoid contamination. (Rowe and Stinnett, 1975). Strict guidelines on the disposal and application of nitrogen compounds can reduce environmental nitrogen inputs and improve groundwater nitrate concentrations in the long term.

6.5 Summary

Many factors influence nitrate contamination of groundwater aquifers. Figure 11 summarizes the different environmental factors that influence nitrate contamination. The factors are interdependent and either amplify or decrease contamination impacts. Case studies should analyze the soil’s nitrate stores, including natural nitrogen-rich deposits, applied fertilizer/manure, historical nitrate stores, and atmospheric nitrogen deposition. This information will help inform how much nitrate is available in the area, whether it is accessible to plants, or if it presents a leaching risk.

Secondly, studies should describe subsurface characteristics, such as geology, sediment type, and redox conditions. The geology and sediment determine the infiltration and contaminant mobility rates, determining how much filtration is possible and whether fast paths circumvent filtration. The sediment type and redox conditions help determine if the conditions are optimal for denitrification and release of nitrogen into the atmosphere.

The movement of nitrate contaminants is impossible without water infiltration; flood irrigation, aquifer recharge, or precipitation provide the necessary water. Nitrates dissolve in the percolating water and get filtered by sediments as the water moves in the subsurface. Another source of nitrate contamination is faulty water well construction, which causes water to mix at different levels or introduces contaminants directly into aquifers.
The other factors that impact nitrate removal are weather, as cold weather limits biotic nitrogen processes, water residence time, and depth of the aquifer. A longer water residence time and more interactions with sediment can increase contaminant removal; water in shallow aquifers have less sediment interactions and higher contaminant concentrations. Nitrate removal is influenced by the depth of the water table and confining aquitard layer; shallow aquifers with a confining layer < 3m deep have shallow flows of water with increased interactions with organic-rich soils. As the depth of the aquifer increases, there are reduced interactions with organic-rich soils and alternate flow paths, complicating nitrate contaminant removal and measurements (Hill 2019).

Finally, groundwater nitrates are taken up by vegetation and released through denitrification processes. Vegetation uptake is temporary, as the nitrogen returns to the soil when the plant dies and decomposes (Hill 2019). Studies indicate vegetation type does not influence nitrate removal from the subsurface (King et al. 2016; Mayer et al. 2007). Uptake is highest during spring.
and summer and when there are elevated groundwater levels (Hill 2019). While uptake does not permanently remove subsurface nitrogen, it supports denitrification processes through organic matter loading of soil and oxygen depletion, creating anoxic conditions. The organic matter loading is present even at deeper soil layers, probably by historical plants (Hill 2019). When creating guidelines to address nitrate contamination, management plans should consider all these factors. The following section covers case studies of agricultural areas and the effects on the underlying aquifers.

7 Case studies of Farming Areas with nitrate contamination of groundwater

7.1 High Plains Aquifer

The High Plains aquifer covers 450,658 square kilometers in eight Midwestern states. It is the primary supplier of agricultural water in the region. The aquifer has predominantly fossil water, which is ten to twenty-five thousand years old. It is largely non-renewable and disconnected from its historical source. Evapotranspiration rates exceed precipitation, leaving little water for recharge. The little recharge happens through infiltration of irrigation water, storm and agriculture run-off, and diffuse infiltration from precipitation. The aquifer lies under Wyoming, Colorado, Kansas, Nebraska, South Dakota, Oklahoma, New Mexico, and Texas (Gurdak et al. 2009). The Ogallala aquifer makes up 80% of the High Plains aquifer (USGS, 2023).

The overlying land is 56% rangeland, 38% agriculture, and 3% urban areas. One-third of the agricultural area is irrigated land in eastern Nebraska, southwestern Kansas, and the west-central part of the Texas Panhandle (Gurdak et al. 2009). It contains over 27% of all irrigated land in the USA, and over 30% of irrigation water is from the High Plains aquifer (Stanton and Fahlquist 2006). Though the irrigated area is a small percentage, water infiltration and chemical application
in these areas raise nitrate contamination in the aquifer (Gurdak et al. 2009). Figure 12A shows the land uses within the aquifer, and part B shows the areas with irrigated agriculture.

![Figure 12: (A) The High Plains aquifer land use. The areas marked with (1) Rangeland, (2) non-irrigated cropland, (3) Irrigated Cropland, and (4) Urban areas. (B) The map shows irrigated cropland above the aquifer. Adapted from (Gurdak et al. 2009).](image)

The surface above the aquifer was historically rangeland, converted to agricultural land. The conversion can impact water quality as chemical applications of nitrate and natural nitrate deposits can leach nitrates into underlying aquifers. McMahon et al. (2006) found that over 57% of the nitrogen found in the unsaturated zone of the High Plains aquifer is from natural deposits. The natural concentration of nitrates in groundwater is 2 – 4mg/L without anthropological intervention. Studies show that deeper aquifers have old water with less nitrate contamination, and shallower aquifers with overlying irrigated agriculture areas have higher concentrations of nitrate, dissolved solids, and other contaminants (Gurdak et al. 2009).
The nitrate contamination measured in the aquifer is below Federal limits; however, the situation can change at any time due to water movement and physiochemical reactions. Further study and management actions are needed to mitigate further deterioration of water quality in the aquifer, mainly since the aquifer has limited nitrate attenuation capacity. Natural nitrate attenuation happens through denitrification processes. It is a prolonged process and can take hundreds to thousands of years to reduce contamination by 1mg/L as nitrogen (Gurdak et al. 2009). Remediation is not a viable path to manage nitrate contamination, and surface land management and systems have a greater probability of success. Nitrate concentrations in recharge water have increased since the 1950s in response to the growing nitrogen fertilizer usage, as seen in Figure 13. The following subsections study two agricultural-rich irrigated regions— one in the west-central panhandle of Texas and the other in Eastern Nebraska.

![Figure 13: Recharge water nitrate concentration from 1940s to early 2000s. Adapted from (Gurdak et al. 2009)](image)

7.1.1 Ogallala aquifer in Texas

The Ogallala aquifer in Texas covers 93,998 square kilometers and extends across the Texas panhandle to Midland. The area has semi-arid to subhumid weather (Bruun et al. 2016). It has the lowest water quality of all areas in the Ogallala aquifer, with nitrate, arsenic, dissolved solids, fluoride, manganese, and iron concentrations regularly exceeding USEPA standards for drinking water (Gurdak et al. 2009). Approximately 4% of the aquifer has nitrate concentrations exceeding MCL of 10mg/L (Malito et al. 2022). The surface sediments comprise gravel, clays, and clay loams in the north and gravel and sandy loams in the south (Nativ and Smith 1985); a
resistant carbonate of siliceous caliche called caprock is present in the subsurface. It is a productive agricultural area, and over 95% of pumped groundwater is used for irrigation (Fahlquis 2003).

Groundwater depth in the south is less than 30.5m, and it is over 122m in the north part of the aquifer in Texas (Fahlquist 2003). Annual precipitation is 50.8cm in the northeast and 33cm in the southwest. This portion of the aquifer gets 0 recharge to 2.54cm/year. The predominant land use is agriculture and rangelands. Over 323 million kilograms of nitrogen was applied to the land between 1997 and 1998, averaging 81.6kg/hectare. Figure 14 shows the study area's nitrate application rates and groundwater concentrations. Cotton is the main crop grown in the study area (Stanton and Fahlquist 2006).
Nitrate concentration levels varied from 0.65 to 21.6 mg/L, with 7% of samples exceeding the MCL of 10 mg/L N. Studies by Stanton and Fahlquist (2006) found that the nitrate concentrations decreased as the unsaturated zone thickness increased. In the study, over 59% of samples indicated that the water age was less than 50 years. Newer water had a nitrate concentration of 4.70 mg/L, whereas older water had 2.24 mg/L N. The nitrate concentration
between a shallow aquifer and a drinking water well was not statistically significant (Stanton and Fahlquist 2006). The following section discusses the local nitrate contamination guidelines.

7.1.1.1 Mitigation Measures

Winter cover crops can reduce nitrate concentrations in soil as they use nutrients and reduce leaching into groundwater. Studies have shown that nitrate loss is high during winter when precipitation is high. The winter crops capture nutrients left from summer harvests and prevent them from leaching below root access so that summer crops can use them. Studies found that rye cover crops reduced soil nitrogen by 160.2 kg/hectare from December to April. Other studies could not quantify the reduction in nitrate leaching by winter crops; additional research can confirm or disprove the effectiveness of these measures (Dozier et al. 2008).

7.1.2 Eastern Nebraska Hydrological unit of High Plains aquifer

The High Plains aquifer lies under over 90% of Nebraska and supplies water for crops like corn, soybeans, alfalfa, and beans. Data from the Quality-Assessed Agrichemical Database for Nebraska Groundwater is represented in Figure 15 and shows the upward trend of groundwater nitrate concentrations since 1974. The median nitrate concentration is higher than background concentrations and is slowly approaching the MCL of 10mg/L N guideline of the USEPA. Figure 16 shows the distribution of wells and the average nitrate concentration in Nebraska. In the eastern part of the state, there is significant agricultural activity, and the nitrate contamination is high and exceeds guidelines. These areas have some shallow and deep aquifers, as seen in Figure 17 (NDEQ 2018); the contaminated areas from Figure 16 correspond with shallow aquifers. In the case study below, the study area has high nitrate contamination and is in Nebraska's eastern portion of the High Plains aquifer.
Figure 15: The median nitrate concentration measured in Nebraska between 1974 and 2017. Adapted from (NDEQ 2018)

Figure 16: The recorded nitrate concentrations measured between 1998 - 2017. Adapted from (NDEQ 2018)
The Eastern Nebraska Hydrological unit of the High Plains aquifer is a heavily irrigated area in Nebraska with extensive agriculture. The overlying surface has rolling hills and plains bisected by numerous streams. The groundwater depth lies between 1.5m and 91.5m from the surface; it has over 1.0 mg/L of dissolved oxygen. Surface and subsurface sediments are mainly sand and gravel with some clay and silt and unstratified glacial till; thick layers of loess soil and glacial till limit recharge to 20% of annual precipitation. The area has subhumid weather and receives between 63.5cm and 68.5cm of rain annually, mainly between May and September (Stanton and Fahlquist 2006). Studies by Dugan and Zelt., (2000) calculated the natural annual groundwater rate for the area to be 10cm – 15cm. The precipitation patterns and associated recharge may change due to the impacts of climate change.

The primary crops grown are soybeans and corn; the secondary crops are sorghum, hay, and wheat. In 1997, manure and fertilizer applications applied an average of 127kg per hectare of nitrogen to croplands (Stanton and Fahlquist 2006). Ferguson (2015) calculated that 154kg/hectare of Nitrogen fertilizer was applied to corn croplands in 2010; no extra fertilizer was applied to the soybean crops planted after corn. The present-day application rate is expected to be lower as agricultural processes have improved (Stanton and Fahlquist 2006). Nebraska is
ranked 6\textsuperscript{th} in toxic pollution, and nitrate contamination is the highest contributor (Mittelstet et al. 2019). Nitrate contamination is a big problem in this part of the aquifer; concentrations varied between 1.96 and 106 mg/L nitrogen in different wells. Over 90% of the measurements were above 4mg/L nitrogen, indicating that anthropological additions raise concentrations above natural background levels (Stanton and Fahlquist 2006). Figure 18, shows the nitrogen application rates for various places in the study area, indicating a high correlation between application rates and nitrate concentrations of underlying aquifers.
Figure 18: Nitrate application rates in Eastern Nebraska Hydrological unit. Adapted from (Stanton and Fahlquist 2006)
Domestic wells get their water from 19 to 176 feet below the water table. Stanton and Fahlquist (2006) found that sample wells near agricultural areas had a median of 1.92 mg/L nitrogen, while shallower groundwater (5 feet below the water table) had 10.96 mg/L nitrogen. The measurements indicate that nitrogen in the agricultural areas reaches groundwater and has not yet contaminated deeper groundwater. The results are from 2003, and the situation could have changed since then. The shallow aquifers, high precipitation, and low evapotranspiration rates make the conditions favorable for nitrate contamination of groundwater (Stanton and Fahlquist 2006).

7.1.2.1 Mitigation Measures

Best management practices in croplands to reduce nitrate contamination include split or reduction in fertilizer application, riparian buffers, treatment by wetlands, terraces, cover crops, and education of residents. The sediment and land use characteristics influence the efficiency and success of the measures. It is essential to study local conditions to pick the appropriate mix of practices that would be most effective (Mittelstet et al. 2019).

Local farmers used nitrogen inhibitors, cover crops, split fertilizing, reductions in autumn fertilization, fertilizer application by a center pivot, soil and water sampling, and center pivot irrigation. They also recommended accounting for nitrates in irrigation water when calculating the amount of fertilizer to apply to a crop (Sixt et al. 2019).

7.1.3 Analysis of Case Study Areas in TX and Eastern Nebraska

There is significant variation in measured nitrate concentrations within the Eastern Nebraska Hydrological unit and Southern High Plains in Texas, even when monitoring locations are close. Eastern Nebraska gets more precipitation, has a higher recharge rate, applies more fertilizer, and has more wells with very high contamination compared to the Texas study area. More research is needed to identify the relative influence of individual factors on contamination. The groundwater age is older in Eastern Nebraska versus the Texas aquifer. The results indicate
complex interactions and influences in play, and further research and modeling are needed to identify which factors are more influential in increasing contamination. In the following section, contamination within the Central Valley aquifer is discussed.

7.2 Central Valley, California

Central Valley is a 51800 square kilometers area in California, a major agricultural powerhouse made up of the northern one-third, known as Sacramento Valley, and the lower two-thirds, known as San Joaquin Valley (SJV), as seen in Figure 19. It is an alluvial basin west of the Sierra Nevada mountains, east of the coastal ranges, north of the Tehachapi mountains, and south of the Sacramento-San Joaquin Delta. The aquifer has perennial streams from the Sierra Nevada, which recharge it (Castaldo et al. 2021). The aquifer underlies an immense agricultural zone. The region's climate is arid to semi-arid, with annual precipitation in Sacramento Valley 33cm and 66cm and 13cm – 46cm in San Joaquin Valley (Burow et al. 2013).

Figure 19: Image of the Central Valley Aquifer in California with the Sacramento and San Joaquin Valley portions. Adapted from (Ransom et al. 2017)
Aquifers in Central Valley are confined, unconfined, and semi-confined and lie within the top 300m of the alluvial plains. The sediments are between 30% - 70% coarse-grained, with the northern Sacramento Valley having finer sediments and the southern San Joaquin Valley with coarse-grained sediments other than a region with Corcoran clay (Burow et al. 2013).

Agriculture production in San Joaquin Valley brings in more than $25 billion in revenue from 250 different crops; it also has three-quarters of dairy animals in the state (Castaldo et al. 2021). Aquifers in the region are among the most contaminated in the nation (Dubrovsky et al. 2010). Like other areas with intense farming activity, it has the highest nitrate groundwater contamination of all nine hydrogeological provinces in the state. Figure 20, shows the increasing trends of fertilizer and manure application in Central Valley, CA, since the 1950s. The increasing nitrate contamination correlates with fertilizer and manure application over the years. Over 450 disadvantaged communities in the Valley are exposed to nitrates as shallow wells are contaminated (Castaldo et al. 2021). Private wells in California are not regulated or regularly monitored and have a higher probability of contamination due to their shallower depth (Ransom et al. 2017).
Figure 20: Nitrogen inputs from nitrogen fertilizer and manure in Central Valley and the growth in population over the time period. Adapted from (Burow et al. 2013)

In areas with coarse sediment, conditions are oxic, and nitrate concentrations are higher than in other areas; deeper in the subsurface, sediments become finer-grained, conditions more anoxic, and denitrification converts some nitrates to nitrogen gas. There are higher nitrate concentrations in shallower aquifers than in deep ones. Groundwater quality in San Joaquin Valley varies significantly due to the heterogeneous sediments from debris from the Coastal Ranges. A highly contaminated zone could lie next to a zone with excellent water quality. Natural nitrate deposits in San Joaquin Valley contribute to high nitrate concentrations zones in the area. Most of the nitrate input in Central Valley is from agriculture, and a small portion is from rural septic systems (Burow et al. 2013).

7.2.1 Analysis of SV & SJV nitrate outcomes
Nitrate concentrations trended higher in oxic zones; in contrast, other geochemical zones had variable concentrations with no clear trends. Conversion of nitrate to nitrogen gas was more significant in the presence of organic material and reducing conditions. In 2010, 80kg/ha of fertilizer was applied in Sacramento Valley and San Joaquin Valley. Long-term studies show that nitrate concentrations in groundwater are increasing faster in San Joaquin Valley than in Sacramento Valley despite following similar agricultural practices. Sacramento Valley has more natural undisturbed land and finer sediments and receives more annual precipitation, leading to anoxic conditions conducive to denitrification and nitrate reduction. In contrast, SJV has granular sediments, natural nitrogen deposits, and oxic conditions (Burow et al. 2013). The results of the case studies show that similar agricultural practices can yield different contamination outcomes based on local conditions such as redox conditions, sediment, hydrogeology, and land use.

7.2.2 Mitigation Measures

In SJV, river-based recharge has doubled since the 1950s as river water is used for irrigation, and excessive groundwater pumping is increasing focused recharge (Castaldo et al. 2021). Studies by Ransom et al. (2017), using hybrid machine learning models, found that proximity to rivers and historical nitrogen inputs, groundwater travel time, and reduced conditions are the highest predictors of nitrate contamination of groundwater. Wells near rivers have lower nitrate concentrations due to the lower nitrate content of the river recharge water. Long-term trends indicate that deeper groundwater will get contaminated as shallow nitrate-contaminated groundwater percolates into deeper areas. Studies indicate that wells within 2km from rivers had lower nitrogen-nitrate concentrations than the ones further on (Castaldo et al. 2021). Supporting studies by Schmidt et al., (2012) indicate that nitrogen-nitrates are diluted in aquifers when river water infiltrates aquifers.

Flood-managed aquifer recharge (MAR) is gaining traction in California, and using excess river water during flood events could reduce nitrate contamination. Mobilization of nitrates during recharge is a concern; studies indicate that denitrification and river water flood MAR could reduce nitrate contamination of groundwater. Nitrate concentrations were higher in shallow
aquifers with younger water, in contrast to the lower concentrations in deeper aquifers with older water (Castaldo et al. 2021). The most significant contamination is usually seen at depths less than 61m from the land surface (McMahon 2000).

California Department of Food and Agriculture (CDFA) has crop fertilization guidelines to reduce nitrate contamination. The best management practices recommend accounting for existing nitrogen inputs from atmospheric deposition, irrigation water, surplus fertilizer, nitrogen-fixing by legumes, crop residues, nitrate mineralization from soil organic matter, manure application, and outputs from volatilization of fertilizer, nitrate leaching, and denitrification before calculating fertilizer requirements for a crop. National Atmospheric Deposition Program (NADP) data calculates that 9kg/ha of atmospheric nitrogen is deposited in Central Valley annually (Geisseler and Horwath, 2023).

In agricultural areas, nitrate leaching is closely linked to irrigation and precipitation events. As irrigation is controllable, CDFA guidelines recommend scheduling irrigation to match evapotranspiration for a crop, applying fertilizer, manure, and water periodically in small amounts to reduce leaching, irrigating uniformly, planting non-legume plants like triticale (hybrid of wheat and rye), ryegrass post-harvest to capitalize on high soil nitrate concentrations, and inject fertilizer into the drip-irrigation system so that it percolates to the root zone. It is imperative to apply fertilizer according to the crop needs; annual and deciduous crops nitrogen utilization follow a sigmoid shape and is plotted as an N-uptake curve, as seen in Figure 21 (Geisseler and Horwath 2023). The plant's nitrate utilization is low during germination, and agriculture practices should consider crop requirements before applying fertilizer.
Figure 21: N-uptake curve for annual crop and deciduous crops. Adapted from CDFA (Geisseler and Horwath 2023)

7.3 Summary of Case Studies

The summary of the four case study areas is covered in Table 1: Summary of case study area’s hydrogeological and local conditions. The areas have different local conditions, fertilizer inputs, and many areas where nitrate concentration exceeds guidelines. Crops have different fertilizer requirements and different tolerances to nitrates in irrigated water. The case study areas in Eastern Nebraska and San Joaquin Valley have higher variability and extreme contamination in some areas. It is clear that multiple conditions influence contamination, and further study and research are needed to identify the relative influence of each condition.
Table 1: Summary of case study area’s hydrogeological and local conditions.

<table>
<thead>
<tr>
<th>Aquifer/Location</th>
<th>Sacramento Valley, CA</th>
<th>San Joaquin Valley, CA</th>
<th>Eastern Nebraska Hydrological Unit</th>
<th>Southern High Plains, Texas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment Type</td>
<td>Finer Sediments(^a)</td>
<td>Coarser Grain, Corcoran clay(^a)</td>
<td>Sand, gravel, some clay, silt, and unstratified glacial till(^b)</td>
<td>Gravel, clays, and clay loams in the north and gravel and sandy loams in the south(^c)</td>
</tr>
<tr>
<td>Depth to Groundwater</td>
<td>3m - 91.4m(^d)</td>
<td>0.3m – 219.5m(^d)</td>
<td>1.5m and 91.5m(^b)</td>
<td>30.5m - 122m(^e)</td>
</tr>
<tr>
<td>Land-use</td>
<td>Cropland, Livestock(^f)</td>
<td>Cropland, Livestock(^f)</td>
<td>Cropland(^g)</td>
<td>Cropland(^e)</td>
</tr>
<tr>
<td>Crop</td>
<td>Cereal grains, hay, cotton, tomatoes, vegetables, citrus, nuts, grapes(^h)</td>
<td>Hay, cotton, tomatoes, vegetables, nuts, grapes, rice(^h)</td>
<td>Corn, soybeans, alfalfa, and beans(^g)</td>
<td>Cotton(^b)</td>
</tr>
<tr>
<td>Fertilizer Input</td>
<td>80kg/hectare(^a)</td>
<td>80kg/hectare(^a)</td>
<td>127kg/hectare(^b)</td>
<td>81.6kg/hectare(^b)</td>
</tr>
<tr>
<td>Climate</td>
<td>Arid-semi-arid(^a)</td>
<td>Arid-semi-arid(^a)</td>
<td>Subhumid(^b)</td>
<td>Semi-arid to subhumid(^c)</td>
</tr>
<tr>
<td>Annual Precipitation</td>
<td>33cm – 66cm(^a)</td>
<td>13 – 46cm(^a)</td>
<td>63.5cm – 68.5cm(^b)</td>
<td>33cm - 50.8cm(^b)</td>
</tr>
<tr>
<td>Annual Recharge Rate</td>
<td>Missing Data</td>
<td>Missing Data</td>
<td>10cm – 15cm(^i)</td>
<td>0 - 2.54cm(^b)</td>
</tr>
<tr>
<td>Redox Conditions</td>
<td>Anoxic(^a)</td>
<td>Oxic(^a)</td>
<td>Oxic(^b)</td>
<td>Oxic(^k)</td>
</tr>
</tbody>
</table>

\(^a\)Burow et al. 2013, \(^b\)Stanton and Fahlquist 2006, \(^c\)Nativ and Smith 1985, \(^d\)USGS, CA State Parks, NOAA 2023, \(^e\)Fahlquist 2003, \(^f\)Castaldo et al. 2021, \(^g\)NDEQ 2018, \(^h\)Faunt and USGS 2009, \(^i\)Bruun et al. 2016, \(^j\)Dugan and Zelt 2000, \(^k\)Mcmahon et al. 2004

8 What cleanup/reduction of nitrate options are available?

Many measures can reduce or slow down nitrate leaching into groundwater. Their appropriateness depends on local conditions, the goal of the management plan, and local land use. The different measures will be discussed in the following sections.
8.1 Riparian areas and natural flooding

Riparian zones are areas along streams, lakes, and water bodies that provide critical habitat for plants and animals. They slow runoff and reduce contamination of streams and groundwater in addition to recharging groundwater (Hill 2019). The vegetated buffer along the stream is the riparian buffer; it can reduce nitrate contamination by restricting its movement (Howarth et al. 2011). Nitrate removal from surface water is higher when there is a broader buffer. In contrast, Mayer et al., (2007) found that subsurface nitrogen removal is independent of the width of the riparian buffer. They theorized that factors such as soil type and hydrology are more influential in subsurface processes. Case studies and models of France and eastern U.S. riparian buffers have shown a removal rate of 5 - 50% agricultural nitrate inputs (Hill 2019).

Riparian zones may be ineffective in nitrate removal in areas with tile drainage systems that bypass these zones. These systems used mainly in agricultural areas have a system of pipes and drains below the soil to drain water away and can be a significant source of nitrate contamination. Redirecting these systems to use riparian buffers has increased nitrate removal. Similarly, storm surges can increase nitrate contamination as stormwater systems and roadside ditches bypass riparian removal zones (Hill 2019).

8.2 Vegetation

Vegetation can reduce the movement of contaminants in the environment by reducing erosion and minimizing movement in the vadose zone. Phyto-stabilization reduces contaminant mobility as the plant roots reduce erosion and hold contaminants that could have eroded and been washed into other areas or moved through the vadose layer to contaminate deeper soils (Sarkar et al. 2021).

8.3 Microorganisms

Anaerobic microorganisms in the soil can reduce the concentration of redox-sensitive pollutants. The organisms can be supported and made more effective by adding organic matter
with electron donors or acceptors (Sarkar et al. 2021). When the carbon content is higher than nitrate, microbes play a significant role in nitrate conversion. Autotrophic denitrifying bacteria can use sulfur and iron to convert nitrates into gaseous nitrogen when organic matter is unavailable. Finally, microbes can convert nitrates through dissimilatory nitrate reduction to ammonium (DNRA) (Hill 2019).

8.4 Biochar & Minerals

Biochar application to soil can reduce nitrate leaching through electrostatic bridge bonding between the two compounds. Biochar made from wood is more effective at reducing nitrate leaching than that made from straw. Its large surface area and high porosity reduce water infiltration and nitrate leaching (Bijay-Singh and Craswell 2021).

8.5 Liners

Liners are commonly used in manure storage lagoons to prevent nitrate leaching into groundwater. Concrete liners are preferred when the water table is high. Earthenware liners typically add clay additives to reduce infiltration (Sahoo et al. 2016).

8.6 Biogeochemical Barriers

Permeable reactive barriers are used to hold contaminants in the soil through chemical bonds and prevent leaching—this enhances soil capacity to reduce the mobility of contaminants (Sarkar et al. 2021).

8.7 Manure application control

Manure application in fields should be made based on assessments of the nitrogen loading and requirements for the area (Almasri 2007). Monitoring programs identify potential areas of nitrate contamination by identifying local land use, and new facilities can be chosen based on groundwater flow, drinking wells, soil properties, and storage needs (Sahoo et al. 2016).
8.8 Fertilizer application and water management

Nitrate pollution increases when excess nitrate fertilizer is used, as the excess gets stored as organic nitrogen in the soil or leaches into groundwater. The nitrate stores decreased when fertilizers with balanced quantities of Nitrogen, Phosphorus, and Potassium were used. A reduction in fertilizer application alone may not be enough, as an increase in precipitation can increase nitrate leaching, and fertilizer application should consider local precipitation and climate conditions. Quemada et al., (2013) ran a meta-analysis of 279 results; they found that water management strategies, including tailoring irrigation to the crop needs, the latest irrigation technologies, and mulched soil, can reduce nitrate-nitrogen leaching by up to 58%. Additionally, refined fertilizer strategies, including time-based fertilization and lower application rates, can reduce leaching by 39%. Implementing efficient agricultural and irrigation practices can lower nitrate contamination and protect environmental health (Gurdak et al. 2009). The amount of fertilizer or manure applied should be reduced when nitrate-contaminated water is used for irrigation (Castaldo et al. 2021).

8.9 Location of Agricultural Zones

Crop rotation and situating fertilizer-intensive crops in lowland areas can reduce nitrate contamination. When fertilizer-heavy crops are in upland areas, excess fertilizer can runoff into adjacent and lowland areas and contaminate a larger area. In contrast, in lowlands, the pollutants have a longer residence time and anoxic conditions, which increase nitrogen release to the atmosphere. Care should be taken to reduce water collection in topographical depressions, which can fasten contaminant travel to the water table. Finally, future land conversions to farmland should consider the composition of underlying sediments, and any area with ample natural nitrate deposits should not be converted (Gurdak et al. 2009). Educating farmers and community members on nitrate contamination hazards and best crop production practices will help reduce excess fertilizer application. (Bijay-Singh and Craswell 2021).
8.10 Well Management

Contamination of deep zones in aquifers increases as pumping activities increase the mixing of newer contaminated water with older water. Wells typically use screens to access water, which can mobilize water from a contaminated area to a less contaminated one as a path is created through the saturated zone of the aquifer. Screening of wells across confining layers and screens into contaminated zones should be avoided. These wells should be constructed to minimize the movement of contaminated water from above or below an aquifer into the aquifer (Gurdak et al. 2009).

8.11 Summary of Options

The above sections describe different options for reducing nitrate contamination in farming communities. Not all options are appropriate for agriculture or livestock yards. Table 2 summarizes which options can be used in the two land-use areas. The land use and management goals help identify appropriate measures for the location.
Table 2: Summary of available remediation options for livestock yards and agriculture.

<table>
<thead>
<tr>
<th>Remediation Options</th>
<th>Livestock</th>
<th>Agriculture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Riparian/Natural areas</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Vegetation</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Microorganisms</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Biochar &amp; Minerals</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Liners</td>
<td>✔</td>
<td>X</td>
</tr>
<tr>
<td>Biogeochemical barriers</td>
<td>✔</td>
<td>X</td>
</tr>
<tr>
<td>Optimize Manure Application</td>
<td>X</td>
<td>✔</td>
</tr>
<tr>
<td>Optimize Fertilizer Application</td>
<td>X</td>
<td>✔</td>
</tr>
<tr>
<td>Land Use Change</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Wells Management</td>
<td>✔</td>
<td>✔</td>
</tr>
</tbody>
</table>

9 Management Framework & Recommendations

There are multiple propositions for reducing nitrate contamination; the effectiveness of the approaches is hard to predict due to the dearth of assessment studies. Research and studies on long-term groundwater contaminant movement, mitigation, and monitoring are needed to understand underlying processes better to improve the measures. This work is urgent since the world is becoming more dependent on groundwater due to climate changes and extreme variations in precipitation events (Sarkar et al. 2021; Gurdak et al. 2009). Further contamination should be minimized as groundwater remediation is expensive, intensive, and impractical (Gurdak et al. 2009).

There is a time lag between groundwater contamination due to its slow movement in the unsaturated and saturated zones. It is essential to consider this pivotal point when creating management plans. It will take decades to see the effects of plans, and current contamination is a legacy of anthropogenic inputs from decades back (Bijay-Singh and Craswell 2021). An area should be assessed for point and non-point nitrogen sources, and all management plans should
consider local sources. Protective measures can be created based on the relative importance of each polluting source. Management plans or regulations to change land use or agricultural processes will need to balance environmental with economic needs and food security, and in some cases, economic needs override environmental needs (Almasri 2007; Bijay-Singh and Craswell 2021). Manure and fertilizer application should be specific to crop needs and conditions.

A management plan should gather all available data and categorize contamination sources before assessing remediation options. It should also include active monitoring and feedback loops as part of the plan to increase long-term resiliency and effectiveness. Figure 22 shows the preliminary steps to create a management plan—data collection, identification, and analysis of remediation options. Multiple remediation options may be implemented concurrently to address contamination. The final decision is made according to contaminant, available removal options, and efficacy. A good management plan should have periodic monitoring and tweaking of plans to maintain or improve effectiveness. Confidence in plans can be increased by using models to predict outcomes (Almasri 2007). The following sections will extend this framework to cropland and livestock yards.
Figure 22: Framework to create management plans to combat nitrate contamination. The first step is contamination analysis, followed by decision-making and implementation. Adapted from (Almasri 2007)

9.1 Cropland

Agricultural practices should be refined to reduce nitrate contamination of the environment. The world should move towards sustainable agricultural practices like no-till farming, interspersion of agriculture plots, and planting location-appropriate native plants and crops. Water-intensive crops should not be planted in areas with known water limitations, and agriculture needs should be balanced with environmental limits instead of putting unsustainable pressure on local water systems. Additionally, policies should encourage sustainable and regenerative agriculture and penalize releases of industrial contaminants (IPCC 2023).

The framework from Figure 23 can be used to identify if the location for a new facility is appropriate or if it can lead to significant nitrate contamination of underlying aquifers. A facility can contaminate downstream drinking water wells, so assessing impacts on local resources when picking a location is essential. After selecting a potential location, nitrogen sources and resources in the area should be identified, and the nitrate concentrations in surface and groundwater
should be monitored at multiple locations upstream and downstream of the facility. A concentration above 1mg/L N would indicate anthropogenic sources of contamination (Dubrovsky et al. 2010); any new facilities with current concentrations above 2mg/L should be dropped since the facility will raise the contamination even higher. Finally, the sediment should be assessed for whether it is well-draining and whether the aquifer is shallow, as this can determine contaminant movement and further contamination.
Is it upstream of drinking wells?

Identify nitrogen sources in area.

Is nitrogen loading above 2mg/L N?

Is sediment well-drained?

Is aquifer shallow?

High Nitrate Contamination Potential

Potential farming land

Yes

No

Yes

No

Yes

No

Yes

No

Figure 23: Framework to identify if a location is appropriate for cropland based on limiting potential aquifer nitrate contamination.
An existing facility should assess and improve its processes to minimize further contamination. Cropland fertilizer applications should be decreased according to crop and soil requirements. Rotation of crops, sustainable farming practices, and conversion of agricultural land to forests or industrial lands can reduce nitrogen loading in the area. Figure 24 shows the best practices to calculate existing nitrogen stores and reduce further contamination when adding fertilizer to crops. The best practices require the identification of local contamination, hydrogeology conditions, continuous reassessment, monitoring, and refinement of processes.

Management plans should contain timelines and intermediate checkpoints to assess efficiency, resiliency, and viability. These plans should contain targeted reductions in contamination and use model results to assess their effectiveness over the short and long term. Management options should be chosen based on the targeted outcome. For example, drinking water quality management can target polluting sources near targeted wells or manage all non-
point and point contamination sources. It is important to involve stakeholders to get their support and input on best practices for the area (Almasri 2007).

Manure can also be applied to cropland to provide organic nutrients to crops. The plants' required quantity is usually much less than the amount generated by livestock facilities. Care should be taken to apply the minimum amount crops need, as excess nitrates can contaminate underlying groundwater. Manure application should be restricted before, after, and during precipitation or flooding events, and application should be avoided in areas with draining soils to minimize nitrate leaching (Sahoo et al. 2016). This section describes the best practices to reduce nitrate contamination from cropland, and the next section will talk about similar practices for livestock facilities.

9.2 Livestock Facilities

Nitrate contamination by livestock facilities is from runoff and leaching from manure lagoons. The contamination from new facilities can be reduced by locating them downstream and a minimum distance of 30 – 90m from local wells. Manure in lagoons can leach into the ground, especially when there is permeable soil, a high-water table, or the bedrock is fractured. The lagoons should be built with concrete or contain liners to reduce leaching, and storage should be covered by compacted soil to reduce aerobic decomposition and promote denitrification.

A facility location should be determined based on herd size, distance from drinking water sources, soil, geology, groundwater flow, groundwater depth, underlying aquifer, bedrock, and waste type (Sahoo et al. 2016). Utah State University Water quality guidelines recommend locating livestock sites in areas with low permeability, such as deep clay soils; in contrast, sandy, gravelly soils with high infiltration are unsuitable as nitrates can leach into groundwater (Utah University Extension 2012). Dairy and ranches with large herds should consider reducing the number of animals or improving feeding and manure disposal strategies (Almasri 2007).
Any new or existing livestock yards should use vegetation buffers to reduce surface flows into the yard, which can pick up contaminants from the location, and roof gutter water should be released outside the yard. Leaching of nitrate from the facility can be reduced by paving the area with concrete to reduce infiltration. Old, abandoned facilities should be remediated by removing contamination sources and planting vegetation which require significant nitrogen inputs (Sahoo et al. 2016).

It is essential to include monitoring and data feedback loops to reassess progress or outcomes and change plans as additional data becomes available. An adaptive plan with active monitoring can provide early data, which is invaluable (Sahoo et al. 2016). It is vital to frequently sample at multiple locations, upstream and downstream of the facility, during different seasons and conditions. Sahoo et al., (2016) recommend that facilities have one upstream and two downstream monitoring points to assess and detect nitrate contamination. Upstream monitoring provides data on local nitrate contamination, and the downstream points provide data on nitrate contamination for the facility.

Most local guidelines recommend sampling of local wells twice a year, usually during spring and fall. The frequency is dependent on local conditions. Livestock yards should be located at least 100-200ft away from drinking water wells and 300-400ft from residential wells and downstream from wells to reduce contamination (Sahoo et al. 2016). The EPA recommends that wells be located 50ft or more away from livestock yards and 250ft or more away from manure stacks (USEPA 2002). It is important to follow local guidelines, which are more restrictive than these guidelines.

10 Conclusion

Nitrate contamination of groundwater is a critical environmental concern as the dependence on groundwater for drinking water increases worldwide. Consumption of contaminated water has many health impacts, such as blue-baby syndrome, cancer, thyroid problems, and high blood pressure (Sahoo et al. 2016; Abascal et al. 2022). The current increased concentrations are the
effect of historical processes, and there is a lag between surface contamination and groundwater contamination. The movement of contaminants from the surface to underlying aquifers depends on the depth of the aquifer. Shallow aquifers with young water – less than 50 years old have more significant nitrate contamination than deep aquifers, as nitrate movement is slow (Stanton and Fahlquist 2006).

The primary pollutant sources are fertilizer, manure industrial activities, septic systems, wastewater treatment effluent, atmospheric deposition, and natural nitrogen deposits. A natural background concentration of nitrate is found in groundwater in undisturbed landscapes. The concentration has increased, indicating anthropological origins for pollution. Farming areas have more significant nitrate contamination measured than urban or undisturbed areas. Contamination has increased worldwide since nitrogen fertilizers were introduced in the 1950s. Fertilizer/manure application rates have been much higher than crop requirements; the extra nitrogen compounds are stored in the soil and slowly move in the subsurface (Stanton and Fahlquist 2006).

Nitrate movement happens when subsurface water percolates during precipitation or irrigation events. As nitrates move further from the land surface, plant roots can no longer access them, and the probability of nitrate contamination increases. Nitrates can be converted to nitrogen and released through denitrification, which happens in anoxic conditions. Remediation of contaminated groundwater is cost-prohibitive, and it is more effective to reduce or slowdown further contamination (Burow et al. 2013). Aquifer recharge can decrease contaminant concentrations through dilution. The High Plains aquifer is largely non-renewable or recharges so slowly that drastic action is needed to address further contamination (Gurdak et al. 2009).

The best practices to further nitrate contamination are to get local hydrogeology, redox, climate conditions, identify the source of pollutants in the study area and, optimize agricultural fertilizer application and irrigation processes to fit local needs, improve livestock lots to reduce runoff and percolation of pollutants, use cover and winter crops and use best practices of well
construction. The effectiveness of these practices should be studied further to improve processes. An essential component in nitrate contamination is monitoring and modeling studies to understand subsurface movement better and create robust processes to reduce the impacts of existing nitrate stores. Even after implementing management plans, continuous monitoring and feedback loops are vital to assessing the effectiveness of measures and areas of improvement. The lack of consistent data and the complexity of modeling interactions between soil, climate, subsurface flows, and contaminant depletion in the areas makes it hard to create a management plan that would be optimal given the numerous interdependent factors (Burow et al. 2013).
11 References


widely underestimated because of fast flow into aquifers. Proceedings of the National Academy of Sciences 118:e2024492118.


