## Addressing Nitrate in California's Drinking Water

# TECHNICAL REPORT 5: Groundwater Remediation and Management for Nitrate

### With a Focus on Tulare Lake Basin and Salinas Valley Groundwater

Report for the State Water Resources Control Board Report to the Legislature



California Nitrate Project, Implementation of Senate Bill X2 1

Center for Watershed Sciences University of California, Davis http://groundwaternitrate.ucdavis.edu

Prepared for the California State Water Resources Control Board

## **Groundwater Remediation**

## **Technical Report 5**

Addressing Nitrate in California's Drinking Water

With a Focus on Tulare Lake Basin and Salinas Valley Groundwater

Report for the State Water Resources Control Board Report to the Legislature

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## Acronyms and Abbreviations

| AF    | Acre Feet   |
|-------|---|
| BD    | Biological Denitrification                        |
| CD    | Chemical Denitrification                          |
| HRT   | Hydraulic Retention Time/Hydraulic Residence Time |
| ISB   | In Situ Bioremediation                            |
| ISRM  | In Situ Redox Manipulation                        |
| MCL   | Maximum Contaminant Level                         |
| MGD   | Million Gallons per Day                           |
| PRB   | Permeable Reactive Barrier                        |
| SV    | Salinas Valley                                    |
| TLB   | Tulare Lake Basin                                 |
| WCBR  | Wood Chip Bioreactor                              |
| WCPRB | Wood Chip Permeable Reactive Barrier              |

### **Unit Conversions**

| Metric t  | o US   | US to                                  | Metric                          |  |
|---|--|--|---------------------------------|--|
| Mass  |  | Mass                                   |                                 |  |
| 1 gram (g)  | 0.04 ounces (oz)                               | 1 ounce                                | 28.35 grams                     |  |
| 1 kilogram (kg)   | 2.2 pounds (lb)                                | 1 pound                                | 0.45 kilograms                  |  |
| 1 megagram (Mg) (1 tonne)                                       | 1.1 short tons                                 | 1 short ton (2000 lb)                  | 0.91 megagrams                  |  |
| 1 gigagram (Gg) (1000 tonnes)                                   | 1102 short tons                                | 1000 short tons                        | 0.91 gigagrams                  |  |
| Distan  | се   | Dis                                    | tance                           |  |
| 1 centimeter (cm)   | 0.39 inches (in)                               | 1 inch                                 | 2.54 centimeters                |  |
| 1 meter (m)   | 3.3 feet (ft)                                  | 1 foot                                 | 0.30 meters                     |  |
| 1 meter (m)   | 1.09 yards (yd)                                | 1 yard                                 | 0.91 meters                     |  |
| 1 kilometer (km)  | 0.62 miles (mi)                                | 1 mile                                 | 1.61 kilometers                 |  |
| Arec  | 1  | Area                                   |                                 |  |
| 1 square meter (m <sup>2</sup> )                                | 10.8 square feet (ft <sup>2</sup> )            | 1 square foot                          | 0.093 square meters             |  |
| 1 square kilometer (km <sup>2</sup> )                           | 0.39 square miles (mi <sup>2</sup> )           | 1 square mile                          | 2.59 square kilometers          |  |
| 1 hectare (ha)  | 2.8 acres (ac)                                 | 1 acre                                 | 0.40 hectares                   |  |
| Volun   | ne   | Volume                                 |                                 |  |
| 1 liter (L)   | 0.26 gallons (gal)                             | 1 gallon                               | 3.79 liters                     |  |
| 1 cubic meter (m <sup>3</sup> ) (1000 L)                        | 35 cubic feet (ft <sup>3</sup> )               | 1 cubic foot                           | 0.03 cubic meters               |  |
| 1 cubic kilometer (km <sup>3</sup> )                            | 0.81 million acre-feet<br>(MAF, million ac-ft) | 1 million acre-feet                    | 1.23 cubic kilometers           |  |
| Farm Pro  | ducts  | Farm Products                          |                                 |  |
| 1 kilogram per hectare (kg/ha)                                  | 0.89 pounds per acre<br>(Ib/ac)                | 1 pound per acre                       | 1.12 kilograms per<br>hectare   |  |
| 1 tonne per hectare   | 0.45 short tons per acre                       | 1 short ton per acre                   | 2.24 tonnes per hectare         |  |
| Flow Rate   |  | Flow                                   | w Rate                          |  |
| 1 cubic meter per day<br>(m <sup>3</sup> /day)                  | 0.296 acre-feet per year<br>(ac-ft/yr)         | 1 acre-foot per year                   | 3.38 cubic meters per<br>day    |  |
| 1 million cubic meters per day<br>(million m <sup>3</sup> /day) | 264 mega gallons per day<br>(mgd)              | 1 mega gallon per day<br>(694 gal/min) | 0.0038 million cubic meters/day |  |

### Summary

This report explores methods and costs of remediation of groundwater nitrate contamination in the Tulare Lake Basin and Salinas Valley. Groundwater cleanup, or remediation, is one of the most difficult actions in the environmental sciences, even when done on the scale of a small contaminant plume (1000s of cubic meters). Remediation of entire groundwater basins has never been attempted at the scale and depths of the Salinas Valley and Tulare Lake Basin, on the order of billions of cubic meters. This analysis shows that direct remediation to remove nitrate from large groundwater basins is extremely costly and not technically feasible. In situ remediation, though technologically infeasible as a regional remedy, is appropriate in certain areas of shallow groundwater with high contaminant levels. Traditional pump and treat (ex situ) methods are too slow to produce results on the regional scale in an acceptable time frame, prohibitively expensive, and impractical to implement.

A novel form of pump-and-treat remediation is possible in the study area, but not yet widely practiced. By monitoring the nitrogen content of pumped irrigation water, and taking that ambient nutrient source into account when calculating additive fertilizer amounts, farmers can reduce the amount of nitrogen input to the aquifer. Such an approach is not unlike phytoremediation and is herein called "pump-andfertilize." Pump-and-fertilize is part of an effective nutrient management program. Due to the nature of irrigation with groundwater, it is as much a source reduction method as it is a form of groundwater remediation.

Hot spot and pump-and-fertilize remediation alone will not solve the problem of groundwater nitrate contamination. A new approach is needed that combines regional groundwater and nitrogen management strategies. This approach would include monitoring, source reduction, maximization of clean groundwater recharge across agricultural landscapes, pump-and-fertilize, and in situ treatment targeted at shallow, high-concentration plumes to place regional water quality on a trajectory toward improvement. Modeling and monitoring of regional groundwater quality are integral to an effective long-term management strategy.

### **1** Introduction

Groundwater remediation is the cleanup of contaminated groundwater to levels that are in compliance with regulatory limits. This involves either ex situ or in situ methods. In the ex situ approach, groundwater is extracted by wells, treated on the surface, and put back in the subsurface by injection wells, percolation basins, or similar means. This approach, referred to as pump-and-treat (PAT), uses water treatment technologies to remove or reduce contaminants in the pumped groundwater. The difficulty and cost associated with this approach largely stems from the often intractable problem of pumping not removing enough of the contamination from the aquifer in a reasonable time frame (e.g., less than a human lifetime). In situ remediation requires a detailed understanding of existing subsurface conditions in order for it to be effective. In the in situ approach, subsurface conditions are created that favor the degradation of the contaminants into less harmful products. The in situ approach is not appropriate for contaminants that are spread over large regions or are recalcitrant to degradation. Both ex situ and in situ methods are typically accompanied by removal or reduction of the sources of contamination.

Groundwater remediation is one of the most difficult tasks in environmental cleanup (NRC 1994; NRC 2000). Historically, groundwater remediation has only been done at the plume scale (<1 km<sup>2</sup>). Recalcitrant contaminants, such as nitrate, are difficult to remove, and can require decades of effort. Moreover, the success rate for cleanup of recalcitrant groundwater contaminants is poor (NRC 1994; NRC 2000). It is not unusual for plumes of recalcitrant contaminants to undergo remediation for several decades without reaching cleanup goals. Plume containment through flow barriers and/or manipulation of groundwater head gradients can be part of a remediation strategy, or it can be a goal in itself when remediation is deemed impossible.

The cost and difficulty of plume remediation rises dramatically with the age<sup>2</sup>, size, and depth of the plume. Older plumes typically have a substantial fraction of their mass residing in the portions of the groundwater system with lower hydraulic conductivity, such as silts and clays in aquifer systems like the Tulare Lake Basin and Salina Valley. Groundwater contamination that entered the subsurface over a time period of months to years will take much longer to flush from the system, on the order of decades to centuries or more, whether active or passive remediation approaches are used. Under such cases (more the norm than the exception), speeding up the cleanup would require increasing the rate of molecular diffusion, an impossibility in all but relatively small aquifer volumes where thermal energy remediation techniques could be applied.

Because of the difficulty and poor success rates of plume remediation, an approach known as monitored natural attenuation (MNA) has become popular in recent years. In MNA, the natural attenuation processes of biochemical transformation and dispersion reduce and dilute contaminant mass to below cleanup goals. Simultaneous monitoring confirms whether MNA is adequately protecting groundwater quality. This approach is only effective for contaminants that can transform to relatively harmless byproducts via biological or chemical transformation.

<sup>&</sup>lt;sup>2</sup> Plume age is defined as the period in which a plume has been migrating in the subsurface.

While it is possible for denitrification to fully degrade nitrate, the combination of circumstances that would favor denitrification is generally lacking in California's alluvial aquifer systems (Fogg et al. 1998). In natural aquifer systems, these circumstances include anaerobic conditions, a carbon source, and substantial microbial activity. Given the very low carbon content of most alluvial aquifer materials in California, and that microbial activity in soils is orders of magnitude greater than in the underlying alluvial deposits, the greatest potential for denitrification is in the biologically active soil zone, found in the upper 1-2 meters of the earth. Soils tend to be orders of magnitude more microbiologically active than the underlying, geologic parent material (Kazumi and Capone 1994). Because of California's semi-arid climate, however, the water table is typically at least 10 m deep, leaving the soil zone largely without the anaerobic conditions needed to drive denitrification. Well below the water table, where anaerobic conditions tend to occur, the natural geologic materials generally lack the carbon source and the microbial activity required for useful rates of denitrification. Given the ongoing spread of nitrate contamination in California's aquifer systems, it is reasonable and prudent to view most nitrate in California groundwater as recalcitrant to denitrification unless protected by thick overlying clay layers. Thus, MNA is unlikely to be a viable remediation strategy.

Favoring nitrate remediation, the regulatory limit is often only a factor of 2 to 10 times lower than the typical nitrate concentrations in contaminated groundwater in the current study areas (see Technical Report 4, Boyle et al. 2012, for discussion of current nitrate concentrations in wells in the study areas). However, this does not mitigate the problem of the scale of the contaminated basins. Plume-scale remediation may be worthwhile in certain parts of the basins, but, there are no examples of remediation of entire groundwater basins on the scale of the Tulare Lake Basin or Salinas Valley.

### 2 Groundwater Remediation Options

Remediation in the classical sense for the basin-scale groundwater nitrate contamination in the Tulare Lake Basin and Salinas Valley is not technically feasible in a reasonable period of time. Once aquifers are regionally contaminated, subsurface heterogeneity, together with the processes of groundwater flow and transport, combine to render the reversal of the contamination extraordinarily difficult. It is nevertheless useful to consider remediation options at multiple scales, to provide context and understanding of the processes involved for policy makers. For context, we examine a scenario in which the basin contamination problem is treated with the PAT method. Additionally at the basin scale, we suggest regional groundwater and nitrate management practices that can be used to improve groundwater quality over the long term. We emphasize that nitrate source reduction is key to any successful long-term solution to the nitrate problem in the study areas. As part of a regional strategy, we also examine the feasibility of removal of hot spots or highly concentrated sources of contamination, including options for local-scale (plume scale and somewhat larger) nitrate remediation.

Part of a regional groundwater and nitrate management strategy involves using existing wells and modified agricultural practices to simultaneously remove contaminated groundwater and reduce nitrate loading at the surface through the use of nitrogen uptake from irrigation water by crops, accompanied by optimized fertilizer application. We refer to this practical, basin-scale approach as pump-and-fertilize. This approach is further described in Section 2.4 of this report.

At the plume scale, several options for the remediation of nitrate impacted groundwater are available; guidance documents have been developed by various agencies to assist in the selection, design and management of remediation systems (see U.S. EPA 1990 and ITRC 2002). Plume-scale remediation options are discussed in Sections 2.1.1 and 2.3 of this report.

Unfortunately, the data needed to accurately estimate the basin-wide volume of groundwater requiring remediation by direct measurement do not exist. Most of the nitrate contamination is in the upper portions of the saturated groundwater systems where little well monitoring data exists, while most of the data on nitrate occurrence are from deeper portions of the groundwater systems where nitrate has either not yet arrived or is gradually increasing due to downward migration from above. We therefore estimated the volume of contaminated groundwater by calculating the fraction of the basin surface area in which well data indicated nitrate contamination and using this fraction to estimate that portion of the total groundwater volume that is contaminated.

#### Estimation of Volume for Basin-wide Remediation

The CASTING database (detailed in Technical Report 4, Boyle et al. 2012) was queried for wells with any nitrate data available between January 1, 2000 and December 31, 2009<sup>3</sup>. Thiessen polygons were created for each of these wells. A Thiessen polygon is defined by a point of interest, in this case, the

<sup>&</sup>lt;sup>3</sup> We note that, for this computation, an (earlier) version of the CASTING database was used that did not include the Central Valley Regional Water Board dairy wells.

well. All the area that lies closer to the particular well than to any other well comprises the Thiessen polygon for that well. The average nitrate concentration in each well during the period from 2000 to 2009 was assigned to each respective Thiessen polygon.

To simplify calculations, and because we were more concerned with the total volume than with the distribution of heterogeneity, we chose to ignore non-aquifer sediments (silts and clays) entirely, although these sediments may store considerable volumes of contaminated groundwater. Therefore, rather than assuming a total porosity to calculate the volume of water requiring remediation, an effective porosity of 0.1 was used.

The area overlying each groundwater basin, taken from Department of Water Resources (DWR) Bulletin 118 (2003), was intersected with the Thiessen polygons for the wells. The areal fractions of each basin contained in its intersected Thiessen polygons were calculated and then multiplied by the total volume of the basin (DWR 2003) to produce a volume underlying each Thiessen polygon. The nitrate concentration (average from the 2000's) from each well was assigned to its corresponding volume. The volumes that contained nitrate levels above ½ the Maximum Contaminant Level (MCL) [scenario 1] (>5 mg/L as N or 22.5 mg/L as nitrate) and above the MCL [scenario 2] (> 10 mg/L as N or 45 mg/L as nitrate), for each basin, are summarized in Table 1.

For scenario 1, using the fraction of wells exceeding ½ the MCL, the estimated volumes of groundwater to be remediated in the Tulare Lake Basin and Salinas Valley are 94.2 km<sup>3</sup> (76.4 million acre feet, AF) and 8.9 km<sup>3</sup> (7.2 million AF), respectively. For scenario 2, using the fraction of wells exceeding the MCL, the estimated volumes to be remediated in the Tulare Lake Basin and Salinas Valley are 39.7 km<sup>3</sup> (32.2 million AF) and 4.2 km<sup>3</sup> (3.4 million AF), respectively.

| Sub-Basin                     | Total Groundwater<br>Volume in Study Area<br>(Million AF) | me in Study Area > ½ MCL (Million AF) |              |
|-------------------------------|---|---------------------------------------|--------------|
| Tulare Lake Basin             |   |                                       |              |
| 5-22.06 – Madera              | 1.2   | 0.31[26%]                             | 0.12 [10%]   |
| 5-22.07 – Delta-Mendota       | 2.6   | 0.13 [5%]                             | 0.13 [5%]    |
| 5-22.08 – Kings               | 93  | 29.73 [32%]                           | 10.34 [11%]  |
| 5-22.09 – Westside            | 52  | 3.10 [6%]                             | 1.35 [3%]    |
| 5-22.10 – Pleasant Valley     | 4.0   | 2.52 [63%]                            | 0.90 [23%]   |
| 5-22.11 – Kaweah              | 34  | 13.98 [41%]                           | 7.39 [21%]   |
| 5-22.12 – Tulare Lake         | 37  | 11.77 [32%]                           | 3.77 [10%]   |
| 5-22.13 – Tule                | 33  | 6.65 [20%]                            | 3.48 [11%]   |
| 5-22.14 – Kern                | 40  | 8.16 [20%]                            | 4.71 [12%]   |
| TLB TOTAL                     | 297   | 76.4 [26%]                            | 32.2 [11%]   |
| Salinas Valley Basin          |   |                                       |              |
| 3-4.01 – 180/400 Foot Aquifer | 6.86  | 2.21 [32%]                            | 0.74 [11%]   |
| 3-4.02 – Eastside             | 2.56  | 1.56 [61%]                            | 1.00 [39%]   |
| 3-4.04 – Forebay              | 4.53  | 2.10 [46%]                            | 1.11 [25%]   |
| 3-4.05 – Upper Valley         | 2.46  | 0.99 [40%]                            | 0.45 [19%]   |
| 3-4.08 – Seaside              | 0.63  | 0.23 [36%]                            | 0.06 [10%]   |
| 3-4.09 – Langley              | 0.36 1  | 0.09 [24%]                            | 0.03 [9%]    |
| 3-4.10 – Corral de Tierra     | 0.49 2  | 0.07 [15%]                            | 0.002 [0.5%] |
| SV TOTAL                      | 17.9  | 7.2 [41%]                             | 3.4 [19%]    |
| STUDY AREA TOTAL              | 315   | 83.6 [27%]                            | 35.6 [11%]   |

Table 1. Total groundwater and remediation volume listed by subbasin (DWR 2003).

<sup>2</sup>From Montgomery Watson (1997), not listed in Bulletin 118.

The estimated volumes of groundwater requiring remediation are based on available nitrate data for wells across the study area. Note that the density of wells having nitrate data is not consistent across the study area. As a result of this heterogeneity, uncertainty in the model is variable and increases inversely with the density of wells in any given region. The se volumes are used to estimate rough costs for remediation options listed below.

#### Hypothetical Plume Size

Plume size, boundary, depth, and volume are site specific. For the purposes of this analysis a typical plume is defined as having a width of 500 m (1,640 ft), a depth from land surface to plume bottom of 75 m (246 ft), and a length of 2000 m (6,562 ft), spanning 100 ha (250 acres), with a total groundwater volume (porosity of 0.1) of 7.5 million cubic meters (6,080 AF). Typical plume characteristics are based on what would be expected for plumes beneath waste discharge areas, lagoons, and excess fertilizer or manure application to agricultural fields. A thorough analysis of site characteristics would be required for accurate plume delineation and cost estimates.

#### 2.1 Pump-and-Treat

Pump-and-treat, a type of ex situ remediation, refers to the extraction of contaminated water from the subsurface followed by treatment and subsequent discharge of treated water to groundwater (i.e., through reinjection or percolation) or surface water. Most commonly known for the remediation of organic chemicals at superfund sites, PAT has been implemented in a variety of applications to address both inorganic and organic constituents of concern. Currently, the application of PAT is shifting toward containment efforts rather than complete plume remediation, protecting public health and limiting the migration of contaminant through the capture and treatment of the leading edge of contaminant plumes (U.S. EPA 2005; U.S. EPA 2007a; U.S. EPA 2007b; Faris 2011). PAT is generally considered when contaminant plumes can be clearly defined; however, for the purpose of this investigation, the extreme example of basin-scale treatment will also be considered.

It is important to be mindful of the long-term nature of nitrate movement into and within the aquifer. Over many years, nitrate is in contact with the heterogeneous porous media of the subsurface, with several key processes affecting their fate and transport, including advection, dispersion, and diffusion. Complete removal of the contaminant is virtually never accomplished in one round of PAT. Water that is pumped from the subsurface comes generally from the highly conductive materials, while water within areas of low conductivity is removed much more slowly, if at all. The concentration of nitrate in the low-conductivity regions is not necessarily less than that in the high-concentration regions. Thus, reinjected, clean water will come into contact with untreated water and diffusion of nitrate from the latter to the former will prolong remediation efforts. These migration processes of diffusion and slow advection are much slower than the groundwater movement in the coarse-grained material of the system. PAT remediation is therefore a lengthy process, with diminishing returns, even for plume-scale contamination.

Options for the treatment of extracted water include existing wastewater or drinking water treatment facilities, newly constructed treatment facilities dedicated to groundwater remediation, constructed wetlands, and remediation basins (ITRC 2000; ITRC 2002). These treatment options can be applied for remediation in a PAT scenario.

Options for the fate of treated water include reinjection wells, percolation basins, infiltration galleries, and discharge to surface water or to storage. For the purposes of this exercise, it is assumed that treated water will be returned to groundwater due to the need to replenish the irrigation and drinking water supplies. Infiltration galleries are not appropriate for any but small-scale recharge projects.

Percolation requires land area for the percolation ponds and allows little control over groundwater recharge rate and depth. This option may be most suitable for recharge from remediation basins due to the low volume rate of output of remediation basin treatment, and the typical placement of remediation basins in areas where space is not a limiting factor. Infiltration basins are also beneficial in regions where protecting the shallow groundwater is the primary goal, as opposed to protecting the deeper water. Hydraulic head in the region below the percolation basin will be increased, causing groundwater flow away from the basin laterally.

Reinjection requires reinjection wells and provides control over the depth and location of recharge. The extraction and injection of water can be used to control hydrologic flow by controlling head gradients. In some situations, decreasing or reversing gradients can be used to contain contaminants by preventing migration beyond the bounds of current contamination. By increasing the local head gradient, flow rate can be increased, thus flushing targeted subsurface regions (Isherwood et al. 1992).

Monitoring will be required of both the effluent from the treatment system to ensure recharge of clean water, and of the groundwater to assess remediation progress. Optimization of the system is fundamental to cost effective long-term operation; extraction from some wells may not be necessary for the same duration as others (U.S. EPA 2005).

#### 2.1.1 Pump-and-Treat Using Drinking Water Treatment

Basin-scale application of PAT using drinking water and wastewater treatment technologies is presented as an extreme option with remediation of the entire aquifer. Local application of this remediation method to hot-spots/nitrate plumes is also considered.

#### Nitrate Treatment

Water treatment to address high nitrate levels consists of two major categories; reduction technologies and removal technologies. Reduction technologies include biological denitrification (BD) and chemical denitrification (CD), both of which transform nitrate through reduction to other nitrogen species, preferably to innocuous nitrogen gas. The removal technologies include anion exchange (IX), reverse osmosis (RO) and electrodialysis/electrodialysis reversal (ED/EDR), which remove nitrate and other constituents, to a concentrated waste stream requiring disposal. Disposal of this waste stream can be costly and disposal options are particularly limited for inland communities.<sup>4</sup> Wastewater treatment plants are generally designed for the removal of organic material but can also include biological nutrient removal (BNR) to remove nitrogen through nitrification and denitrification.<sup>5</sup> In the selection of the most appropriate treatment method, it is important that co-contaminants are taken into consideration.<sup>6</sup> Cocontaminants must also be considered when re-injecting the treated water. Discharge or injection permits often need to be obtained, and removal of other constituents may be required. Each of the above treatment technologies has the potential to remove other constituents of concern to varying degrees, in addition to nitrate. For example, biological treatment has been used for removal of both perchlorate and nitrate, while reverse osmosis can address many co-contaminants simultaneously including arsenic, salt, nitrate, and others.

Biological treatment was successfully deployed for treatment of nitrate contaminated groundwater in San Diego, CA, decreasing nitrate levels from ~18 mg/L to <4.5 mg/L as nitrate (4 mg/L to <1.0 mg/L as

<sup>&</sup>lt;sup>4</sup> See Technical Report 6, Section 3 (Jensen et al. 2012), for more information on these technologies in the context of drinking water treatment.

<sup>&</sup>lt;sup>5</sup> See Technical Report 3, Section 5 (Dzurella et al. 2012), for more information on wastewater treatment technologies for nutrient removal.

<sup>&</sup>lt;sup>6</sup> See Technical Report 6, Section 3 (Jensen et al. 2012) for additional information on the impact of water quality parameters on the selection of treatment.

nitrate) with discharge to a nearby creek (Envirogen 2010). In an assessment of exsitu remediation options for perchlorate, biological treatment was found to be the most commonly considered alternative, accounting for 69% of case studies reported (NASA 2006). Treatment for perchlorate and nitrate can be similar; both anion exchange and biological treatment are employed for the removal of these constituents. Capital and operations and maintenance costs of biological treatment have been described as being lower than costs for anion exchange, especially when the cost of waste brine disposal for anion exchange is considered (Harding ESE 2001 from NASA 2006). "In exsitu denitrification, the University of Colorado has shown that a complete denitrification system costs approximately \$60 per 3,780 L treated (Silverstein 1997)" (ITRC 2000, p. 40).

In Southern California, large desalters have been used to address salinity. Consisting predominantly of reverse osmosis treatment (sometimes supplemented with anion exchange treatment), these large treatment plants are also being used to reduce high nitrate levels. Chino Desalters I and II are drinking water treatment plants combining RO and IX technologies. Using the combined treatment technologies, nitrate levels are decreased from 70-300 mg/Las nitrate (16-68 mg/L as N) in the influent to 22-35 mg/L as nitrate (5-8 mg/L as N) in the effluent with influent TDS of 1100 mg/L (CDA 2010) (blending is also used, see Technical Report 6, Jensen et al. 2012, for more information).

For the purposes of this investigation, we assess only one round of extraction, treatment, and reinjection (per unit of water) to remove nitrate from the groundwater. Accordingly, these scenarios also assume no additional nitrogen inputs into the groundwater. However in practice, as discussed above, reinjected, clean water will come into contact with untreated water and mass transfer of nitrate from the latter to the former in the presence of subsurface heterogeneity will prolong remediation efforts.

Two treatment options will be considered: biological treatment and a combined treatment system using reverse osmosis and anion exchange (RO/IX). Biological denitrification was selected as an appropriate treatment option based on the prevalence of its use in remediation scenarios. Although biological denitrification is not commonly used in the U.S. for drinking water treatment, two full-scale biological denitrification plants are being implemented in California for drinking water treatment (Webster & Crowley 2010; Brown & Bernosky 2010).<sup>7</sup> In the context of PAT remediation, biological denitrification reduces nitrate to nitrogen gas rather than concentrating nitrate in a waste stream. The combined RO/IX treatment system, while capable of addressing many constituents of concern (including nitrate), produces brine that is costly to dispose of.

#### Basin-Scale Pump-and-Treat Remediation with Drinking Water Treatment

For the remediation of an entire basin, the portion of groundwater impacted by nitrate would need to be extracted, treated and recharged. From above (Table 1), for scenario 1, using the fraction of wells exceeding ½ the MCL, the corresponding total volumes to be remediated in the Tulare Lake Basin and Salinas Valley are 94.2 cubic kilometers (76.4 million AF) and 8.9 cubic kilometers (7.2 million AF),

<sup>&</sup>lt;sup>7</sup> See Technical Report 6 (Jensen et al. 2012) Section 3.4.5 for related case studies.

respectively. For scenario 2, using the fraction of wells exceeding the MCL, the corresponding total volumes to be remediated in the Tulare Lake Basin and Salinas Valley are 39.7 cubic kilometers (32.2 million AF) and 4.2 cubic kilometers (3.4 million AF), respectively. We do not consider this basin-scale PAT scenario to be either economical or feasible. This scenario is presented for context and to convey the scale of the problem.

For complete aquifer treatment, multiple large treatment plants would be required throughout the Tulare Lake Basin and Salinas Valley; the number, location, and distribution of plants would require an analysis of pipeline and pumping costs (for transport to and from the plant) relative to treatment plant costs. While it would be less costly to build and operate one very large treatment plant than multiple smaller plants, the cost of transporting water across the regions of interest would be insurmountable. In this simplified hypothetical example, the cost of treatment is assessed on the basis of a \$/1000 gallons cost for a large plant (10 million gallons per day (mgd)). Pipeline and pumping costs for transport of water from remote locations to a large centralized facility are not included and would increase the total cost.

Factors affecting treatment cost include facility capacity (how much water), source water quality (including nitrate concentration), environmental factors (temperature and pH), and target effluent nitrate concentration. In this analysis, the focus is the removal of nitrate. Costs of nutrient removal in wastewater treatment include numerous processes other than denitrification and are thus not directly applicable. Instead, treatment costs for biological denitrification are used as a proxy for simulation of denitrification in BNR. Treatment costs are based on direct contact with facilities<sup>8</sup> and include capital and O&M costs adjusted to 2010 dollars. Costs reported are for complete plant operation and would therefore include monitoring and pumping costs. Total capital costs were converted to annualized capital costs per 1000 gallons (\$/kgal) based on Eqn. 1.

An amortization value of 0.0802 was used which corresponds with an interest rate of 5% over 20 years (Eqn. 2).

Amortization Factor = 
$$(1+i)^N/((1+i)^N - 1)/i)$$
(Eqn. 2)Where i = interest rate and N = number of years

Annual O&M costs were calculated based on Eqn. 3 to convert total annual O&M costs to \$/kgal.

O&M Cost (\$/kgal) = [O&M Cost (\$)] / [Flow (MGD) \* 1000 kgal/mgal \* 365 days/year] (Eqn. 3)

<sup>&</sup>lt;sup>8</sup> Cost estimation is based on drinking water treatment costs reported by BIOLOGICAL DENITRIFICATION treatment systems and a combined RO/IX system (See Table 2).

Annualized Capital Cost (\$/kgal) and O&M Cost (\$/kgal) were summed to determine Total Annualized Cost (\$/kgal). The corresponding costs of treatment using a) biological denitrification, and b) reverse osmosis combined with anion exchange, are listed in Table 2. For reference, the costs of treatment using anion exchange alone are also provided. Listed biological treatment costs are based on a published cost analysis for a 10 MGD drinking water treatment plant (Meyer et al. 2010). Costs for the RO/IX combined scenario are based on reported costs of a drinking water treatment plant using reverse osmosis and ion exchange with a brine line for disposal (CDA 2010). Costs of ion exchange treatment alone are based on a published costs analysis for a 10 MGD drinking water treatment plant using evaporation ponds for brine waste management (Meyer et al. 2010).

|   | Capital Cost<br>(\$/kgal) | O&M Cost<br>(\$/kgal) | Total Annualized Cost<br>(\$/kgal) |  |
|---|---------------------------|-----------------------|------------------------------------|--|
| Biological Treatment <sup>1</sup>   | 0.43                      | 0.75                  | 1.18                               |  |
| Reverse Osmosis and Ion<br>Exchange <sup>2</sup>  | 0.83                      | 1.80                  | 2.63                               |  |
| Ion Exchange <sup>3</sup>   | 0.36                      | 0.87                  | 1.23                               |  |
| <sup>1</sup> 10 MGD system, Meyer et al. (2010). Other costs a vailable for smaller systems from Webster & Togna (2009), and<br>Carollo Engineers (2008).<br><sup>2</sup> CDA (2010).<br><sup>3</sup> 10 MGD system, Meyer et al. (2010). |                           |                       |                                    |  |

| Table | 2. | Drinking | water | treatment | cost | estimation. |
|-------|----|----------|-------|-----------|------|-------------|
| 10010 |    |          |       |           |      | countration |

Based only on treatment costs and the calculated volume to be treated, the total annualized cost of remediation in the Tulare Lake Basin and Salinas Valley is listed in Table 3. The total annualized cost of remediation across the entire study area would be \$32.1 billion [scenario 1] and \$13.7 billion [scenario 2] using biological treatment and \$71.6 billion [scenario 1] and \$30.5 billion [scenario 2] using a combined RO/IX system. The duration of remediation would depend on the number of facilities and their design capacity; however, costs listed above are based on a 20 year amortization. To remediate the entire basin under scenario 2 (nitrate above the MCL, the lesser total volume) in a 20 year time frame, using multiple 10 mgd treatment plants, more than 140 plants would be required in the TLB and more than 15 plants would be required in the SV. This does not account for the proximity to high nitrate areas or the distribution of treatment plants that would be required. For remediation of the estimated volume of groundwater exceeding ½ the MCL, additional plants would be required. The significantly lower costs of biological treatment in this remediation scenario illustrate the importance of accounting for disposal costs. The use of the removal technologies (RO/IX), especially on such a large scale, would not be possible without complete optimization of waste recycling or an inexpensive means of disposal. Such an operation would be more feasible with coastal access to the ocean for disposal of waste brine; water treatment facilities with high brine/concentrate waste volumes (e.g., desalters and desalination plants) are typically located near an ocean. As mentioned above, the costs of the RO/IX combined treatment scenario are based on a treatment plant with access to a brine line. In the context of drinking water treatment, the management of waste brine is discussed is greater detail in Technical Report 6, Section 6.4 (Jensen et al. 2012).

|       | Total Annualized Remediation Cost (2010 \$)                   |              |                     |                     |  |
|-------|---|--------------|---------------------|---------------------|--|
|       | Biological Denitrification Treatment Combined RO/IX Treatment |              |                     |                     |  |
|       | Scenario 1 Scenario 2   |              | Scenario 1          | Scenario 2          |  |
|       | (> ½ MCL) (> MCL)   |              | (>½ MCL)            | (> MCL)             |  |
| TLB   | 29.4 billion  | 12.4 billion | 65.5 billion        | 27.6 billion        |  |
| SV    | 2.8 billion   | 1.3 billion  | 6.2 billion         | 2.9 billion         |  |
| TOTAL | <i>32.1</i> billion   | 13.7 billion | <i>71.6</i> billion | <i>30.5</i> billion |  |

 Table 3. Estimated basin-wide pump-and-treat water treatment costs using drinking water treatment technologies.

We note that only a small portion of all groundwater in the two study areas is used for drinking water. The remaining remediated groundwater would be ultimately (re-) pumped and used for crop irrigation, a water use for which the nitrate regulation does not need to be met, and for which elevated nitrate levels can help meet crop nitrogen needs. Assuming that future nitrate loading to groundwater was to not exceed maximum allowable nitrate levels, this scenario would illustrate the cost of one-time complete aquifer remediation to address legacy contamination. However, as previously mentioned, significant low conductivity material present in the aquifers will provide diffuse sources of nitrate for decades, requiring more than one round of PAT remediation, thus, this estimate is likely to be a low estimate of cost and time requirements.

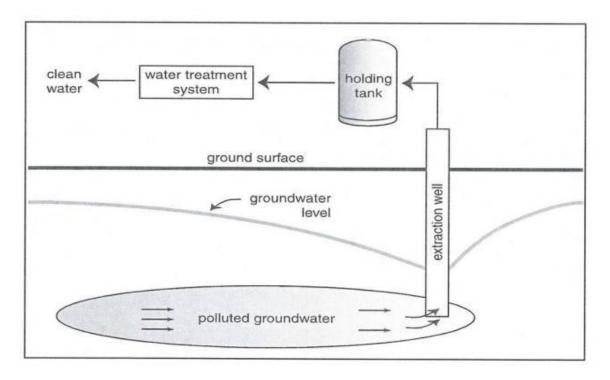
Basin-wide remediation, by whatever means, will be a long-term process. Short-term solutions would be needed to address nitrate levels in public and private drinking water supply wells during the period of time needed for complete aquifer remediation. These (short- and intermediate-term) costs would need to be added to the cost for remediation.<sup>9</sup> If additional treatment is required to avoid groundwater degradation due to constituents other than nitrate, costs would likewise increase. Measures to ensure a significant reduction of ongoing nitrogen loading to groundwater would also need to be implemented simultaneously, further adding to the cost of this scenario. Again, this scenario was presented for completeness only; we do not consider basin-wide pump-and-treat to be either economical or feasible.

#### Plume-Scale Pump-and-Treat Remediation with Drinking Water Treatment

PAT remediation at the local level can be implemented to address current and historical discharges of nitrogen that have created highly concentrated nitrate plumes (e.g., beneath an unlined waste discharge pond). Remediation of such known hot-spots in the vicinity of drinking water sources has the potential to avoid the need for drinking water treatment for nearby water systems and household wells. Through remediation of high-nitrate plumes, contamination can be mitigated before nitrate leaches deeper into the aquifer and disperses to impact a larger area. Remediation of a highly concentrated nitrate plume is more cost effective than remediation of a much larger volume of water with diluted contaminant levels, such as a basin-wide scenario as presented above. It is important to keep in mind that nitrate contamination is generally dispersed basin-wide and from numerous non-point and point sources. A

<sup>&</sup>lt;sup>9</sup> See the analysis of alternative water supplies in Technical Report 7 (Honeycutt et al. 2012).

plume-scale remediation scenario is only applicable to point-source pollution. PAT remediation of a contaminant plume is illustrated in Figure 1.



#### Figure 1. Pump-and-treat remediation - plume-scale application. (Source: U.S. EPA 2001b.)

Locations of hot spots and plume delineation would be required to locate the extent and boundary of the high-nitrate plume.<sup>10</sup> Optimization of placement of extraction and reinjection wells would be needed to ensure capture of the contaminant plume. For the purposes of this analysis, a typical plume is defined as discussed above in the Section *Hypothetical Plume Size*.

Drinking water treatment options and costs in this scenario are the same as those listed in Table 2 above (\$/kgal), which include pumping, but not new well construction. Two treatment types are considered here; however, the selection of the appropriate treatment technology will be dependent upon the nitrate concentration, the presence and concentration of co-contaminants (e.g., arsenic, salt, perchlorate, etc.), availability of affordable disposal options, and additional site-specific characteristics. As in the consideration of basin-wide remediation, costs are for a large treatment plant (10 mgd). If a smaller treatment plant were deemed more appropriate, total capital and O&M costs would decrease; however, the cost per 1000 gallons generally increases as plant size decreases. The need for additional extraction, monitoring and reinjection wells will increase total costs. Preliminary costs associated with plume delineation are also excluded.

The calculated total annualized costs of plume-scale remediation in this scenario are \$2.3 million and \$5.2 million, for biological treatment and combined RO/IX treatment, respectively. Using a 10 mgd

<sup>&</sup>lt;sup>10</sup> A nitrogen loading a nalysis of the study a reas, along with a cumulative nitrogen loading map is presented in Technical Report 2 (Viers et al. 2012).

plant, the entire plume volume would be remediated over a period of 6 months; however total annualized costs are based on a 20 year amortization. In the actual application of drinking water treatment technology for remediation of a plume of this size, a smaller plant would be more appropriate, having a capacity of about 0.3 mgd for remediation over 20 years. The priorities for a given site would determine whether the more appropriate option would be the use of a large plant for faster remediation or the use of a smaller plant for remediation over a longer period of time with lower upfront capital costs, but long-term O&M costs. To address multiple plumes across the study area, a plausible option would be the use of a portable treatment system that could be used to sequentially address multiple plumes over a long duration. The costs and sizing of such a system would require additional research.

It is somewhat counter-intuitive to treat extracted groundwater to drinking water standards and then return the clean water to the aquifer, rather than using treated water directly for potable water supply. This scenario was presented for completeness, with the intent of showing how treating highly contaminated nitrate plumes can avoid dispersion of nitrate to a wider impacted area.

#### 2.1.2 Pump-and-Treat Using Remediation Basins – Wood Chip Bioreactors (WCBRs)

Denitrification with solid carbon sources has been used in treatment of wastewater, groundwater, and agricultural runoff. The most common tested applications are denitrification walls for shallow groundwater, basins or beds for concentrated discharges, and horizontal layers for leachate. Typically, shredded or chipped wood is used as the carbon source. Wood chips provide biochemical oxygen demand that strips all available oxygen from the water, creating the habitat for denitrifying bacteria. These bacteria use the carbon of the wood chips as an electron donor in the process of biological denitrification.

Above-ground Wood Chip Bioreactors (WCBRs) for remediation of nitrate with wood chip biomass are simple to install and have been proven effective in agricultural runoff treatment (Blowes et al. 1994; Moorman et al. 2010; Schipper et al. 2010), and decentralized wastewater treatment (Leverenz et al. 2010). A typical installation consists of a basin 1 to 3 meters deep, lined with an impermeable layer that is filled with wood chips. Water to be treated is injected into one end of the basin through a manifold and removed from the basin at the other end.

Longevity of the treatment system becomes more important with increasing cost and difficulty of installation. Sub-surface (below-grade) installations are more difficult to maintain, while at-grade or above-grade containerized bioreactors can be maintained and monitored very easily, however, sub-surface systems allow use of the over-lying land. Moorman et al. (2010) found a half-life of 36.6 years for wood chips under anoxic conditions in a bioreactor treating agricultural drainage. When the wood chips were exposed to oxygenated water periodically, this dropped to 4.6 years. Robertson et al. (2000) concluded that wood chip bioreactors operated to maintain anoxic conditions could function without replacement of the chips for decades with a consumption rate of about 3% of original wood chips after 7 years of operation.

A variant of this technology also incorporates wetland plants such as the common cattail, *Typha latifolia* (Leverenz 2010). The plants themselves take up nitrate, increasing the efficiency of the system. The roots of the plants preferentially fill in voids in the wood chip media that could otherwise develop into preferential flow paths leading to short-circuiting of the bed. The plants are also visual indicators of the function of the WCBR. A well-functioning, planted WCBR should have healthy plants at the upstream end and unhealthy or no plants at the downstream end, where available nitrogen should be eliminated.

Two anoxic treatment wetland systems (WCBRs planted with wetland plants) have been installed at safety roadside rest areas by the California Department of Transportation to remove nitrogen from restroom wastewater (Leverenz 2011). The systems, which have been in operation for approximately six months, are located near Shandon, CA, and El Centro, CA, and treat approximately 15,140 and 37,850 liters per day (4,000 and 10,000 gal/d), respectively. Each system is composed of two horizontal plug flow reactors operated in parallel, with a total wood chip volume of 344 cubic meters (450 cubic yards) for each system. The hydraulic retention times/hydraulic residence times (HRT) for these systems are approximately 9 and 3.6 days, respectively. The influent nitrate concentrations for both systems range from 20 to 40 mg nitrate-N/L, while the effluent has no detectable nitrate.

A one year experiment conducted by Blowes et al. (1994) tested the performance of a pair of pilot-scale WCBRs in treating agricultural tile-drain runoff. These 200 liter (53 gallon), unplanted bioreactors treated up to 60 liters (16 gallons) per day from inflow concentrations up to 27 mg/L as nitrate (6 mg/L as N) to effluent concentrations below the detection limit (0.09 mg/L as nitrate, 0.02 mg/Las N).

Residence time is the key parameter for sizing bioreactors. Robertson and Cherry (1995) observed that groundwater flow rate was inversely related to the nitrate removal efficiency of sub-surface wood chip denitrification walls used for treatment of groundwater. This is due to the dependence of removal rates on hydraulic residence time in the reactor. Residence times in WCBRs vary with temperature, influent concentration and desired effluent concentration, but typical values range from 1.3 to 15 days (Blowes et al. 1994; Robertson et al. 2000; Greenan et al. 2009; Leverenz 2010; Schipper et al. 2010; Moorman et al. 2010).

The porosity of wood chips in a packed basin ranges from 0.3 to 0.5 (void volume over total volume) (Robertson et al. 2000; Hamel & Krumm 2008). Assuming the middle of that range, and a 10-day hydraulic residence time, a reactor designed to treat 38 liters (10 gallons) per minute (equivalent to 54,510 liters (14,400 gallons) per day) would require about 1,380 cubic meters (1,800 cubic yards) of wood chips.

Wood chip prices per cubic yard from commercial vendors are typically between \$7 and \$20, depending on location, season, and quality. Higher quality chips have less fines and inorganic material than low quality chips. Fines may reduce porosity in the wood chip bed, thus creating the potential for reduced flow through parts of the bed, and reduced denitrification efficiency. Inorganic materials such as sand, metal (from nails, etc.), or paint will have no significant effect on denitrification at typical levels found in low-quality chips, such as chips made from pallets or construction/demolition waste.

In a PAT scenario, at-grade<sup>11</sup> WCBRs could be used to enhance denitrification of pumped well water. The limiting factors on this treatment technology would be the cost and supply of wood chips, the depth of the groundwater level, and the cost of pumping. Additionally, water quality regulations present a possible complicating factor for use of the WCBR technology for PAT. WCBRs do not treat for all constituents, and thus the effluent may require further treatment prior to use as drinking water or reinjection to groundwater.

In the first several months of operation, WCBRs produce effluent with high dissolved organic carbon content. This problem is simple to mitigate through cascade aeration, but does add some cost as well as requiring space.

### 2.2 Phytoremediation of Nitrate in Groundwater

#### 2.2.1 Background

Phytoremediation is defined in the 1999 U.S. EPA Phytoremediation Resource guide as "the direct use of living plants for in situ remediation of contaminated soil, sludges, sediments, and ground water through contaminant removal, degradation, or containment" (U.S. EPA 1999, p. vii). Some phytoremediation schemes rely on the ability of plants to take up contaminants into their tissues, which are then harvested or otherwise removed, while others use the plants to produce a soil environment for microbial degradation of contaminants. Phytoremediation can be conducted with terrestrial or wetland plant species. Phytoremediation is most useful as a method of interception of contaminants on their path to the aquifer, though treatment of aquifer contaminants in situ is possible for shallow aquifers under certain circumstances.

Terrestrial plant phytoremediation can be used to intercept nitrate from septic leach fields and other shallow subsurface applications, such as land application of pumped groundwater (a pump and treat alternative) or wastewater from municipal or industrial sources. Contaminated runofffrom flood or furrow irrigated agricultural fields could also be treated via phytoremediation. The pump and fertilize concept described in Section 2.4 of this report is essentially a phytoremediation option, whereby the constituent nitrogen in pumped groundwater for irrigation is accounted for in the calculation of fertilizer input rates. Within the study area, another example of the use terrestrial plants to reduce groundwater nitrogen loading is the land application of effluent and solid wastes from food processing and wastewater treatment facilities.<sup>12</sup>

Application of phytoremediation with terrestrial plants is limited to the vadose zone and the top surface of the saturated zone. Roots of these plants do not grow deeply into the saturated zone even when that is very shallow.

<sup>&</sup>lt;sup>11</sup> The top of the basin is level with the surrounding land surface.

<sup>&</sup>lt;sup>12</sup> See Technical Report 2, Section 6.2 (Viers et al. 2012) and Technical Report 3, Section 5.2 (Dzurella et al. 2012) for a dditional information.

Dense plantings with large evapotranspiration rates can create a zone of depression in a shallow water table, causing flow towards the phytoremediation site, enabling the remediation of saturated-zone groundwater; however, this in situ application is unlikely to be feasible in most of the study area, due to lack of sufficiently shallow groundwater. Again, in general, nitrate phytoremediation projects have been more successful when implemented as part of a long-term strategy to control nitrogen flux to groundwater rather than as treatment for contaminated groundwater. Targeted applications, designed to treat contaminated flows at their source, have been tested and found effective (Schnoor 1995; U.S. EPA 1999; Perry 2009), and could be implemented in the study areas.

Typical terrestrial plants used for nitrate phytoremediation include phreatophyte trees (e.g., poplar, willow, cottonwood, aspen), grasses (e.g., rye, bermuda, sorghum, fescue), and legumes (e.g., clover, alfalfa, cowpeas) (Schnoor 1997). Phreatophyte trees transpire much more water than typical agricultural crops (Blaney 1958). Root depths of the listed tree species are essentially never over 3 – 4 meters (9.8 – 13.1 feet), and can be much shallower depending on soil conditions (Crow 2005). The mature root systems of rye and sorghum can extend to around 1.4 meters (4.6 feet) in ideal conditions, while alfalfa and clover taproots can extend to over 3 meters (9.8 feet), but are rarely over 4 meters (13.1 feet) (Weaver 1926). These rooting depths are sufficient for the uptake of nutrients (and other contaminants) in leachate of septic systems (typical leach field depths range from 1 to 2 meters (3.3 to 6.6 feet) below ground surface).

#### 2.2.2 Phytoremediation of Nitrate

McKeon et al (1996), in an investigation of phytoremediation with 2 phreatophyte species, estimated 4.1 metric tonnes (4.5 short-tons) per year of nitrate removal on the 24 hectare (59.3 acres) site, assuming no grazing and non-manipulated canopy coverage rate (25% coverage was assumed). Maximum nitrate concentration in the plume was 1,200 milligrams per liter. Plume volume at time of the study was  $2 \times 10^6$  m<sup>3</sup> (1,620 acre feet). They further estimated that pumping the groundwater to irrigate the trees would result in full remediation to acceptable levels (44 mg/L) of the entire plume in 20 years. This form of phytoremediation was entirely based in the accumulation and assimilation of nitrate in and by the plants.

Phytoremediation of contaminated flows in constructed wetlands is mediated primarily through enhanced denitrification, although accumulation and assimilation also occur. In a review of this technology, Horne (2000) found removal rates of established stands of wetland plants from 540 to 1220 mg/L per m<sup>2</sup> per day. This type of remediation requires that the water to be treated is either pumped from the aquifer, or intercepted before entering the aquifer.

#### 2.2.3 Required Acreage for Complete Treatment

Complete phytoremediation requires transpiration of 100% of the flow to be treated, thereby removing all of the contaminant of interest. As an example of a small-scale phytoremediation application, we assume phreatophyte trees are used to treat the leachate from a septic system on a 4-person household. Phreatophyte trees typically transpire around 3000 liters (793 gallons) of water per tree per

year, and typical phytoremediation plantings are at a density of 3700 trees per hectare (1500 per acre) (Schnoor 1997). Assuming a typical flow rate of 800 liters (211 gallons) per day for a household of 4 persons (Tchobanoglous et al. 2003), a septic system phytoremediation site would need an area of roughly 16 by 16 meters (52 feet by 52 feet) of trees to transpire all of the wastewater flow from the septic system. This simple exercise ignores the problems inherent in planting trees over a leachfield, such as root growth into the leach field apparatus. Though the details of such an application would need to be dealt with, it is conceivable that phytoremediation of septic leachate could be used in rural residential areas where parcel sizes are large enough to accommodate plantings of this size, but small enough (high septic system density) that septic systems contribute a substantial amount of nitrogen to groundwater.

At a larger scale, the outflow of a wastewater treatment plant such as the Visalia municipal plant, with a flow of 12.25 MGD, would require about 3800 acres of trees for complete transpiration, or 150 ha (307 acres) of trees per MGD. The Visalia plant currently applies 7.1 MGD of its effluent to 910 ha (2250 acres) of silage and cotton crops, with the balance of the effluent wasted to a 97 ha (240 acre) percolation basin. At the 150 ha (307 acres) per MGD rate, 882 ha (2180 acres) of trees would be required for complete transpiration of 7.1 MGD. Table 4 summarizes the agricultural lands applied effluent flows in comparison to the acreage required for complete transpiration based on the 150 ha (307 acres) per MGD estimate.

#### 2.2.4 Phytoremediation Conclusions

Phytoremediation is most useful for interception of contaminated flows rather than as an insitu treatment, except in areas of very shallow groundwater. Sufficient plantings for complete phytoremediation of nitrate require substantial areas (150 ha (307 acres) per million gallons per day with phreatophyte trees). Currently, many wastewater treatment facilities in the study areas apply effluent to adequate acreage; however, this can be misleading, as the rate of transpiration of agricultural crops is much lower than that of the optimal plant species.

Table 4. Acreages of land used for application of effluent from wastewater treatment facilities in the study areas, compared to estimates of the acreage needed for complete transpiration using phreatophyte trees.

| Facility Name                         | Reported<br>Ag-applied<br>Flow<br>(MGD) | Reported<br>Ag Acreage | Est. Acreage<br>for Complete<br>Transpiration | Reported<br>as Pct of<br>Estimate |
|---------------------------------------|---|------------------------|---|-----------------------------------|
| WOODLAKE WWTF                         | 0.46                                    | 35                     | 141   | 25%                               |
| MCFARLAND WWTF                        | 0.55                                    | 75                     | 169   | 44%                               |
| KING CITY DOMESTIC WWTF               | 0.435                                   | 65                     | 134   | 49%                               |
| TAFT WWTF                             | 1.2                                     | 185                    | 368   | 50%                               |
| PORTERVILLE WWTF                      | 3.7                                     | 620                    | 1136  | 55%                               |
| CUTLER-OROSI WWTF                     | 0.6                                     | 106                    | 184   | 58%                               |
| TULARE WWTF                           | 10.8                                    | 2000                   | 3316  | 60%                               |
| DELANO WWTF                           | 4.28                                    | 1145                   | 1314  | 87%                               |
| KERN SANITATION AUTHORITY WWTF        | 3.9                                     | 1100                   | 1197  | 92%                               |
| NORTH OF RIVER WWTF                   | 5.5                                     | 1740                   | 1689  | 103%                              |
| VISALIA WWTF                          | 7.105                                   | 2250                   | 2181  | 103%                              |
| BAKERSFIELD WWTP #3                   | 9.76                                    | 3148                   | 2996  | 105%                              |
| LEMOORE NAS WWTF (naval services)     | 0.95                                    | 306                    | 292   | 105%                              |
| FRESNO CO #41-SHAVER LAKE WWTF        | 0.5                                     | 161                    | 154   | 105%                              |
| GONZALES WW                           | 0.265                                   | 85                     | 81  | 105%                              |
| LINDSAY WWTF                          | 0.65                                    | 210                    | 200   | 105%                              |
| MILLERTON NEW TOWN WWTF AND RECYCLING | 0.355                                   | 114                    | 109   | 105%                              |
| FRESNO REGIONAL WWTF                  | 9.78                                    | 3670                   | 3002  | 122%                              |
| BAKERSFIELD WWTP #2                   | 13.7                                    | 5476                   | 4206  | 130%                              |
| WASCO WWTF                            | 0.9                                     | 390                    | 276   | 141%                              |
| LAMONT WWTF                           | 2                                       | 1150                   | 614   | 187%                              |
| SANGER INDUSTRIAL WWTF                | 0.25                                    | 188                    | 77  | 245%                              |
| MRWPCA REG TRTMT & OUTFALL SYS        | 14                                      | 12000                  | 4298  | 279%                              |
| HANFORD WWTF                          | 2.45                                    | 4000                   | 752   | 532%                              |
| ARVIN WWTF                            | 1.1                                     | 6000                   | 338   | 1777%                             |
| LEMOORE WWTF                          | 2                                       | 13333                  | 614   | 2171%                             |

#### 2.3 In Situ Denitrification

As an alternative to groundwater extraction and treatment, under appropriate conditions, nitrate impacted groundwater can be addressed in situ. In situ methods can be less costly than ex situ options and have the ability to directly target the groundwater contaminant plume while taking advantage of naturally occurring processes of denitrification. Two major categories of in situ denitrification are considered: Enhanced In Situ Biological Denitrification (EISBD)/In Situ Redox Manipulation (ISRM) and Permeable Reactive Barriers (PRBs).

The In Situ Bioremediation (ISB) Team of the Interstate Technology and Regulatory Council (ITRC) developed a detailed reference document as a guide for in situ remediation options (ITRC 2002). The ITRC (2000, 2002) specifically addresses options for the remediation of nitrate impacted groundwater and states, "All indications point to enhanced in situ biodenitrification as a reasonable remediation alternative for nitrate (NO<sub>3</sub>) contaminated groundwater" (ITRC 2002, p. iv). See Figure A-1 of the Appendix for a detailed decision-tree on the application of ISB for nitrate. Extensive information is also available in the literature on the use of PRBs for the remediation of various groundwater constituents (U.S. EPA 1998; ITRC 1999; U.S. EPA 2002; FRTR 2002).

Important considerations in the application of in situ denitrification are the mobility and mixing capability of water and contaminants in the subsurface, redox conditions, and the maximum depth of the contaminant plume. The key to successful in situ remediation is the exposure of the contaminant plume to the treatment zone; both ISB and PRBs can operate as a barrier through which contaminant migration is blocked as nitrate is destroyed within the plume. When injecting a carbon substrate, the substrate must be available across the plume, for remediation to occur. Unfortunately, subsurface heterogeneity of material properties, such as permeability, render any such injection procedure very inefficient because most of the injectate flows preferentially in relatively localized volumes of the subsurface, thereby bypassing most of the contaminant volume. PRBs have the advantage that the contaminated groundwater moves passively through the PRB for nitrate to be removed. If the PRB can be sufficiently deep and laterallyextensive, cleanup can be very effective for the region down gradient of the PRB.

In situ remediation options rely on denitrification in the subsurface to reduce nitrate to other nitrogen species; denitrification requires an electron donor for the reaction to proceed. Nitrate can be reduced through biological denitrification or chemical denitrification. Generally in situ denitrification through the injection of a carbon source (EISBD and ISRM) reduces nitrate through biological denitrification, while PRBs can operate through biological and/or chemical denitrification, depending on the design of the system. PRB remediation and ISB can be combined and sometimes the barrier configuration of ISB is referred to as a PRB. These remediation options are examined separately below in greater detail.

#### **Biological Denitrification**

Denitrification occurs naturally in the environment as part of nitrogen cycling, but can be promoted in the subsurface by providing appropriate conditions. Control and monitoring of water quality characteristics, including temperature, pH, salinity, and oxidation reduction potential (ORP), can be fundamental to the stability and efficiency of biological denitrification processes (WA DOH 2005). For biological denitrification, near neutral pH is preferred (7-8) and temperatures below 5°C (41°F) can inhibit denitrification (WA DOH 2005). Biological denitrification uses denitrifying bacteria to reduce nitrate to innocuous nitrogen gas in the absence of oxygen (anoxic conditions). The reduction of nitrate proceeds stepwise in accordance with Eqn. 4.

$$NO_3^{-} \rightarrow NO_2^{-} \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
 (Eqn. 4)

Denitrifying bacteria require an electron donor (substrate) for the reduction of nitrate to nitrogen gas. Autotrophic bacteria utilize sulfur or hydrogen as an electron donor and inorganic carbon (typically carbon dioxide) as a carbon source for cell growth (Eqns. 5 and 6), while heterotrophic bacteria consume an organic carbon substrate, like methanol, ethanol or acetate (Eqn. 7) (Mateju et al. 1992; Kapoor & Viraraghavan 1997).

 $11S^{0}+0.5CO_{2}+10NO_{3}^{-}+2.54H_{2}O+1.71NH_{4}^{+} \rightarrow 0.92C_{5}H_{7}O_{2}N+11SO_{4}^{-2}+5.4N_{2}+9.62H^{+}$ (Eqn. 5) H<sub>2</sub> + 0.35 NO<sub>3</sub>^{-} + 0.35 H^{+} + 0.052 CO\_{2} \rightarrow 0.010 C\_{5}H\_{7}O\_{2}N + 0.17 N\_{2} + 1.1 H\_{2}O(Eqn. 6)

 $1.08 \text{ CH}_{3}\text{OH} + \text{NO}_{3}^{-} + \text{H}^{+} \rightarrow 0.065 \text{ C}_{5}\text{H}_{7}\text{O}_{2}\text{N} + 0.467 \text{ N}_{2} + 0.76 \text{ CO}_{2} + 2.44 \text{ H}_{2}\text{O}$ (Eqn. 7)

Eqns. 5 through 7 illustrate the overall denitrification reaction defining the stoichiometric relationship between electron donor, carbon source and nitrate in the production of cells and the conversion of nitrate to nitrogen gas. Not all nitrogen is converted to nitrogen gas. Some nitrogen is required for cell growth. The governing stoichiometric equation indicates the necessary dose and varies with the substrate used. For example, the stoichiometric factor for acetic acid is 0.82 moles of acetic acid per mole of nitrate (Dördelmann et al. 2006).

Various species of bacteria are responsible for denitrification, including *Thiobacillis denitrificans, Micrococcus denitrificans, Pseudomonas maltophilia* and *Pseudomonas putrefaciens* (Kapoor & Viraraghavan 1997). Denitrifiers are naturally present in the subsurface and bioaugmentation is not typically required (i.e., denitrifiers generally do not need to be added). Due to slower bacterial growth rates, autotrophic denitrification offers the advantage of minimizing biomass accumulation; however, autotrophic denitrification requires alkalinity to supply the inorganic carbon source for cell growth (Della Rocca et al. 2006).

#### **Chemical Denitrification**

The general mechanism of chemical denitrification involves the transfer of electrons from an electron donating metal to nitrate. As in biological denitrification, nitrate is reduced in accordance with Eqn. 4. However, in contrast with biological denitrification, chemical denitrification often reduces the nitrogen in nitrate to the least oxidized form, ammonium (Eqn. 4a) (Huang et al. 1998; Hao et al. 2005).

| $NO_3^{-} \rightarrow NO_2^{-} \rightarrow NO \rightarrow N_2O \rightarrow N_2$ | (Eqn. 4)  |
|---|-----------|
| $NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$                                  | (Eqn. 4a) |

Nitrate is exposed to an electron donating metal by passing the treatment stream through granular media. Particle size, surface area and surface chemistry are important media characteristics related to the efficiency of nitrate removal.

Due to the extensive research focused on the use of zero valent iron (ZVI) in chemical denitrification, ZVI will serve as a preliminary example. There is some variation in the use of ZVI. Forms of application include powdered iron, stabilized iron as nanoparticles, and iron filings. Relevant reactions are listed in Eqns. 8 through 13 (Huang et al. 1998; Hao et al. 2005; Xiong et al. 2009). Nitrate can be reduced to

nitrite (Eqn. 9), ammonia (Eqn. 10) or nitrogen gas (Eqn. 13) by ZVI. Following nitrate reduction to nitrite, nitrite can then be reduced to ammonia (Eqn. 12). Nitrate can also be reduced by the hydrogen gas that is produced from corrosion reactions (Eqn. 8) to ammonia (Eqn. 11).

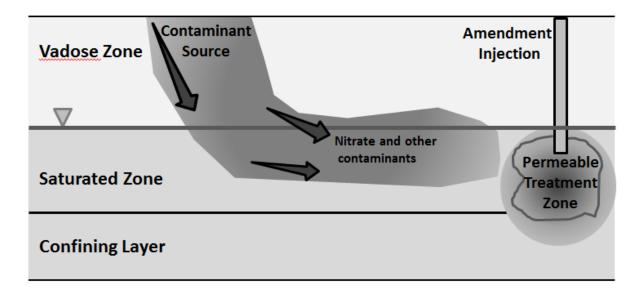
| $Fe^{\circ} + 2H^{+} \rightarrow H_{2(g)} + Fe^{2+}$                             | (Eqn. 8)  |
|--|-----------|
| $Fe^{\circ} + NO_3^{-} + 2H^+ \rightarrow Fe^{2+} + NO_2^{-} + H_2O$             | (Eqn. 9)  |
| $4Fe^{\circ} + NO_{3}^{-} + 10H^{+} \rightarrow NH_{4}^{+} + 4Fe^{2+} + 3H_{2}O$ | (Eqn. 10) |
| $NO_3^+ + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O$                                | (Eqn. 11) |
| $3Fe^{\circ} + NO_2^{-} + 8H^+ \rightarrow 3Fe^{2+} + NH_4^+ + 2H_2O$            | (Eqn. 12) |
| $5Fe^{\circ} + 2NO_{3}^{-} + 6H_{2}O \rightarrow N_{2(g)} + 5Fe^{2+} + 12OH^{-}$ | (Eqn. 13) |

The reduction of nitrate by iron is characterized by an increase in pH and consumption of hydrogen ions. pH is a significant controlling factor for this treatment method (Hao et al. 2005). The kinetics of nitrate reduction by ZVI have been thoroughly covered in the literature to determine the reaction rate under various conditions. For example, Alowitz & Scherer (2002) examined the nitrate reduction rates of three types of iron; findings indicate that reduction rate increases with decreasing pH.

# 2.3.1 In Situ Bioremediation/In Situ Redox Manipulation (With Injection of Carbon Source) – Local

In situ bioremediation (ISB) "requires simultaneous evaluation of subsurface hydrogeology, contaminant interactions, and biology/biochemistry. It necessitates the ability to scientifically understand, predict, and monitor the collocation of contaminants, substrates, nutrients, and microbial processes in situ to achieve bioremediation. It is a system designed to establish optimized subsurface conditions, utilizing injected substrates and nutrients to enhance natural biodegradation, the ultimate result of which is accelerated destruction of the target contaminant..." (ITRC 2002, p. 7).

In situ bioremediation/redox manipulation (ISRM) is accomplished by injecting an electron donor into the groundwater plume such that bacteria can utilize the electron donor in the denitrification process, reducing nitrate to nitrogen gas (Figure 2). The addition of injectate enables denitrification to occur much faster than it would naturally (i.e., natural attenuation) (ITRC 2000). ISB requires plume delineation, monitoring wells, and injection wells. "This technology has the potential of remediating sizeable nitrate plumes in groundwater systems" (ITRC 2000, p. iii). Nevertheless, as mentioned above, experience shows that geologic heterogeneity typically results in very poor contact between any injectate and the groundwater contamination due to preferential flow and bypass. Additional information specific to the application of ISRM is available in the literature (see DOE 2000).



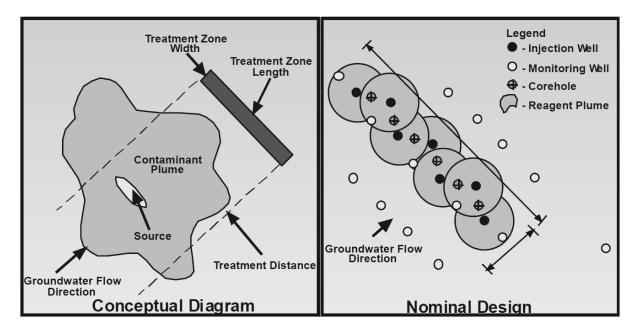
#### Figure 2. Hypothetical in situ bioremediation scenario. (Source: adapted from DOE 2000.)

For successful implementation and operation of an ISB system, a thorough characterization of the site and ISB system is essential, including the following (ITRC 2002; See also Figure A-1 of the Appendix):

- site history
- hydrologic parameters
- contaminant definition
- geochemical parameters
- potential risks
- analysis of contaminant transformations
- plume delineation and source control
- analysis of subsurface interactions (e.g., ORP, O<sub>2</sub>, appropriate carbon source, limiting nutrients)
- regulatory and permitting requirements
- pilot testing
- monitoring

According to the ITRC, advantages of ISB include low-cost, rapid remediation, and the potential for "complete plume remediation," while disadvantages of this remediation option include "impact to geochemistry, regulatory concerns, and biomass buildup" (ITRC 2000, p. 15). While biomass management is fundamental, in part, to avoid uneven distribution of injectate, a problematic concern is the buildup of biomass and the potential for well and aquifer clogging, which can be detrimental to the remediation system. Management of biomass can be accomplished through selection of the optimal carbon source and through various operational practices. Acetate has been shown to limit biomass buildup, pulsed injection can minimize both biomass buildup and oxidizers, while acids and biocides have been utilized to control biofouling (ITRC 2002). Variability in the hydraulic conductivity across the plume can also reduce the efficiency of an ISB project; low conductivity areas will have limited to no contact with the injectate, leaving the nitrate in these regions untreated.

ISB can be implemented in a number of configurations to remediate and contain nitrate contamination including general well placement designed for maximal plume remediation, a downstream barrier configuration (Figure 3), a daisy well configuration (Kahn & Spalding 2003), and in parallel with PRBs (discussed separately). Using injection wells, the remediation depth is limited primarily by the permeability of the subsurface and the depth of injection wells. The electron donor (carbon source) can be delivered through reinjection by mixing extracted nitrate contaminated water or by alternating injections of amendment and nitrate laden water (pulsed injections); the latter limits the risk of biomass accumulation in the vicinity of the injection well.





#### Application of In Situ Bioremediation to Address Nitrate Impacted Groundwater

#### Case Study: Nebraska (Khan & Spalding, ITRC)

In Nebraska, research by the University of Nebraska-Lincoln (UNL) used a daisy well configuration to promote biological denitrification of groundwater surrounding an inactive municipal well, with acetate as the substrate (Khan & Spalding 2004). Reduction wells (15 cm diameter) were placed 18 m from the centrally located municipal well, in a circular configuration. Oxidation wells (5 cm diameter) were placed similarly, but at a distance of 9 m from the central municipal well. Oxidation wells were included for the injection of an oxidizer to decrease residual carbon and oxidize any nitrite to nitrate. Site characteristics include a shallow, unconfined aquifer of 22 m thickness. The heterogeneous aquifer is composed of predominantly sand and gravel. Modeling software (Modflow and Modpath) facilitated system design. The extraction flow rate of the system was 12.6 L/s (~0.3 mgd or ~200 gpm) resulting in an appropriate residence time of the carbon source for denitrification to occur (~ two days). The maximum screened depth of the wells was ~25 m.

The acetate dosage (pulse length) was varied and alternated with injection of extracted nitrate contaminated water. No clogging problems were detected over a three month period. Nitrate levels decreased by ~45%, from an initial nitrate concentration of 55.7 mg/L as nitrate (12.6 mg/L as N) to a final nitrate concentration of 29.3 mg/L as nitrate (6.6 mg/Las N). While water quality improved to meet regulations with respect to nitrate, "the total plate count [for coliform] exceeded the maximum permissible limit (500 cfu/mL)" (Khan & Spalding 2004, p. 3382). For long-term operation, the injection line, accessories, and injection wells should be cleaned regularly (with a hydrogen peroxide solution). Hydrogen peroxide can also be injected in the oxidizing wells to decrease dissolved organic carbon (DOC) levels in extracted water; however, this was unnecessary as extracted DOC levels in this project were close to background levels.

Reported costs associated with the remediation system are (Khan & Spalding 2004):

- Capital and Installation \$75,000 (2004 dollars)
- Chemicals

•

| 0   | Acetate  | \$0.05/1000 L (0.19/1000 gal) |
|-----|----------|-------------------------------|
| 0   | Cleaning | \$0.06/1000 L (0.23/1000 gal) |
| 0&M |          | \$0.16/1000 L (0.61/1000 gal) |

Other UNL remediation projects include similar systems that are successfully addressing nitrate concentrations as high as 177 mg/Las nitrate (40 mg/Las N) (ITRC 2000). The daisy well configuration surrounding a municipal well is a specific scenario that would likely be operated continuously for the protection of a drinking water source, rather than an option to specifically remediate a plume.

#### Case Study: Mineral Processing Facility (Garret & Hudson)

Large scale in situ bioremediation was used at a 28 ha (70 acre), shut down mineral processing facility to address nitrate levels ranging from ~45 mg/L as nitrate (10 mg/L as N) to more than 10,000 mg/L as nitrate (2,258 mg/L as N), with the highest concentrations found beneath an evaporation pond (Garrett & Hudson 2005). Over the three-year study period, an average of 41% reduction in nitrate levels was achieved across the 19 ha (48 acre) nitrate plume using methanol as the amendment for denitrification. Initially, a total of 24 injection wells and 14 monitoring wells were used; injection wells were placed both upstream and downstream of the contaminant source. Thirty-five more injection wells and 18 more monitoring wells were placed within the pond area, while 22 injection wells and seven monitoring wells were placed in another contaminated area on site. In addition to methanol, a nutrient solution was injected. In regions treated for a longer duration (>2 years) of the project, nitrate levels were decreased by 69%. Costs of the remediation system were not discussed; however, the system was designed to be as simple as possible, in part to minimize capital and O&M costs.

#### Case Study: New Mexico (Nuttall & Dutta, Dutta et al., Mohr, Faris)

Lastly, a research project by the University of New Mexico (Nuttall & Dutta N.D.) implemented in situ bioremediation using a bio-barrier (aka. bio-curtain) design. The technology consists of a radially arranged set of injection wells that maintain appropriate electron donor level for denitrification in a ring

about the extraction well. The site, located in the South Valley of Albuquerque, NM, spanned 223 ha (550 acres) with a total plume volume of more than 6 billion L (1.6 billion gal) and nitrate levels approaching ~1,330 mg/Las nitrate (300 mg/L as N). The objective of the pilot scale study was to assess the feasibility of both plume remediation and containment with injection of molasses and nutrients. The pilot system was tested for more than a year with nitrate levels reduced to < 4.4 mg/Las nitrate (< 1mg/L as N) (Dutta et al. 2005). After four months, biomass buildup resulted in clogging and interrupted system operation; a bleach solution was subsequently used for biomass management. The use of an inexpensive amendment as electron donor and the ability to recharge the curtain repeatedly allow for a potentially cost-effective remediation system with minimized operation and maintenance demands (Dutta et al. 2005). According to researchers,

"The ability to direct groundwater flow using a biofilm barrier could be used to channel contaminated groundwater to an active treatment zone while also contributing to bioremediation of the water. In situations where groundwater flow is minimal, pumping strategies to draw the contaminated groundwater into an active treatment zone could be enhanced with biofilm barrier technology. This technology has commercial value for assisting agricultural businesses, such as feedlots, hog farms, and fertilizer suppliers, in reducing their environmental impact and ensuring the availability of s afe drinking water" (Nuttall & Dutta N.D., p. 205).

Following subsequent research and consideration of various remediation options,<sup>13</sup> the New Mexico Office of Natural Resources Trustee (ONRT) opted to utilize ISB to address the nitrate plume in Mountain View, NM (Mohr 2009). Although the bio-curtain falls into the category of ISB, the terminology is not particularly clear for this unique system as it is also called a PRB. For reference, the following is excerpted from a published article (Mohr 2009, p. 417) discussing remediation at this location:

"It is anticipated that if a biodenitrification barrier could be constructed within and down the gradient of the Mountain View contamination site, natural groundwater gradient flow through the barrier would stimulate denitrification (Faris, 2007a). Barriers to successful in situ biodenitrification include the proper placement of food, need for additional nutrient injections, and the potential for clogging or biofouling (Faris, 2007a). Typical biobarriers require injection of the food every 10 feet; given the size of the Mountain View nitrate plume, 460 injection points would be required to build one biobarrier (Faris, 2007b). The estimated cost of building the biobarrier to remediate the Mountain View nitrate plume is approximately \$1.5 million, with another \$500,000 for soil and groundwater testing and assessment (Faris, 2007a)."

The New Mexico site is further discussed below in Section 2.3.2 on Permeable Reactive Barriers (PRBs).

<sup>&</sup>lt;sup>13</sup> The following remediation options were considered for remediation of the nitrate plume in Mountain View, NM,: "taking no action, pumping the nitrate-contaminated water for agricultural or industrial use, pumping the contaminated water and treating it for reinsertion into the a quifer or for other beneficial use (ex situ biodenitrification), or treating the nitrate in place through manipulation of natural biodentrification processes..." (Mohr 2009, p. 415).

#### Estimation of Costs of ISB/ISRM

In addition to that reported in the above research, cost information for ISB/ISRM systems is available in the literature through various agencies (ITRC 2000; DOE 2000; U.S. EPA 2001a; ITRC 2002; ITRC 2008; www.frtr.gov); however, it is important to note that the costs for remediation projects are site specific, varying with location, site and water quality characteristics. Capital and O&M costs for ISB/ISRM are highly dependent on depth to the plume, as related to drilling, injection, and pumping costs.

Cost components of Enhanced In Situ Biological Denitrification (EISBD) consist of the following categories (ITRC 2000, p. 39): "Chemical Amendments, engineered Amendment Injection Systems, well Construction, system Maintenance, and Monitoring."

The majority of available cost information is for the use of ISB to address contaminants other than nitrate, thus, the costs associated with nitrate remediation of the Mountain View, NM, nitrate plume are likely the best example of nitrate plume remediation. General cost information for ISRM is available in the literature (see DOE 2000).

#### Application of ISB to the TLB and SV

For the purposes of this analysis, a typical plume is defined as discussed above in the Section *Hypothetical Plume Size*. The total plume volume of the typical plume is greater than that discussed above for the New Mexico site (due to greater depth); the additional depth makes it difficult to accurately extend the published cost estimates of the NM site to our typical plume. While the feasible depth of ISB for remediation is theoretically dependent on the depth of injection wells, remediation to greater depths will be more costly and less reliable, due, in part, to inconsistencies in subsurface geology. It is expected that the cost of ISB remediation for a typical plume in the study area would exceed that of the NM site (>\$2 million), whereas for a more shallow plume, this may not be the case.

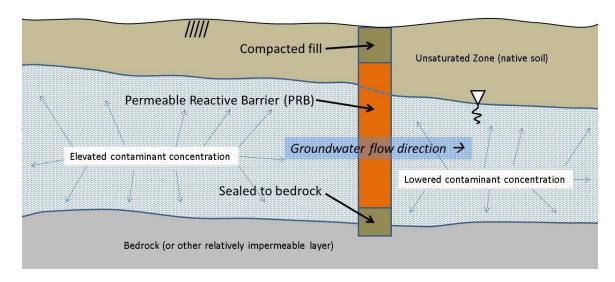
It is important to note that the costs presented here are just one example of nitrate plume remediation costs using ISB; there are numerous configurations, amendments, and site specific variables that affect remediation costs. Obstacles associated with the application of ISB in the TLB and SV might include:

- Plume depth, hydrologic and geologic factors (lack of strong confining layer at shallow depth)
- Depth to groundwater, often exceeding 50 feet to 100 feet
- Limited access for site characterization, injection, extraction and monitoring wells, depending on location (e.g., the middle of an operating dairy or an actively farmed field)
- Cooperation of stakeholders and public perspectives/education
- Project funding sources (especially for legacy contamination and the lack of a clearly definable responsible party)
- Regulatory and permitting requirements

However, the extensive research and experience thus far with ISB for nitrate impacted groundwater (in Mountain View, New Mexico) offers a precedent for the potential application of this technology as a plume-scale remediation option.

#### 2.3.2 In situ Denitrification Using Permeable Reactive Barrier – Local

PRBs can be used to remove nitrate from groundwater in situ through biological denitrification or chemical denitrification (see above for more information). Barriers containing reactive media (e.g., ZVI, solid phase organic carbon, oil coated sand) can be installed in the path of groundwater flow (Figure 4), supplying the necessary components for denitrification.



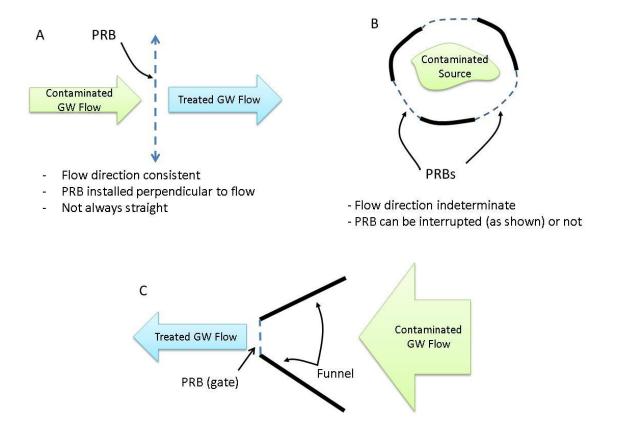
#### Figure 4. General schematic of a permeable reactive barrier.

The denitrification zone of PRBs can also be augmented by injection of amendments to provide optimal conditions. PRBs can be implemented in several configurations including cross-flow continuous barriers to treat diffuse contaminant plumes, funnel and gate installations that channel contaminated flow through a narrow reactive barrier, and reactive vessel designs for containment of point-source plumes before they have spread (Figure 5). According to the U.S. EPA (2001c, p. 2):

- "PRBs work best at sites with loose, sandy soil and a steady flow of groundwater.
- The pollution should be no deeper than 50 feet.
- Since there is no need to pump polluted groundwater above ground, PRBs can be cheaper and faster than other methods.
- There are no parts to break, and there is no equipment above ground so the property can be used while it is being cleaned up.
- There are no energy costs to operate a PRB because it works with the natural flow of groundwater."

PRB remediation systems can require significantly less maintenance than alternative remediation options; however, plume depth will be a significant determining factor affecting the feasibility of application. Trenching is a significant portion of the costs associated with the implementation of PRBs

and the deeper the required barrier, the more costly the project. For depths greater than 30 feet, specialized equipment may be necessary; PRBs can be installed as deep as 120 feet or more, but costs will increase with depth (Gavaskar et al. 2000; NFESC 2002 as cited in Perry 2008). Based on U.S. EPA recommendations (2001c) PRBs are generally more appropriate for contamination less than 15 m (50 ft) deep.



#### Figure 5. Permeable reactive barrier configurations: A) continuous, B) reactive vessel, C) funnel and gate.

One area of research focuses on the selection of the most appropriate amendment for biological denitrification using PRBs. For example, Hunter (2001) examined the use of vegetable oil as an electron donor in biological denitrification. The use of an insoluble substrate minimized biomass blockage, a problem common with the use of soluble substrates like ethanol, methanol, and acetate. The barrier was composed of soybean oil-coated sand and effectively decreased the nitrate levels from a starting concentration of ~89 mg/L as nitrate (20 mg/L as N) to below the MCL for a period of 15 weeks, with a flow rate 1100 L/week. After 15 weeks, insufficient oil remained for denitrification. High chemical oxygen demand, TSS, and turbidity in the effluent of the reactor indicate a longer sand bed was needed; however, the author suggests that in situ application of this type of biological reactor would decrease these factors naturally. With a withdrawal point far enough from the barrier, subsequent drinking water treatment requirements would be limited to disinfection. The most significant problem encountered in this study was the exhaustion of substrate; an effective means of substrate addition must be found (injection for example), but this was not explored. The estimated life of the PRB was 2.5-12.5 years

depending on several key factors including flow, nitrate concentration and dissolved oxygen concentration.

# **2.3.2.1** Application of Permeable Reactive Barriers (PRBs) to Address Nitrate Impacted Groundwater

Numerous examples of the application of PRBs for treatment of groundwater impacted by nitrate and other contaminants are available in the literature (U.S. EPA 1998; ITRC 2000; Blowes et al. 2000; U.S. EPA 2002; DOD 2002; FRTR 2002). PRBs can be implemented as a stand-alone denitrification barrier or can be augmented by the injection of amendments.

#### Case Study: Tennessee (FRTR)

An example of chemical denitrification, an iron-based PRB was installed in Tennessee for the remediation of nitrate and uranium; initial nitrate concentrations ranged from 20 to 150 mg/L (assumed to be nitrate as NO<sub>3</sub><sup>-</sup>) (FRTR 2002; FRTR 2011). A total of 503,000 liters (133,000 gallons) of groundwater were treated using a PRB 67 m (220 ft) long and 7.6 m (25 ft) deep in a funnel and gate configuration. An iron and peat mixture was used to address nitrate; levels were reduced by 75%. Installation costs for this demonstration project were \$943,000. Operation and maintenance costs were not provided.

#### Case Study: Canada (Robertson et al.)

Robertson et al. (2000) discuss several examples of the use of biological denitrifying PRBs to address nitrate contamination from septic tanks, and one example that addresses the runoff/drainage from an agricultural field. At these sites the barrier was composed of 15% – 100% cellulose and nitrate concentrations were reduced between 58% and 91%, from as high as 252 mg/Las nitrate (57 mg/L as N) (Robertson et al. 2000). These PRBs successfully removed nitrate from groundwater through passive treatment, with results indicating a lifespan of ten years or more before necessary restocking of the PRB.

#### Case Study: New Mexico Revisited (Faris, ONRT, Intera)

Current plans for remediation of the Mountain View, NM, nitrate plume discussed above (see the case study listed in Section 2.3.1 of this report), include the use of several PRBs for the most concentrated portions of the plume (Faris 2011; ONRT 2011). The remediation plans at this site consist of multiple PRBs using an ISB (in situ bioremediation) bio-curtain configuration. The remediation costs are budgeted for \$4 million and are planned to "remove 450,000 pounds of nitrate from the groundwater plume hot-spots allowing the remainder of the plume to naturally attenuate to below State groundwater standards in less than 20 years" (ONRT 2011). An extensive remedial investigation of the Mountain View site began in mid-2009 resulting in the compilation of a detailed report, for the New Mexico Environment Department (NMED) and New Mexico Office of Natural Resources Trustee (ONRT), including monitoring data, plume delineation, characterization of the subsurface and hydrogeology, and an assessment of the feasibility of remediation (Intera 2010). The breadth of this report highlights an important part of any remediation project; the costs of preliminary planning, site characterization, monitoring, and feasibility studies must be considered, as they can be significant. The Mountain View, NM, nitrate plume has a long history, with numerous projects investigating and cataloging the site; the costs to finalize site characterization and feasibility (for the development of the Intera report) were

\$250,000 (Faris 2011). This figure excludes pre-existing monitoring wells and additional past investigative efforts.

Additional unique variations of the application of PRBs might also be considered including circular barriers around wells and installation in drainage channels.

#### 2.3.2.2 Costs of PRBs Reported in the Literature

At the Mountain View, NM, site, the latest total cost estimate budgets the project around \$4 million for multiple PRBs to address hot-spots, removing 450,000 pounds of nitrate over a period of 4 years. Additional details of the remediation plans for this site are currently in development.

As indicated above, PRB remediation costs are largely dependent on the required depth of the barrier. As reported by Gavaskar et al. (2000), estimated costs for trenching to depths of 30 feet range from \$2 – \$10 per sq. ft., while excavation deeper than 80 feet can range from \$2 – \$55+ per sq. ft. PRB installation costs have been estimated to range from \$50 – \$300 per vertical foot using Caisson-based construction<sup>14</sup> (Gavaskar et al. 2000).

The following example capital costs are summarized for a PRB remediation system of a Chlorinated Volatile Organic Compounds (CVOC) plume at Dover Air Force Base (AFB).<sup>15</sup> Although the Dover AFB site is for CVOCs rather than nitrate, comprehensive costs are included here as a representative example of PRB costs for a PRB system of the same scale as the Dover AFB site. In this example, the PRB depth, width, and thickness for the funnel and gate project were 39 ft, 68 ft, and 4 ft, respectively, which captures 50 ft of the plume across 25 vertical ft (Gavaskar et al. 2000). The estimate includes preconstruction costs as well as the costs of materials and construction (Appendix B of Gavaskar et al. 2000). Preconstruction costs include "site assessment, site characterization, laboratory testing, PRB modeling and design, procurement of materials and construction contractors, and regulatory overview...and can constitute as much as 50% of the total capital investment in the PRB" (Gavaskar et al. 2000, p. 128). O&M costs refer to any ongoing costs over the life of the project. Estimates provided by Gavaskar et al. (2000) for a full-scale PRB at Dover AFB (operating at 10 gpm which would equate to ~5.3 million gal/year) are:

<sup>&</sup>lt;sup>14</sup> Caissons are steel temporary retaining walls installed progressively during excavation to maintain integrity of the walls, and removed after fill has been placed.

<sup>&</sup>lt;sup>15</sup> The exact dimensions of the plume were not reported; however, the operating capacity of the PRB system, estimated to be 10 gpm, would equate to ~5.3 million gal/year. Please refer to Gavaskar et al. (2000) for a dditional information.

- Capital Costs
  - Preconstruction: \$365,000
  - PRB Construction (including materials): \$587,000
  - Total Capital Cost: \$947,000
- O&M Costs
  - Annual Operating Costs: \$148,000
  - o Additional Long-term Maintenance (every ten years): \$421,000
  - Total Annual O&M Cost: \$190,100

The most significant elements of the annual operating costs listed above include quarterly groundwater sampling of 40 wells (\$80,000), quarterly CVOC analysis (\$20,000) and data analysis, reporting and regulatory review (\$40,000); these O&M costs highlight the importance of accounting for sampling, chemical testing, and data analysis. O&M costs can vary widely with not only the scale of contamination, but also monitoring and reporting requirements.

Capital costs for PRBs can be greater than those of PAT remediation, but the long-term ongoing operations and maintenance cost savings can make PRBs the more financially prudent option. Estimated costs for a PAT system comparable to the above PRB system at Dover AFB (capable of the same level remediation) indicate a break-even point of the PRB for this site after 8 years of operation assuming a 30 year project duration and a 20 year medialife.

In McGregor, TX, PRB trenches were constructed over one mile long and 25 ft deep for the remediation of perchlorate contaminated groundwater; the initial perchlorate concentration was reported as 27,000 ppb (ug/L)(DOD 2002). Less than one month after start-up, perchlorate levels were reduced by a minimum of 90% (DOD 2002). Installation of the PRB totaled \$833,000. "Capital cost avoidance has been estimated at more than \$3 million compared to *ex situ* technologies. In addition, operation and maintenance costs are estimated at \$5,000 per year versus \$100,000 per year for the *ex situ* technologies" (DOD 2002, p. 2). In addition to treating for perchlorate rather than CVOCs, the significantly lower O&M costs for the McGregor PRB remediation, in comparison with the Dover PRB remediation, is assumed to be due to differences in site characteristics, sampling regime, and reporting requirements.

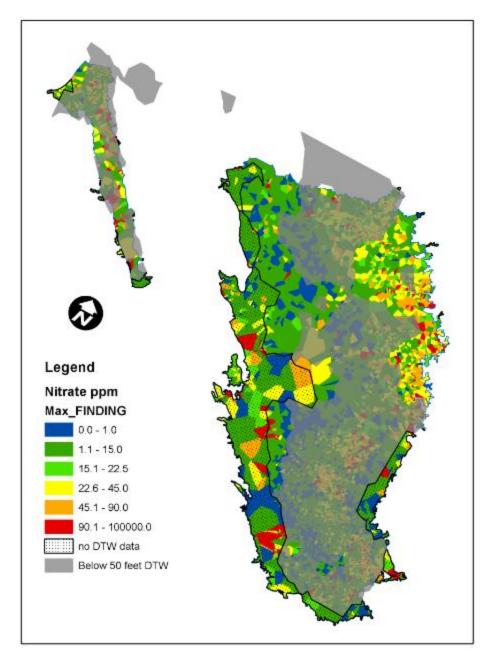
The use of PRBs for remediation at the McGregor, TX, and Dover, DE, sites are provided only as examples of the full-scale application of PRBs; it is important to keep in mind that these PRBs were used to address contaminants other than nitrate and costs are not only variable across sites, but also across contaminants. Additional costs of PRB remediation are listed in the literature on a case study basis (Gavaskar et al. 2000; U.S. EPA 2001d; U.S. EPA 2003).

#### 2.3.2.3 Application of PRBs Within the Study Areas

Costs associated with the use of PRBs for remediation in the Tulare Lake Basin and Salins Valley are expected to be similar to those described above, depending on plume size and site considerations.

However, it is important to note that the costs presented here are just examples of plume remediation costs using PRBs; there are numerous configurations, amendments, and site specific variables that would affect remediation costs.

The application of PRBs for the remediation of nitrate contaminated groundwater in the Tulare Lake Basin and Salinas Valley would be limited to areas with shallow contamination which accounts for only a small portion (about 26%) of the area of interest. From Figure 6, it is apparent that the northeast region of the Tulare Lake Basin study area is the most likely part of the study areas to be appropriate for PRB treatment for two reasons: first, the shallow groundwater in that region makes PRB treatment possible, and second, the high concentrations of nitrate in that region affords better return on the cost to implement than installations in areas with lower concentrations of nitrate. Because the PRB systems are capable of treating water at high nitrate concentration as easily as at low concentration, the best benefit to cost is found in the former.





#### 2.3.2.4 Biological Denitrification with Wood Chip Substrate

As a plausible alternative to chemical substrates, wood chip PRBs (WCPRBs) are examined as an example of PRB application in the Tulare Lake Basin. WCPRBs can be implemented as vertical denitrification walls to intercept flow of high-nitrate, shallow groundwater moving in predictable flow paths.

The eastern slopes of the northern Tulare Lake Basin are heavily planted with citrus crops that require large amounts of nitrogen fertilizer. Although a definite link has not been established between the applied fertilizer and the groundwater nitrate levels, wells in these areas are prone to elevated nitrate levels. In the same area, the groundwater levels are frequently less than 50 feet below ground surface. The groundwater gradient in this area is to the southwest, toward one of the more heavily populated parts of the study area. This eastern portion of the Tulare Lake Basin represents the most favorable conditions for in situ treatment with WCPRBs in the study area. A brief discussion of the effort and estimated cost of employing this remediation option follows.

In the Tulare Lake Basin, typical infiltration rates of 1 foot per year, and typical down-gradient movement of 50 to 100 feet per year imply that a WCPRB placed 50 feet deep (starting from the groundwater surface) could intercept groundwater flow from nearly a mile up-gradient. Assuming a required residence time of 10 days and groundwater flow velocity of 100 feet per year, the denitrification wall would need to be 2.74 feet thick. Assuming a denitrification wall of 50 foot depth, starting at 30 feet below the ground surface, and running for a half mile to intercept the infiltrate from a half-section field (Figure 7), a WCPRB would require about 21,500 cubic yards of excavation, and about 13,400 cubic yards of wood chips. Assuming a low-estimate cost for excavation of \$20 per cubic yard, \$10 per cubic yard for backfilling, wood chips delivered at \$20 per cubic yard, the cost to install such a WCPRB would be roughly \$779,000, not including the costs of site inspection, plume delineation, permitting, and monitoring.

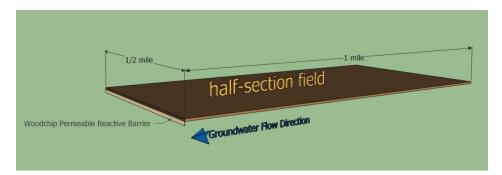


Figure 7. WCPRB for treatment of infiltrate from a single half-section field or orchard, assuming 100 feet per year lateral groundwater travel, 1 foot per year of infiltration, and 10-day residence time in the WCPRB. Over 13,400 cubic yards of wood chips would be required.

As a sub-regional approach to remediation, WCPRBs could be installed for miles roughly parallel to groundwater depth contours (Figure 8). Interception and treatment of nitrate contaminated groundwater from a strip of impacted agricultural land approximately one mile wide, with WCPRBs following depth to water contours from 20 miles north of Visalia to 20 miles south east of Visalia, would require placement of about 40 miles of WCPRB at a cost on the order of \$62.5 million. Considering that the area of impacted groundwater along the eastern edge of the basin varies from 2.5 to 5 miles in width, multiple WCPRBs would need to be placed in sequence perpendicular to the groundwater flow gradient, totaling on the order of 120 miles of WCPRB. Implementation of this WCPRB example is estimated to cost roughly \$180 million, and require over 1.6 million cubic yards of wood chips (with the same assumptions as the ½ section example above).

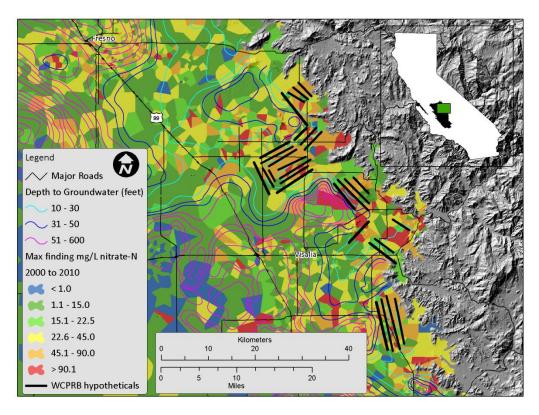


Figure 8. Hypothetical placement of 120 miles of WCPRBs (thick black lines) to intercept and treat infiltrate from a high nitrate-loading area with shallow groundwater.

At these scales, the supply of wood chips for bioreactors will likely become limiting. However, the hypothetical ½-mile application described above would consume the equivalent of about 15% of the yearly delivered volume of a single typical medium-sized wood chip supplier in the central valley (based on interviews with regional woodchip delivery companies). Therefore, it is feasible that the 120 miles of WCPRB could be installed over a period of several years.

#### 2.3.2.4 Wood Chip Bioreactor (WCBR) Treatment of Tile-Drain Effluent

Another targeted application of wood chip biological denitrification technology incorporates the use of tile drains as collectors of infiltrate, with treatment of the collected irrigation infiltrate in a bioreactor. Robertson et al. (2000) demonstrate this application. In a similar approach, a 9-year field-scale experiment by Moorman et al. (2010) used a pair of shallow WCPRBs placed on either side of a tile drain to treat agricultural drain water prior to entry into the tile drain. This treatment resulted in a reduction from 97 mg/L to 39 mg/L nitrate as  $NO_3^-$  (22 mg/L to 8.8 mg/L nitrate as N).

Such smaller scale, on-farm technologies could be used to target high-nitrate crops before the contamination reaches the groundwater, and should reduce costs when compared with treatment options restricted to treating diluted or deep water. Similar to the WCPRB application above, this technology is applicable only in limited areas – though not the same areas. Tile drains are only used in a small portion of the agricultural areas in California, specifically, those areas with very shallow, perched groundwater (on the order of 1 to 3 meters depth to water). Tile drains are used in the lower Salinas

Valley and the north-western Tulare Basin (southern San Joaquin). Data on the distribution of tile-drains is not available in the public record, so a survey of agricultural practices, combined with investigation of tile-drain effluent nitrate concentrations, would be required before an evaluation of this application could be accomplished. No extensive on-farm testing of WCBR treatment of tile-drain effluent has been conducted to date in California. Based on the rate constants in Leverenz (2010), a typical installation designed to treat a 100 acre field would cost between \$20k and \$35k and would require approximately 1 acre of land.

Regional Water Quality Control Boards have issued waste discharge permits for in situ treatment of leaking sub surface tanks (petroleum) using injection of oxidizing agents, and PRBs of zero-valent iron for treatment of groundwater plumes contaminated with heavy metals. WCPRBs would require similar permits.

#### 2.3.2.5 PRB Conclusions

Permeable reactive barriers are useful as in situ treatment for nitrate, however, in the Tulare Lake Basin and Salinas Valley, feasibility of PRBs is limited by depth to groundwater (a quarter of the study area has shallow enough groundwater). PRBs are most cost effective when used to treat relatively high concentrations, further restricting their regional value. As with any in situ treatment regime, drinking water supplies may need to be protected by other means until remediated groundwater reaches drinking water wells. Woodchips are a viable alternative to more expensive materials (e.g., iron powder) in the Tulare lake Basin, where chipped orchard trees supply ample material for large scale implementation of WCPRBs.

Obstacles associated with the application of PRBs in the TLB and SV include:

- Plume depth, hydrologic, and geologic factors
- The limited area within the SV and TLB with a shallow enough depth to groundwater allowing for PRBs. Of the 22,660 square kilometers of the study area, only 26% (6,000 square kilometers) has groundwater at 50 feet depth or less, the recommended (U.S. EPA 2001c) maximum depth to groundwater for application of PRBs.
- The time lag for remediated water to reach drinking water wells
- Limited access for site characterization, PRB installation, and monitoring wells (depending on location, e.g., the middle of an operating dairy or actively farmed field)
- Cooperation of stakeholders and public perspectives/education
- Project funding sources (especially for legacy contamination and the lack of a clearly definable responsible party)
- Regulatory and permitting requirements

### 2.4 Pump and Fertilize (PAF) at the Basin Scale

Full, basin-scale application of pump-and-treat (PAT) methods is not practical, due to the prohibitively high costs associated with the required construction and operation of a vast network of contaminant capture wells for decades, possibly centuries. Moreover, vast amounts of groundwater would have to be treated and reinjected. The construction and energy costs alone would be enormous. Pump-and-fertilize (PAF) refers to accounting for any nitrate already present in irrigation water when determining fertilizer needs. The PAF option could be done at a small fraction of the cost of pump-and-treat (PAT) but requires changes in land, fertilizer, and irrigation management. Many of these changes are technically feasible. Some farmers in the study area already employ improved farm management practices that include pump and fertilize.<sup>16</sup>

#### 2.4.1 Overview of Pump and Fertilize

Traditional PAT involves construction of contaminant recovery wells to capture the contamination. In agricultural groundwater basins such as the TLB and SV, however, there already exist thousands of irrigation wells that provide most of the groundwater used in the region. These existing irrigation wells capture a significant fraction of the recharge, including any high nitrate water stemming from crop irrigation and fertilizer application. PAF would use the existing wells and the existing pumping schedule of those wells to capture nitrate contaminated groundwater. PAF could potentially include the drilling of new irrigation wells specifically to capture high nitrate, shallower groundwater. Furthermore, since this water is used to grow crops, PAF would use crops to remove nitrate-N from irrigation water by applying less commercial fertilizer, commensurate with the amount of N already in the pumped irrigation water. PAF is, in effect, a regional phytoremediation approach that makes use of existing irrigation wells and nitrogen uptake by crop production. PAF is therefore an intrinsic element of proper nutrient management efforts. Unless additional irrigation wells are installed specifically to capture high nitrate at l., 2012). It has to be operated as part of a farm's nutrient management efforts. Unless additional irrigation wells are installed specifically to capture high nitrate groundwater for irrigation, PAF may not necessarily be called out as an active remediation scheme, but may simply be considered part of a farm's nutrient management.

The PAF approach requires more careful management of both, nitrate-Ninirrigation water and the nitrogen applied as fertilizer. The amount of N applied to each field through irrigation water needs to be measured, and commercial (or organic) fertilizer applications must be adjusted downward to account for nitrogen applied with the irrigation water. Because nitrate concentrations in pumped groundwater can vary considerably in space and time, frequent monitoring and adaptive nutrient management is required.

Some long-term remediation at the basin-scale is possible by using nitrate contaminated groundwater to grow crops and by reducing the nitrate concentration of water percolating below the crop root zone. To ascertain how much reduction in nitrate loading this method could accomplish, pilot field projects

<sup>&</sup>lt;sup>16</sup>See Technical Report 3 (Dzurella et al. 2012) for more information on extent of use of best management practices by growers in the study a rea.

would need to be conducted, quantifying the improvement in nitrate leaching or in groundwater quality beneath the fields. Regional groundwater contaminant transport modeling studies would also need to be conducted to assess the necessary time scale of this remedial action to achieve the stabilization and reduction of groundwater itrate concentrations to acceptable levels. Such models would provide the basis for regional groundwater quality management with respect to nitrate but also with respect to other contaminants such as arsenic and salts that also affect drinking and irrigation water quality. Moreover, groundwater quality management models would help estimate how much of the downward migrating nitrate would be captured by existing and additional wells, depending on pumping rates and schedules. Ultimately, the goal would be to manage groundwater quantity and quality jointly to improve the sustainability of both.

A disadvantage of the PAF approach is that many existing irrigation wells are designed to pump at large extraction rates, requiring that they are drilled to relatively large depth drawing water across multiple aquifer layers and allowing for sometimes large water level drawdowns near the well. Shallow-to-intermediate depth nitrate contaminated groundwater is therefore not efficiently intercepted by these wells (also see Technical Report 4, Boyle et al., 2012). An alternative option to better capture high nitrate shallow-to-intermediate depth groundwater is to drill intermediate-depth irrigation wells that would intercept contaminated groundwater before it further penetrates the deeper subsurface. This approach would require a significant and careful capital investment because shallower wells would have smaller capture zones, and therefore a much larger numbers of such wells would need to be drilled and operated. The above-mentioned groundwater quality management models would be an integral tool in the evaluation of the potential costs and benefits of constructing additional shallow to intermediate depth irrigation or capture wells.

A number of factors will determine the cost for an extensive pump and fertilize scheme, including the type of irrigation system, the number of wells on a farm, and the degree to which groundwater is used for irrigation purposes (exclusively or mixed with surface water). There is also cost associated with creating and setting up such a program on-farm, including costs for education, training, and planning, as well as for infrastructure changes. Of those factors, we here consider only the cost of testing water quality on a sufficiently regular basis to provide the farmer with confidence in the fertilizer nitrogen content of groundwater applied as irrigation water. Based on an informal survey of analytical costs for testing nitrate in water, the estimated cost is approximately \$15/test for nitrate. Testing for other forms of nitrogen (ammonium or organic nitrogen) is more expensive, but generally not necessary for purposes of managing pump-and-fertilize: the total concentration of non-nitrate N in groundwater is typically less than 2 mg N/L. Additionally assuming that sample collection and shipping costs \$15, the total cost is \$30 per sample. If a nitrate sensor or nitrate test kit is used, the sample cost may be lower, albeit the cost for sample collection, in-field analysis, and instrument maintenance remains.

Within the study area, we estimate that there are between approximately 6,000 and 20,000 agricultural irrigation wells (see Section 9.5 in Technical Report 2, Viers et al., 2012). These wells pump, on average, 7.9 km<sup>3</sup> (6.1 million acre-feet) per year (see Technical Report 4, Boyle et al., 2012) and are active throughout much of the 3.8 million acres of irrigated cropland within the study area (see Technical Report 2, Viers et al., 2012).

To estimate cost, we assume each well is tested five times during each irrigation season to ensure that varying nitrate levels are adequately captured for the farmer to properly account for the nutrient value in the irrigation water. Per well, the sampling is then on the order of \$150 per year. We note that on many wells, it will not be necessary to sample more than once or twice per irrigation season (\$30 - \$60 per year) once a sufficiently long record is established showing relatively constant nitrate values over the season. The analytical cost is only a small fraction of the amount of fertilizer value gai ned in this process: Assuming that a typical well pumps at least 200 acre-feet per irrigation season, and assuming that water contains an average 22.5 mg/L nitrate (5 mg N/L, half of the MCL), the amount of nitrogen "fertilizer" obtained from a well is 2,800 lb N per year, at a 2012 value of approximately \$1,400, if used to replace commercial fertilizer.

For 6,000, 10,000, or 20,000 active wells, the total annual cost of regular nitrate data collection to estimate the irrigation water fertilizer value, is \$0.9 million, \$1.5 million, or \$3 million for the entire study area, at least initially; and likely lower in the longer term.

The median nitrate concentration in public supply wells during the last decade varies by groundwater sub-basin (see Technical Report 4, Boyle et al. 2012). The wells in the Westside and Tulare Lake Central Basin sub-basins typically have median nitrate concentrations well below 10 mg/L as nitrate. There, pump-and-fertilize may be of limited use until nitrate levels rise in the future – a likely consequence of the long-term groundwater transport processes – unless networks of shallow production wells are installed to provide capture of the upper aquifer portions. In the Kern sub-basin, median nitrate concentration is 16 mg/L as nitrate, while the median concentration in the Salinas Valley main aquifer and in the Kings, Kaweah, and Tule subbasins range from 20 to 25 mg/L as nitrate (see Technical Report 4, Boyle et al. 2012). The overall median nitrate concentration is 21 mg/L as nitrate. In 7.85 km<sup>3</sup> (6.1 million acre-feet) of irrigation water, this concentration gives over 35,000 GgN/yr. At current nitrogen fertilizer costs exceeding \$1 per kg N (\$0.50-\$0.75/lb N), the theoretical "fertilizer value" of irrigation water is over \$35 million. If a pump-and-fertilize program can take advantage of at least one-third to half the groundwater's fertilizer value, the net savings in fertilization costs could still be in the range of \$10 - \$20 million, exceeding the necessary investment in monitoring nitrate concentration in the groundwater by one order of magnitude.

There are multiple potential on-farm challenges to adopting a pump-and-fertilize program. Perhaps the largest is information, education, and training. Farmers may be unaware of the fertilizer value of their irrigation water, and/or do not have the means to properly interpret groundwater quality data for their irrigation wells in terms of accounting for its fertilizer value. Some farms have complex and seasonally varying irrigation setups with varying input from one or more wells and surface waters, making proper accounting of the fertilizer value that much more difficult and prone to error. For some of the high fertilizer need crops, the amount of nitrogen applied with irrigation water from groundwater (on the order of 10 - 100 kg N/ha depending on nitrate concentration and groundwater use), may be thought to be too insignificant to be used.

Nonetheless, basic pump-and-fertilize management - proper accounting for the nitrogen content of irrigation water in nutrient management planning - is an essential part of modern nutrient management.

Additional pump-and-fertilize management components, such as requiring that a larger number of agricultural wells be screened only in the shallower (higher nitrate) portions of the aquifer, would need to be evaluated for their cost and feasibility.

#### 2.4.2 Understanding the Value of Irrigation Water Nitrogen

Nitrogen in groundwater pumped for irrigation has been shown to be important both, for crop nitrogen uptake and in field effluent nitrogen loads. In a detailed mass-balance study of a corn field in Yolo County, California, King et al (2009) found that influent irrigation water nitrate was an important constituent in post-irrigation runoff nitrogen content. In the endorheic (hydrologically closed) Tulare Lake Basin, field runoff eventually percolates to groundwater unless it is artificially captured and stored. Although the Salinas Valley does drain to the ocean (via the Salinas River and Elk horn Slough), it is also subject to percolation of irrigation runoff waters.

Martin et al (1982) conducted a field-calibrated modeling study of nitrogen uptake by corn in Nebraska, with results that showed that nitrogen uptake efficiency by corn from irrigation water was actually higher than that from synthetic fertilizer nitrogen. This finding suggests that, in some cases, it may be possible to replace commercial fertilizer nitrogen with irrigation water nitrate nitrogen at a replacement rate of less than 1:1 (irrigation water N to commercial fertilizer N), further supporting the above economic valuations.

#### 2.4.3 Current Use of Irrigation Water Nitrate in Fertilizer Calculations

The expert panels conducted for the current study (see Technical Report 3, Dzu rella et al, 2012) indicated that although irrigation water nitrate testing is somewhat common, properly reducing fertilizer applications based on irrigation water nitrate content is less of a common practice. In areas of high groundwater nitrate, growers tend to make more of an effort to account for it. The complexity of the irrigation water source, the irrigation scheduling, and the need for technical expertise are the most important barriers. Many growers operate irrigation regimes that incorporate both surface water as well as multiple wells (at varying levels of nitrate concentration), meaning the pumping and piping (which are not static) contributes significantly to the complexity of accounting for irrigation water nitrate. In the Tulare Lake Basin, farms are much larger than in the Salinas Valley, increasing the tendency for complex irrigation modes. Growers also indicated some reluctance to test water in wells on leased land, citing privacy concerns of landlords. In the end, while more and more growers in the study area are aware of the issue, the complexity and associated learning curve keeps proper accounting a less common practice.

A survey of growers in the Salinas Valley was conducted in 2001 (MCWRA 2002). This survey was voluntary. Of 314 growers who received the survey, 107 growers responded, which represented 49% of the irrigated agricultural acres in the Salinas Valley. No conclusions are drawn regarding the applicability of these results to non-surveyed growers. The survey found that 66% of the area was farmed by growers who stated they accounted for nitrate in some of their calculations of fertilizer application rates. Monterey County Water Resources Agency recommends to growers that they account for

irrigation water nitrogen content. In a fact sheet produced by MCWRA, (1999), a detailed description of how to take this nutrient source into account is presented, and it appears that farmers in that region use it (MCWRA 2002). No such technical assistance is widely available to growers in the Tulare Lake Basin.

In Nebraska, and in Australia, farmers are encouraged to account for irrigation water nitrogen (nitrate) when calculating the amount of fertilizer they will apply. The Nebraska Cooperative Extension office offers advice and training to this end, including tables of irrigation water nitrogen content by region (of Nebraska) that can be used by farmers in the absence of irrigation well water nitrogen monitoring data (Ferguson et al 1994). The Queensland (Australia) Department of Environment and Resource Management Reef Protection Package (2009) (addressed specifically to sugar-cane growers in coastal areas where nitrogen leaching to groundwater impacts coral reefs in the near-shore ocean environment) gives their recommended method for calculating the amount of reduction in fertilizer nitrogen necessary to account for nitrate in irrigation water. Both the Queensland and Nebraska methods recommend that a 1-for-1 reduction (nitrogen in irrigation water for nitrogen in fertilizer) be made.

# 2.5 Management of Groundwater Recharge

In the Tulare Lake Basin the dominant source of groundwater recharge is irrigation, while infiltration of surface water from streams is a secondary source. Direct precipitation also contributes some recharge. A basic premise of regional groundwater quality management is that if most of the recharge to a basin is contaminated with recalcitrant compounds like nitrate, the groundwater quality is more vulnerable and likely non-sustainable. If however, a less contaminated source of recharge, such as stream infiltration or recharge ponds can be augmented to decrease the ratio of contaminated-to-clean recharge, regional groundwater quality will improve and is more sustainable. A good example of the effects of relatively clean recharge from streambed infiltration can be seen in the vicinity of the Leaky Acres recharge facility in Fresno, where groundwater nitrate tend to be lower than groundwater that is receiving most of its recharge from irrigation (Technical Report 4, Boyle et al., 2012). There is also evidence suggesting that recharge from the Salinas River results in lower groundwater nitrate concentrations near the river.

As climate change results in less storage of surface water in California reservoirs owing to earlier snow melt and flood control requirements, subsurface storage of water will become increasingly necessary to mitigate the loss of snow water storage. Moreover, if some of this earlier winter runoff can be captured and diverted to streams and groundwater recharge operations, the volumes of 'clean' recharge will increase. The beneficial effects of clean recharge on the nitrate problem would need to be estimated through regional scale modeling of the groundwater quality under various pumping, irrigation, and recharge scenarios.

# **3** Summary and Conclusions

The basin-scale pump-and-treat (PAT) approach is not recommended for implementation in the study areas due to its economic and logistic impracticality. Hot-spot source reduction through local-scale remediation methods such as injection wells and PRBs for in-situ treatment in targeted areas, together with regional scale management of irrigation water nitrate and optimized fertilizer application (pump-and-fertilize, PAF) are the most promising actions and will likely improve groundwater quality over the long term. The benefits of these measures, and the time necessary for these changes to occur, can be estimated through agricultural-field scale monitoring at focus sites and through regional scale modeling of groundwater quality. Some farmers are applying PAF now, but technical support and incentives are needed to encourage broader implementation, especially in the Tulare Lake Basin, but also in Salinas Valley.

Implementation will require regional groundwater quality management models for determining the combinations of N source reductions, localized remediation, irrigation water and N management (PAF), streambed recharge, and groundwater pumping distributions that will bring about improvement in the groundwater quality on a time scale of decades to centuries. The long time frame required for such actions to succeed will present both policy and implementation challenges. The policy must still be developed based on current scientific knowledge, some of which is presented in this chapter, together with science that will come from the needed groundwater quality management models. Because the effects of any practices set into motion by policy will unfold slowly, it will be important to use an adaptive management approach, in which predictions of trends in groundwater quality are regularly checked against monitoring data that are then used to recalibrate models, assumptions, and policies.

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# Appendix

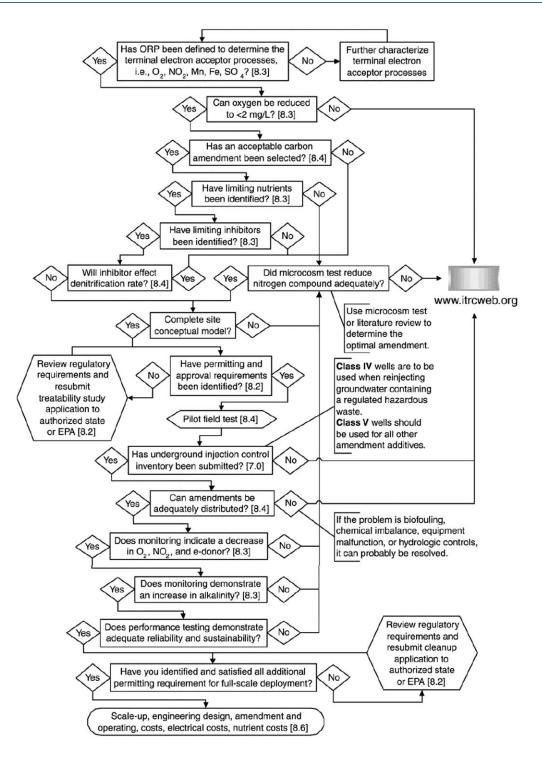


Figure A-1. Decision-tree for the application of in situ bioremediation for nitrate (reproduced with permission from ITRC 2002).