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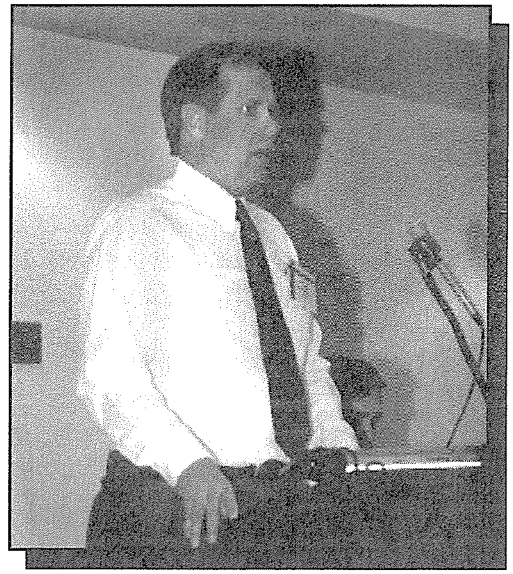

A TECHNOLOGY FOR IN SITU DENITRIFICATION OF GROUNDWATER

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Nitrate contamination in groundwater is an important health concern. In New Mexico, nitrate contamination is found in several communities and in many states as well as throughout most of the populated world. The source of nitrate contamination includes over fertilization, improper disposal of animal wastes, human wastes from septic tanks, and industrial waste streams. This topic is of potential importance to the ranchers and farmers of New Mexico as the Eastern portion of the New Mexico continues to grow in population and in drinking water demands. Through research sponsored by the Waste-management Research and Education Consortium (WERC), the University of New Mexico has developed a promising innovative natural biological process to convert hazardous nitrate into harmless nitrogen gas. The technology uses the indigenous bacteria commonly found in soil and groundwater. This cost-effective and efficient technology can be applied underground directly to the contaminated water or soil. The process may also be used for pollution prevention to protect our valuable drinking water from future contamination by nitrates. Plans are underway to demonstrate this process at an orphan nitrate plume site located in Albuquerque's South Valley. Satellite field tests using this technology also are being considered in Minnesota and California. The process and its potential application to nitrate contamination in New Mexico is presented here along with information on the importance of this little known groundwater contamination problem.

INTRODUCTION

Background on Health Hazards

"The U.S. Environmental Protection Agency has determined that nitrate poses an acute health concern at certain levels of exposure" (Cook 1996). The drinking water standard in the U.S. is 10 ppm N-NO_3^- while Germany and South Africa have a standard half that of the U.S., that is, 5 ppm. Health effects include methemoglobinemia (blue-baby syndrome) in infants, cancer, disruption of thyroid function, and birth defects. Methemoglobinemia is a condition caused by the inability of blood to deliver enough oxygen to the body. It is the most well-known effect of exposure to elevated levels of nitrate in drinking water. It is estimated that over 12 million people in the United States drink water contaminated by nitrate at levels above the EPA's 10 ppm standard (Cook 1996). Nitrate contamination in groundwater is both a national and a global problem faced by most densely populated countries. In the early 1980s, surface treatment became standard in Europe while in the late 1980s, France and Israel began testing in situ biodenitrification (Jandi et al. 1988; Mercado et al. 1988; Hamon and Fustec 1991). A recent study predicts a factor of about five cost savings when using in situ remediation versus pump and treat remediation (Quinton et al. 1997). In situ biodenitrification is still a developing technology with opportunities for cost reduction in drilling and a need for improvement in the amendment delivery system. At the University of New Mexico, we hope to demonstrate an improved version of this technology using new drilling methods such as Geoprobe Systems (Division of Kejr Engineering, Inc.) and improvements in the design of the delivery system which will enhance mixing and avoid potential formation plugging.

Background on the Mountainview Plume in Albuquerque's South Valley

To demonstrate this technology, we are considering a location in the Mountainview area of Albuquerque's South Valley. A migrating groundwater plume of nitrate contamination has existed in the Mountainview area of Albuquerque's South Valley since 1961. The source is believed to be a former vegetable farm. Currently, the plume is classified by New Mexico Environmental Department (NMED) as an orphan site meaning that the State of New Mexico is ultimately responsible for its restoration. The plume covers an area of about 0.8 square miles. Nitrate contamination extends about 30-feet deep in the uppermost saturated Rio Grande valley-fill sediment. A Mountainview infant was hospitalized with blue-baby syndrome after ingesting contaminated well water in 1980. Based on the last door-to-door "water fair", seven private water-supply wells contained dangerous nitrate levels. The plume has damaged health, environment and property values, has interfered with public welfare, water rights and the use of property, and continues to migrate and threaten other water-supply wells.

In Situ Denitrification Process

The philosophy underlying the development of this technology is to enhance natural or intrinsic remediation where possible. The following quote by Carson (1962) seems most appropriate in describing our efforts: "Nature herself has met many of the problems that now beset us, and she has usually solved them in her own successful way. Where man has been intelligent enough to observe and to emulate Nature he, too, is often rewarded with success." The denitrification of water by heterotrophic bacteria was established as a potable water treatment technique in the early 1980s (Gauntlett and Zabel 1982).

Biochemical Reactions

This section describes the biochemical reactions employed in biodenitrification of groundwater and soil. This process converts hydrocarbons into water and carbon dioxide using nitrate as the electron acceptor. Figure 1 shows the complete nitrogen cycle found in nature with the denitrification pathways illustrated in bold. The overall denitrification reaction is defined as:

nutrient + bacteria + nitrate > nitrogen gas + water + carbon dioxide

$$NO_3^- \rightarrow NO_2^- \rightarrow N_2\uparrow \qquad (1)$$

Using acetate for the organic nutrient, the overall balanced reaction is:

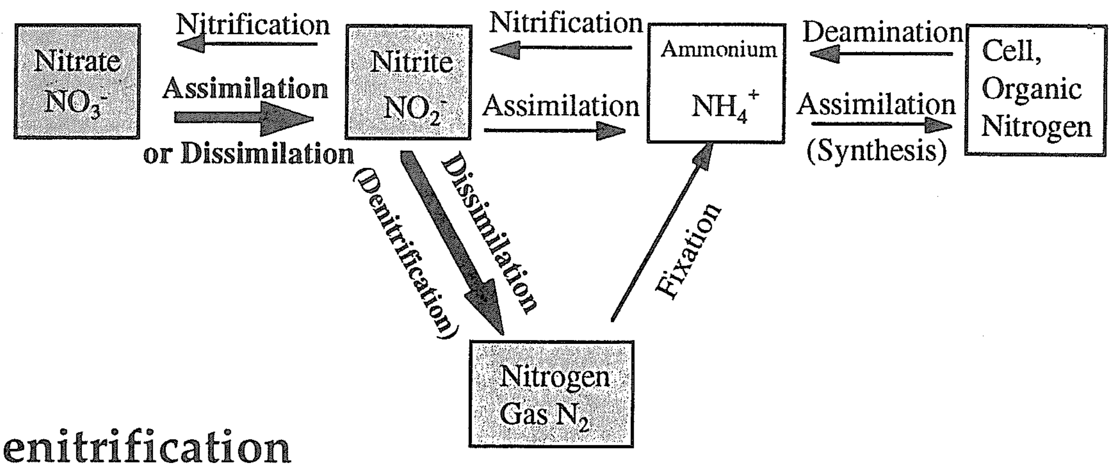
$$5CH_3COO^- + 8NO_3^- + 3H^+ \rightarrow 4N_2\uparrow + 10\,HCO_3^- + 4\,H_2O \quad (2)$$

In practice, there are two rate-limiting reactions; first the conversion of nitrate to nitrite

$$CH_3COO^- + 4NO_3^- \rightarrow 4NO_2^- + 2HCO_3^- + H^+ \qquad (3)$$

and, subsequently, the conversion of nitrite to nitrogen gas.

$$3CH_3COO^- + 8NO_2^- + 5H^+ \rightarrow 4N_2\uparrow + 6HCO_3^- + 4H_2O \qquad (4)$$



Denitrification

$$NO_3^- \longrightarrow NO_2^- \longrightarrow N_2$$

$$NO_3^- \longrightarrow NO_2^- \longrightarrow (NO) \xrightarrow{fast} N_2O \xrightarrow{fast} N_2$$

Figure 1. Nitrogen cycle with emphasis on denitrification

Almeida et al. (1995a, b) and Wang et al. (1995a, b) suggest that nitrite further reacts to NO and then to N_2O before final conversion to N_2, nitrogen gas.

Organic nutrient sources for denitrification may include acetate, lactate, glucose, methanol or ethanol. Our experimental results show in Figure 2 that both nitrate and nitrite can be completely bioremediated in about 17 days under certain physical and biological conditions.

This process combines in situ processing with bioremediation. In situ techniques do not require excavation of the contaminated soils, so therefore are less expensive, create less dust, and release less contaminants than ex situ techniques. Also, it is possible to treat a large volume of soil at once. In comparison, pump and treat technology is expensive and is not believed to be cost effective at the Albuquerque South Valley site. Bioremediation is a treatment process that uses naturally occurring microorganisms (bacteria) to transform hazardous nitrate (NO_3^-) into nontoxic nitrogen gas. Bioremediation in this case can take place under anaerobic conditions. Anaerobic biological activity occurs in the absence of oxygen. Under anaerobic conditions, nitrate is the electron acceptor, whereas for aerobic conditions, oxygen is the electron acceptor. In aerobic conditions, microorganisms use available atmospheric oxygen in order to function. In both cases, microorganisms will convert organic nutrients into carbon dioxide and water.

The goal of anaerobic in situ bioremediation of nitrate contaminated groundwater is to supply nutrients (acetate, i.e., vinegar and phosphate) to the indigenous microorganisms in the soil and as the anaerobic bacteria multiply consuming the nutrients, they will chemically transform nitrate (NO_3^-) into harmless nitrogen gas (N_2).

Engineered in situ bioremediation of groundwater accelerates the biodegradation processes that take place in the saturated zone. For sites at which both the soil and groundwater are contaminated, this single technology is capable of treating both. Generally, an in situ groundwater bioremediation system consists of extraction wells to remove groundwater, an aboveground system where nutrients are added to the contaminated groundwater, and injection wells to return the "conditioned" groundwater to the subsurface where the microorganisms transform the contaminant (nitrate).

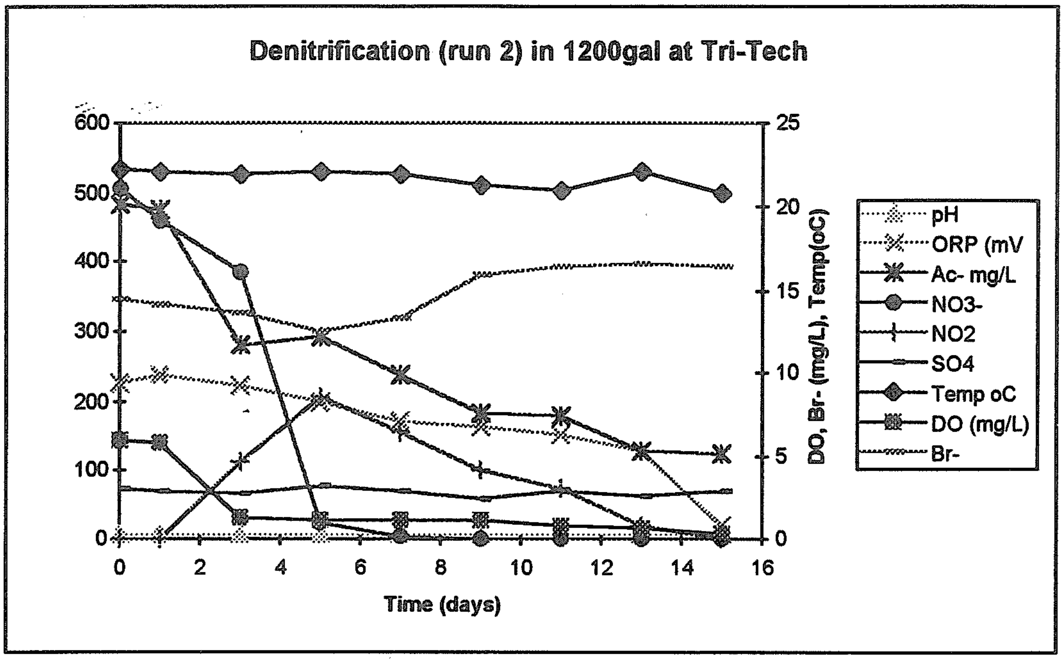


Figure 2. Concentrations versus time curves measured during denitrification in a 1,200-gallon tank.

APPLICATIONS

Presently the in situ concept is under evaluation at the Mountainview site. The project consists of three phases. Phase I, now complete, was a survey and biotreatability testing of nitrate contaminated groundwater samples from several locations in Albuquerque's South Valley. A summary of the Phase I data is tabulated in Table 1. Wells MVMW-C and Tri-Tech are only a tenth of a mile apart and are located in a nitrate plume which originated in the 1950s by over fertilization. Well MVMW-1 is immediately adjacent to one of the wastewater disposal lagoons of a dairy in Albuquerque's South Valley.

All three samples were amended with sodium acetate and trimetaphosphate to stimulate the denitrification process using the indigenous bacteria. In all three cases, the denitrifying bacteria are those naturally occurring within the groundwater. Conversion times for reduction of nitrate to levels below the EPA limit of 45 ppm (or 10 ppm N-nitrate) was 11 days. These results indicated that denitrifying bacteria were present in the groundwater and with proper amendment, the denitrification process proceeds rapidly. Many additional studies were performed using groundwater from the Tri-Tech site and they all produced similar successful results. At the Tri-Tech site, to date, we successfully denitrified above ground tanks containing contaminate water quantities of 55 gallons and 1,200 gallons. The denitrification time for these larger samples ranged from six to seventeen days. The concentration versus time curves for a typical test in the 1,200 gallon tank is given in Figure 2.

The data show that complete nitrate conversion to nitrite occurs in about 5 days followed by the completion of nitrite conversion to nitrogen gas in 15 days. Phase II studies are currently ongoing and will include the in situ testing of the process. Details of the phase II tests will be presented in a future paper.

CONCLUSIONS

At present it is believed that groundwater nitrate contamination caused primarily by over fertilization and from animal farms such as dairies. There are severe potential health problems associated with

Table 1. Results from Denitrification Tests on Water Samples from Albuquerque's South Valley

Sample	Error (%)	MVMW-1	MVMW-C	Tri-Tech
Sand (g)		8	8	8
Vol H_2O (mL)		160	160	160
Denitrification Time (days)		11	11	11
Initial Conditions:				
Acetate (mg/L)	5	1434.97	1569.02	1389.3
NO_3^- (mg/L)	5	1107.25	259.9	412.9
NO_2^- (mg/L)	5	8.15	0	0
$SO_4^=$ (mg/L)	5	434.5	136.72	73.3
TMP (mg/L)	5	20	20	20
pH of water		6.8	7.63	7.85
Temp (°C)		20	20	20
Final Conditions				
Acetate (mg/L)	5	618.55	1299.7	986.4
NO_3^- (mg/L)	5	1.875	1.89	1.8
NO_2^- (mg/L)	5	0	1.04	19
$SO_4^=$ (mg/L)	5	423.4	136.74	73.45
pH of water		7.8	8.72	8.2
Temp (°C)		20	20	20

TMP = Trimetaphosphate

drinking nitrate contaminated groundwater ranging from methemoglobinemia (blue-baby syndrome) to cancer. The problem occurs in many states and in most of the major countries throughout the world. Over 12 million people in the United States drink water contaminated by nitrate at levels above EPA's 10 ppm standard.

In situ bioremediation is a promising innovative technology for denitrification which has been demonstrated in Israel and France. These overseas experiments indicated that there are opportunities for reductions in cost and improved performance reliability. The University of New Mexico's Center for Radioactive Waste Management, in cooperation with the New Mexico Environment Department and WERC, is planning to demonstrate an improved version of the in situ denitrification technology at a nitrate contaminated site in Albuquerque's South Valley. For this technology to be fully successful, drilling costs must be reduced using new methods, and mixing of the substrate and nutrients with the nitrate contaminated groundwater must be complete and effective. We hope to demonstrate that our improved technology can achieve these improvements.

The long-term solution to the nitrate problem is pollution prevention. Countries such as Israel have aggressively begun pollution prevention programs but they estimate it will take 10-30 years for these programs to have an impact. In the interim, groundwater remediation is necessary. It also will be necessary to remediate those plumes where natural remediation processes are not occurring. Hence the development of an effective in situ denitrification process is necessary.

Acknowledgment

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