



PROJECT: Groundwater Denitrification Using a Permeable Reactive Barrier

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Abstract

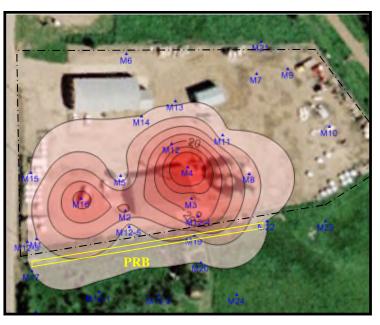
The trigger for this PINTER & Associates Ltd. (PINTER) risk management project was a groundwater nitrate plume caused by long term handling and storage of fertilizers. The nitrate plume was shown to be migrating off-site to the south towards sensitive receptors including potable water wells. Conventional treatments or full-scale remediation proved too costly and disruptive to site operations and nearby residents. Therefore, PINTER developed and designed an innovative and cost-effective permeable reactive barrier (PRB), where nitrate impacts would be removed in situ with minimal disturbance to the surrounding environment. PINTER's approach allowed for a cost savings of over 50% compared to a conventional 'dig and dump' or lagoon treatment approach. After site characterization, groundwater modeling, risk analysis, literature review, cost/benefit analysis of various alternatives and detailed design, PINTER installed a permeable reactive barrier in June 2012. Three separate transects of monitoring wells consisting of wells upstream, within the PRB and downstream of the PRB were installed in order to monitor the performance of the PRB. Monitoring results from the first fourteen months following installation show a steady decline of nitrate concentrations within the PRB. Nitrate removal expressed as a percentage was greater than 95% in the latest monitoring event. Early results show that the PRB is performing the intended purpose of removing nitrate by biological denitrification from groundwater flowing through it. Downstream receptors are no longer at risk from the groundwater nitrate plume.

Groundwater Denitrification Using a Permeable Reactive Barrier

1. Introduction

The trigger for the remediation project was the observation of elevated groundwater concentrations of nitrate during a third party investigation and clean-up. Viterra Inc. retained PINTER & Associates Ltd. in September 2010 to undertake a detailed Phase II Environmental

Site Assessment (ESA) and assist with ongoing environmental management of the Site. Previous investigations on the Site indicated shallow soil and groundwater on the Site were impacted by nutrients which have accumulated over the 40 year operation of the Site as a fertilizer distribution center. The figure to the right shows the nitrate plume as determined by PINTER's ESA work, along with the location of the installed permeable reactive barrier (PRB). Nitrate concentrations in the groundwater were as high as 1,200 milligrams per Litre (mg/L) and were traveling off-site to the south towards potable water wells.



Health Canada's maximum acceptable concentration (MAC) for nitrate in potable groundwater is 45 mg/L.

1.1. Project Objectives

Three primary objectives were set out in the Proposal-Agreement as follows.

- i. Prevent further expansion of the nitrate plume towards the adjacent property and sensitive receptors by reducing nitrate concentrations below 45 mg/L, the Health Canada MAC.
- ii. Implement a durable, cost-effective and maintenance-free system capable of long-term operation in excess of 15 years.
- iii. Improve the aesthetics and usefulness of the work area and minimize disruptions to the ongoing site operations.

Objectives not set out in the proposal, but which were integral to project success included; staying within budget, maintaining an aesthetically pleasing and safe worksite, maintaining a positive working relationship with the adjacent landowner, improving the appearance and function of the work area, and protecting the public during the remediation activities.

1.2. Evaluation and Selection of Remediation Options

Upon request from Viterra, PINTER developed preliminary designs and a comprehensive cost/benefit analysis on six alternatives for risk management of the identified groundwater nitrate

plume. Options had to meet each of the project objectives listed above. The six alternatives evaluated were:

- i. Installation of a lagoon and French drain system to treat groundwater on site.
- ii. Injection of Hydrogen Release Compound Extended Release (HRC-X) throughout the source area.
- iii. Excavation and Removal of soils across the source area.
- iv. Phytoremediation along the drainage ditch to the south of the site.
- v. Ongoing site monitoring in conjunction with improving site infrastructure and housekeeping.
- vi. Installation of a PRB to remove nitrate through biological denitrification from the groundwater plume traveling south.

The lagoon system, injection of HRC-X across the site, and excavation were eliminated due to high costs, uncertainty over whether risk management objectives could be met, and anticipated disruptions to site operation. The phytoremediation option was eliminated as it would take several seasons for results to become apparent. Monitoring alone was determined to be insufficient. Groundwater modeling and a risk analysis showed that without action, the



downstream receptors would eventually be compromised even without further additions to the source area.

It was decided to install a PRB (shown left) to intercept and nitrates through remove biological denitrification from groundwater the traveling south of the property. А literature search showed that PRBs been used had successfully for denitrification in the past; however they have mainly been used in small applications scale (PRB volume less than 100 cubic

metres) for denitrification of nitrate plumes related to sewage, at concentrations averaging only 50 mg/L of nitrate. PINTER's challenge was to design and install a much larger scale PRB to deal with nitrate concentrations in groundwater of up to 1,200 mg/L. PINTER's final design was based on detailed site information gathered during the course of two ESAs on the property and an extensive literature review encompassing both field applications of PRBs and laboratory based denitrification work. PINTER relied on in-house expertise and experience in the disciplines of hydrogeology, bioremediation, contaminant transport, groundwater modeling, biochemistry and project management to successfully meet the challenge. Nitrate specific remediation expertise was provided by Dr. Mehdi Nemati of the Chemical and Biological Engineering Department of the University of Saskatchewan.

2. Background Theory

2.1. Nitrification

The source of nitrate (NO_3^-) at the Site is the ammonia (NH_3) present in the fertilizer. The biochemical process that converts ammonia to nitrate is called nitrification. Nitrification theory describes a two-step process by which ammonia is first converted to nitrite (NO_2^-) which is in turn converted to nitrate. Oxygen is consumed at each step as an electron acceptor, and because the organisms responsible are autotrophic (derives energy from inorganic material) the process also decreases alkalinity. PINTER's assessment of the site indicated that nitrification was occurring on the site, although the process was incomplete up to approximately 10 metres (m) south of the southern property line.

2.2. Denitrification

Denitrification is a biochemical process which reduces nitrate under anaerobic conditions to nitrogen gas (N_2) through multiple steps $(NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2)$. There are several variations of denitrifying bacteria which contribute to the reduction of nitrate to nitrogen gas. They are classified as either autotrophic bacteria or heterotrophic bacteria (use organic carbon as an energy source). In each case, an electron donor is required to complete the oxidation-reduction reaction. Denitrification tends to occur in concentrated areas where oxidizable organic matter is readily available and anaerobic conditions dominate. Unlike the nitrification process the denitrification process results in increased alkalinity. PINTER's assessment indicated that an organic carbon source was the limiting factor needed to drive the denitrification process on the Site.

3. Construction and Design

The PRB was constructed in June 2012, approximately 6 m south of the southern property line of the Viterra site on the neighbouring property. The oxidizable organic matter chosen for the PRB was pine shavings (see photo below). Pine shavings were selected given their low nitrogen content compared to other types of wood. Furthermore, field applications of PRBs with pine as a carbon source have been shown to be effective in removing the majority of influent nitrate for more than 15 years after installation.



The PRB was constructed by removing native soils, mixing them pine shavings with on an approximate 2:1 volumetric basis, and returning the mixture to the excavated area. The amount of pine shavings used was determined by calculating the expected nitrate mass flux and using a mass balance approach to provide enough carbon to remove nitrate for a period of at least 30 years. In total, 960 m^3 of native soils were mixed with 480 m³ pine shavings and placed into the 120 m long x 4 m deep x 2 m wide trench. The PRB was constructed

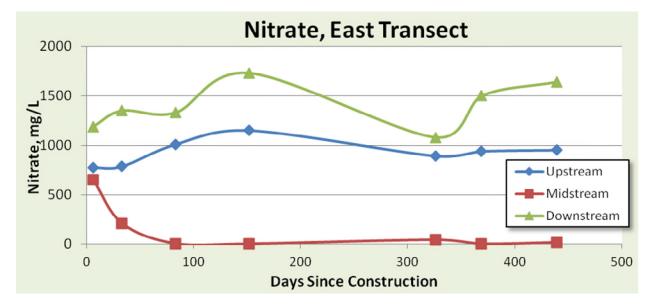
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in 20 m sections to ensure the excavated areas were filled at the end of each working day for public safety.

Groundwater monitoring wells were installed upon completion of the PRB to monitor the efficacy of the denitrification process. Nine wells were installed along three transects of the PRB. Each transect consisted of an upstream well, a midstream (center of the PRB) well, and a downstream well. Each transect allowed for monitoring of denitrification rates as groundwater moves from upstream, through the PRB, to the downstream well.

4. Results

Three key laboratory measured parameters were tracked in the area of the PRB; nitrate, Dissolved Organic Carbon (DOC), and alkalinity. Nitrate concentrations immediately upstream of the PRB have consistently maintained an average value of approximately 500 mg/L. According to literature convention, the nitrate removal within a PRB is based on the difference between the upstream nitrate value and the midstream (centre of the PRB) value. To date the PRB is effectively removing more than 95% of the nitrate from incoming groundwater. The DOC and alkalinity are significantly elevated within the PRB compared to surrounding wells, indicating that the PRB is functioning according to design. The following figure shows the measured nitrate concentrations in the upstream, midstream, and downstream wells of the east transect since construction. The east transect has the highest concentration of nitrate.



Although a decreasing trend in nitrate concentrations in the downstream wells is anticipated, it has not yet been apparent. Horizontal groundwater velocities in the area of the PRB are estimated to be about 1.5 m per year. The downstream wells are approximately 4 m south of wells within the PRB, therefore noticeable reductions in the downstream wells are anticipated in either the fall of 2014 or spring of 2015.

5. Project Highlights

5.1. The Innovation

At a scale not reported in any literature, PINTER's innovative design and construction of a PRB was able to cost-effectively reduce concentrations of nitrates in the groundwater to levels below criteria. The PRB has prevented expansion of the nitrate plume onto adjacent lands. With these achievements, PINTER met all three of the objectives set out in the proposal.

The geochemistry of a fertilizer nitrate plume is significantly different than sewage related plumes shown in literature, including but not limited to the presence of concentrations of sulphates and ammonia in excess of 1000 mg/L. With a volume of 960 m^3 , the PRB in this present work is approximately six times larger than any shown in literature and is remediating nitrate concentrations more than ten times higher than any previous work.

PINTER's success with this design means the technique is now a proven remediation or risk management tool and opens the door to other similar remediation projects worldwide where cost may be prohibitive and/or site specific considerations exclude more traditional approaches. PINTER applied for and received tax credits for portions of this work under the federal Scientific Research and Experimental Development (SR&ED) Tax Incentive Program. The program is meant to encourage Canadian businesses to conduct research and development in Canada.

PINTER's innovative work on this project has been featured in an article in the May/June 2013 issue of Environmental Science Engineering magazine, and also at the 2014 Water Technologies Symposium in April 2014. Further submissions and presentations are anticipated as ongoing monitoring results come in.

5.2. Complexity

The decision to locate the PRB on the adjoining property was driven by the desire to allow the maximum amount of nitrification upstream of the PRB, and minimize disruption Making use of the to the site. natural drainage to help keep the saturated, PRB therefore maintaining anaerobic conditions was also a benefit (see photo below). Constructing the PRB on the adjoining property required some clear discussions with the landowner regarding what the project was, why it was being done, and what the benefits to him would be.



The extremely high concentrations of nitrate, sulfate and ammonia present at the Site were well beyond anything that had been attempted with a PRB in the past. This PRB needed to be much larger, and contain a much higher proportion of woodchips than anything seen in literature to ensure its long-term effectiveness. Laboratory scale testing and computer modelling were both used to aid in the design. Results of the testing and modelling suggested that the PRB could achieve nitrate reductions greater than 90%. This allowed for the design to be finalized with a high degree of confidence.

One critical aspect of PRB design is that the hydraulic conductivity of the PRB must be greater than the surrounding soils, making the PRB the preferential path for groundwater flow. Otherwise much of the groundwater might bypass the PRB completely. Extensive testing of the PRB and surrounding area shows that the hydraulic conductivity within the PRB is approximately 20% higher than surrounding soils.

Contrary to the complexity of the PRB design was the simplicity of its installation. Conventional "dig and dump" remediation or lagoon installation require a lot of heavy equipment and truck traffic either hauling contaminated material out or clean material in. The PRB was installed with the use of a single trackhoe and skid steer, with one flat deck semi delivering the necessary pine shavings.

5.3. Social and Economic Benefits

5.3.1. Economic Sustainability

PINTER's approach provided a substantial cost savings for Viterra with a cost reduction of more than 50% compared to a conventional wastewater lagoon treatment system, or excavation and removal of the source area. Additional cost savings will be realized annually as there will be no ongoing maintenance or operational costs associated with the PRB, and site operations were never disrupted. Finally, Viterra's potential for future liabilities has been significantly reduced.

The project budget was set at \$205,900. PINTER was able to complete the project on time and on budget using sound project management practices. A project budget cost summary is provided in the following table.

SUMMARY BUDGET RELATIVE TO ACTUAL COSTS		
Element	Budget	Actual Cost
Engineering	\$ 89,000	\$ 84,300
Disbursements	\$ 25,900	\$ 20,680
Contractor	\$ 25,000	\$ 21,360
PRB materials	\$ 15,000	\$ 10,760
Monitoring	\$ 28,500	\$ 22,400
Laboratory	\$ 22,500	\$ 21,500
analysis		
TOTALS	\$ 205,900	\$ 181,000
Total Remaining From Approved Budgets : \$29,900		

5.3.2. Social Sustainability

PINTER and Viterra were able to partner with a local contractor and the Village to hire local workers for the duration of the onsite work for security, labour and equipment increasing project

efficiency, ensuring public safety, and providing an opportunity for residents to participate in the improvement and protection of the community and surrounding environment.

The adjacent landowner benefited by having his property and potable water protected, and by having access to his land improved. Prior to the PRB's construction the area possessed steep slopes and was not suitable for agriculture use. During the PRB construction the area was landscaped to reduce the slopes and direct more surface water towards the PRB. As a result the landowner was able to access the land and bale it for the first time in the fall of 2013.

5.4. Environmental Benefits

This project is of direct benefit to the surrounding environment, citizens of the Village, and to Viterra. The potential hazards to the environment and the public posed by the groundwater nitrate plume reaching sensitive off-site receptors no longer exist. In addition, the carbon footprint of the total onsite remediation and mobilization to the site was significantly less than if a conventional treatment was used.

A renewable carbon source in the form of wood chips was the only thing added to the Site. There are no undesirable emissions from the PRB as the primary byproduct of the denitrification process is nitrogen gas. Nitrogen is the major constituent of ambient air, thus its release into the environment is not of concern. The system does not require any ongoing maintenance or power for operations.

Also, previous to the work on the Site, the only use the area had been put to by the landowner was as a waste dump for metal debris and garbage. During the installation of the PRB, the garbage in the area was disposed of and the metal debris recycled.

5.5. Aesthetic Success

A notable advantage of using a PRB is the absence of any visible infrastructure associated with the solution (see photo right). Previous to the installation of the



PRB the steep slopes and metal debris in the area posed a potential hazard to anyone attempting to walk through. Now the area appears as any other part of the landowner's property and the PRB would never be noticed unless it was pointed out to a casual observer.

5.6. Meeting Client's Needs

The PRB has so far met all of the client's needs as described in the Project Objectives (Section 1.1). At the midpoint of the PRB nitrate concentrations have been shown to be reduced by more than 95%, well below the Health Canada MAC for potable groundwater. The PRB will remain operational for at least the next 15 years with absolutely no maintenance required. The installation of the PRB had very little impact on site operations and the area of the adjacent landowner's property where it was installed is now more useful than it was before the PRB

installation. All of this was achieved with a very modest budget compared to the alternatives, and at minimal risk to the public or the workers responsible for the construction.

6. Conclusions

PINTER has shown in this work that the principles of PRB denitrification can be successfully applied to nitrate plumes related to fertilizer storage at a large scale. PINTER's PRB volume was 960 cubic meters and influent nitrate concentrations were as high as 1,200 mg/L. Currently the PRB is reducing nitrate concentrations from incoming groundwater by more than 95%.

This work demonstrates that PRBs can be a cost-effective long-term risk management solution for shallow groundwater nitrate plumes. These plumes are quite common in agricultural areas throughout the world, and often lead to potable water supplies being compromised. PRBs can effectively protect sensitive receptors with minimal disturbance to the surroundings. PINTER has developed significant expertise in this area through this work and has been contracted to design and install several more PRBs for denitrification in 2014.