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# Ethanol-based *in situ* bioremediation of acidified, nitrate-contaminated groundwater

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ARTICLE INFO

*Article history:*
Received 30 April 2014
Received in revised form
28 May 2014
Accepted 11 June 2014
Available online 23 June 2014

*Keywords:*
Nitrate
*In situ* bioremediation
Denitrification
Groundwater
Vadose zone
Ethanol

ABSTRACT

A novel approach for the *in situ* bioremediation of acidified, nitrate-contaminated groundwater was developed. Ethanol was introduced into the groundwater to enhance the activity of intrinsic denitrifying micro-organisms. Infiltration of the carbon source was made via an infiltration gallery constructed in the unsaturated zone to avoid clogging problems and to allow wider distribution of ethanol in the groundwater. The changes in the groundwater geochemistry and soil gas composition were monitored at the site to evaluate the efficiencies of the infiltration system and nitrate removal. Moreover, the impact of pH and ethanol addition on the denitrification rate was studied in laboratory. A reduction of 95% was achieved in the groundwater nitrate concentrations during the study. Neither clogging problems nor inefficient introduction of ethanol into the saturated zone were observed. Most crucial to the denitrifying communities was pH, values above 6 were required for efficient denitrification.



## 1. Introduction

Nitrate from agriculture and farming is among the most frequent groundwater contaminants worldwide. Contamination arises from both point (septic tanks, leaking sewage pipes etc.) and non-point sources (fertilizers in agriculture etc.). Finland has been one of the largest suppliers of farmed fur in the world. This line of business is regionally very focused as 95 percent of the country's fur farms are found in Ostrobothnia region in Western Finland (Antikainen et al., 2009). In this area, fur farms make a significant contributor to overall phosphate and nitrate emissions to surface and groundwaters (Antikainen et al., 2009; Environmental Centre of Western Finland, 2009).

In the past, fur farms were frequently built on aquifers that were only later classified as valuable for water supply. As requirements for the management of animals waste were lacking, groundwater contamination by nitrate and nitrite were likely to happen. Later on, in the 1980s, new permissions to build fur farms onto these classified aquifers were no longer granted and since 2008, fur farming was no longer allowed there unless the farm met more strict regulations for the management of animal feces. In spite of this, groundwater contamination by nitrate and nitrite is expected to remain a problem in many of these aquifers.

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http://dx.doi.org/10.1016/j.watres.2014.06.013

Transformation of nitrate and nitrite to nitrogen gas by heterotrophic micro-organisms (denitrification) can be used in the *in situ* bioremediation of groundwater. This often requires introduction of additional carbon (C) source into the groundwater as intrinsic denitrification very often becomes carbon-limited in nitrate-contaminated aquifers (Rivett et al., 2008).

Present techniques are based on the idea that the C source is introduced directly into the groundwater. Various C sources and ways of introducing them into the saturated zone have been tested. In early studies, direct introduction of liquid C sources, such as formate (Soares et al., 1991; Smith et al., 2001), methanol, ethanol (Janda et al., 1988; Soares et al., 1991), acetate (Böckle et al., 1986; Soares et al., 1991), sucrose (Mercado et al., 1988; Soares et al., 1991) into the saturated zone was attempted. However, aquifer clogging problems due to gas formation or biomass growth and consequent malfunction or need for well maintenance were frequently reported (for review see Matějů et al., 1992; Soares and Abeliovich, 1998). Various technical solutions such as pulsing techniques (Khan and Spalding 2004; Peyton, 1996) and daisy well systems (Khan and Spalding, 2003, 2004; Gierczak et al., 2007) were then tested to overcome these problems, which, however, persisted to varying extent.

*In situ* permeable reactive barriers (PRBs) containing various solid C sources, such as straw (Boussaid et al., 1988; Warneke et al., 2011), sawdust (Robertson and Cherry, 1995; Robertson et al., 2000; Schipper and Vojvodic-Vukovic, 2001; Warneke et al., 2011), compost (Robertson et al., 2000), woodchips (Warneke et al., 2011), among others, have also been studied.

Nitrate contamination problems associated with fur farms in the Ostrobothnia region are now recognized but cost-effective remediation methods are still lacking. Aquifers in the region run typically so deep and in fracture zones that the construction of PRBs becomes expensive and technically challenging. Moreover, animal houses, the source of pollution, cover large areas at fur farms meaning that the remedial actions often need to cover large areas as well. Third relevant character of the groundwaters for which an *in situ* treatment is sought for is that they are poorly buffered and thus very prone to acidification (Rivett et al., 2008; Wilhelm et al., 1996). In the region, pristine groundwaters are typically slightly acidic (pH 5.8–6.4) (Lahermo et al., 1990). Introduction of extensive amounts of urea into the ground likely results in accumulation of nitrate and further acidification of the groundwater. Low pH often decreases the rate of denitrification significantly although the optimum pH for denitrification varies markedly in different soils (Šimek et al., 2002; Saleh-Lakha et al., 2009).

The current study was preceded by pilot scale investigations (Martin et al., 2009), where ethanol and acetate were compared as the enhancers of denitrification in sand columns at low temperature. Ethanol was regarded as slightly better option for field experiments as it had wider range of concentrations with good removal of nitrate, and lower tendency for nitrite production during the treatment. Moreover, ethanol enhanced denitrification at pH as low as 5.5 in the pilot study, which was an additional asset considering the field conditions.

The objective of the current work was to study whether liquid C source (ethanol) could be efficiently introduced into the contaminated groundwater via an infiltration gallery constructed in the unsaturated zone. The feasibility of this novel approach was tested and the operational results of a 2-year field experiment are reported. Factors limiting intrinsic denitrification were investigated in laboratory microcosms.

## 2. Material and methods

### 2.1. Site description

The research site (N 63° 20.25′, I 22° 45.04′) was located at Karkauskangas aquifer in Uusikaarlepyy municipality, in southern Ostrobothnia. Karkauskangas aquifer is an anticlinic, deep-rooted esker typical for the Ostrobothnia region (National Board of Survey, 1992), and has a total area of 2.89 $km^2$. The aquifer sediments at the site contained primarily glasifluvial sand and gravel and silt. In the south-western end of the aquifer, a small fur farm (minks and foxes) comprising two animal house units (90 m in length and 2 m in width each, Fig. 1) was in operation from 1988 to 2006. The animal houses standing on legs of roughly 1 m in height were built on bare, non-isolated land. Moreover, liquid and solid animal feces were not regularly collected and the infiltration of various substances from them was not limited in any way.

### 2.2. Aquifer parameters

Prior to the installation of the treatment system, and to find an optimal location for it, the aquifer in the area shown in Fig. 1 was characterized in terms of the properties and layering of the sediments, and groundwater geochemistry, flow direction and velocity.

Aquifer sediments and sediment layers were characterized based on drilling logs and soil type determinations. The grain size distributions were either analyzed by sieving and subsequent sedigraph measurement or estimated by eye. Twenty-five observation wells (52 mm in diameter) were installed in

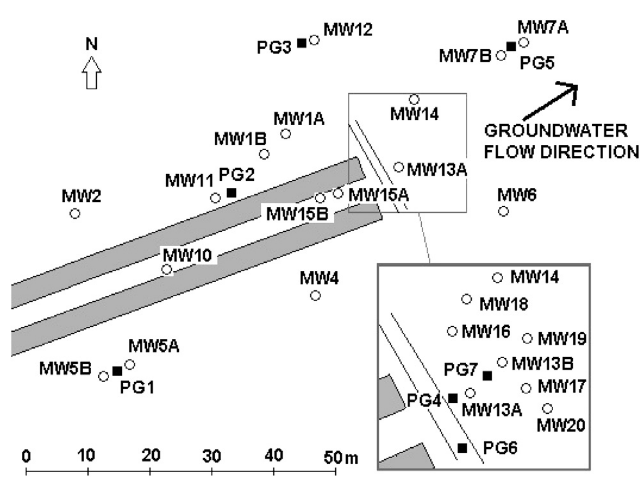


**Fig. 1 – Animal houses and the source of the contamination (animal feces) under them (gray rectangles), infiltration system (two straight lines), groundwater monitoring wells (○), pore gas wells (■), and groundwater flow direction at the Karkauskangas aquifer.**