

Simulating nitrate transport in an alluvial aquifer: a three-dimensional N-dynamics model

F. Wang¹, J. Bright¹, J. Hadfield²

¹ *Lincoln Environmental, P.O. Box 133, Lincoln, Canterbury, New Zealand*

² *Environment Waikato, Hamilton, New Zealand*

Abstract

The transport and transformation of nitrogen (N) and dissolved organic carbon (DOC) originating from point sources such as effluent discharge or pond seepage are described by using a mechanistic mathematical model. The model describes the transport and transformations of N species and other relevant chemical substances (i.e., oxygen and DOC). Rates of microbial transformations, such as mineralisation, nitrification and denitrification, are described by a Monod-type expression. A numerical code describing three-dimensional multi-component transport has been developed from FEMWATER, a finite-element numerical program developed for simulating water flow and single-component solute transport. The code was used to simulate the transport of nitrogen, discharged from the Waitahanui wastewater treatment plant, into an alluvial aquifer located east of Lake Taupo in the North Island, New Zealand. Reasonable agreements were achieved between measured and simulated concentrations at sampling wells both for non-reactive solute (chloride) and for reactive solute (organic-N, ammoniacal-N, nitrate-N and DOC). The sensitivity of nitrate-N concentrations at wells downstream of the soakage trench to effluent discharge rate and the chemical composition (i.e., nitrogen and DOC concentrations) of

the effluent was explored through numerical simulations. Simulation results show that nitrate-N concentration at downstream wells is most sensitive to the nitrogen concentration of the discharged effluent, and then to the rate of effluent discharge. The concentration of DOC in the effluent may significantly affect the rate of denitrification and thus the nitrate-N concentration in downstream wells.

Keywords

transport model, numerical simulation, nitrogen transport, denitrification, alluvial aquifer.

Introduction

One of the most common groundwater contaminants is nitrate (NO_3^-), which may originate from point or non-point sources. Effluent discharge from wastewater treatment plants and effluent seepage from wastewater treatment ponds are two common point sources of nitrate in New Zealand aquifers. A big concern is the extent to which these sources may increase nitrate concentrations in groundwater and under what conditions effluent from these ponds or plants may be sustainably assimilated by groundwater. Therefore it is necessary to predict the development of nitrate plumes and to identify

major factors affecting nitrate concentrations in groundwater by using mathematical modeling and numerical simulations.

Effluent from wastewater treatment point sources usually passes through an unsaturated zone before reaching the groundwater table. Therefore, a saturated-unsaturated three-dimensional transport model is required to describe the transport of effluent in the unsaturated zone and underlying aquifer. An important nitrogen (N) species of effluent either discharged from wastewater treatment plants or leaking from wastewater treatment ponds is ammonium, which may quickly be oxidised into nitrate in the unsaturated zone and the top layer of aquifers where oxygen is available. Once nitrate is formed, it will be transported with the groundwater. The mechanisms reducing the nitrate concentration in groundwater are mainly hydrodynamic dispersion and denitrification. To predict concentrations of nitrate originating from effluent, both nitrification (as a source of nitrate) and denitrification (as a sink for nitrate) must be included in a mathematical model. The rate of nitrification can't be predicted without knowing ammonium concentrations. Since denitrification occurs only in an anaerobic environment where oxygen concentration is low and organic compounds are available (as energy and carbon sources) (Korom, 1992), the calculation of denitrification rate would require prediction of oxygen and organic carbon concentrations. A detailed description of effluent transport in the unsaturated zone and its underlying aquifer would thus require a multi-component transport model including ammonium-N, nitrate-N, carbon and oxygen.

Researchers have developed models that predict the simultaneous transport of nitrate, oxygen and organic carbon and calculate the rate of denitrification using multiple-Monod expressions (e.g., Widdowson *et al.*, 1988; Kindred and Celia, 1989; Frind *et al.*, 1990;

Kinzelbach *et al.*, 1991; Postma *et al.*, 1991; Lindstrom, 1992). Widdowson *et al.* (1988) proposed a sophisticated model that takes into account the kinetics and interactions of organic carbon (as a substrate), oxygen and nitrate (electron acceptors), and ammonium (mineral nutrient), as well as their physical transport in one dimension. In their model, the aquifer was assumed to consist of a mobile water phase and a biological phase of microorganisms attached to the surface of the aquifer matrix. Kindred and Celia (1989) proposed a model that describes multiple-nutrient uptake kinetics coupled to a one-dimensional transport model. Baveye and Valocchi (1989) reviewed mathematical models for biologically reacting solutes in aquifers. Kinzelbach *et al.* (1991) presented a model describing the interactive transport of oxygen, nitrate, organic substrates and microbial mass in two dimensions, including the possibility of diffusion-limited exchange between different phases in the aquifer. However, the above models didn't consider effluent transport in the unsaturated zone, where nitrification and dispersion affect the input concentration of nitrate to groundwater. Their model applications were limited to one- or two-dimensional cases. MacQuarrie and Sudicky (2001) presented a three-dimensional, multi-component transport model considering physical, geochemical and biochemical processes affecting the evolution of a wastewater plume in groundwater. They used the model to simulate the transport of wastewater-derived nitrogen and carbon at a small-scale field site. In their simulation transport was assumed to be two-dimensional within the vertical profile. To apply such models to three-dimensional cases would require an amount of computer resources not usually available. Transport of nitrate and denitrification were included in models that describe the transport and biodegradation of organic compounds in aquifers (see Essaid

et al., 1995; Hunter *et al.*, 1998; Schäfer *et al.*, 1998; Brun and Engesgaard, 2002). The focus of these models is the fate of volatile and semi-volatile organic compounds, such as hydrocarbons and pesticides. Their level of detail describing transformations involving carbon compounds is greater than necessary for our modelling, in which nitrate is the major concern and organic carbon is the likely limiting factor for denitrification.

Past numerical simulations of nitrogen transport at field sites were usually two-dimensional (Kinzelbach *et al.*, 1991; MacQuarrie *et al.*, 2001). To our knowledge, three-dimensional numerical simulations of nitrogen transport at field sites with consideration of relevant microbial transformations have not been reported in the literature. The objectives of this paper were: (1) to present a mathematical model that describes three-dimensional simultaneous transport of ammonium, nitrate, oxygen and organic carbon originating from effluent discharge or pond seepage in variably saturated porous media; and (2) to apply the model to predicting the development of nitrate plumes in an alluvial aquifer at a field site in New Zealand.

Model description

For modelling the transport and transformation of nitrogen originating from effluent discharge or pond seepage, simultaneous transport and transformations of organic-N (*ON*), ammonium-N (*AN*), oxygen (*O*), substrate (*S*) (organic compounds) and nitrate-N (*NM*) in a three-dimensional unsaturated zone and aquifer domain are considered. Of the chemical components, organic-N and ammonium-N are sources of nitrate, oxygen is an electron acceptor for mineralisation, nitrification and aerobic decomposition of organic-C, and the substrate provides energy and carbon for all microbial reactions. Following Kinzelbach *et al.* (1991), we assume that aquifers are

composed of three phases: a liquid phase (*l*), a bio-phase (*b*) and a solid phase (*s*). Oxygen and nitrate exist in the liquid phase and bio-phase. Oxygen enters the aquifer via recharge water and is consumed by aerobic processes (decomposition of organic matter and nitrification). Nitrate comes from effluent discharge and from nitrification, and it may be transformed into gaseous nitrogen through denitrification. The substrate in the bio-phase, which is available for microbial reactions, is supplied from recharge water and by release from solid phase, and is consumed by all microbial reactions. All microbial reactions take place in the bio-phase. The exchange of mass between phases is controlled by mass transfer coefficients.

With the above assumptions, which are summarised in Table 1, we may write the mathematical model as a set of mass balance equations, and the equations describing relevant source and sink terms, and initial and boundary conditions.

Mass balance equations

The mass balance equations for the five chemical components are given below.

Organic-N (*ON*)

$$\frac{\partial(\theta_l c_l^{ON})}{\partial t} + \frac{\partial(\rho_s c_s^{ON})}{\partial t} = L(c_l^{ON}) + \mathfrak{R}_{b \rightarrow l}^{ON}, \quad (1)$$

$$\frac{\partial(\theta_b c_b^{ON})}{\partial t} = -\mathfrak{R}_{b \rightarrow l}^{ON} - \mathfrak{R}_{min}^N, \quad (2)$$

where c_l^{ON} , c_s^{ON} and c_b^{ON} are concentrations of organic-N in the liquid phase (M/L³ water), solid phase (M/M solids) and bio-phase (M/L³ bio-phase), respectively, θ_l and θ_b are volumetric fractions of the liquid phase (L³ water/L³ medium) and bio-phase (L³ bio-phase/L³ medium), respectively, ρ_s is the bulk density (M solids/L³ medium), $\mathfrak{R}_{b \rightarrow l}^{ON}$ is the rate of organic-N transfer from bio-phase to liquid phase (M/T/L³ medium),

Table 1 – Summary of the N-dynamics model

Component	Symbol	Phases			Source Processes	Sink Processes
		Liquid	Bio-phase	Solid		
Organic-N	<i>ON</i>	√	√	√	Effluent discharge	Mineralisation
Ammonium-N	<i>AN</i>	√	√	√	Effluent discharge mineralisation	Nitrification
Nitrate-N	<i>NN</i>	√	√		Effluent discharge nitrification	Denitrification
Substrate	<i>S</i>	√	√	√	Effluent discharge	Organic-C decomposition, denitrification
Oxygen	<i>O</i>	√	√		Supply via air diffusion	Organic-C decomposition, nitrification

Note: √ represents that the chemical exists at this phase.

\mathfrak{R}_{\min}^N is the rate of organic-N mineralisation (M/T/L³ medium), and L is a differential operator representing the advection and dispersion terms.

Ammonium-N (*AN*)

$$\frac{\partial(\theta_l c_l^{AN})}{\partial t} + \frac{\partial(\rho_s c_s^{AN})}{\partial t} = L(c_l^{AN}) + \mathfrak{R}_{b \rightarrow l}^{AN}, \quad (3)$$

$$\frac{\partial(\theta_b c_b^{AN})}{\partial t} = -\mathfrak{R}_{b \rightarrow l}^{AN} + \mathfrak{R}_{\min}^N - \mathfrak{R}_{nit}^N, \quad (4)$$

where c_l^{AN} , c_s^{AN} and c_b^{AN} are concentrations of ammonium-N in the liquid phase (M/L³ water), solid phase (M/M solids) and bio-phase (M/L³ bio-phase), respectively, $\mathfrak{R}_{b \rightarrow l}^{AN}$ is the rate of ammonium-N transfer from the bio-phase to liquid phase (M/T/L³ medium), and \mathfrak{R}_{nit}^N is the rate of nitrification (M/T/L³ medium).

Oxygen (*O*)

$$\frac{\partial[(\theta_g H^O + \theta_l) c_l^O]}{\partial t} = L(c_g^O) + L(c_b^O) + \mathfrak{R}_{b \rightarrow l}^O, \quad (5)$$

$$\frac{\partial(\theta_b c_b^O)}{\partial t} = -\mathfrak{R}_{b \rightarrow l}^O - \mathfrak{R}_{nit}^O - \mathfrak{R}_{aer}^O, \quad (6)$$

where H^O is the Henry's law constant for oxygen (L³ water/L³ air), θ_g is the volumetric content of the gas phase (L³ air/L³ medium), c_l^O and c_b^O are concentrations of oxygen in the liquid phase (M/L³ water) and bio-phase (M/L³ bio-phase), $\mathfrak{R}_{b \rightarrow l}^O$ is the rate of oxygen transfer from the bio-phase to liquid phase (M/T/L³ medium), and \mathfrak{R}_{nit}^O and \mathfrak{R}_{aer}^O are rates of oxygen consumption by nitrification and aerobic decomposition of organic-C (M/T/L³ medium).

Substrate (S)

$$\frac{\partial(\theta_l c_l^S)}{\partial t} = -\frac{\partial(\rho_s c_s^S)}{\partial t} = L(c_l^S) + \mathfrak{R}_{b \rightarrow l}^S + \mathfrak{R}_{s \rightarrow l}^S, \quad (7)$$

$$\frac{\partial(\theta_b c_b^S)}{\partial t} = -\mathfrak{R}_{b \rightarrow l}^S + \mathfrak{R}_{aer}^S - \mathfrak{R}_{den}^S, \quad (8)$$

$$\frac{\partial(\theta_s c_s^S)}{\partial t} = -\mathfrak{R}_{s \rightarrow l}^S, \quad (9)$$

where c_l^S , c_b^S , c_s^S are concentrations of substrates in the liquid phase (M/L³ water), solid phase (M/M solids) and bio-phase (M/L³ bio-phase) respectively, \mathfrak{R}_{aer}^S and \mathfrak{R}_{den}^S are rates of substrate consumption by aerobic decomposition of organic-C and denitrification (M/T/L³ medium) respectively, and $\mathfrak{R}_{s \rightarrow l}^S$ and $\mathfrak{R}_{b \rightarrow l}^S$ are exchange rates of substrates between phases (M/T/L³ medium).

Nitrate-N (NN)

$$\frac{\partial(\theta_l c_l^{NN})}{\partial t} + \frac{\partial(\rho_s c_s^{NN})}{\partial t} = L(c_l^{NN}) + \mathfrak{R}_{b \rightarrow l}^{NN}, \quad (10)$$

$$\frac{\partial(\theta_b c_b^{NN})}{\partial t} = -\mathfrak{R}_{b \rightarrow l}^{NN} + \mathfrak{R}_{nit}^N - \mathfrak{R}_{den}^N, \quad (11)$$

where c_l^{NN} and c_b^{NN} are concentrations of nitrate-N in the liquid phase (M/L³ water) and bio-phase (M/L³ bio-phase), $\mathfrak{R}_{b \rightarrow l}^{NN}$ is the rate of nitrate-N exchange between the liquid phase and bio-phase (M/T/L³ medium), and \mathfrak{R}_{den}^{NN} is the rate of nitrate-N consumption by denitrification (M/T/L³ medium).

Source and sink terms

Adsorption

By using the linear isotherm, we have

$$c_s^\gamma = \kappa_d^\gamma c_l^\gamma, \quad (12)$$

where γ represents organic-N (ON) or ammonium-N (AN) and κ_d^γ is a coefficient

of solute distribution between the solid and liquid phases (L³ water/M solid).

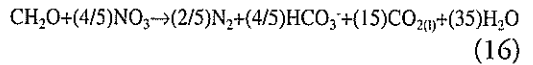
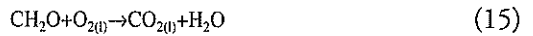
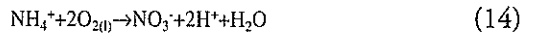
Mass transfer between phases

$$\mathfrak{R}_{b \rightarrow l}^\gamma = \alpha^\gamma (c_b^\gamma - c_l^\gamma), \quad \mathfrak{R}_{s \rightarrow l}^\gamma = \beta (c_s^\gamma - c_l^\gamma), \quad (13)$$

where α^γ and β are coefficients of mass exchange between phases (1/T), and γ represents chemical component ON, AN, O, S, or NN.

Nitrogen and carbon transformations

Reaction stoichiometry of nitrification, aerobic decomposition of organic carbon and denitrification may be approximated (MacQuarrie and Sudicky, 2001) as:



N and C transformation rates are calculated using multiple Monod kinetics model as:

$$\mathfrak{R}_{min}^N = V_{min}^{\max} (1 - fo) \frac{c_b^{ON}}{K_{min}^{ON} + c_b^{ON}} \frac{c_b^O}{K_{min}^O + c_b^O}, \quad (17)$$

$$\mathfrak{R}_{nit}^N = V_{nit}^{\max} (1 - fo) \frac{c_b^{AN}}{K_{nit}^{AN} + c_b^{AN}} \frac{c_b^O}{K_{nit}^O + c_b^O}, \quad (18)$$

$$\mathfrak{R}_{aer}^S = V_{aer}^{\max} (1 - fo) \frac{c_b^S}{K_{aer}^S + c_b^S} \frac{c_b^O}{K_{aer}^O + c_b^O}, \quad (19)$$

$$\mathfrak{R}_{den}^N = V_{den}^{\max} fo \frac{c_b^S}{K_{den}^S + c_b^S} \frac{c_b^{NN}}{K_{den}^{NN} + c_b^{NN}}, \quad (20)$$

where V^{\max} is a maximum rate (M/T/L³ medium), K is a half-rate concentration (M/L³ bio-phase), and fo (dimensionless) is a switch function between aerobic and denitrifying bacteria growing conditions, which is expressed as (Kinzelbach *et al.*, 1991),

$$f_o = 0.5 - \frac{1}{\pi} \arctan\left(\left(c_b^o - O_t\right) f_{st}\right), \quad (21)$$

where f_{st} and O_t are the slope and the threshold oxygen concentration, respectively.

Oxygen consumption

Oxygen consumption in processes of nitrification and aerobic organic carbon decomposition may be calculated as:

$$\mathfrak{R}_{nit}^O = \frac{1}{y_{nit}^O} \mathfrak{R}_{nit}^N, \quad \mathfrak{R}_{aer}^O = \frac{1}{y_{aer}^O} \mathfrak{R}_{aer}^S, \quad (22)$$

where y_{nit}^O is the ratio of N consumption to oxygen consumption in the process of nitrification (M nitrogen/M oxygen), and y_{aer}^O is the ratio of substrate to oxygen consumed in the process of aerobic organic-C decomposition (M substrate/M oxygen).

Substrate consumption

Substrate (organic carbon) consumption in the process of denitrification is calculated as:

$$\mathfrak{R}_{den}^S = \frac{1}{y_{den}^S} \mathfrak{R}_{den}^N, \quad (23)$$

where y_{den}^S are ratios of N consumption to substrate consumption in the process of denitrification (M nitrogen/M substrate), respectively.

Boundary conditions

Cauchy boundary conditions are used for boundaries with specified solute fluxes, such as land surfaces, the bottom faces of soakage trenches and treatment ponds. Dirichlet boundary conditions are used for soil-water interfaces such as rivers and lakes.

Numerical model and verification

The mathematical model consists of 11 partial differential equations (Equations (1) to (11)), which are coupled by source or sink

terms expressed by Equations (12), (13) and (17) to (23). To solve these transport equations, the distribution of flow velocity must first be obtained by solving the equation describing water flow in the saturated and unsaturated subsurface. Assuming that the total concentration of dissolved chemicals is small, the effect of water density on flow velocity can be neglected and thus the equations for water flow and solute transport can be solved sequentially.

FEMWATER, a well-known and tested computer code, was modified to simulate flow and the transport of multiple reactive solute in the saturated-unsaturated zone of the subsurface. A detailed description of the numerical scheme used in FEMWATER can be found in Lin *et al.* (1997). An operator-splitting method was used to separate the transport (partial differential equations) and reaction (algebraic equations) operators, and solve them iteratively within each time step. The transport operator was further separated into a pure dispersion part and a pure advection part, which are solved by the Galerkin finite element method and the particle tracking method, respectively.

Since FEMWATER has been widely used and tested, verification of the numerical code was conducted only for reactive solute transport with Monod source/sink terms. Tests for three-dimensional cases were conducted by reducing or increasing the half-rate constant of the Monod expression, leading to a zero- or first-order rate expression for nitrification and denitrification, and then comparing results obtained from our code with those from the original FEMWATER code that can model the transport of single component chemical with zero- or first-order decay. With both the increased and reduced half-rate constants, the simulation results from our code converged to those from the original FEMWATER code.

Simulating nitrogen transport in an alluvial aquifer

Site description

Since November 1988 treated effluent from the Waitahanui wastewater treatment plant at Taupo has been discharging into the subsurface just above the groundwater table of an alluvial aquifer that supplies water for much of the Waitahanui community. The aquifer comprises at least 30 m of pumiceous sand, which is the reworked alluvial product of the Taupo volcanic eruption. The depth to the groundwater table ranges from 1.5 m near Lake Taupo to 5.5 m near the wastewater treatment plant. The transmissivity and effective porosity were estimated to be 900–2500 m²/day and 0.38–0.43, respectively (Hadfield, 1995). The region of this investigation (see Figure 1) is the triangular area defined by Lake Taupo, Waitahanui River and the boundary between the volcanic plateau and alluvial sediments; its area is about 0.8 km².

The high ambient groundwater quality at Waitahanui enables the contaminant plume to be delineated by nitrate-N, chloride and electrical conductivity over a distance of nearly 500 m. Nitrate-N concentrations are attenuated (by denitrification, diffusion and dispersion) below health guidelines for drinking water before reaching the nearest domestic wells. Hadfield (1995) conducted a comprehensive investigation of the geological, hydrological and hydrogeological conditions of the area and constructed a two-dimensional numerical model of water flow and conservative solute transport in the alluvial aquifer. The discrepancy between his simulation results and measured data suggests that denitrification occurs in the aquifer. Therefore, an N transport model considering denitrification may better predict the distribution of nitrate and reduce the discrepancy between model predictions and measured data. As denitrification occurs only

at anaerobic sites with available substrates, it may be more accurately modelled by the N model described here, which models the simultaneous transport of oxygen, substrates and N species, than by models that describe denitrification as a first-order or zero-order degradation. Since the plume in the aquifer is three dimensional, a two-dimensional model cannot predict the distribution of concentrations of chemicals along the vertical direction and thus cannot calculate rates of N transformations accurately. Therefore we shall use our three-dimensional N-dynamics model to simulate the transport and transformations of N species (organic-N, ammonium and nitrate) and relevant chemical components (oxygen and Dissolved Organic Carbon) at this site.

Effluent discharge

The Waitahanui wastewater treatment plant was commissioned in November 1988. The effluent discharge rate and its chloride and nitrogen concentrations were measured from 1990 to 1994. After 1994, no measurements were taken on the rate of effluent discharge or the chemical composition of the effluent. Based on monitoring data, it is estimated that there has been no significant change in chloride concentration since the commissioning of the plant. However, nitrogen concentration has been decreasing due to improvements in the efficiency of the sewage treatment plant. With the increase in the population of the area, the rate of effluent discharge has increased with time and thus the annual nitrogen loading into the groundwater has been approximately constant.

Groundwater sampling

Groundwater table and quality surveys were conducted in 25 piezometers on two occasions in July 1993 and March 1994 (Fig. 1). Of these piezometers, 12 were selected to monitor temporal changes of

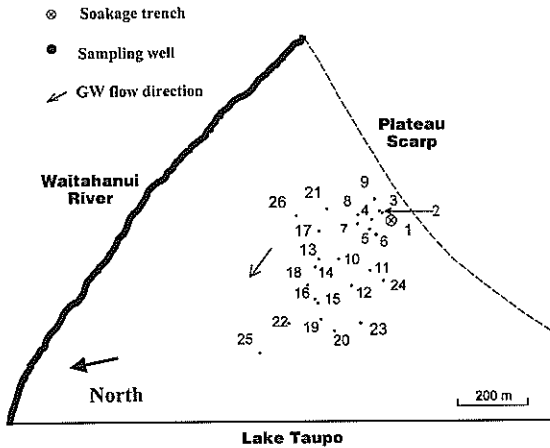


Figure 1 – Map showing the model domain and locations of sampling wells and the soakage trench for discharging treated wastewater.

groundwater table and contaminant concentrations. During the monitoring period from July 1993 to June 1994, ten measurements of groundwater table and ten water samples were taken approximately monthly. Samples were taken from the top 0.4 m of the water column below the groundwater table, which was isolated using a pneumatic packer. The depth distributions of contaminants were investigated at two driven piezometers located near sampling wells 2 and 17, respectively. Samples were extracted at four or nine depths below the groundwater table.

All samples collected were analysed for concentrations of chloride, ammonium-N, and nitrate-N. Samples collected on September 1999 and March 2000 were also analysed for dissolved organic carbon (DOC) and dissolved oxygen (DO).

Selection of model parameters

Chemicals simulated in the model were chloride, organic-N, ammoniacal-N, nitrate-N, oxygen and DOC. Values of the model parameters related to chemicals transport are shown in Table 2. The values of some parameters are specified based on values reported in the literature or calculated from

reaction stoichiometry. Dispersivity values were obtained by calibrating the simulated chloride plume against the measured one. Other parameters were obtained by calibrating simulated results from the simultaneous modelling of organic-N, ammoniacal-N, nitrate-N, oxygen and DOC against measured concentrations. Concentrations of the simulated chemicals in the treated effluent, ambient groundwater, Waitahanui River, Lake Taupo and rain water are shown in Table 3.

Following Hadfield (1995), the aquifer is assumed to be homogeneous and its hydraulic conductivity and porosity are approximately 40 m/day and 0.4, respectively. The soil in the unsaturated zone is a highly permeable sand or sandy loam. Since no measured data were available, soil hydraulic conductivity, moisture content, and water capacity curves were taken from the technical report (Lin *et al.*, 1997).

The lateral boundaries (Fig. 1) are specified by either pressure-head (along Lake Taupo and the Waitahanui River) or water-flux (along the plateau scarp). As is shown in Figure 2, the upper boundary is the land surface and its elevation changes with its horizontal position. The lower boundary is set at the bottom of the aquifer, which is assumed to be horizontal and is 35 to 42 m below the ground surface.

The aquifer was discretised into 19 layers with thicknesses between 1 m (for the top layers) and 5 m (for bottom layers) (see Figure 2). Each layer is divided into a number of hexahedrons. Most of hexahedrons are $50 \times 50 \text{ m}^2$ in the horizontal plane. Smaller hexahedrons ($5 \times 50 \text{ m}^2$) were used for areas near the effluent discharge trench.

To model the effluent discharge from the trench, the discharge rate and the physical mixing between discharged effluent and groundwater must be accurately represented

Table 2 – Values of model parameters used in numerical simulations.

Name	Symbol	Value	Unit	Source
Longitudinal dispersivity	α_L	10	m	1)
Transverse dispersivity	α_T	0.04	m	1)
Distribution coefficient of organic-N	κ_d^{ON}	5.0	l water/g solid	2)
Distribution coefficient of ammoniacal-N	κ_d^{AN}	5.0	l water/g solid	2)
Bio-phase fraction	θ_b	0.05	// l	1)
Exchange coefficient	α	0.1	day ⁻¹	1)
Exchange coefficient	β	0.0002	day ⁻¹	1)
Maximum mineralisation rate	V_{min}^{max}	1.0	mg/l/day	1)
Maximum nitrification rate	V_{nit}^{max}	10.0	mg/l/day	1)
Maximum aerobic C-decomposition rate	V_{aer}^{max}	0.001	mg/l/day	1)
Maximum denitrification rate	V_{den}^{max}	1.0	mg/l/day	1)
Half rate concentration	K_{min}^{ON}	6.0	mg/l	1)
Half rate concentration	K_{min}^{ON}	0.2	mg/l	1)
Half rate concentration	K_{nit}^{AN}	6.0	mg/l	1)
Half rate concentration	K_{nit}^O	0.2	mg/l	1)
Half rate concentration	K_{aer}^S	6.0	mg/l	3)
Half rate concentration	K_{aer}^O	0.2	mg/l	3)
Half rate concentration	K_{den}^{NN}	6.0	mg/l	1)
Half rate concentration	K_{den}^S	6.0	mg/l	1)
Ratio of N to O consumed in nitrification	y_{nit}^O	0.219	dimensionless	4)
Ratio of substrate to O consumed in aerobic organic-C decomposition	y_{aer}^O	0.375	dimensionless	4)
Ratio of N to substrate consumed in denitrification	y_{den}^S	0.934	dimensionless	4)
Threshold oxygen concentration	O_t	0.2	mg/l	3)
Slope of the function representing oxygen effect on denitrification	f_{sl}	10.0	(mg/l) ⁻¹	3)

Notes:

- 1) Obtained through model calibration;
- 2) Based on the assumption that the aquifer material has a moderate adsorption capacity;
- 3) From Kinzelbach *et al.* (1991); 4) Calculated from reaction stoichiometry (equations (14)-(16)).

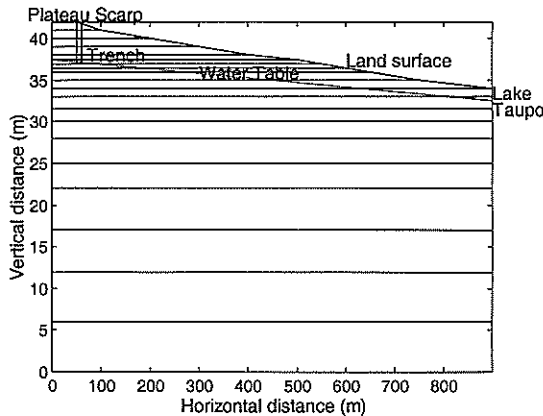


Figure 2 – A cross-section view from the Plateau Scarp near the soakage trench along the groundwater flow direction to Lake Taupo. Horizontal lines show the discretisation of the model domain in the vertical direction.

in the model. Here the effluent discharge trench (36 m long and 1.4 m wide) is represented in the model as an inner flux-specified boundary over the horizontal face of a numerical element. The boundary is 50 m long and 5 m wide and located at a depth of 5 m below the ground surface. This guarantees that the discharge rate is represented accurately. At the same time the mixing effect caused by the forced discharge is accounted for, though not accurately, through using a flux-specified elemental face larger than the actual size of the trench.

Model calibration

Due to limited available data, we use the average values of model inputs to model the flow and transport in the aquifer. Therefore calibration results represent only the average state of groundwater flow and plume distribution, and are compared against the average measured data when calibrating model parameters. Based on measurements, we set the rate of treated effluent discharge at 89 m³/day. Concentrations of chemicals in the discharged treated effluent are shown in Table 3.

Table 3 – Concentrations of chemical species used in numerical simulations.

Species	Initial value	Source	River	Lake	Rainfall water
Chloride	3.55	40.0	3.0	9.3	1.0
Organic-N	0.0	2.0	0.0	0.0	0.3
Ammonium-N	0.019	13.8	0.014	0.005	0.2
Nitrate-N	0.13	23.7	0.193	0.005	0.2
DO	6.0	2.06	6.0	6.0	7.0
DOC	2.0	7.7	0.0	0.0	2.0

Groundwater table contour

Measured data (Hadfield, 1995) show that the seasonal variation in groundwater table is less than 0.5 m near the discharge trench and less than 0.25 m away from the trench. Hence the average state of groundwater flow can be approximated by a steady-state solution. By using a constant rate of rainfall recharge and constant specified pressure heads or fluxes on boundaries, a steady-state groundwater table was obtained through numerical simulation. Following Hadfield (1995), the rate of rainfall recharge was set to 350 mm/year. The pressure head along Lake Taupo is 356.5 m (above sea level) and the pressure head along the Waitahanui River increases from 356.5 m, at the intersection of the lake and the river, to 362.5 m at the upstream point of the model domain. Water input through seepage along the plateau boundary was estimated from the water balance at about 11,200 m³/day. The distribution of seepage flux along the boundary was determined by model calibration. Simulation results showed that the flux was not constant, but increased from 0.14 to 0.34 m³/day/m² toward the lake.

Chloride distribution

Due to its conservative property, chloride was simulated first to calibrate the dispersivities of the aquifer. The best agreement (i.e., the sum of the squared error between measured and simulated concentrations is

minimum) was achieved when longitudinal and transverse dispersivities were 10 m and 0.04 m. The comparison between measured data and simulation results are shown in Figures 3, 4(a) and 5. The very low value of transverse dispersivity is consistent with the high permeability of the aquifer material (pumiceous sands) and the near steady-state flow condition. As discussed by Gelhar (1997) and tested by a field experiment at a site near Regina in Canada (Van der Kamp *et al.*, 1994), transverse dispersivity may be very low in highly permeable sand and gravel aquifers under very steady flow conditions. Figure 3 shows that simulated chloride concentrations in most of the sampling wells are in agreement with measured ones. Significant discrepancy exists in some wells however. This might be caused by the small-scale spatial variation of hydraulic properties in the aquifer. Figure 4(a) shows that the measured vertical distribution of chloride in sampling well 17 and in a piezometer close to well 17 is in reasonable agreement with the simulated distribution. Figure 5 compares simulated (thick line) and measured (thin line) chloride plumes, with a cutoff concentration of 6 mg/l at the plane just below groundwater table. It shows that the complex irregular measured plume could not be exactly matched by the simulated plume. But the agreement between the two plumes is still reasonably good, given that the spatial variation in hydraulic properties was not considered in our simulation.

Ammoniacal-N and nitrate-N distribution

Measured data show that treated effluent consists of about 5% organic-N, 35% ammoniacal-N and 60% nitrate-N. It is believed that the small amount of organic-N is quickly mineralised into ammonium, since

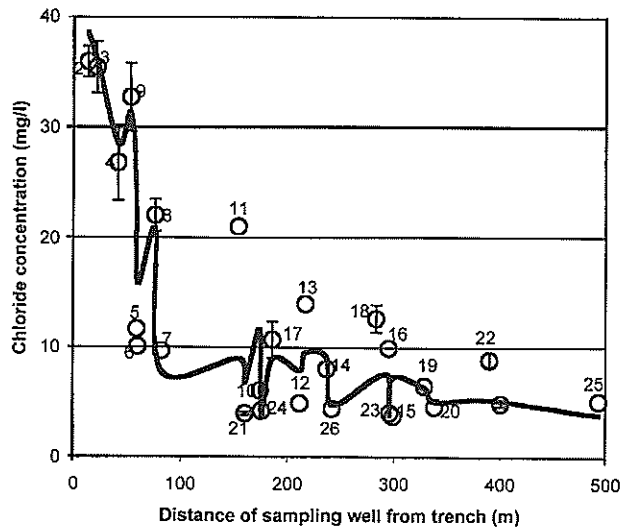


Figure 3 – Comparison between simulated chloride concentrations (thick line) and measured concentrations (circles for averages and vertical segments for one standard deviation from the averages) at sampling wells.

no organic-N was detected in groundwater samples. Simulation results are compared against measured data in Figures 4(b), 6 and 7. Figures 4(b) and 6 show that simulated nitrate-N concentrations of groundwater samples are significantly larger than measured ones when denitrification is not included in the simulation. The Mean Squared Error (MSE) (shown in Figure 6) between model predictions and measurements decreased from 24.9 (mg/l)² to 15.0 (mg/l)² when denitrification is included in modelling. Figure 7 also shows that when denitrification isn't considered, the simulated nitrate-N plume occupies a significantly larger area than the measured plume, and that the discrepancy was significantly reduced by adding denitrification in our simulation. Therefore denitrification played an important role in reducing nitrate-N concentrations of groundwater at this site. Figure 8 shows that ammoniacal-N exists only at wells close to the effluent discharge trench and it is soon oxidised into

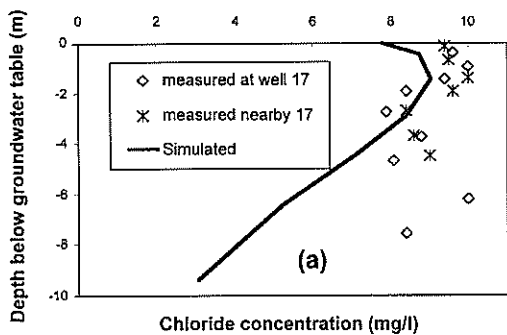


Figure 4 – Comparison between simulated and measured vertical distributions of (a) chloride, (b) nitrate-N, (c) DOC, and (d) oxygen, at well 17; DN represents denitrification.

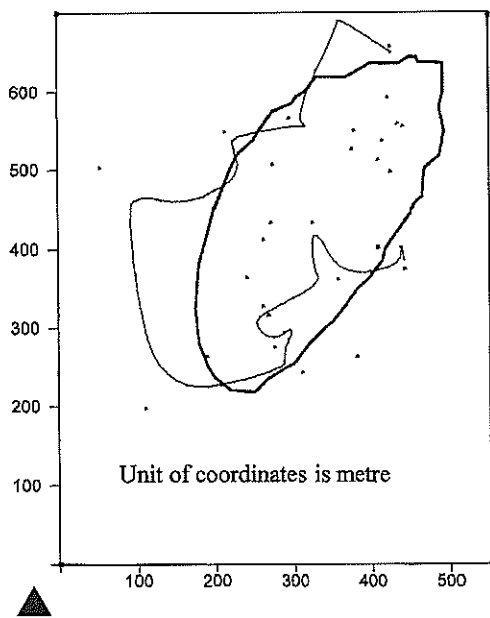
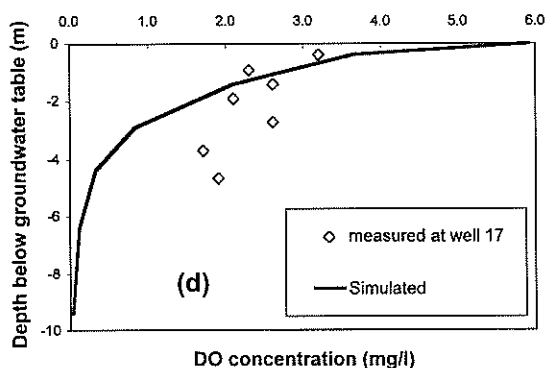
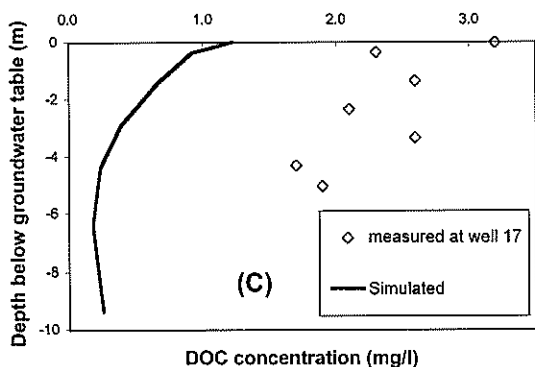
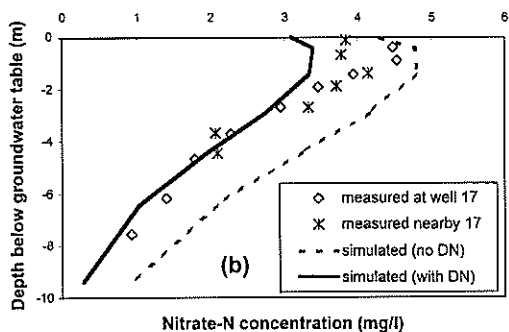


Figure 5 – Comparison between measured (thin line) and simulated (thick line) chloride plumes with a cutoff concentration of 6 mg/l at the plane just below groundwater table. Symbols represent locations of sampling wells; units of both coordinates are metres.

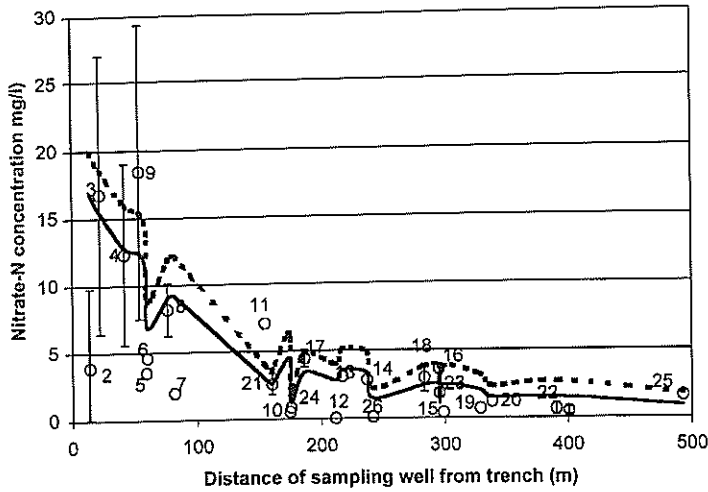


Figure 6 – Comparison between simulated and measured nitrate-N concentrations at sampling wells. The solid line is simulation with denitrification; the dashed line is simulation without denitrification. Circles are averages and vertical segments are one standard deviation from the averages.

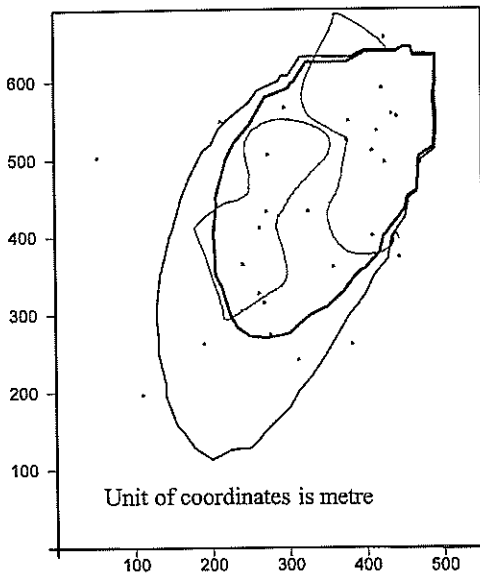


Figure 7 – Comparison between nitrate-N plumes with a cutoff concentration of 2 mg/l at the plane just below groundwater table. Measured values are shown by the thinnest line; simulated values are shown by the thickest line (for simulation with denitrification) and second thickest line (for simulation without denitrification). Symbols represent the locations of sampling wells; the units of both coordinates are metres.

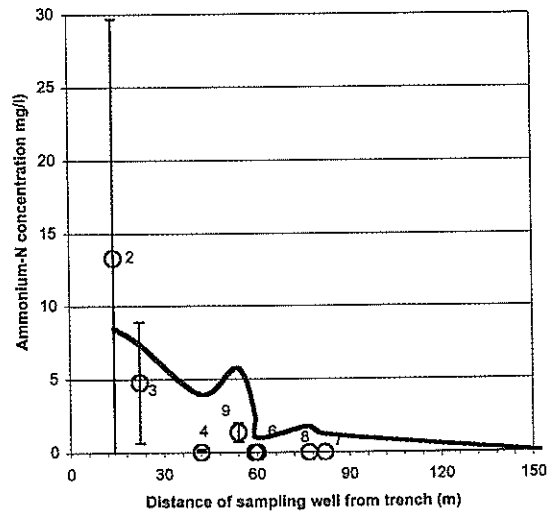


Figure 8 – Comparison between ammoniacal-N concentrations at sampling wells. Simulated values are shown by the solid line and measured values by circles (averages) and vertical segments (one standard deviation from the averages).

nitrate. The simulated ammoniacal-N concentrations are higher than measured ones at all wells except at well 2, although a large value of the maximum nitrification rate, 10 mg/l/day, was used. Further increasing the maximum nitrification rate only slightly increased nitrate-N concentrations at wells close to the discharge trench, and other factors, such as smaller effluent ammonium concentrations, may have contributed to the lower measured ammoniacal-N concentrations. We therefore chose not to change the maximum nitrification rate of 10 mg/l/day in our simulations.

DOC and DO distribution

Figures 4(c) and 8 show the comparison between simulated and measured DOC concentrations at sampling wells. The simulated DOC concentrations are significantly lower than measured values at wells 2, 3, 4, 5 and 17, which are close to the discharge trench. This suggests that the actual DOC concentration in the discharged effluent may be higher than the concentration used in our simulation. Figure 9 shows that both the measured and simulated concentrations of DOC decreased with distance away from the trench until 80 m, where DOC started increasing with distance. The DOC concentrations at wells close to the trench are higher than at other wells, probably because the effluent itself provides a major source of the organic carbon that is used in denitrification. The recovery of DOC concentration with distance from plume centre is caused by the decreasing denitrification rate and thus the consumption rate of DOC. Simulated and measured concentrations of dissolved oxygen (DO) are compared in Figures 4(d) and 10. It is evident that the DO concentration is low at wells close to the discharge trench and decreases with depth below the water table. This is the result of

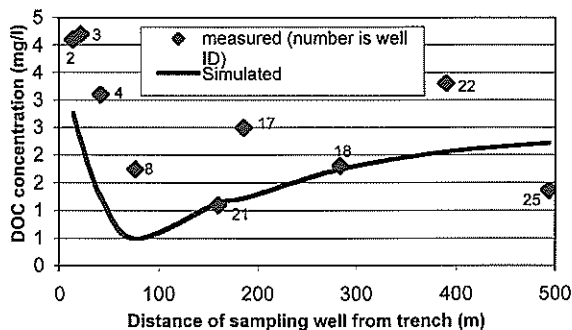


Figure 9 – Comparison between simulated (solid line) and measured (diamonds) dissolved organic carbon (DOC) concentrations at sampling wells.

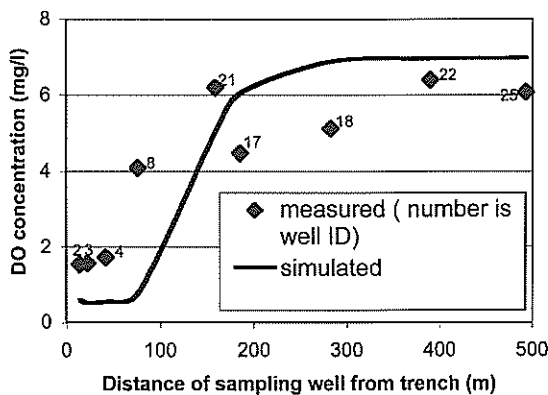


Figure 10 – Comparison between simulated (solid line) and measured (diamonds) dissolved oxygen (DO) concentrations at sampling wells.

aerobic degradation of DOC, organic-N mineralisation, and nitrification, which occur mainly in the area surrounding the trench.

Sensitivity of the nitrate-N plume to model inputs

Due to the lack of detailed measurements of model inputs, the model was calibrated under steady-state flow and transport conditions. Numerical simulations were conducted to investigate how nitrate-N concentrations at wells downstream of the trench are affected by factors such as temporal

variation in effluent discharge, the DOC concentration of the effluent, and the rate of nitrogen loading from effluent discharge.

Seasonal variation in effluent discharge

Measured data show that both the rate of effluent discharge and the N concentration of treated effluent change with time. Two simulations were conducted that consider temporal variations in effluent discharge rate and in nitrogen concentration of effluent. Results are shown in Figures 11 and 12. It is evident that nitrate-N concentrations at wells 3 and 6 (thin solid lines (3) and (5)), which are only 22 and 60 m away from the trench, followed the temporal variations in effluent discharge rate and in nitrogen concentration of discharged effluent (dotted lines (1)). Nitrate-N concentration at the closest domestic well (well 13, as shown in thick solid line (7)) changed only slightly with variations in effluent discharge. In other wells downstream of well 13, nitrate-N concentrations changed even less with time (not shown here), due mainly to solute dispersion. Since the variation in N concentration decreases with increasing distance from the soakage trench, it is reasonable to use an average rate of effluent discharge in running simulations for long time periods, if the area of interest is sufficiently far away from the effluent discharge source.

Dissolved Organic Carbon concentration of the effluent

Figure 13(a) shows that nitrate-N concentrations at wells along the plume central line decrease with increasing concentration of DOC in treated effluent. As shown in Figure 13(b), increasing the amount

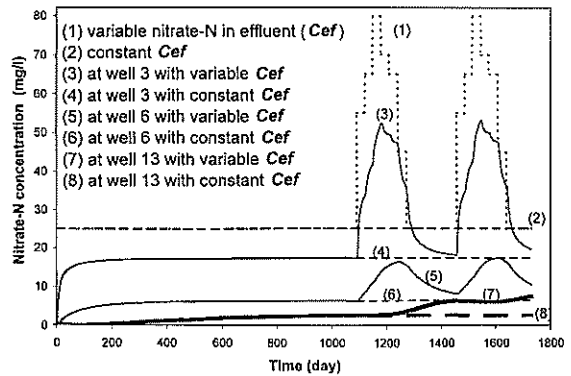


Figure 11 – Influence of the temporal variation in nitrate-N concentration of treated effluent (*Cef*) on nitrate-N concentrations at sampling wells 3, 6 and 13, which are 22, 60 and 217 m from the soakage trench, respectively.

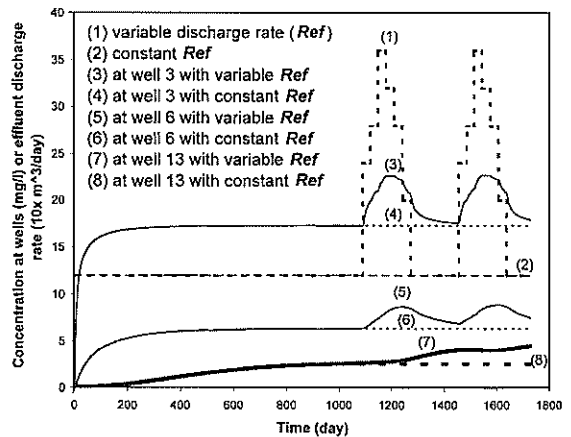


Figure 12 – Influence of the temporal variation in effluent discharge rate (*Ref*) on nitrate-N concentrations at sampling wells 3, 6 and 13, which are 22, 60 and 217 m from the soakage trench, respectively.

of DOC available from the solid phase of the aquifer or from recharging water (i.e., increasing the value of *b*) may enhance denitrification.

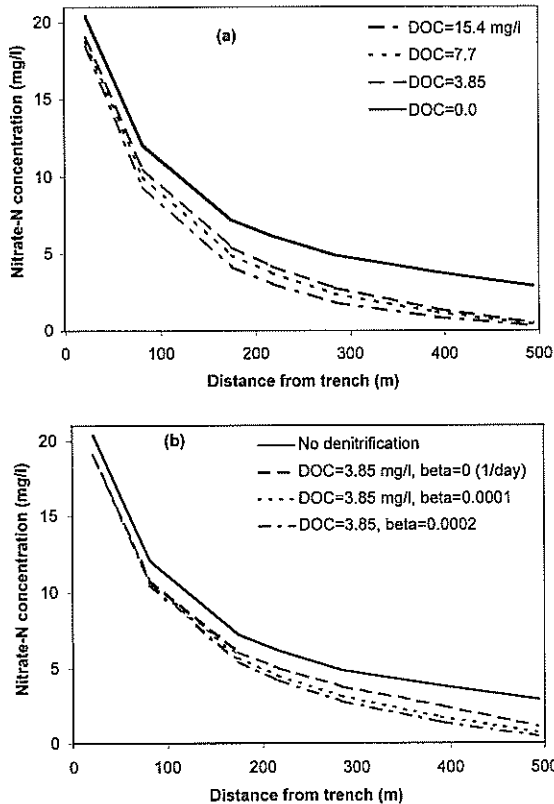


Figure 13 – Nitrate-N concentration at sampling wells along the central line of the plume as affected by: (a) effluent dissolved organic carbon concentration, (b) the availability of dissolved organic carbon from the aquifer solid phase (represented by the model parameter β - beta)

cause the nitrate-N concentration at the closest well to reach the limit for drinking water; the limit will be reached at an effluent discharge rate of 120 m³/day if no natural denitrification occurs in the aquifer. If the nitrate-N concentration is 100 mg/l, an effluent discharge rate of 120 m³/day will lead to a nitrate-N concentration at the closest well of about 20 mg/l, far exceeding the drinking water standard.

Nitrogen loading from effluent discharge

Figure 14 shows that the nitrate-N concentration at the closest domestic well is determined by both the effluent discharge rate and the nitrate-N concentration of the effluent. Given the nitrate-N concentration of the effluent, the larger the rate of effluent discharge, the higher is the nitrate-N level at the closest domestic well (well 13). If nitrate-N of the treated effluent is only 25 mg/l, nitrate-N concentration at the closest domestic well is predicted to not exceed the drinking water standard (11.3 mg-N/l), even if the rate of effluent discharge is as high as 480 m³/day. If the nitrate-N concentration of the effluent is doubled, an effluent discharge rate of 170 m³/day will

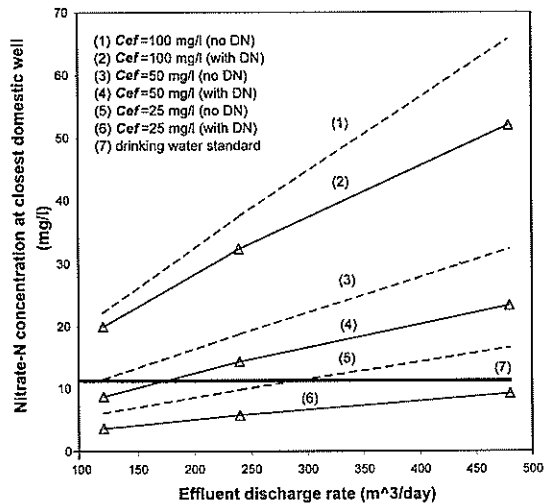


Figure 14 – Simulated nitrate-N concentration at the closest domestic well, as affected by effluent discharge rate and by nitrate-N concentration of the effluent.

Conclusions

The fate of N originating from effluent discharge and pond seepage in the subsurface was described with a three-dimensional multi-component transport model. Since the model describes the simultaneous transport and transformations of oxygen, substrate, and organic and inorganic N species, it provides a useful tool to analyse the influences of various management factors on the level of nitrate concentrations in groundwater. The model was used to simulate the transport and transformation of effluent (nitrogen and carbon) discharged from a wastewater treatment plant to the subsurface just above the groundwater table of an alluvial aquifer. Given the limitations of field data, the acceptable agreements between simulated and measured nitrate-N distributions in both vertical and horizontal profiles demonstrate that the model can reasonably represent the actual processes that control the fate of N in aquifers. Simulation results suggest that denitrification occurs in groundwater at the site.

The simulation results show that nitrate-N concentrations at wells downstream of the soakage trench are controlled mainly by the rate of effluent discharge, the N concentration of the treated effluent and the rate of denitrification under the given hydraulic conditions. Seasonal variations in effluent discharge rate and nitrate-N concentration of the effluent affect significantly the nitrate-N concentrations near the effluent soakage trench. This influence decreases gradually with increasing distance from the trench.

The presented model may be applied to investigate the influences of effluent seepage from treatment ponds on the groundwater quality of underlying aquifers, to analyse the efficiency of various remediation approaches and to optimise the design of bio-remediation systems for nitrate-N polluted aquifers. These model applications will be explored in future

work. Use of this or a similar model to solve practical problems of nitrate contamination of groundwater requires comprehensive field data. It is important to have detailed information on microbial transformations (e.g., denitrification), in addition to sufficient hydrological data characterising groundwater flow conditions.

Acknowledgments

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