

Florida Onsite Sewage Nitrogen Reduction Strategies Study

Task D

Selection of Existing Data Sets for Calibration

Draft Report

June 2009



HAZEN AND SAWYER Environmental Engineers & Scientists In association with



OTIS ENVIRONMENTAL CONSULTANTS, LLC

Florida Onsite Sewage Nitrogen Reduction Strategies Study

TASK D DRAFT REPORT

Literature Review of Nitrogen Fate and Transport Modeling

Prepared for:

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June 2009

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Section 1.0 Introduction

1.1 Project Background

As a result of the widespread impacts of nitrogen on groundwater, the management of nitrogen sources, particularly onsite wastewater treatment systems (OWTS), is of paramount concern for the protection of human health. Mathematical models of groundwater flow and solute transport historically have been utilized for simulating concentration and plume distribution of contaminants and assisting in management practices by providing representations of groundwater behavior. An appropriate model can provide guidance for land-use planning and remedial approaches. As part of the Florida Onsite Sewage Nitrogen Reduction Strategies (FOSNRS) Study, a groundwater flow and transport modeling tool is being developed to provide a management tool for potential impacts of nitrogen from OWTS. The primary objectives of the model development are to:

- create a user-friendly flow and transport model (i.e., a programmed Microsoft Excel spreadsheet), and
- develop a model that can be used to predict nitrogen concentrations and mass flux/loading at a point or plane down-gradient of an OWTS or systems assuming the model:
 - adequately represents the identified processes that govern the fate and transport of OWTS-generated nitrogen in groundwater, and
 - should also be capable of simulating temporally variable source input and account for non-uniform spatial distribution of OWTS sources.

The following presents a literature review to assess the current state-of-knowledge regarding the mathematical modeling of nitrogen and nitrate movement and distribution in groundwater related to OWTS. The review will attempt to identify existing models that may satisfy the above-stated objectives, modeling approaches that can be useful, relevant input and calibration parameters and the level of effort required in developing a modeling tool. As part of the literature review, a database of the references was developed in conjunction with this summary report. This database (see separate Excel file "CSM_D-1 Nitrogen Modeling Studies") includes a summary table of the relevant fea***WORKING DRAFT - DO NOT CITE OR DISTRIBUTE***

1.0 Introduction

tures and parameters of each modeling study. As a result of the large number of identified sources, some modeling studies not deemed valuable to this effort are mentioned in this report but are not described in detail and the reader is directed to the database for further information.

1.2 Nitrogen in Ground Water; Conceptual Considerations

Nitrogen is an important concern for water quality and nitrates represent perhaps the most common groundwater pollutant. Animals, crops, ecosystems, and human health can be adversely impacted by the presence of nitrogen in water supplies. Of these concerns, nitrate impacts to human health are a primary consideration. The consumption of nitrates has been linked to various illnesses, including cyanosis in infants and some forms of cancer. As a result, in the United States, a maximum allowable nitrate concentration of 10 mg/L as N has been established as protective of human health (Canter 1996). Other agencies around the world have also established such standards for nitrates in groundwater.

A survey of community service wells and private domestic wells performed by the U.S. Environmental Protection Agency (EPA) indicated that over half of these water supply wells contained detectable levels of nitrate (Canter 1996). The sources of this contamination are various, and include agricultural and domestic fertilizer applications, natural sources, wastewater treatment applications, and the use of OWTS. The last category is often of concern, as nearly 25% of the population in the U.S. and 30% of all new development utilize OWTS (Lowe et al., 2007). In Florida, nearly a third of all households are serviced by OWTS and 92% of water supplies come from groundwater (Briggs et al. 2007, Lowe et al. 2007).

Nitrogen transport in the subsurface is a complex process, especially when considering the nitrogen inputs from OWTS. The objectives of model development therefore requires the development of a conceptual understanding that includes the relevant fate and transport processes, parameters, and simulation approaches that will appropriately achieve the goals of the model. Figure 1-1 summarizes the conceptual understanding of the inputs of nitrogen and the transformative and advective processes that lead to nitrogen contamination of groundwater. The model development should result in a tool that will consist of the adequate level of complexity to represent these processes to accurately simulate the fate and transport of nitrogen species.



Figure 1-1: Nitrogen Processes Occurring in a Typical OWTS (Heatwole and McCray 2007)

Proper OWTS design, installation, operation, and management are essential to ensure protection of the water quality and the public served by that water source. Assuming soils and site conditions are judged suitable, a wide variety of OWTS are designed and implemented (U.S. EPA, 1997, 2002; Crites and Tchobanoglous, 1998; Siegrist, 2001). Conventional OWTS rely on septic tanks for the primary digestion of raw wastewater followed by discharge of septic tank effluent (STE) to the subsurface soils for eventual recharge to underlying groundwater (Crites and Tchobanoglous, 1998; Metcalf and Eddy, 1991; U.S. EPA, 2002). However, increasing uses of alternative OWTS rely on additional treatment of the STE prior to discharge to the environment in sensitive areas or may eliminate use of a septic tank altogether.

Septic tanks are anaerobic and have long solids retention times (e.g., years) that can enable digestion resulting in a reduction of sludge volume (40%), biochemical oxygen demand (60%), suspended solids (70%) and conversion of much of the organic nitrogen to ammonium (Reneau et al. 2001). Septic tanks are also important as they attenuate instantaneous peak flows from the dwelling unit or establishment. The effluent discharged from the septic tank (i.e., septic tank effluent or STE) then flows to subsequent engineered treatment or the directly to the soil treatment unit where the processes of soil adsorption, filtration, and transformation (biological and chemical) occur.

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Nitrogen waste products are a considerable component of septic tank effluent. Total nitrogen, composed primarily of organic nitrogen products and ammonium-nitrogen, is typically assumed to range between 20-190 mg-N/L in untreated waste water, and 26-125 mg-N/L in STE (Canter 1996, Crites and Tchobanoglous, 1998, Lowe et al., 2009). Furthermore, in a recent study that evaluated the composition of raw wastewater and STE, the median total nitrogen concentration in STE specific to Florida was determined to be 65 mg-N/L (average = 61 mg-N/L) (Lowe et al., 2009). In terms of mass loading to the subsurface, the median loading rate was determined to be 10 g-N/capita/d (average = 13.3 g-N/capita/d) (Lowe et al., 2009). McCray et al. (2005) suggested that an average subdivision can generate up to 2880 kg/km² annually. While this value is significantly higher than estimates of naturally generated deposition (600-1,200 kg/km² annually), it is much lower than the loading that results from fertilizer application (10,000-20,000 kg/km² annually). Nonetheless, OWTS should be considered a potential contributor to groundwater nitrogen concentrations.

The first stages of nitrogen transformation related to OWTS occur in the septic tank. Organic nitrogen is mineralized to the inorganic form (ammonia) via the process of ammonification, followed by volatilization to ammonium ions.

$$NH_3(aq) + H_2O \rightarrow NH_4^+ + OH^-$$
 (equation 1)

Once the liquid portion of the wastewater enters the drainfield through the subsurface infiltration system, nitrogen species (specifically ammonium and nitrate) are further transformed in the soil by nitrification and denitrification. Nitrification is a two step process by which ammonium is converted first to nitrite than to nitrate via biological oxidation.

$$NH_4^+ + O_2 \rightarrow NO_2^- + O_2 \rightarrow NO_3^-$$
 (equation 2)

Although a two step process, it can be assumed to be a one step process since the conversion of ammonium to nitrite is relatively rapid. Nitrification is either described as a zero-order or first-order reaction or via Monod kinetics. This particular reaction is of importance, as it represents the transformation from the relatively immobile nitrogen form (ammonium) to the highly mobile form (nitrate). Most studies of OWTS with suitable unsaturated soil have indicated that little ammonium reaches the underlying groundwater and that most impacts to groundwater from nitrogen are in the nitrate form. Nitrate behaves essentially as a conservative solute, with virtually no sorption or retardation processes affecting its movement in the aquifer. It is, however, subject to transformative processes.

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Denitrification is the transformation of nitrate to N_2 gas.

$$5(CH_2O) + 4NO_3 + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$$
 (equation 3)

Denitrification occurs in oxygen-free conditions, and is therefore seen in anoxic zones in the soil and groundwater. This reaction is typically described as first-order. However, nitrogen transformations are probably best modeled using Monod kinetics, which result in zero-order rate constants for concentrations typical of nitrate-impacted groundwater. The process, while studied extensively, is not well understood or well quantified. Previous studies identifying significant processes that lead to the reduction of nitrate concentrations identify denitrification rates as relatively small, and that most reductions occur as a result of mixing with ambient groundwater (to be discussed in more detail later in this review).

The development of a conceptual understanding of nitrogen fate and transport from source to receptor indicates that there are potentially a large number of processes that can be simulated depending on the objectives of the model. In the literature review that follows, researchers have in some cases used simplifying assumptions to account for certain processes if data is not available or the model does not need to simulate the process to achieve desired outputs. In other cases, researchers use relatively complex mathematical models in attempt to model multiple transformation or transport processes as accurately as possible. For example, the development of a model that considers all of the sequential steps of denitrification. The approach chosen is highly dependent on the goals of the modeling and the data available, as well as the scale that is to be represented.

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Section 2.0 Literature Review

The following presents a summary of available research related to the modeling of fate and transport of nitrogen in groundwater. Modeling research directly related to nitrogen is presented, as well as modeling for general solute transport. The purpose of the summary is to:

- assess the state-of-knowledge of modeling nitrogen fate and transport in the vadose zone and in groundwater,
- identify the relevant processes, parameters and data used in the simulation of nitrogen transport,
- identify the modeling methods that enable quality simulation with an appropriate level of complexity in the context of the important processes that govern nitrogen fate and transport in the subsurface, and
- identify the merits and drawbacks of the various modeling studies and develop a guidance in designing the mathematical approach to address the project objectives.

2.1 Modeling Research Summary

The literature review discovered over 70 reports or articles related to the modeling of nitrogen fate and transport. Additionally, the review discovered more than 20 modeling codes or solutions not specific to a particular contaminant that could potentially be applied to the simulation of nitrogen in the subsurface, based on the conceptual understanding of the processes governing nitrogen movement and transformation. Only a very small number of models specific to OWTS were discovered, and generally were concerned with land-use planning related to septic tank density.

A relatively large number of studies investigated the behavior of nitrogen in the vadose zone. These models were typically physically-based deterministic solutions of the Richards' equation for groundwater flow with a variation of the advective-dispersive equation (ADE) to simulate solute transport. Some researchers used a stochastic solution approach; this approach assumes that vadose zone parameters are too heterogeneous

to be captured by a physical model, and that transport through the unsaturated zone is better modeled by using probabilistic functions for model input parameters.

The review identified fewer models considering nitrogen in the saturated zone. This may be in large part due to the fact that nitrate acts as a conservative solute in groundwater and therefore the development of complex models to describe this movement are not necessarily valuable or appropriate. A number of mass-balance models were created for nitrates in the saturated zone, because such a model could satisfy the objectives of the study. The models in this category consist of land-use planning models, studies identifying nitrate sources, and studies of specific groundwater systems. Modeling efforts that were not specific to nitrogen also tended to fall in this category, as researchers were concerned with developing methods that provided appropriate approximations of the ADE. Because solutions to this equation are approximate, many researchers were developing or comparing solution methods in order to identify the method that provided the most accurate solution.

Fewer still have considered the combined simulation of nitrogen in the vadose and saturated zone, and among these only a handful simulated flow and transport processes at the field scale. The latter category of models is often developed at the watershed scale and included impacts to surface water bodies. The inputs and the models themselves are often fairly large and complex, and include data and simulations for climate, streamflow characteristics and fluxes, and land-use and vegetative patterns. Simulations and calibration procedures are usually time-consuming and complex, and require a considerable amount of input data.

Additionally, a large body of research has exclusively modeled the denitrification processes. In fact, numerous simple models have been developed that generate empirical expressions for denitrification at particular sites of interest. As a result, broad applicability and transferability of the models described to other sites is questionable.

2.2 Vadose Zone Models

Many modeling studies were identified that addressed solute transport in the vadose zone, of which a majority of the models selected for this review specifically simulated nitrogen transport. The studies could generally be classified as either deterministic physical models or stochastic, probabilistic models. Among the studies that examine the problem of nitrogen fate and transport, physically-based deterministic models for the vadose zone are generally solutions of the Richards' equation combined with a one-dimensional solution of the ADE for representing vertical flow and transport (in the "z" direction) and assuming horizontal flow vectors are not significant, although in some cases dispersion was also considered.

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Addiscott and Wagenet (1985) provided a summary of soil leaching models and provided brief descriptions of modeling approaches and specified studies that applied the various methods. The key distinction the authors make when comparing the modeling approaches is comparing deterministic models with stochastic modeling approaches. The authors note that in most cases the selection of methods is based on the preferences of the researchers and tend to ignore the fact that models are intended for different purposes.

Among the physically-based models, most studies examine the problem of nitrogen transport in the unsaturated zone related to the impacts of fertilizer applications. These include studies by Bakhsh et al. (2004), Hansen et al. (1991), Jabro et al. (2001), Johnson et al. (1999), Moreels et al. (2003), and Johnsson et al. (1987). Generally, these modeling studies used numerical computer simulation programs designed for onedimensional solutions of the Richards' equation coupled with the ADE or a variation of the ADE that contains provisions for partially-saturated flow and transport. In some cases, these programs are relatively complex, requiring large amounts of computing power and time, as well as complex data inputs. For example, (Bakhsh et al. 2004) used an updated version of the Root Zone Water Quality Model (RZWQM) to simulate nitrogen transport in a watershed in Iowa that is potentially impacted from corn and soybean field fertilizer applications. The RZWQM simulates solute transport using a one-dimensional solution to the Richards' equation and ADE. Input data for meteorological parameters includes daily minimum and maximum temperature, hourly wind speed, and solar radiation. Additionally, a full suite of soil and crop management inputs are required as well. Jabro et al. (2001) used the SOIL-SOILN model to simulate nitrogen transport. This model simulates fluid flow and heat transport using a coupled program that solves the ADE for fluids and the Fourier equation for heat transport. Again as with the RZWQM, inputs are complex including meteorological, soil, and crop management data. Simulations were performed for a three-year period and showed generally good model performance.

Other unsaturated zone models simulated nitrogen movement associated with the practice of wastewater treatment via land applications. Modeling studies by Reynolds and Iskandar (1995) and Beggs et al. (2005) looked at effectiveness of this practice at minimizing the impacts of effluents. Beggs et al. (2005) used HYDRUS 2D to look at the effectiveness of using subsurface drip irrigation as a means of treating STE. HYDRUS 2D, like the RZWQM, uses the Richard's equation for flow and the ADE with reaction parameters (including rate constants for nitrification and denitrification) for transformation and transport. The study showed an appropriately designed system could reduce annual nitrogen percolation through the soil column. Reynolds and Iskandar (1995) used the previously developed computer code WASTEN to simulate various scenarios of wastewater

land application at a treatment facility at Fort Dix, New Jersey. The code utilizes a subroutine for the ADE and can also simulate transformation processes such as nitrification and denitrification. Additionally, WASTEN is capable of simulating the effects of plant uptake, evapotranspiration, leaching, and rainfall.

Selim and Mansell (1976) and Mironenko and Pachepsky (1984) developed onedimensional analytical solutions of the ADE for the simulation of solute transport through soils. Selim and Mansell develop a solution that can simulate constant source or pulse source inputs, and can also simulate reversible linear adsorption and irreversible sorption. No parameters for reactions are provided. In comparison to other solutions, the model performed more favorably at lower pore velocities, and performed similarly at higher pore velocities. Mironenko and Pachepsky developed a solution that could simulate adsorption as well as biological or chemical transformations. The heterogeneity of the soil pore scale was addressed by introducing mobile and immobile transport domains. The model was then used to simulate nitrogen transport and denitrification in a soil column. The results are presented as relative concentrations (C/C_0) vs. pore volumes, as shown in Figure 2-1. The researchers were able to reasonably match observed data using a model calibration procedure to determine input parameter values.





Two modeling studies were found that simulated wastewater vadose zone transport associated with OWTS. Huntzinger and McCray (2003) used HYDRUS2D to examine the problem of soil pore clogging and its impact on the effectiveness of wastewater soil absorption systems. Results indicated the importance of understanding the influence of clogging on system design to optimize residence times and treatment of wastewater. Heatwole and McCray (2007) applied HDYRUS1D to estimations of nitrogen contamination flux from a proposed housing development in Weld County, Colorado. The modeling

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used some site-specific data, and statistically-based N-transformation rate parameters to simulate nitrate impacts to the groundwater below. The model was highly sensitive to nitrogen mass-flux input and the denitrification rate coefficient. The latter sensitivity is important, because published denitrification rates are highly variable and therefore the estimates can potentially have a high degree of uncertainty. In contrast, nitrogen mass flux inputs to the subsurface are less uncertain.

In contrast to the physically-based models, a stochastic modeling approach was developed by Jury (1982) for one- or two-dimensional transport of solutes through the vadose zone. The transfer function model (TFM) considers that the spatial distribution of the physical, chemical and biological transport mechanisms are not well known especially when considering a heterogeneous media such as the soil column. Therefore, the model simulation is independent of site-measured characteristics and the behavior of a solute entering the soil matrix is based on probabilistic functions rather than physical functions; in other words, the model produces outputs based on the probability that a solute will reach a defined depth in the soil column. This is done using the probability density function (PDF), a mathematical operator that can estimate solute concentrations at a given depth based on the average and variance values of either travel time or input water flux at the surface. As a result, the model can consider uniform spatial distribution of input water flux or spatially variable inputs. Models in this category, while using agricultural problems as examples, could potentially have simulation capabilities for a variety of sources.

Studies by White (1987) and White et al. (1998) used applications of the TFM at the field scale to address the problem of nitrogen leaching in pasture lands in New Zealand. The first study developed a probability distribution for solute transport times from observed data related to numerous rainfall events and soil moisture conditions. The transfer function was then calibrated against measured quantities of nitrate leached. The TFM was capable of representing the measured data with reasonable accuracy. The researchers suggest that predictive simulations using a TFM are possible using a time and space-averaged value for solute travel times. However, this would require numerous additional studies to characterize a variety of soil types. The second study is similar, using a TFM to simulate nitrate leaching in a soil near Palmerston North, New Zealand. Results are generally good; however, there is a consistent tendency of the TFM to over-estimate the nitrate leaching in this case.

A number of studies compared modeled solute transport through the vadose zone using the TFM and an analytical solution of the ADE. Jury and Sposito (1985) used data collected from soil core and soil solution samplers to calibrate and validate results using both modeling methods. Based on the data collected, model parameters were optimized.

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In the case of the ADE analytical solution, the parameters were pore-water velocity (V) and a field-scale dispersion coefficient (D). For the TFM, the parameters were mean and variance of travel time through the media. Parameters were estimated using three methods: a sum of squares method, a method of moments, and maximum likelihood estimation. The parameter estimations for the solution sampler data had relatively high uncertainties, owing to the deviations between the shape of the average data curve and the model estimates of the curve, and the small number of replicate measurements. Therefore, a comparison of performance could not be done. For the soil core samples, the TFM was determined to have provided a better representation of the data.

Dyson and White (1987) conducted a similar study comparing the two modeling approaches for the transport of chloride through a structured clay soil. Also considering soil cores, the researchers found that the TFM model, using an assumption of a log-normal distribution of travel times (characterized by the mean and the variance), could model the flux-averaged breakthrough curves well. Also, the ADE could model the breakthrough curves equally well when the velocity and dispersion parameters were optimized via the least squares method.

2.3 Saturated Zone Flow and Transport Models

Due to the scope of the problem related to the protection of groundwater, the modeling of fate and transport of contaminants in aquifers has been a significant objective for research. A relatively large body of numerical, analytical and mass-balance models has been developed to study the movement of solutes in the saturated zone. Additional effort aims to provide accurate simulation of solute reactions and adsorption. Among many studies that develop general solutions of flow and transport, numerous models have been focused on the behavior of nitrogen (specifically nitrate) in the saturated zone. These can be either site-specific or more broadly-focused nitrate transport models that can potentially be applied to any site or problem.

Among the aquifer models, the simplest form of simulating solute fate and transport is the mass-balance model. This type of model ignores aquifer parameters that influence groundwater direction and velocities and transformative processes. The objective is to simply balance source and groundwater inputs and outputs (usually expressed as fluxes or rates) based on observed data. Typically, these models have numerous simplifying assumptions.

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A simple mass-balance equation was developed and then compared the modelpredicted results to field data for three communities in California (Hantzche and Finnemore 1992):

$$n_r = \frac{In_w(1-d) + Rn_b}{(I+R)}$$
 (equation 4)

where: $n_r = net$ nitrate concentration in recharge groundwater, $I = volume rate of waste water entering the soil averaged over the gross developed area (inches yr⁻¹), <math>n_w$ is the total nitrogen concentration of wastewater (mg L⁻¹), d = the fraction of nitrate-nitrogen loss due to denitrification in the soil, R = average recharge rate of rainfall (inches yr⁻¹), and n_b = background nitrate-nitrogen concentration of the rainfall (mg L⁻¹).

Results were plotted as mean nitrogen-nitrate concentration versus wastewater recharge relative to rainfall recharge (I/R) and include comparison to field data values from the different sites in the study (Figure 2-2). In general, model-predicted results compared favorably with the concentrations measured in the field. The authors note that the model has the following limitations:

- The equation considers only vertical components of groundwater recharge, and does not consider fluxes from upgradient areas.
- The predicted concentrations are long-term values, as loading rates may take many years to develop and may be affected by the nature and thickness of the vadose zone.
- Results cannot be applied to a single point, as in considering a specific water supply well.
- This method does not account for other sources of nitrogen, such as fertilizer or animal wastes.

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Figure 2-2: Results of Modeling with Comparison to Field Data (Hantzche and Finnemore 1992)

DeSimone and Howes (1998) used a mass-balance solution to estimate fate and transport rate values based on observed field data. The source of nitrogen in this study was a waste treatment facility in Cape Cod, Massachusetts. The objective of the research was to use a mass-balance method to identify the key hydrogeochemical processes, estimate rate values for these processes, and ultimately estimate potential mass flux into nearby surface water bodies.

Calculated wastewater input fluxes from the treatment facility, waste loads to the aquifer, and the observed concentrations at downgradient sampling points were considered and input into the mass-balance equation. Based on the observed data, values for advective and transformative processes were estimated. The researchers determined that within the unsaturated zone, nitrification and ammonification processes were the most important to nitrogen transport, whereas in the saturated zone denitrification and sorption of ammonium had the most influence. They concluded, based on the estimated fate and transport processes, that approximately 75% of the input waste load could potentially reach the nearby surface water body.

Mass-balance models are often utilized as land-planning tools. The objective in most cases is to estimate the optimal lot size or housing density to minimize the impacts from OWTS. A few examples are summarized below.

Rogers, Golden and Halpern (1988) developed a groundwater-dilution model based on mass-balance inputs for the State of New Jersey. The ultimate goal of the model was to assess optimal numbers of households and lot sizes in new developments using septic systems to minimize the impact of nitrate groundwater contamination on surface waters. In this case, the model considers dilution of nitrate contamination by recharge fluxes alone as a way to reduce the waste mass flux into the aquifer, and does not consider upgradient groundwater inputs or transformative processes in the soil or the aquifer.

A very simple modeling approach ultimately defines carrying capacity as acres required per household to optimize nitrate dilution from precipitation recharge so as not to exceed the groundwater protection standards. The equation, from an earlier study by Trela and Douglas (1978) is as follows:

$$H = \frac{V_e C_e}{(V_i + C_i)C_q}$$
 (equation 5)

Where: H= carrying capacity; V_e = Volume of septic effluent entering system; C_e = Nitrate concentration in septic effluent; V_i = Volume of infiltrating precipitation; C_i = Nitrate concentration in precipitation; and C_q = Water quality standard for nitrate.

Two example runs considering varying target nitrate concentrations are provided, but not verified with field data.

A similar dilution-based mass-balance model for land use planning was developed for Pennsylvania (Taylor 2003). Through a mass-balance equation, the model is intended to estimate appropriate lot sizes to allow for adequate dilution of the input nitrogen to minimize the impacts of a septic system:

$$V_{s}C_{s} + V_{r}C_{f} + V_{g}C_{g} = (V_{s} + V_{r} + V_{g})C_{o} + (V_{s} + V_{r} + V_{g})C_{d}$$
 (equation 6)

Where V_s = volume of septic tank effluent (gpd), C_s = Concentration of nitrate in septic tank effluent (mg/L), V_r = Volume of groundwater recharge/infiltration (gpd), C_f = nitrate concentration in fertilizer that reaches the groundwater (mg/L), V_g = Volume of upgradient recharge water (gpd), C_g = nitrate concentration in upgradient groundwater (mg/L), C_o = nitrate concentration of groundwater leaving the site (mg/L), and C_d = concentration of nitrate lost due to denitrification.

In order to arrive at these terms, this mass-balance approach utilizes a number of site parameters including hydraulic conductivity, gradient, average recharge rate due to precipitation, and mass of fertilizer applied as examples. These parameters are then used in empirical relationships to define the needed inputs for the mass-balance equation. Un-

like the model developed for the state of New Jersey, this model does consider upgradient groundwater flux. The model conceptualization is shown in Figure 2-3.



Figure 2-3: Conceptual Model for Mass-Balance Approach (Taylor, 2003)

This model, as with the other mass-balance models, has several simplifying assumptions, such as: complete mixing of wastewater and recharge water within a specified aquifer thickness; complete conversion of nitrogen to nitrate; and neglecting most chemical transport and reactive processes including diffusion, dispersion, adsorption, and denitrification. The author provides an example use of the model to calculate the optimal lot size for a hypothetical development in Pennsylvania and makes land-use recommendations based on the results. However, as with the previously described model, the modelpredicted results are not verified with field data.

While examination of available research indicated mass-balance models are often used for land planning tools, some researchers have utilized them for nitrate source identification or as a predictive tool. Tinker (1991) compared the results from three mass-balance models, along with other investigative tools, to help identify possible sources of nitrate impacts on wells in Wisconsin. Tinker used a mass-balance model developed by Wehr-

mann (1984), the BURBS model and a combination of the two models to determine if the nitrate in the groundwater was primarily from fertilizer applications or wastewater treatment.

The Wehrmann mass-balance model uses estimates of water volumes and nitrate concentrations to evaluate the diluted nitrate leaving the area of the subdivision in question. In this case, the model considers upgradient groundwater and also pumped water volumes. The primary source for this model is septic effluent:

$$V_b C_b + V_i C_i + V_s C_s - V_p C_p = (V_b + V_i + V_s - V_p)C_o$$
 (equation 7)

Where V_b = Volume of upgradient groundwater, C_b = Nitrate concentration in upgradient groundwater, V_i = Volume of precipitation infiltration, C_i = Nitrate concentration in the infilitration, V_s = Volume of septic effluent introduced beneath subdivision, C_s = Nitrate concentration in the septic effluent, C_p = Nitrate concentration in the pumped groundwater and C_o = Diluted nitrate concentration leaving the subdivision. The BURBS model is similar, but also considers contributions from turf, impervious land, and natural land. A bulk nitrogen-nitrate concentration (C_{BURBS}) is used in the water contribution from these three sources. The combined mass-balance expression is as follows:

$$V_{b}C_{b} + (V_{t} + V_{i} + V_{n} + V_{s} - V_{p})C_{BURBS} = (V_{b} + V_{t} + V_{i} + V_{n} + V_{s} - V_{p})C_{o}$$
 (equation 8)

With terms defined as above and also V_t = Volume of recharge water from turf, V_i = Volume of water recharged from impervious land and V_n = Volume of water recharged from natural lands.

The author predicted that a majority of the nitrate in the groundwater could be accounted for by OWTS and fertilizer applications, and the mass-balance modeling agreed with that prediction, based on sampling results from residential wells.

Frimpter et al. (1990) developed a simple mass balance equation to predict the potential nitrate impacts to municipal supply wells based on loading rates from natural and anth-ropogenic sources. The model can consider individual sources and therefore is a potential tool for determining septic tank density in new developments. Assumptions of the model are steady-state conditions, complete mixing, and modeling nitrate as a conservative solute. The author provides example calculations in which nitrate concentrations are predicted based on source density and flow rates of withdrawing municipal supply wells.

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Beyond mass-balance models, a variety of approximations of the ADE or similar governing equations that apply to nitrates were found in the literature. Methods of simulation were variable, from simple analytical solutions to complex numerical codes.

Lerner and Papatolios (1993) developed a unique, simple analytical expression for predicting nitrate concentrations in pumped groundwater:

$$C_{t} = C_{o} + \left(C - C_{o}\right) \left[1 - \exp\left(-\frac{Rt}{bn}\right)\right]$$
 (equation 9)

Where C_t = Time variant pumped concentration, C_o = Initial groundwater nitrate concentration, C = Concentration of nitrate in groundwater in area of influence of the pumping well, R = Recharge rate, b = Aquifer thickness, t = Time, and n = Porosity.

This expression considers nitrate in the saturated zone with source inputs mostly originating from recharge waters. C_o is arrived at by estimating leaching rates of nitrate through the vadose zone. The model considers only nitrate in groundwater as an initial concentration and does not consider source input rates or flux. The model was applied to a pumping station in England, and predictive calculations were performed. In the two years following the model simulations, field data was collected and then compared to the simulations to verify if the model predictions agreed with the actual observed nitrate concentrations. The model predicted future nitrate concentrations with reasonable accuracy. Also, a sensitivity analysis was done to determine sensitive parameters in terms of conservative solute transport for this system (in this case, porosity, aquifer thickness and estimated leaching rates from the vadose zone that determine C_o).

Young et al. (1976) also develop an analytical approach to predicting future nitrate concentrations in groundwater in a fractured sandstone aquifer in England. The investigators used an unsaturated zone flow model to forward model nitrate impacts to groundwater based on current land use practices. However, the exact analytical approach is not described, except to describe important parameters and processes.

MODFLOW and MODPATH are two commonly used numerical modeling codes that have been widely utilized by both academic and industry hydrogeologists. MODFLOW is a three dimensional, finite difference modeling codes that has a wide variety of capabilities for modeling multiple layers of an aquifer system and heterogeneous parametric distributions. The model code is often employed with a graphical pre- and post-processor to assist with the construction of the input files. MODPATH is an extension of MODFLOW that utilizes model-calculated groundwater velocities and flow vectors to give particle tracking of groundwater movement. The tracking of the groundwater movement can be time-stepped to give estimates of travel time.

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Puckett and Lowdery (2002) constructed a MODFLOW groundwater flow and transport model and used it in conjunction with sample analyses and water-aging to determine the relationship between agricultural practices and nitrate concentrations in groundwater in a glacial outwash aquifer in Minnesota. The model was constructed as a three layer model with assigned boundary conditions based on the conceptual understanding of the hydrogeologic system. The model was calibrated against observed water levels at monitoring wells in the study area, and MODPATH was used to compute groundwater travel times and flow paths. The modeling was used to indicate expected groundwater travel times and correlated with the groundwater aging aspect of the study, and showed generally good agreement between the two methodologies. Although no transport modeling was done, an extension of MODFLOW, MT3DS is a full transport modeling code and can consider adsorption and chemical processes in numerous ways. This could be a potential extension of the study to further validate the conceptual understanding of the groundwater system.

A study by Molenat and Gascuel-Odeux (2002) provides an example of nitrate modeling using a combination of MODFLOW and MT3DS. In this study, these model codes were coupled to simulate different spatial distribution scenarios of nitrate inputs from agricultural practices in the Kervidy watershed in Brittany, France. The initial simulation of groundwater flow and nitrate distribution was done as a steady-state simulation, and simulation results matched field observations well. Two scenarios reduced the uniform spatial distribution of nitrate recharge from the initial 100 mg/L to 80 mg/L and 60 mg/L, respectively. The other four scenarios redistributed the nitrate recharge to the watershed hillsides, but retained the initial rate of 100 mg/L. The results of the scenarios indicate that the impacts to groundwater could be reduced by reducing the nitrate inputs on the hillsides more than reducing nitrate inputs over the entire watershed.

A simple distributed transport model was developed to simulate and predict ground water nitrate concentrations. Based on a numerical code developed by Bear (1979), a study was completed for the Great Ouse Chalk aquifer in England by Carey and Lloyd (1985). The chalk is a fine-grained fractured limestone aquifer that has seen increasing impacts from nitrate pollution. For the modeling, a groundwater flow and transport model was constructed using numerous computation cells representing small volumes of the aquifer with the nitrate concentrations into and out of the model cells calculated using a massbalance approach. The model assumed that the concentration of nitrate in groundwater recharge was constant, but that the rate of recharge varied. Nitrate sources in this case were natural land, plowed land, and nitrogen inputs that resulted from fertilizer applications. The downward migration of nitrate is solved via a simple equation that calculates a velocity based on porosity and recharge. The model was calibrated using observed groundwater and nitrate concentration data, and a sensitivity analysis was performed to

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assess the effects of various parameters. The model was able to simulate past trends of groundwater behavior and nitrate concentration reasonably well. Further, the model predicted an increasing trend in nitrate concentrations, but the severity of the increase was dependent on changes in land practices.

Hendry et al. (1983) apply this methodology to the problem of nitrate transport in an aquifer in England with impacts resulting from agricultural practices. The researchers apply a numerical model among other investigative techniques to test two hypotheses of nitrate fate and transport; 1) that the resulting concentrations observed are a result of mixing with upgradient groundwater, and 2) that the vertical concentration distributions are due to denitrification processes. Based on the modeling and other investigations, they conclude that the denitrification processes are dominant.

2.4 Combined Vadose Zone and Saturated Zone Models

The research that examines the combined fate and transport of nitrogen species in both the vadose and saturated zones is limited. However, some models have been developed either on the watershed or field scale that does in fact couple the two zones for simulations of contaminant transport. Among these are several models that could effectively simulate nitrogen transport.

Mehran et al. (1983-1984) developed a two-dimensional numerical solution for the fate and transport of soluble nitrogen species in both the vadose and saturated zones. This model resulted in two separate codes that simulate the vadose zone and saturated zone simultaneously. The vadose zone is represented by the finite-difference code UCD-RANN and the saturated zone by the finite-element code FLOWS.

The model considers numerous parameters for both flow zones including all relevant flow parameters indicated in Darcy's Law (i.e., hydraulic conductivity, gradient, porosity), and transport and transformative parameters in both the vadose zone and saturated zone. Among others, these parameters include saturation index, pressure head, and root zone uptake of nitrates as well as first-order rate constants for nitrification and denitrification, and the retardation factor for ammonium transport in the vadose zone. The retardation factor is defined by:

$$R=1+\left(\frac{\rho_b}{n}\right)(K_d)$$
 (equation 10)

Where R = retardation factor, ρ_b = bulk density of the soil, n = effective porosity, and K_d = soil distribution coefficient.

The model, shown conceptually in Figure 2-4, also provides equations for boundary conditions that are necessary to define the model dimensions.



(Mehran et al. 1983-1984)

The outputs of the model include nitrate concentrations at various depths through time for the vadose zone and time-variable depth and distance nitrate concentrations in the aquifer. The researchers provide a model demonstration on a hypothetical aquifer system, shown in Figure 2-5. In this case, a constant nitrate concentration is imposed on the water table, however, it is probable that a varying rate of concentration input can be applied using this code. An example output for the vadose zone simulation is shown in Figure 2-6.

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(Mehran et al. 1983-1984)

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2.5 Nitrate Modeling at the Watershed Scale

Numerical modeling codes also have been applied to the watershed scale for the simulation of groundwater flow and nitrate leaching in the unsaturated zone and the resulting impacts to surface water bodies. These models represent perhaps the most complex of the models reviewed, requiring large input data sets and complex numerical codes for the simulations. Sonnenburg et al. (2003) and Refsgaard et al. (1999) present modeling of watersheds in Denmark using large scale models. The researchers utilize the code MIKE SHE, which uses numerical solutions for overland 2-D and channel 1-D flow, 1-D unsaturated flow, and 3-D saturated flow. The conceptual model is illustrated in Figure 2-7.





Refsgaard et. al. conceptualized and constructed groundwater flow and transport models to consider nitrate impacts on two watersheds in Denmark. The intention of the study was to show that such a model could be shown to be a reliable tool for specific watersheds, and that reasonable model performance at such a scale was possible. This model was a coupled model using the MIKE SHE code and the Daisy code, which simulates the percolation of water and nitrate at the bottom of the vadose zone. Input, verification, and calibration data for the model were found in GIS-linked databases which provided data for agricultural practices, topography, groundwater data, stream-flow and climatic

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variables. Representative model grids were constructed using topography and catchment delineation data from the databases. The researchers use an up-scaling method to transfer some field-scale data to the catchment scale. Model parameters were assessed using various transfer functions, and the results of the simulation were validated by comparing model simulated results to observed results for annual water balance, river run-off, and groundwater nitrate concentrations.

Simulations were done for the Karup and Odense watersheds and validation of the model based on watershed-specific water balances over a five-year period and ground-water nitrate concentrations over the same period was also performed. Validation results for the Karup watershed were extremely good, and the simulations of the Odense watershed were acceptable although not at the same level as the simulations for the Karup watershed. The results indicate that similar models can be useful tools for assessing nitrate contamination at such a scale for other watersheds, provided access to adequate databases is available.

Conan et al. (2003) used MODFLOW and MT3DMS coupled with the watershed modeling code SWAT (Soil and Water Assessment Tool) to simulate nitrogen fate in a watershed in Brittany, France that has been impacted by livestock practices. The model considers the full range of transformative processes for nitrogen species, such as ammonification, nitrification, and denitrification. Hydraulically, the combined models simulate groundwater flow, nitrogen transport, and surface water flows and concentrations. Model structure is constructed using digital elevation models and used field data sets for stream flow, groundwater levels and nitrogen concentration over a three-year period. Data collected was used for initial input parameters and calibration of the model. Results were generally good, with some exceptions. The stream flow simulations consistently overestimated flows in June and underestimated flows in December. Simulations done with the SWAT model alone consistently underestimated nitrogen levels in the surface waters, but the coupled model performed much better, perhaps due to being able to account for the stream baseflow. Groundwater concentrations were also well simulated by the coupled model.

Heng and Nikoladis (1998) developed a highly complex, multidimensional watershed scale model for the transport and transformation of nitrogen from non-point sources. The model (NTT-watershed) generates a grid system based on topography and subsurface properties can also be vertically discretized to represent vegetation, overland flow, and the groundwater zones. Flow and solute inputs into the model are temporally and spatially variable and can consider transport and transformation of organic nitrogen, ammonium, and nitrate. For this study, the model was applied to the Muddy Brook watershed in Connecticut. Input, calibration, and validation data was collected over a two-year pe-

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riod and included nitrogen species concentrations, field parameters, stream-flow values, precipitation rates, and land use practices and applications (i.e. fertilizer use). Simulations were performed and the model matched groundwater, stream-flow, and concentration data reasonably well. Results indicate that future models for other watersheds can be developed in a similar manner to assist with management planning.

Weintraub et al. (2004) used the GIS-based watershed modeling tool WARMF for investigating watershed-scale impacts from OWTS in Summit County, Colorado. WARMF is a modeling tool that estimates total maximum daily loads (TMDL) based on a series of modules with various inputs. The model was constructed using a Digital Elevation Model (DEM) of the Blue River Watershed and included input data for regional meteorology, point sources, and land use. Additional data was collected in the field for surface water quality, soil properties, well data and spatial distribution of OWTS. The model was enhanced by including a biozone module that simulated the transformative processes in the soil column beneath the OWTS. After constructing the model, simulations were performed representing a period from fall 1998 through fall 2002. Model simulations were compared to observed data, and a calibration was done to adjust the input parameters to improve the fit to observed hydraulic and concentration data. The calibrated model was then used to assess various management scenarios including converting housing subdivision from OWTS to a centralized sewer system. The results for nitrogen indicate that although nonpoint loading is reduced, the loading to the river increases due to the increased nitrogen loading from the treatment plant. This suggests that conversion to a sewer system would require a higher level of nitrogen treatment at the plant.

Geza and McCray (2007) also applied the WARMF model to assess the influence of various point and non-point sources including OWTS in the Turkey Creek watershed in Colorado. As with the previous study, a DEM was used to build the model that included land cover and soil type data. Data was also input regarding population, wastewater loading per person, and effluent concentration. Stream flow and water quality data from a previous study was used and a simulation period of five years (1998-2003) was used as a calibration run. Calibration was done using UCODE, an automatic calibration tool and a sensitivity analysis was also done. The analysis showed that groundwater concentrations for nitrate were most sensitive to soil parameters, land cover parameters, and input concentrations of ammonium. However, the model was not sensitive to denitrification rates. Stream concentrations were most sensitive to sediment transport parameters.

Once a calibrated model was completed, four management scenarios related to OWTS were performed. Stream concentrations of nitrate were shown to be highest when the stream segment was located close to an area with a high density of OWTS as compared to locations downstream, an effect likely due to dilution. Soil water concentrations in-

creased with increasing population, but decreased when OWTS were converted to sewer systems.

2.6 General Fate and Transport Modeling

Numerical or analytical codes for modeling groundwater flow and solute transport have had numerous applications. The use of a particular method, solution, or transport parameter depends largely on the contaminant of interest, the objectives of the modeling, and in some cases site-specific characteristics. For the most part, models in this category are limited to the saturated zone. Within the summary below, several models have been identified that do not model nitrate fate and transport specifically. However, because the codes can consider the important fate and transport processes, they can be useful in developing a model to simulate nitrate in the subsurface. Among the codes identified, 13 analytical solutions to the ADE were found in the literature. These solutions consider different methods, spatial and temporal simulations, and different transport parameters such as retardation, decay, or dispersion. Analytical solutions are appealing in that they can be programmed into a spreadsheet relatively easily, and can therefore be part of a user-friendly modeling tool. Four such spreadsheet programmed solutions are discussed below.

The governing equation in most cases is a variation of the ADE with either chemical (production of solute or degradation) or physical reaction (sorption) or both. An example featuring one-dimensional advection-dispersion with retardation and first-order degradation is shown from Elmore (2007):

$$R\left(\frac{\delta}{\delta t}C\right) = -v_x\left(\frac{\delta}{\delta t}C\right) + D_x\frac{\delta^2}{\delta t^2}C - kRC \qquad (equation 11)$$

Where R= retardation factor; C = solute concentration; t = time; v_x = average pore water velocity; x = distance from source; D_x = dispersion coefficient; and k = first-order degradation constant.

Virtually all the analytical solutions considered either first-order reaction, equilibrium linear reversible sorption, or a combination of both. Leij et al. (1993) provide expressions for the partitioning of the solute in the mobile and immobile phases. For degradation, the majority of solutions use a first-order degradation rate constant for the solute. Sun et al. (1999) develop a three-dimensional reactive model for the saturated zone via an analytical solution that can simulate degradation as sequential first-order reactions. Example contaminants that can be simulated with this process include tetrachloroethylene (PCE) and its degradation daughter products and the denitrification process from nitrate to nitrite to ammonia to nitrogen gas. A unique three-dimensional code for the simulation of a reactive solute in a variably saturated porous media was developed by Srivasta and Yeh

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(1992). Equations are based on the Richards' equation for flow in variably saturated media and the conventional ADE. This model also considers adsorption via a mobileimmobile partitioning condition and employs the use of a first-order decay function. The solutions are performed using a Galerkian finite element method and a Picard iterative process.

A number of solutions simulate transport considering different source orientations. This may be an important consideration for nitrate contamination from OWTS, as the impacts to groundwater may be from multiple sources that are not necessarily point sources. Carslaw and Jaeger (1959) derived solutions to the three-dimensional advection-dispersion equation utilizing Green's functions, which were extended to develop an aquifer transport model for a contaminant from a horizontal plane source at the top of the water table (HPS)(Galva 1987). This results in estimates of contaminant transport that are more accurate than simulations using a point source when considering a groundwater contaminant source that may be distributed over a relatively large planar area, such as a source associated with a landfill or a development utilizing OWTS.

Galva provides the mathematical background to the development of the HPS model, and provides example numerical simulations using a FORTRAN code to illustrate the applicability of the model. Simulation one uses various retardation rates, zero decay, and a continuous source rate. Simulation two varies the retardation rate and the period of source emissions. Finally, simulation three considers constant source input rates with variations in retardation and decay coefficient. Results for the second simulation are shown in Figure 2-8. Results are presented as predicted solute concentrations at a specified point (200 meters down-gradient) through time.

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Figure 2-8: Model Output for HPS Model, Simulation Two (Galya 1987)

The model simulations indicate the sensitivity of the varied parameters such as decay factor, retardation factor and the temporal period of source emission. The authors also point out that while this model is useful for quick estimates, the simplifying assumptions required for the analytical solution make it impractical for hydrogeologically complex systems.

Heatwole and McCray (2006) applied the HPS to the problem of wastewaters derived from OWTS. The research demonstrates that the HPS model has the appropriate parameters and model structure to accurately simulate fate and transport of nutrients from OWTS, including nitrogen, phosphorus, and fecal coliform. Using an analytical solution of the HPS model in a FORTRAN code, simulations of an example nitrate plume resulting from an OWTS are run using baseline parameter inputs. Additionally, a sensitivity analysis of input parameters was included. Groundwater velocity is indicated as the most sensitive parameter, and is therefore indicated as an important factor when trying to es-

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timate potential groundwater impacts. The HPS model is identified as a potentially useful tool for simple simulations in support of regulatory compliance and OWTS planning.

Similarly, Domenico (1987) provided an three-dimensional analytical solution that allows the user to input source dimensions in the x, y, and z directions creating a vertical plane source in contrast to the horizontal plane source described above. A further development of this source orientation was presented in Ollila (1996) for estimating natural attenuation of groundwater contaminants. Superposition of the rectangular source orientations developed by Domenico can provide for simulation of concentration profiles and asymmetric concentration cross sections.

More complex source orientations are proposed by Leij et al. (1991). In the development of this analytical solution, solutions are provided for representing rectangular, circular, cylindrical, and parallelepipedal source regions (Figure 2-9).



Figure 2-9: Source Orientations (Leij et al. 1991)

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Some researchers utilized novel approaches to the solution of the contaminant transport problem using analytical solutions. Hwang et al. (1985) incorporate a local analytical solution in a numerical model framework. By developing an analytical element at a node in the framework, a relationship with that node and its neighboring nodes is developed via a mathematical relationship. However, such an approach may require large amounts of computing power for more complex problems. Tang and Aral (1992) provide a solution for a layered aquifer that includes the main aquifer body and surrounding aquitards. Different values for degradation and retardation and other parameters are input for the aquifer and aquitards. This approach can therefore simulate different flow regimes in the same system and also can simulate the effects of diffusion into and out of aquitards.

Among the analytical solution models, some researchers created spreadsheet solutions to the ADE that can potentially be useful, simple tools for simulating nitrogen transport in the subsurface. These studies include Ollila (1996), Elmore (2007), Karahan (2006), and Karahan and Ayvaz (2005). While the equations themselves are typical solutions to the partial differential equation of the ADE, the use of a spreadsheet can be a very efficient method of calculating the solutions. Spreadsheets have the advantage of being relatively easy to program and use, wide availability, and iterative solution capabilities.

2.7 Parameter Estimation

Determining appropriate input parameters and the process of parameter estimation for fitting a groundwater model to observed data are an important yet difficult process. Parameter values can never be completely accurate, due to natural variations or incomplete data sets. Uncertainty related to input and calibration parameters leads to uncertainty in outputs. As such, some research has been performed specifically regarding parameter estimation. The objective of this research is to reduce the uncertainty as much as possible when estimating parameters, either as inputs to a model or through the calibration process.

A process of estimating parameters related to the transport of nitrogen and phosphorus from OWTS was developed by McCray et al. (2005). Cumulative frequency distributions (CFDs) were developed from data collected in the available literature to create statistical distributions for effluent concentrations, and nitrification and denitrification rates. In cases where inadequate data was available to produce a CFD, the mean, median and standard deviation was reported. These diagrams indicate the frequency of a reported value. The 50% value is the most frequently reported, whereas the 80% value means that 80% of the reported values are less than that value. Considering this for effluent concentrations as an example, the selection of the 90 percentile value would be considered as very conservative. This may be an appropriate choice if a simulation is intended to provide a protective concentration for a drinking water well.

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The resulting CFD diagram (for an example see Figure 2-10) can be useful for selecting appropriate water quality input parameters when data is limited either for a site or in the literature. This is particularly true for nitrification and denitrification rates.





Yanyong et al. (1992) describe a statistical process in the estimation of model parameters based on the observed data of the actual system. The method suggests using probability distributions of errors in the observed data to appropriately adjust parameters to reduce model residuals as much as possible. The researchers provide this as a direct method of estimating parameters, as opposed to performing a trial and error method to fit the model to the data. Therefore, the task of parameter fitting is less tedious, creates more optimal parameter sets, and has a statistical justification for the parameter values that were selected.

Regardless of the method chosen to estimate parameters, the analysis of uncertainty should also be included with any modeling effort. It is important to quantify the level of uncertainty as related to the simplifying assumptions of the model used and the quality of the data and how this influences the results.

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2.8 Nitrification and Denitrification Modeling

The simulation of the nitrification process has not received much research beyond the use of Monod kinetics, zero-order or first-order mathematical expressions and is mostly expressed as part of a larger model if the transformation of ammonium to nitrate needs to be represented. However, the simulation of denitrification has resulted in numerous approaches to the problem. This is perhaps due to the complexity of the biogeochemical processes associated with denitrification. The methodology ranges from empirically-based expressions to complex numerical codes. The review of the literature identified 20 studies related to the modeling of denitrification. Heinen (2006) provides a comprehensive summary of over 50 denitrification models, mostly simple empirical expressions. Heinen and other researchers identify numerous influencing factors such as pH, water content, dissolved oxygen, and others that may be beyond the scope of such a modeling tool. The modeling of denitrification is not discussed in great detail in this review. The research is provided for possible reference if desired.



Section 3.0 Discussion and Analysis

The models addressed in the review represent potential approaches to the model tool being developed for this project. The models were grouped in such a manner since each zone of interest requires different parameters, inputs, and assumptions; the modeling tool being developed will likely consider simulations in the vadose and saturated zones. In addition to identifying models for the different zones, various modeling methods were also identified; mass-balance modeling, analytical modeling, numerical modeling, and transfer function modeling. Each of these has their own advantages and disadvantages.

Mass-balance models are probably the simplest of the models found in the research review. These models are largely based on estimates of mass flux or volumes, and as such do not necessarily require prior knowledge of the subsurface characteristics. These types of models can have value for predicting mass flux in a generalized sense. In fact, many researchers use mass- or flux- balance calculations to assist in estimating input rates and concentrations for transport modeling. However, these models require numerous simplifying assumptions and typically cannot be used to predict solute concentrations at specified points in time and space. Furthermore, they do not account for hydrogeochemical processes; thus, any change in mass flux that may be influenced by such characteristics is represented as a fractional loss that is assumed to be constant over time.

Analytical models are a deterministic approach that simulates systems based on relatively simple, but widely used equations of flow and transport. This approach does require prior knowledge of subsurface characteristics, but the mathematics behind the analytical solution is relatively simple and flexible. Input parameters are relatively few and can be readily adjusted. Therefore, an analytical solution can be applied to multiple sites or hypothetical sites. Furthermore, the solutions can be programmed into a spreadsheet program for ease of use. However, analytical solutions cannot simulate highly heterogeneous systems. Therefore, it is important to consider the level of spatial variability of a system and how accurately this variability must be represented.

Numerical modeling has the most applicability when considering heterogeneous systems that operate under non-steady conditions that are impractical with analytical solutions. This is usually the case when estimating flow and transport in the vadose zone. As with analytical solutions, these models are very flexible. Often, however, numerical models

3.0 Discussion and Analysis

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are extremely complex, require relatively large amounts of input data (when compared to analytical solutions or mass-balance models), and require the use of computational methods. Furthermore, numerical models are often site-specific and not easily extended to other sites. Nonetheless, when considering a system that is highly heterogeneous or if boundary conditions cannot be simplified to constant, steady conditions, they are extremely useful.

The final category, transfer function models, operates on the assumption that deterministic models cannot appropriately account for the spatial variation in subsurface characteristics. This modeling approach, instead of relying on broadly applied parameter values, generates a probability distribution to account for water and solute movement. The major drawback to this model type is the lack of field studies to validate them and the likely resistance from regulatory agencies to their use since they do not rely on physical site characteristics. However, it is possible to couple stochastic methods with analytical models to better assess the uncertainty associated with the results.

When considering the modeling of denitrification, four approaches are possible. The first considers the details of the process, which may require inputs of temperature, pH, microbial population and growth dynamics, soil-moisture, and carbon availability in the modeling to capture the reduction functions that lead to denitrification. Secondly, models such as the analytical solution by Sun et al. (1999) could consider the reaction as a sequential first order process. The third approach simply identifies the process as a single first-order reduction, and therefore uses rate constants as an input parameter. Finally, recent work at Colorado School of Mines involves linking denitrification and nitrification rate constants to soil type and water content in analytical models. This provides an improvement over using only rate constants, without the need to consider all the biogeochemical processes at play. Considering the complexity of the denitrification process and the relative lack of understanding of how it works, the first approach is likely impractical. This may also be true when attempting to model denitrification as a sequential process, as the modeling would require rate constants for each step. Given the goals of the project and the level of influence of the process, the third approach may be sufficient to capture the denitrification process, while requiring the least amount of data collection. Field data and application of various models will be undertaken in this project to determine the appropriate level of complexity.

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Section 4.0 Conclusions

A review of the literature, the conceptual understanding of the transport of nitrogen as related to OWTS, and the goals of the project are all taken into consideration when beginning to describe the tool that will be developed. From this, several conclusions and some suggestions for the modeling tool can be developed.

The literature review was intended to identify the state-of-knowledge of nitrate fate and transport modeling, identify past models that may have provide good templates for the model developed by the FOSNRS Study, and assist in identifying key parameters and processes that need to be represented in a predictive tool.

As with any model development project, the appropriate approach can depend on numerous factors. When conceptualizing a model, several key questions need to be posed, such as:

- Will this model be constructed to represent a specific site of interest or be a predictive tool with broad applicability to a variety of sites?
- What is the desired output?
- What is the most appropriate method of calculating the output?
- Will this model require calibration to existing data sets?
- What, if any, regulatory requirements constrain the model choice?

The modeling tool that is being developed to simulate nitrate fate and transport will require certain features, some of which include:

- ease-of-use;
- ability to simulate time-variable OWTS inputs;
- simulation of transport and fate in both the vadose zone and saturated zones;

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- representation of the numerous advective-dispersive and transformative processes that affect nitrate transport;
- simulation of temporal and spatial concentrations and mass loading downgradient of the source;
- include the impacts of seasonal rainfall variation on the source function; and
- incorporate critical OWTS operating characteristics that strongly influence nitrogen reduction.

Based on the above questions and objectives, many conclusions about the models and model types in the research summary can be made. No simple model (analytical or mass-balance) identified in the literature can currently achieve all of the above-described goals. Also, numerical models are generally not considered a useful tool for system design or regulatory compliance where broad applicability is desired. Thus, development of a new modeling tool is likely required and rigorous numerical modeling may be needed as a first step to determine the most important parameters to include.

A strictly mass-balance modeling approach will likely be inappropriate, as it either does not consider the known physical processes that influence nitrate transport or makes simplifying assumptions about these processes. Furthermore, the output will not satisfy the objectives of the model (time-variable estimations of concentrations at specific spatial points). Nonetheless, these approaches have value in the conceptualization of model inputs and should not be ignored. Transfer function models have not been widely applied and will likely encounter regulatory resistance, since they are based strictly on probabilities and do not directly consider measured site characteristics. Both analytical and numerical modeling methods are the most promising approaches when considering the FOSNRS Study model to be developed. These approaches will have wide applicability, regulatory acceptance, and are capable of estimating the important hydrogeochemical properties associated with nitrate fate and transport.

The modeling tool will need to consider transport and transformation (chemical and physical) in the vadose zone, because the Nitrogen transformations that occur in this zone have considerable influence on the mass-flux input into the underlying aquifer. This can be a numerical one-dimensional solution of the Richards' Equation as suggested by (Bakhsh et al. 2004) or (Heatwole and McCray 2007) coupled with the ADE applied to the unsaturated zone as found in (Selim and Mansell 1976). A one-dimensional formulation can likely be implemented in a spreadsheet. Additionally, the modeling will need to consider temporally and spatially variable inputs for multiple OWTS, as would be found

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in a community development. This could be addressed through a series of onedimensional vadose zone models that could provide input to a multi-dimensional groundwater flow and transport model such as those suggested by (Ollila 1996) or (Galya 1987). Both of these studies use the horizontal plane source model or some variation and are also capable of transient simulations. However, the models likely will not be capable of interacting with each other in the vadose zone (i.e., strictly vertical flow is assumed). Nonetheless, the value of including these model features is important when simulating the areal distribution of OWTS in a potential housing development and the temporal variation of source input due to changes in wastewater input rate and precipitation recharge. These combined models can likely be implemented in a spreadsheet or using Fortran or C++ programming while maintaining simple and straight-forward input requirements. Of course, no similar model is available to our knowledge, so considerable model research and development must be achieved by this project. Within the models identified by the research review, the model developed by (Mehran et al. 1983-1984) is an example of a coupled modeling code for the transport and transformation of nitrogen but it lacks certain features for simulating nitrogen fate and transport related to OWTS.

The literature review has suggested the most likely processes and parameters that will need to be considered when developing the modeling tool. The fate and transport of nitrogen products is a result of advective movement, retardation via adsorption, and the transformative processes of nitrification and denitrification. These processes are to be calculated in the model tool via the solutions of the appropriate equations using the necessary parameters, described below. Key parameters to consider for simulation should consist of:

- physical parameters of the media such as bulk density, water content, and soil characteristics;
- advective-dispersive parameters such as hydraulic conductivity, hydraulic gradient, porosity (or groundwater velocities), and dispersivity values;
- retardation factor values for ammonium sorption; and
- rate coefficients for transformative reactions, typically first-order rate constants

A majority of the parameter values needed for model input can be collected during site characterization. McCray et al. (2005) utilize CFD's for the estimation of initial parameter values if utilizing literature values but the approach results in an uncertain model output where the degree of uncertainty must be quantified.

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Within the models identified by the research review, the model developed by (Mehran et al. 1983-1984) is a representative example of a coupled modeling code for the transport and transformation of nitrogen. Additionally, many analytical models were found in the literature review (nitrate-specific and general analytical solutions) that are appropriate for the modeling tool, since these can be programmed into a spreadsheet and can be user-friendly.

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Section 5.0 References

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