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Understanding nitrogen and carbon biogeotransformations and transport dynamics in saturated soil columns

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ABSTRACT

Nitrogen, originating from fertilizers, wastewater irrigation, livestock, septic tank leakages and other waste disposal sites, poses a major threat to surface and groundwater resources. Both hydrological and biogeochemical processes should be considered for accurate prediction of transport and transformations of nitrogen compounds. In this study, an attempt was made for better prediction of the existing advection-dispersion-reactive transport model by a coupled sorption-biodegradation sink term including advanced biokinetics and inhibition effect for nitrogen movement in saturated soil. The model addresses all the major biogeochemical transformations occurring in the soil similar to the flooded soil environment. The proposed numerical model was validated using a laboratory scale cylindrical soil column with immobile mixed bacteria operated under saturated conditions. Soil column experiments were performed to understand the dispersion, sorption, leaching and biodegradation of nitrogen (100 mg/L of NH_4^+, NO_3^-) and carbon (3000 mg/L of acetate) compounds during wastewater infiltration. It was observed that the model simulations matched closely in the case of sorption experiments for NH_4^+, NO_3^- and acetate with average model efficiency (E) of 0.986. In the case of sorption with leaching experiments, the model prediction was average for both NH_4^+ and NO_3^- at both low and high flow rates. The model predictability was improved by introducing a calibrated parameter λ which accounted for microbial activity in continuous column experiments when compared to the values obtained from the batch system, which was calculated by back fitting. As a result, the numerical model simulated the breakthrough profiles of NH_4^+ ($E = 0.812$), NO_3^- ($E = 0.701$) and acetate ($E = 0.611$) well. Further, this study implies that relatively shallow aquifers with sandy soil are vulnerable to NO_3^- contamination at around 10 days if continuous wastewater irrigation is practiced. Hence, long-term studies under field conditions under different irrigation scenarios in addition to simulation modeling must be carried out to generalize flow and nitrogen compound transport under various soil types.

1. Introduction

The use of treated, partially treated and untreated urban wastewater in agriculture has been a common practice for centuries in developing countries. The use of wastewater in the agricultural sector has enormously substituted both water and nutrient demands in the form of nitrogen. Nitrogen (N) is an important agricultural input which plays a major role in crop production (Tavakkoli and Oweis, 2004). It is important to use an optimum amount of water and nitrogen for best management of crop production in agricultural fields because the application of an excess amount of water can cause nitrogen leaching below the root zone (Chen et al., 2007, Gheysari et al., 2009; Wang et al., 2010), thus causing economic losses for farmers. Due to the lack of regulation and monitoring in this regard, most of the groundwater resources are contaminated which can cause a health threat to humans. Effective management of groundwater quality requires a thorough scientific understanding of complex physical, chemical and biological processes that govern the transport in the subsurface environment.

NO_3^- transport in flooded soil is governed by a complex interplay between chemical, biological and physical factors such as flow conditions (Fillery et al., 1984, Antonopoulos, 1993), nitrogen sources, climate, soils, microbial ecology, soil oxic condition, plant uptake, geology, groundwater geochemistry, the land surface area contributing to the well, and travel time in the, aquifer (Reddy et al., 1989; Lee et al., 2006; Desimone and Howes, 1998; Rubol et al., 2013; Ma et al., 2016a, b). A good understanding of transport (advection and dispersion) processes along with chemical and biological reactions (adsorption, biotransformation) is essential for developing a model for sustainable irrigation practices and policymaking. Moreover, modeling tools open a window for irrigation scheduling, water and nutrient addition according to crop needs, and deciding remediation technology (Zhao et al., 2009). But, the knowledge about contaminant loading, solute velocity, dispersion, transformation rates and soil properties is essential.

Numerous laboratory scale controlled column experiments were carried out to address the leaching and sorption process (Jellali et al., 2010, and Al-Darby and Nasser, 2006) and biotransformation

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(Munoz-Leoz et al., 2011, Liang et al., 2012, Mekala and Nambi, 2016). The biodegradation process was mostly considered as first order kinetics for simplification (Zhao et al., 2014). Moreover, the studies that have considered the biodegradation process ignore the effect of substrate inhibition on biodegradation which seems to greatly affect the reaction rates. The evaluation of column experiments with numerical models allows quantification of individual processes and their parameters (Wehrer and Totsche, 2008).

Several numerical reactive transport models have been developed and are used to explain the contaminant transport in saturated (Lee et al., 2006, MacQuarrie and Sudicky, 2001, Chowdary et al., 2004, Kinzelbach et al., 1991) and unsaturated porous media (Tindall et al., 1995; Berlin et al., 2013, Gaonkar et al., 2016). Most of these models address the microbial degradation as lumped parameter ignoring the processes of vital importance such as nitrification and denitrification and also lack experimental validation. Though models such as HYDRUS by Simunek and van Genuchten (2008) and RT3D by Clement et al. (1998), are able to give the spatial and temporal distribution of water flow and NO_3^- transport, they are more complicated, data intensive and appropriate for field studies. For simplification and scientific understanding of the nitrogen dynamics, there is always a need for a simple one-dimensional model. Some researchers have developed numerical models to simulate the transport and transformation of NO_3^- through laboratory column experiments (Chun et al., 2009, Peyrard et al., 2011 and Tafteh and Sepaskhah, 2012). But they consider only a single process and also represent microbial degradation in simple kinetics. In addition, modeling the fate and transport of nitrogen species in flooded soil is quite complicated due to a series of nitrogen transformation processes (Yoshinaga et al., 2004; Evans et al., 2006) and coupled physical, chemical and biological processes (Nakasone et al., 2004; Liang et al., 2004).

In this study, the vertical transport and dynamics of nitrogen in an agricultural soil under flooded conditions are simulated. The model considered in this study accounts for all the important N-transformation processes namely, sorption, leaching, nitrification and denitrification with substrate inhibition effect which usually is not taken into consideration. Moreover, the model accounts for efficiency factor to consider the deviation in biokinetic constants between batch and column studies. In addition, the model requires a minimum number of parameters that will effectively quantify N-transformation processes which can assess the risk of groundwater contamination. The ultimate goal is to provide a simple but comprehensive model that can estimate N leaching loads in groundwater governed by the bio and hydrogeochemical pathways which can improve fertilizer management.

2. Materials and methods

This study was conducted in a saturated soil column of 35 cm depth packed with wastewater irrigated soil. The soil was obtained from wastewater irrigated fields near the wastewater treatment plant of Indian Institute of Technology, Madras Tamil Nadu, India (IITM) at 1 m depth by continuous coring which was dried, sieved and stored for subsequent studies. This method of soil sampling would provide an easy and representative way for nitrifier and denitrifier enrichment from the soil (Elbanna et al., 2012, Song et al., 2000). The physicochemical properties of the soil are as shown in Table 1.

Table 1
Soil physicochemical properties.

Parameters	Values
pH	7.58
EC	406.9 μs/cm
OC	0.89%
CEC	22.8 mEq/100 g
C, H, N, S	0.64%, 0.46%, 0.07%, 0.05%
Gravel	5.51%
Sand	76.86%
Silt and clay	13.01%
Soil type	Well graded, loam sand
NO_3^- (2 M KCl extraction)	21 mg/kg
NH_4^+	6 mg/kg

2.1. Experimental studies

2.1.1. Batch experiments

The distribution coefficient in terms of sorption process between soil and the liquid phase was established by isotherm models in batch experiments for NH_4^+, NO_3^-, and acetate. Adsorption studies were carried out in triplicate with sterilized soil slurries for various initial concentrations 5, 10, 50, 100, 300 and 500 mg/L of NH_4^+, NO_3^- and acetate in 250 mL conical flasks. 5 g of sterilized soil was added to 100 mL of solute solution in distilled water and kept for shaking at 140 rpm for the equilibrium time determined using kinetic studies. The solutes NH_4^+, NO_3^-, and acetate attained pseudo-equilibrium state at times 6, 3 and 10 h respectively. The experimental results were fitted using different isotherm models and the sorption parameters were estimated. After the adsorption experiments, the entire soil mixture was centrifuged and the liquid was decanted. The soil was air dried overnight and then added to 100 mL of deionized water and kept on a shaker at 140 rpm for the equilibrium time for desorption experiments. The desorbed aqueous concentrations were analyzed and fitted using isotherm models. The Fourier Transform Infrared (FTIR) (ATR-FTIR, Bruker co., Germany) using KBr crystal disc in the spectral range 400 to 4000 cm^{-1} and at a scan rate of 30 scans was used to characterize the functional groups and the bonding mechanisms in plain soil and sorbed soil. The samples were oven dried at 200 °C and analyzed. The IR peaks obtained in sorbed soil were compared with plain soil. The zeta potential analyzer (Horiba SZ-100) was used to measure the electrophoretic stability and repulsion between charged particles based on the theory of Marian Smoluchowski in 1903. Charged particles disperse towards oppositely charged electrodes with a velocity proportional to zeta potential.

Biodegradation studies were carried out to establish biokinetic constants for aerobic nitrification and anoxic denitrification separately. Mixed microbial consortium was isolated from soil and sludge taken from wastewater treatment plant of IITM and enriched to carry out nitrification and denitrification studies. Based on their activity for NH_4^+ oxidation and NO_3^- reduction, a substrate-biomass profile was established. It was fitted for various biokinetic models and the best accurate fit was selected based on model efficiency. The complete details of the methodology, analysis, and results of batch studies with biokinetic modeling can be obtained from our previous studies Mekala and Nambi, 2016.

2.1.2. Continuous column studies

Column experiments were performed in an acrylic column of length 50 cm and diameter 5.2 cm. The feed was supplied with the help of a peristaltic pump at a flow rate of 0.153 cm/min. The column was wet packed and equilibrated till it reached a steady flow condition. The initial concentration of bacteria in soil was established by plate count. The inlet feed of 100 mg/L for NH_4^+ and NO_3^- and 3000 mg/L for acetate was supplied and their outlet concentrations were monitored with time. The excess substrate concentrations assured a continuous supply of electrons for redox reactions and avoided circumstances of substrate inhibition (Somasundaram et al., 2011). The operating conditions for the column studies were as given in Table 2. The following column experiments were conducted: (i) tracer studies with bromide; (ii) column experiments containing sterile soil for sorption studies of NH_4^+, NO_3^- and acetate; (iii) column experiments with sterile soil for understanding sorption and leaching of NH_4^+ and NO_3^-. These experiments were carried out at two different flow rates and in this case, the feed containing solute was continuously supplied for first 12 h and then replaced with pure