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Edge of Field Technology to Eliminate Nutrient Transport from Croplands: Specific Focus on Denitrification Bioreactors

Michael Aide, Indi Braden and Sven Svenson

Additional information is available at the end of the chapter

Abstract

Tile drainage effluent from agriculture fields is beneficial to production agriculture; however, nitrate and phosphate transport from production fields to surface water resources is an environmental concern. The David M. Barton Agriculture Research Center (Cape Girardeau County, Missouri, USA) has a 40 ha controlled subsurface tile drainage/irrigation technology with associated denitrification bioreactor. Nitrate-bearing effluents from the controlled subsurface tile drainage/irrigation technology under a corn (*Zea mays* L.)-soybean (*Glycine max* L) rotation is sufficient to be an environmental concern. Nitrate-bearing effluent passage through the denitrification bioreactor typically promotes sufficient nitrate reduction (denitrification) that the bioreactor effluent water is less than 10 mg NO_3-N/L. Phosphorus, ammonium-N, and sulfate-S concentrations are not appreciably influenced by denitrification bioreactor passage.

Keywords: bioreactors, nitrate, controlled drainage, water quality, denitrification

1. Introduction

1.1. Impact of nutrient migration from cropland to fresh water

Hypoxia is considered as oxygen depletion in a water column to the point that living aquatic organisms may no long survive. Hypoxia in the northern Gulf of Mexico is defined as a dissolved oxygen concentration smaller than 2 mg/L. Hypoxia may be a naturally occurring phenomenon in selected marine environments (fjords, deep ocean basins, etc.); however,

human activities are increasingly associated with the expanding of existing hypoxia zones [1]. One large hypoxia zone exists in the northern Gulf of Mexico, adjacent or superimposed on the Louisiana/Texas continental shelf.

Factors believed to be influencing the areal extent and the degree of oxygen depletion in the northern Gulf of Mexico include (i) nutrient concentrations flowing from the Mississippi River, (ii) eutrophication, (iii) microbial biomass respiration at the ocean floor, and (iv) water column stratification and attendant oxygen depletion. Mississippi River nutrient concentrations have increased in the twentieth century and continue to increase to the present time. The current concentrations of nitrogen and phosphorus in the Mississippi River and other rivers has been attributed to increased use of nitrogen and phosphorous fertilizers, the potential for nitrogen and phosphorus to become transported from crop fields to tributaries of the Mississippi River, and atmospheric deposition of oxidized nitrogen gases arising from the combustion of fossil fuels.

Eutrophication follows when aquatic systems receive these nutrients and increase primary production, including algae. The increased growth of phytoplankton exceeds the food web's capacity to consume the phytoplankton, permitting a portion of the phytoplankton to sink to the ocean bottom, supporting bacterial growth. Water column stratification isolates the reduced oxygen-bearing deep water layers. Organisms that are more predatory and higher in the food chain vacate the region, while other less mobile species perish. Disruption of commercial fishing is common. Hypoxia typically persists until weather patterns and storms remix the water column.

1.2. Review of controlled subsurface irrigation and drainage technologies

1.2.1. Nitrogen, phosphorus, and tile drainage

The United States Environmental Protection Agency (USEPA) maximum contamination level for nitrate-N is 10 mg NO_3-N/L and the scientific literature is replete with manuscripts addressing nitrate levels in groundwater and surface water exceeding this concentration [2–9]. Watersheds having N-fertilized row crop and metropolitan/suburban areas are known to contribute N runoff to tributaries, supporting hypoxia in the Gulf of Mexico [4].

Surface water runoff from intensively fertilized agricultural fields or urban landscapes, soil erosion, livestock and poultry operations, and effluent discharge from subsurface drainage technologies are important nutrient sources for freshwater contamination [10–15]. Nitrate concentrations emanating from subsurface drainage systems frequently exceed the USEPA maximum contamination levels [3, 5, 8, 16]. Phosphorus concentrations emanating from surface- or subsurface-drained landscapes are markedly most severe if the soils have a low P sorption capacity or have been heavily amended with phosphate manure/fertilizers [14, 17–23].

Dinnes et al. [4] reviewed the literature and noted that agricultural investigations aimed at reducing N losses from tile-drained soils include (1) properly adjust timing and rate of nitrogen fertilization, (2) quantify soil organic matter mineralization to reduce overapplication of nitrogen fertilizers, (3) using appropriate yield goals when making fertilizer recommenda-

tions, (4) encourage prescription fertilization practices, (5) employ nitrification and urease inhibitors, (6) employ remote sensing technologies to monitor crop nutrient status, (7) diversify crop rotations and cover crops, (8) manage plant residues, and (9) install riparian buffers and drainage control strategies. Drainage control strategies essentially manage soil water to promote anoxic soil conditions resulting in denitrification.

Kladivko et al. [7] effectively demonstrated that narrow-spaced lateral drainage lines have a greater capacity to promote nitrate removal. Fisher et al. [24] compared controlled subsurface drainage technologies with open drainage systems and documented that 30–75 cm water table depth maintenance reduced nitrate soil water concentrations and improved corn uptake of nitrogen. Randall et al. [8] investigated corn-soybean rotations in Minnesota and documented that nitrate leaching correlated with rainfall, that the soybean phase supported nitrate tile drain discharges because of residue mineralization and residual nitrate concentrations from the previous corn planting. Randall et al. [8] also observed that summer intervals exhibited the smallest nitrate leaching because the evapotranspiration rates exceeded the precipitation rates.

Phosphorus studies have centered on P runoff and P leaching [25–27]. Organic P and colloidal P may be mobile in controlled drainage systems [7, 17, 23]. Djodjic et al. [19] noted that dissolved reactive phosphorus was not effectively predicted by total P and that preferential water flow pathways did not allow for equilibrium assumptions. In a review, Hart et al. [28] noted that catchment studies typically show that 62–91% of surface runoff is associated with particulate P.

1.2.2. Denitrification bioreactors

Numerous ground and surface waters exceed the USEPA nitrate-N concentration of 10 mg NO_3-N/L drinking water limit [5, 6, 29, 30]. United States Environmental Protection Agency (USEPA) reports that a 45% reduction in nitrogen loads in the Mississippi River Basin is a goal to reduce water impact. In the Midwest, 15 million ha have artificial drainage capacities. The reported elevated nitrogen loads include 81 [31] and 88 kg N/ha [32], whereas more typical nitrogen loads are 25–35 kg N/ha, likely associated with nitrate-N effluent concentrations of 10–25 mg NO_3-N/L [33]. An emerging technology involves the design and construction of permeable reactive subsurface-packed beds having carbonaceous materials to support nitrate denitrification [34–36].

In a review by Christianson [37], denitrification bioreactors in the upper Midwest were effective in reducing nitrate-N effluent concentrations: 32.5 [38, 39], 40–65 [30], 50–60 [40], and 47% [41]. Denitrification bioreactors rely on microbial denitrification

$$5C + 4NO_3^- + 2H_2O = 2N_2 + 4HCO_3^- + CO_2.$$
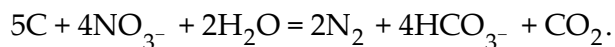
The process requires a (i) carbon source (electron donor), (ii) low dissolved oxygen (DO) concentrations, (iii) denitrifying bacteria, and (iv) nitrate as an electron acceptor and results in either nitrogen gas (N_2) or nitrogen oxides (N_2O) production [40]. The microbial reaction pathway may be described as

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O.$$
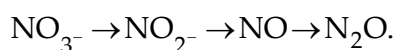
Each step is catalyzed by nitrate reductase, nitrite reductase, nitric oxide reductase, and nitrous oxide reductase, respectively. The release of bicarbonate may modify the reactor pH. Low pH, low temperature, suboxic dissolved oxygen levels, and low C/N ratios act individually or collectively to support greater N_2O/N_2 ratios [37, 42, 43].

The reduction half reaction and associated log K_r and $E^o{}_H$ values for nitrate-dinitrogen gas couple may be written as [44]

$$1/5NO_3^- + 6/5H^+ e^- \rightarrow 1/10N_2 + {}^3\!/\!4H_2O \, LogK_r = 21.1 \text{ and } E^o{}_H = 1.248 \text{ volts V.}$$

The IUPAC convention would list the reaction as

$$E_H (volts V) = E^o + \left(RT/nF\right)\left\{\ln\left[NO_3^-\right]^{0.2}\left[H^+\right]^{1.2}/\left[N_2\right]^{0.1}\right\},$$

where $[H_2O]$ has unit activity Activity, R=001987 kcal/mole deg., T is temperature in Kelvin, and F is 23.061 kcal/volt g. eq. Given the partial pressure of nitrogen gas at 0.79 and a pH near neutrality, the E_H is a linear function of the nitrate concentration.

Denitrification reactor design is a complex function of reactor length and retention times suitable to reduce dissolved oxygen concentrations for the anaerobic process to facilitate nitrate reduction [42, 45]. Excessive retention times may promote sulfate-S reduction and mercury methanogenesis [37, 42]. Retention time is largely a function of reactor water flux, with greater water flow rates reducing the retention time. Chun et al. [41] observed that denitrification bioreactor nitrate reduction responded to first-order kinetics, whereas Schipper et al. [22] noted that field-scale bioreactors were better simulated using zero-order kinetics.

2. Materials and methods

2.1. Existing physical infrastructure

Located in Cape Girardeau County (Missouri, USA), the David M. Barton Agriculture Research Center hosts the Crop Science Unit. The Crop Science Unit has a controlled subsurface drainage and irrigation system. The controlled drainage system consists of a series of parallel 10 cm (4 in.) subsurface conduits having a parallel 10 m (30 ft) spacing collecting into 20 cm (8 in.) conducts for transport of surplus drainage water to field ditches. Irrigation and drainage are monitored by stop-log boxes fitted with adjustable baffles strategically arranged in the field to permit the restriction of water flow, allowing irrigation/drainage water to be added/removed

throughout the system by gravity flow. The irrigation pumping system consists of five wells, each with capacity to pump 265 L/min (70 gal/min).

The denitrification bioreactor was constructed in June 2014. Sampling ports allow water sampling from the denitrification bioreactor at the influent and effluent tile lines. The denitrification bioreactor has dimensions of 10 m width, 20 m length, and 0.7 m thickness. The top of the denitrification bioreactor is approximately 0.6 m below the soil surface. Oak (*Quercus* sp.) wood chips having an approximately 5 cm (2 in.) equivalent circular diameter with 1 cm thickness constitute the denitrification bioreactor-packed bed fill (**Figure 1**).
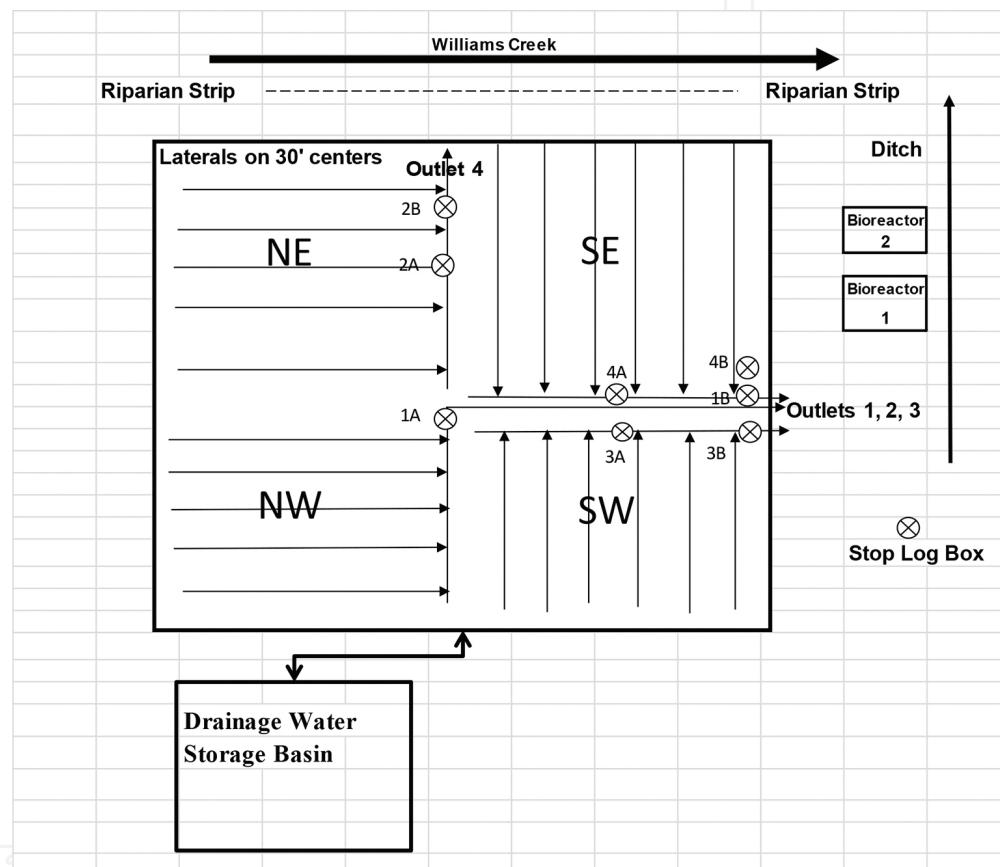

Figure 1. Technology development at the Crop Science Unit (40 ha or 100 acres).

2.2. Soil resources

The soils of the Wilbur series (USA Soil Taxonomy: coarse-silty, mixed, superactive, mesic Fluvaquentic Eutrudepts) consist of very deep, moderately well-drained soils that formed in alluvium. Six pedons show uniform silt loam textures throughout their soil profiles and display Ap-Bw-Cg horizon sequences [46]. Moderate medium platy structures in the near-surface horizons typically part to weak medium subangular blocky structures in the Bw horizons. The deeper Cg horizons generally show moderate coarse prismatic structures that part to weak medium subangular blocky structures. The dominant soil matrix colors are dark brown to dark

yellowish brown in the Ap and Bw horizons, transitioning to light gray, gray, light brownish gray, and grayish brown in the Cg horizons. Iron-Mn accumulations and Fe depletions are evident throughout the soil profiles, especially in the Cambic and Cg horizons.

Soil pH generally ranges from slightly acid (pH 6.1–6.5) to neutral (pH 6.6–7.3) in the near-surface horizons to strongly acid (pH 5.1–5.5) and very strongly acid (pH 4.5–5.0) in the Bw and upper Cg horizons, whereas the deepest Cg horizons have moderate to slight acidity (pH 5.6–7.0). The soil organic matter contents are generally low (less than 2%) and decline with increasing soil depth. Soil phosphorus (extraction using Bray1-P) and sulfur (extraction using 2 M KCl) have their greatest concentrations in the near-surface horizons, showing a continuous P and S decline with increasing soil depth. The exchangeable cations are dominated by calcium (Ca), especially in the near-surface soil horizons. The total acidity is appreciable, particularly in the deeper soil horizons; however, some Wilbur pedons show reduced total acidity expressions in the deeper Cg horizons. The cation exchange capacity is low (<12 cmol$_{p(+)}$/kg) to medium (12–18 cmol$_{p(+)}$/kg) and roughly corresponds with the clay and soil organic matter contents.

Mechanical analysis indicates that silt is the dominant separate in all six pedons, with the sand separate being less than 10% and composed almost entirely of very fine sand. The clay mineralogy is mixed, with an abundance of hydroxyl Al-interlayered vermiculite, smectite, hydrous mica, and kaolinite. Smectite shows relatively greater abundances in the deeper soil horizons.

2.3. Soil water assessment

Field soil water measurements involve (i) water table height using piezometer tubes, (ii) irrigation water rates using flow meters, (iii) rainfall monitoring using a US Class A rain gauge, and (iv) volumetric soil moisture distribution using gravimetric samples and bulk density. Estimates of total tile drainage flow were obtained using electronic water elevation sensors in the stop-log boxes and box geometry to calculate water flow, where water was applied from Williams Creek with a centrifugal pump system. Levees were designed by field survey and established with a levee plow.

2.4. Crop production to assess nutrient uptake

Corn (*Zea mays* L.) was planted from 2008 to 2015 on 0.77 m (30 in.) row spacing. Phosphorus (P) and potassium (K) fertilization was applied using variable rate technology based on grid soil sampling. From 2012 to 2015, corn nitrogen fertilization rates were 378 kg N/ha (344 N lbs N/acre) as half of the urea was applied 1 week prior to planting and half applied 2 weeks after planting. Yield goals were 13,200 kg/ha at an established population of 85,000 plants/ha. Tissue testing (N, P, K, Ca, Mg, S, Na, Al, Fe, Mn, Zn, B, and Cu) and plant biomass accumulation were documented to assess nutrient uptake patterns at V7, R1, and R6 corn growth stages. Plant organ sampling includes biomass and nutrient accumulation in root, stem (culm), leaf, and seed, with total plant uptake and biomass accumulation based on the summation of the product of the plant organs biomass and concentration.

2.5. Field and laboratory protocols

Water sampling of tile drain and denitrification bioreactor influent and effluent was conducted weekly for the spring 2015 drainage season and daily for the denitrification bioreactor/ Williams Creek assessment. Water was collected in precleaned plastic collection bottles and stored in refrigeration cabinets until analyzed. Samples were analyzed for pH, NO_3-N, NH_4-N, H_2PO_4/HPO_4, SO_4-S, Ca, Mg, K, and Na at the University of Missouri's Fisher Delta Research Center using standard protocols. Nitrate concentrations were determined using an ion-specific electrode, ammonium concentrations were determined using colorimetric indophenol blue, phosphorus was determined using colorimetric ammonium molybdate, and sulfate-S was determined using the $BaCl_2$ turbidimetric method. Water pH was determined using a combination pH electrode. Exchangeable cations were extracted using 1 M ammonium acetate (pH 7) extraction. Water and soil calcium, magnesium, potassium, and sodium concentrations were determined using air-acetylene atomic absorption spectroscopy.

3. Research involving controlled subsurface irrigation and drainage at the David M. Barton Agriculture Research Center

This portion of the research project is a long-term assessment of controlled subsurface irrigation/drainage technologies with associated denitrification bioreactors. Tile drainage water chemistry and nitrate-ammonium concentrations available in soil from 2010 to 2013 are documented [47, 48]. These 4 years of investigation reveal soil nitrate concentrations generally showed an increase immediately after soil nitrogen fertilization practices and were sufficiently abundant to promote their transport from the soil resource to the tile drain effluent waters. The tile drainage chemistry data indicated (i) appreciable transport of nitrate-N in tile drain effluent waters (mean of 32 mg NO_3-N/L in 2008, mean of 80 mg NO_3-N/L in 2009, mean of 10 mg NO_3-N/L in 2010, and mean of 15 mg NO_3-N/L in 2012); (ii) denitrification soil pathways partially reduced a portion of the soil nitrate-N when the controlled drainage system establishes winter/early spring anoxic soil conditions, and (iii) the best strategy for reducing nitrate-N concentrations in tile drain effluent waters was adjusting: (i) N fertilization rates and (ii) the timing of their application.

Tile drainage from the 2014 soybean system illustrated pH levels near pH 6.5 ± 0.5 across all of the sampling sites for the duration of drainage. Greater nitrate sampling was performed in 2014 than 2013 because of the longer drainage interval; however, tile drainage effluent nitrate-N concentrations averaged from less than 10 mg NO_3-N/L for many of the sampling sites/times to more than 80 mg NO_3-N on at least four occasions (**Figure 2**). Ammonium concentrations in the tile drain effluents ranged from 0.25 mg NH_4-N/L to near 5 mg NH_4-N/L. The presence of appreciable nitrate and ammonium concentrations was reflective of a large nitrate pool remaining from the previous corn production and to a smaller extent soil organic matter mineralization. Phosphorus concentrations ranged from 0.1 to 3 mg P/L, thus phosphorus concentrations represent an environmental impact given they frequently exceed

0.2 mg PO_4-P/L. Sulfate-S concentrations ranged from 2.5 to 5.5 mg SO_4-S/L; however, these SO_4-S concentrations were not considered an environmental hazard.
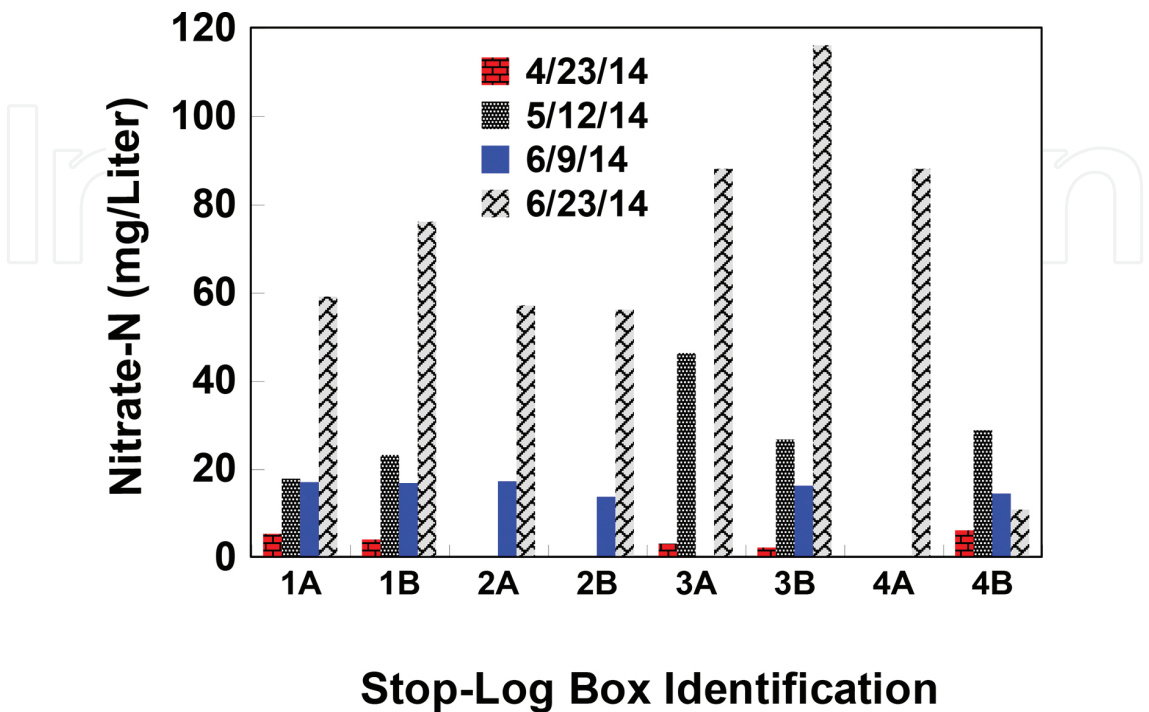

Figure 2. Drainage water nitrate-N concentrations from stop-log boxes in 2014.

Soil nitrate concentrations have been periodically monitored to estimate the soil nitrate pool for plant uptake and leaching potentials. The soil nitrate concentrations typically have fluctuated based on (i) the corn-soybean rotation stage, (ii) nitrogen (urea) fertilization rates and timing, (iii) soil denitrification (either intentionally establishing perched water tables by restricting drainage during the noncropping season and cropping season rainfall patterns), (iv) crop uptake (corn-soybean rotation and off-season cover crop establishment), and (v) soil mineralization and residue decomposition. Soil sampling established that nitrate-N concentrations were (i) greater after urea application for corn and (ii) dependent on rainfall patterns. Approximately 10–50% of the nitrate pool migrated from the upper 15 cm to the 15–30 cm layer within 1 month of application, with smaller portions of the nitrate pool ultimately percolating to deeper soil layers. As an example, 2013 (corn portion of the rotation) witnessed an April planting with urea (292 lbs/ac or 328 kg/ha) application just prior to 15 May 2013. On 15 May 2013, the majority of the urea was converted to ammonium with a portion of the ammonium converting to nitrate via nitrification reactions. On 7 June, the majority of the nitrogen application was nitrate, with a portion of the nitrate leaching into the 15–30, 30–45, and 45–60 cm deep soil layers (**Table 1**). Soil nitrate concentrations postcorn harvest (data not shown) and 24 March 2014 soil nitrate concentrations were comparatively smaller. A substantial portion of the field nitrogen pool was documented to be associated with grain and residue production (approximately 60%) and the remainder associated with the soil nitrate pool and lost from the soil system because of tile drainage effluents or soil denitrification reactions.

Depth (cm)	NO$_3$-N	NH$_4$-N
	mg N/kg	
15 May 2013 (corn)		
15	12.5–18.6	9.7–25.7
30	11.3–16.1	0.5–0.9
45	8.3–8.6	1.1–1.5
60	7.6–7.1	0.7–0.9
7 June 2013 (corn)		
15	14.4–21.4	3.2–5.8
30	15.0–16.7	3.4–7.9
45	14.5–15.6	2.2–3.4
60	14.4–14.6	0.7–3.4
24 March 2014 (soybean)		
15	6.9–7.9	0.3–1.4
30	7.0–7.7	0.2–0.6
45	6.9–7.9	0.2–0.7
60	7.0–7.7	0.2–1.4

Multiple replications.

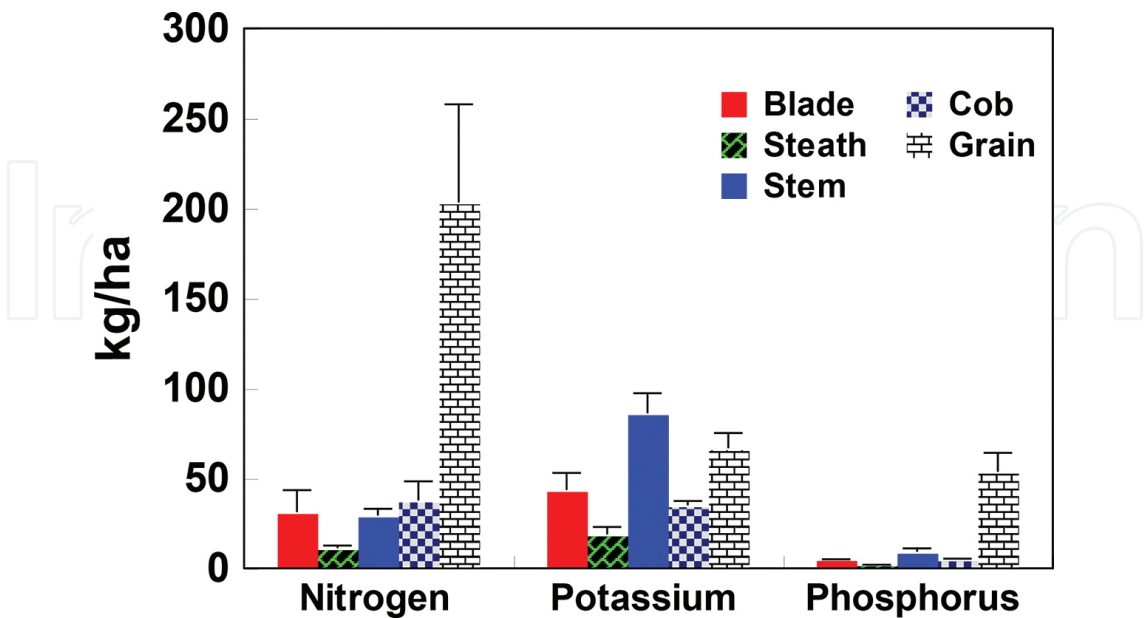**Table 1.** Soil nitrate and ammonium concentrations.

Figure 3. Concentrations of nitrogen, potassium, and phosphorus in 2014 corn by plant organs (Error bars are the standard deviations of three replicates.).

The associated corn biomass (**Figure 3**) demonstrates that nitrogen is primarily associated with grain (65%) and is thus removed from the soil landscape by harvest. Similarly, potassium (27% associated with grain) and phosphorus (74% associated with grain) demonstrate different harvest removals.

4. Research involving controlled subsurface irrigation and drainage with denitrification bioreactors at the David M. Barton Agriculture Research Center

4.1. Spring drainage water study: denitrification bioreactor inlet and outlet water chemistry for Spring 2015

The 2015 growing season was the first operational year for the denitrification bioreactor. Nitrate-bearing tile drainage water from land cultivated to corn (*Zea mays* L.) entered the denitrification bioreactor during the "drainage season." Mean phosphate, ammonium, nitrate, and sulfate concentrations and water pH are presented (**Table 2**) to illustrate the baseline chemistry and document that tile drainage effluent has sufficient nitrate-N to be considered as an environmental hazard.

Sampling sites	PO_4-P	NH_4-N	NO_3-N	SO_4-S	pH
			mg/L		
1A	0.3	0.9	21	2.7	6.8
1B	0.23	1.5	25.6	2.6	6.8
2A	0.19	1	16.4	2.7	6.6
2B	0.37	1	11.2	2	6.5
3B	0.2	0.7	15.8	1.6	6.9
4B	0.21	0.7	22	2.2	6.8
Bioreactor influx	0.23	0.8	59.1	4	6.7
Bioreactor effluent	0.25	0.9	38.6	2.1	6.6

Tile drainage sampling (1A, 1B, 2A, 2B, 3B, and 4B), mean of 12 sampling times from 20 March 2015 to cessation of drainage on 6 July 2015.

Table 2. Mean phosphorus, ammonium, nitrate, and sulfate concentrations and pH of tile drainage waters collected during the spring 2015 drainage season.

Nitrate-N concentrations were substantially reduced by passage through the denitrification bioreactor, except for 29 May 2015 that was postnitrogen fertilization and a heavy rain event with large water volumes migrating through the bioreactor (**Figure 4**). From March through early May, the influx of nitrate-N averaged 17 mg NO_3-N/L (standard deviation of 12 mg NO_3-N/L), whereas the effluent concentrations were 5 mg NO_3-N/L (standard deviation of 3 mg NO_3-

N/L). Nitrate concentrations from late May to mid-June and following nitrogen fertilization, the influx of nitrate-N averaged 69 mg NO_3-N/L (standard deviation of 31 mg NO_3-N/L), whereas the effluent concentrations were 21 mg NO_3-N/L (standard deviation of 40 mg NO_3-N/L).
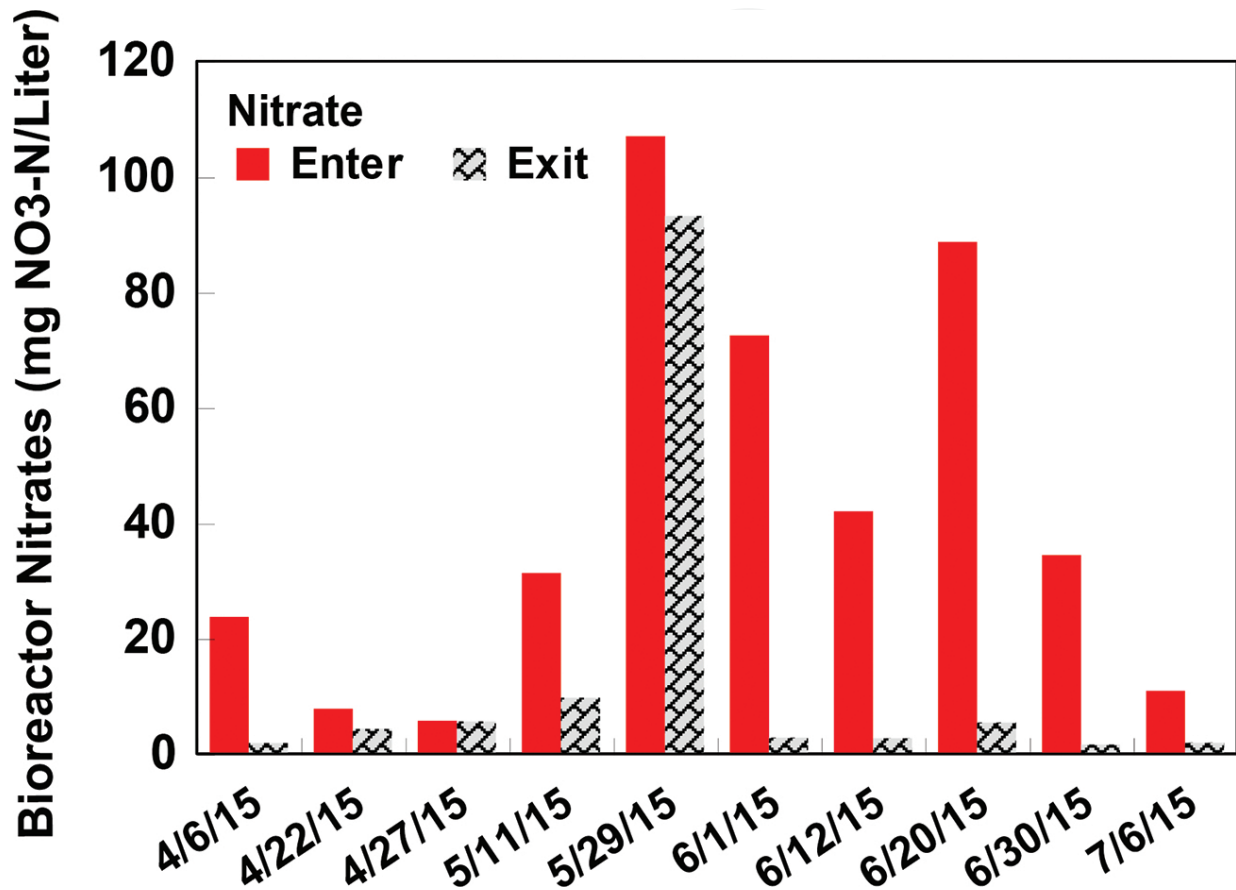

Figure 4. Denitrification bioreactor nitrate-N concentrations at the receiving and exiting terminals.

Ammonium concentrations were not appreciably influenced by bioreactor passage. Ammonium-N concentrations were generally less than 1 mg NH_4-N/L, except for 22 April 2015 (1.3 mg NH_4-N/L influx and 0.4 mg NH_4-N/L effluent) and 30 June 2015 (3.0 mg NH_4-N/L influx and 2.4 mg NH_4-N/L effluent). Phosphorus and sulfate concentrations and water pH were not appreciably influenced by fluctuations during the drainage season and were not significantly altered by denitrification bioreactor passage.

4.2. Williams Creek impoundment and denitrification bioreactor efficiency

In the winter of 2015, Williams Creek waters were pumped and impounded by a levee system and then allowed to infiltrate/percolate through the soil and entered the tile drainage system. Water captured by the controlled subsurface drainage technology was transported to the denitrification bioreactor.

4.2.1. Williams Creek water and stop-log box 4B captured soil water

Williams Creek water is classified as a calcium-carbonate type water with a pH range from 7.92 to 8.05, implying dissolved calcium carbonate was influencing pH. Soil water pH sampled from stop-log box 4B ranged from 6.36 to 7.15 with a mean near 6.75. Presumably, the soil's cation exchange complex buffered soil drainage water and reduced the pH of waters originating from Williams Creek.

The soil water comparisons for calcium, magnesium, potassium, and sodium (**Table 3**) reveal that calcium concentrations are greater in the Williams Creek impoundment trial than the spring 2015 drainage trial. The field was limed with calcite limestone in the winter of 2014–2015 and limestone requires a lengthy time interval to dissolve, perform cation exchange, and complete acid neutralization, thus increasing the calcium saturation of the cation exchange complex. Additionally, Williams Creek may be assumed to be a water solute calcium source.

ID	Ca (ppm)	Mg (ppm)	K (ppm)	Na (ppm)
6/12/2015				
4B	5.5	24	2.1	11.3
In	5.3	9.1	2.9	14.1
Out	8.9	11.6	2.8	13.8
12/13/2015				
4B	61	9.4	4.5	12.8
In	52	8.7	3.7	11.1
Out	54	8.6	3.5	11.2
12/14/2015				
4B	36	6	2.8	8.9
In	33.5	5.7	2.7	7.4
Out	35.5	5.8	2.6	8.3

Table 3. Soil water concentrations of calcium, magnesium, potassium, and sodium.

Williams Creek waters show elevated nitrate concentrations, ranging from 12.7 mg NO_3-N/L on 25 November 2015 to 672 mg NO_3-N/L on 4 December 2015 (**Figure 5**). Soil water shows a nitrate-N increase to 33.1 mg NO_3-N/L on 2 Dec 2015 and 44 mg NO_3-N/L on 3 December 2015, suggesting that the soil resource is influenced by nitrate-N originating from Williams Creek. Soil water nitrate-N concentrations are consistently smaller than the water from Williams Creek, implying that the soil resource is reducing nitrate-N concentrations by a combination of two processes: (i) dilution of Williams Creek nitrate-N concentrations with the preexisting soil water and (ii) denitrification soil processes.

Nitrate-N concentrations in soil water after 7 December 2015 show a gradual decline. Between 27 November and 29 November 2015, approximately 2.94 in. of rainfall occurred, inferring that rainfall acted to dilute the soil water nitrate-N concentrations. Williams Creek and soil water both demonstrated greater nitrate concentrations on 2 December 2015.
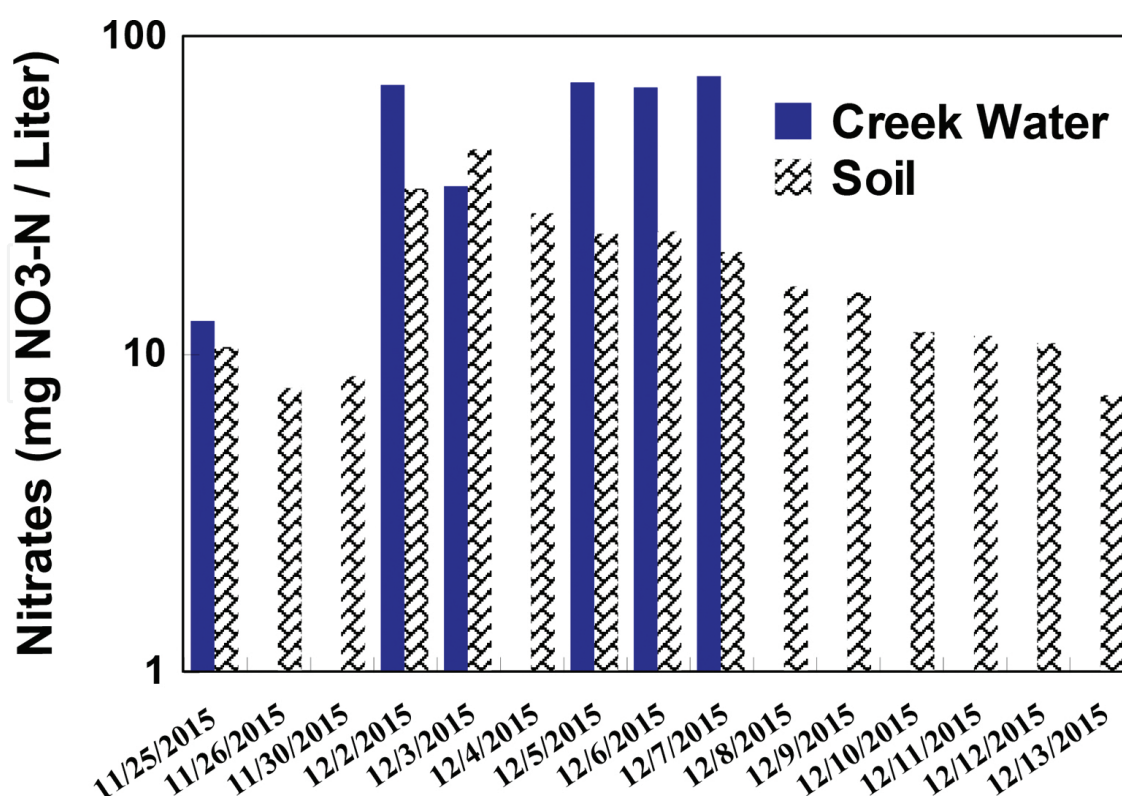
Figure 5. Nitrate concentrations from Williams Creek and stop-log box 4B. (Note: Log scale.) On 4 December 2015, Williams Creek showed 691 mg NO_3-N/L. (Data not shown on graph for graphics clarity.) Pumping from Williams Creek stopped on 8 December 2015.

Ammonium concentrations are generally small, less than 2 mg NH_4-N/L for Williams Creek and generally less than 1 mg NH_4-N/L for soil waters. Williams Creek water has the greatest ammonium concentration on 7 December 2015 (1.7 mg NH_4-N/L), approximately 3 days after the greatest nitrate-N concentrations, whereas soil water has the greatest ammonium concentration on 9 December 2015 (1.7 mg NH_4-N/L). Mean phosphorus concentrations are 0.36 mg PO_4-P/L for Williams Creek waters and 0.39 mg PO_4-P/L for the field sampling site waters, with the concentration differences being not significant. These phosphorus concentrations are considered sufficiently abundant to support water eutrophication. Sulfate concentrations were not significantly different between the Williams Creek waters (mean SO_4-S at 1.4 mg SO_4-S/L) and the field sampling site waters (mean SO_4-S at 1.2 mg SO_4-S/L).

4.3. Denitrification bioreactor nitrate reduction potential with Williams Creek source water

pH of the denitrification bioreactor inlet and effluent waters were not significantly different for each sampling date; however, the inlet water pH varied from a low pH of 6.33 (30 November 2015) to pH 7.07 (12 December 2015) and the effluent water pH varied from pH 6.31 (30 November 2015) to pH 7.18 (12 December 2015).

Denitrification bioreactor outlet nitrate-N concentrations were slightly too appreciably smaller than the corresponding inlet nitrate-N concentrations (**Figure 6**). The highest nitrate-N concentrations occurred on 2 December 2015, which corresponds with the nitrate-N concen-

tration rise associated with stop-log box 4B. Nitrate-N concentrations from 2 December to 7 December 2015 ranged from 35.1 mg NO_3-N/L to 20.6 mg NO_3-N/L for the inlet concentrations and from 25.3 mg NO_3-N/L to 17.2 mg NO_3-N/L for the outlet concentrations. From 8 December to 13 December 2015, the inlet and outlet nitrate-N concentrations became increasingly smaller, and the outlet nitrate-N concentrations continued to be smaller than those of the corresponding inlet concentrations.
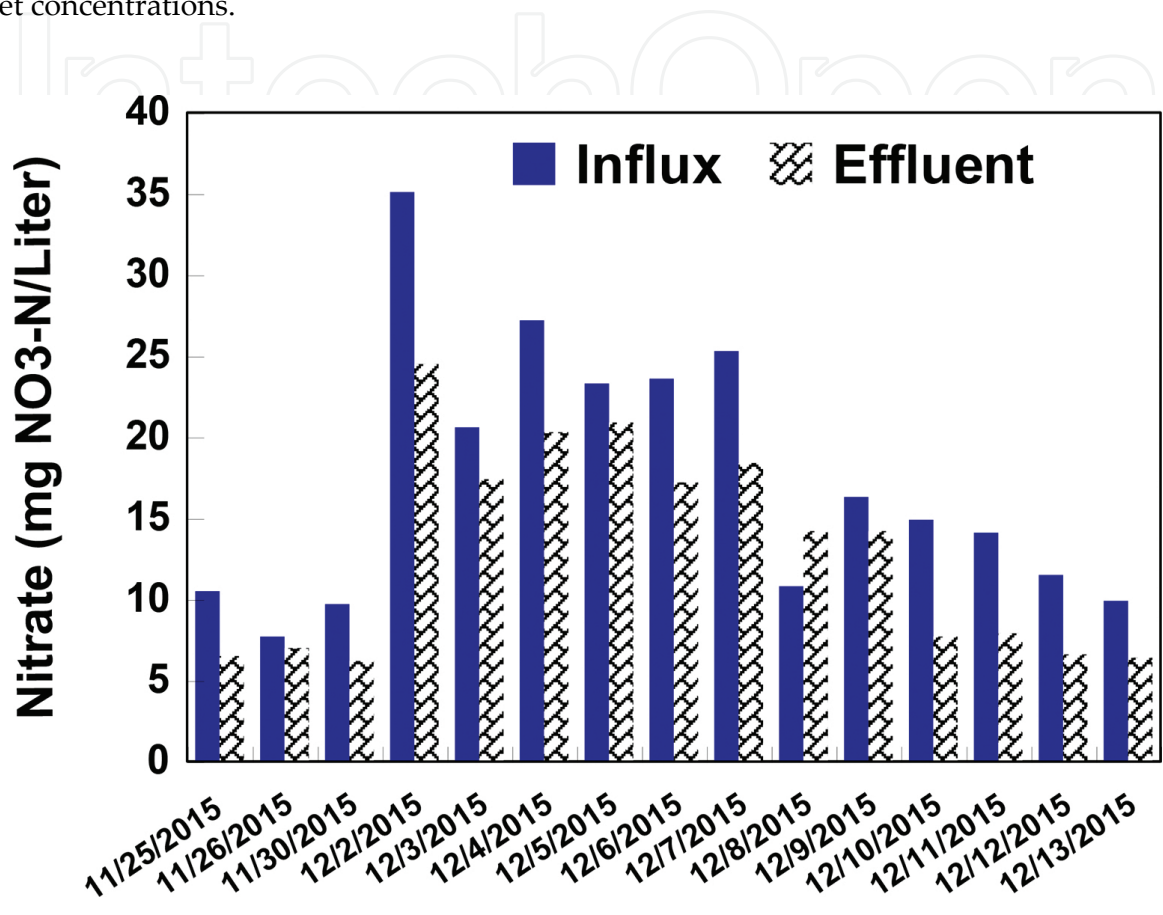

Figure 6. Water nitrate concentrations from the inlet (influx) and outlet (effluent) from the denitrification bioreactor.

Ammonium-N concentrations were substantially smaller than the corresponding nitrate-N concentrations. Ammonium-N concentration differences between the inlet and outlet waters suggest that the denitrification bioreactor sequestered ammonium-N or nitrification processes oxidized ammonium to nitrate (**Figure 7**). Denitrification bioreactor's mean phosphorus concentrations were smaller for the effluent (0.29 mg PO_4-P/L) than the inlet concentrations (0.38 mg PO_4-P/L); however, the concentration differences were not significant. Denitrification bioreactor's mean sulfate concentrations were greater for the effluent (1.1 mg SO_4-S/L) than the inlet concentrations (1.0 mg SO_4-S/L); however, the sulfate-S concentration differences were not significant.

Denitrification bioreactors in these field trials reduced effluent nitrate-N concentrations via denitrification pathways. Approximately 50% or greater nitrate-N reductions were observed when the flow volumes per unit time were sufficiently small for equilibrium attainment.
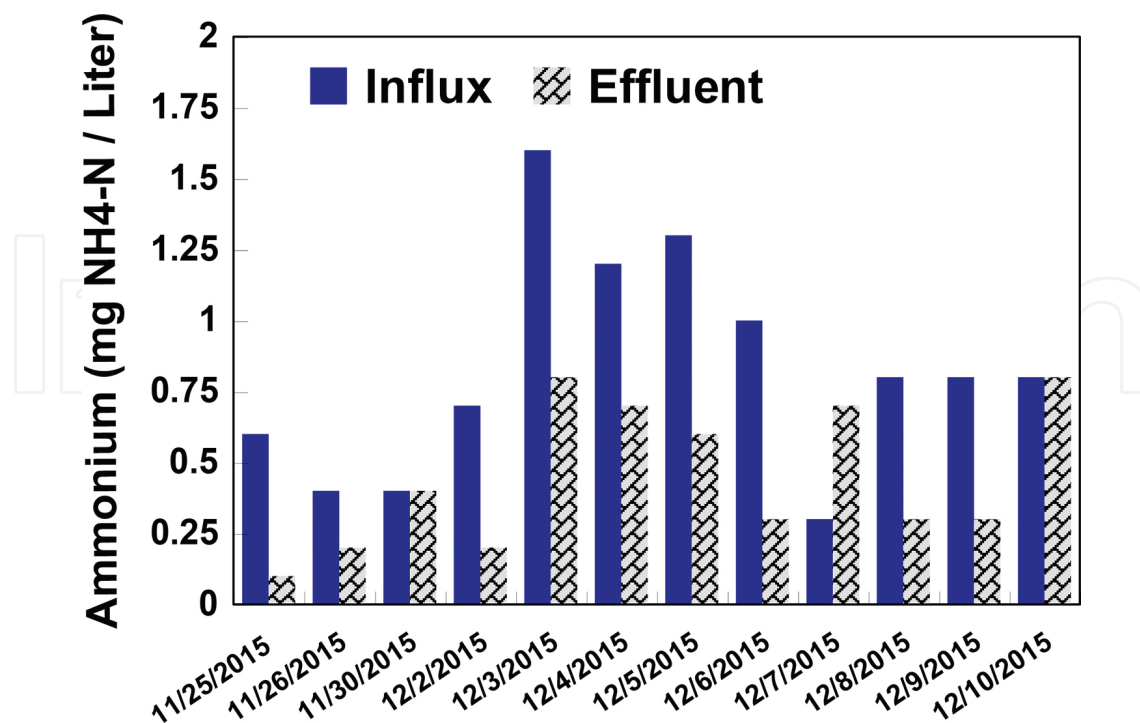
Figure 7. Water ammonium concentrations from the inlet (influx) and outlet (effluent) from the denitrification bioreactor.

5. Prospectus for future endeavors

(1) Development of effective crop nutrient management systems to improve crop uptake efficiency and reduce nitrate leaching.

(2) Development of "Soil Health" research initiatives to quantify soil structure attainment and carbon sequestration.

(3) Continue research on denitrification bioreactor design to reduce nitrate tile drainage. Engineering parameters based on reactor size, preferential bed packing materials, equilibrium thresholds, elimination of preferential flow path attainment, and pH maintenance require additional scrutiny.

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