CALIFORNIA LEAFY GREENS RESEARCH BOARD
April 1, 2015 – March 31, 2016

SUMMARY: Optimizing nitrate removal from tile drain water

This was the final year of a 4-year project investigating the feasibility of removing nitrate-nitrogen (NO_3-N) from tile drain water through the use of a denitrification bioreactor. A bioreactor filled with waste wood chips was constructed on a Monterey County farm in 2011; tile drain water was channeled through the bioreactor before release to the farm's drainage ditch. NO_3-N was reduced by approximately 8-10 PPM per day of retention time in the bioreactor; however, with tile drainage exceeding 100 PPM NO_3-N, it was impractical to retain water long enough for complete NO_3-N removal. This year's work investigated the possibility of using carbon enrichment (providing soluble carbon to increase the activity of the denitrifying bacteria in the bioreactor) to speed the process and make this remediation approach more practical. Using industrial methanol as a carbon source we demonstrated that with carbon enrichment nearly all NO_3-N in drainage water could be denitrified in less than 2 days of retention time in the bioreactor. The economics of this remediation technique are discussed.

Project title: Optimizing nitrate removal from tile drain water
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Cooperating personnel: Ken Johnson and Luke Coletti, Monterey Bay Aquarium Research Institute

Objective: Demonstrate the ability to reliably and economically remove nitrate from tile drain effluent from coastal vegetable farms to meet environmental water quality targets.

Procedures:

A pilot-scale denitrification bioreactor was constructed in spring, 2011, on a tile-drained commercial vegetable farm near Castroville. A pit of approximately 930 ft^3 volume was dug, lined with polyethylene sheeting and filled with chipped wood waste obtained from the Monterey Regional Waste Management District. The wood chips are unfinished construction wood waste crushed in a tub grinder. Total porosity of the chips as initially packed into the bioreactors was approximately 80%, with free-draining porosity of about 55%. A pump in the collection sump of the farm's tile drain system continuously pumped into one end of the bioreactor, and water flowed by gravity out of the other end of the bioreactor into the surface ditch draining the farm.

From 2011-2013 the flow rate through the bioreactor was maintained at approximately 2 gallons per minute, equivalent to about 2 days of hydraulic residence time (HRT) calculated on the basis of total porosity, or 1.3 days of HRT calculated on free-draining porosity. Denitrification within the bioreactor reduced the nitrate-nitrogen (NO_3-N) concentration of the tile drain water by approximately 16-20 PPM during the summer, somewhat less than that in winter. However, since the tile drainage typically ranged between 120-200 PPM NO_3-N, water exiting the bioreactor was still quite high in NO_3-N. Experiments in 2014 showed that the addition of soluble carbon (C, either from methanol or glycerin) dramatically increased the rate of denitrification. Both materials are available in industrial quantities; methanol is a product of

oil refining, while glycerin is a byproduct of biodiesel refining. Work in 2015 centered on the development of a system to scale C injection based on real-time NO_3-N monitoring of inlet NO_3-N concentration, with the goal of eliminating NO_3-N in outlet water while minimizing release of dissolved organic carbon (DOC) and nitrous oxide (N_2O), both of which can have negative environmental effects.

To allow replicated measurements under controlled environmental conditions six laboratory-scale bioreactors were fabricated from 6" diameter PVC pipe, each of approximately 16 liter volume. The lab bioreactors were filled with aged wood chips from the field bioreactor. The lab bioreactors were placed in a room at UC Davis maintained at 62 ^oF, the mean summer temperature of tile drain water at the field site. Peristaltic pumps were used to continuously apply NO_3-N solution to the reactors, at a rate equivalent to a 2 day HRT (based on total porosity), again to simulate field conditions. Two of the reactors received just NO_3-N solution, while the other reactors received that same NO_3-N solution augmented by C at varying concentrations. Preliminary work in 2014 showed that the denitrification of 1 PPM NO_3-N required approximately 1.4 PPM injected C (if from methanol), or 2.0 PPM injected C (if from glycerin); the work in 2015 was intended to confirm these ratios, and to document the effect of C enrichment on the emission of N_2O. In all lab bioreactors the inlet solution contained 160 PPM NO_3-N. For bioreactors receiving injected C, the effects of C:N ratio were determined by comparing performance at C levels insufficient to achieve complete denitrification (120 PPM for methanol and 160 PPM for glycerin) with C sufficient to achieve complete denitrification (230 PPM for methanol and 320 PPM for glycerin).

Nitrous oxide emission from the laboratory bioreactors was measured on two separate days for each combination of C source and concentration. Bioreactors were sealed with an air-tight PVC cap and air was circulated through the headspace of the bioreactors at approximately 0.7 L min^{-1}. After an hour of calibration four headspace air samples were collected 15 minutes apart using a hypodermic needle and syringe, and stored in evacuated glass tubes until analysis by gas chromatography. Matching samples of outlet water were gathered for determination of dissolved N_2O. The water samples were injected into sealed glass tubes containing 2 M NaOH to stop biological activity in the water. After 24 hours of equilibration to allow dissolved N_2O to come to equilibrium with the air in the tube, the headspace in these tubes was resampled and stored in evacuated glass tubes until analysis by gas chromatography. The concentration of dissolved N_2O in outlet water was then calculated using Henry's Law.

At the field bioreactor methanol was injected at a constant rate of 140 PPM C from 22 April until 5 May, 2015, to ensure the establishment of bacteria capable of metabolizing methanol. The C injection rate was increased to 270 PPM on 5 May and maintained through 17 June. Inlet and outlet samples were collected on 12 days during this period and analyzed for both NO_3-N and NO_2-N; DOC concentration was determined on 5 of those days.

On 17 July an optical nitrate sensor (in-situ ultraviolet spectrophotometer, ISUS) was installed. This sensor, designed and constructed by scientists at the Monterey Bay Aquarium Research Institute and generously loaned to this project, allowed real-time NO_3-N monitoring of the tile drainage. A carbon enrichment system was developed in which methanol was injected proportionally to the inlet NO_3-N concentration at a ratio of approximately 1.4:1 (C:N, w/w basis), the ratio suggested by the laboratory experiments as being adequate to allow complete denitrification. This C enrichment system operated from 15 Aug. through 6 Oct. The water flow rate was increased on 17 Sept. to reduce HRT (total porosity basis) from 2 days to 1.7 days; this flow rate was maintained through 6 Oct.

Inlet and outlet NO_3-N and NO_2-N concentrations were determined on samples collected on 14 different days during the period of proportional C enrichment, with DOC measured on 6 days. On each of four days, 4 replicate samples of outlet water were collected 15 minutes apart for measurement of dissolved N_2O. Water sample NO_2-N and NO_3-N concentrations were measured spectrophotometrically. DOC was determined by UV-persulfate oxidation after filtration through 0.30 µm glass fiber filters.

Results and discussion

Results from the laboratory bioreactor study confirmed that carbon enrichment, regardless of C source, dramatically enhanced the rate of denitrification (Table 1). NO_3-N concentration of inlet water (160 PPM) was only marginally reduced in the unenriched control columns, while C enrichment had the capacity to completely remove NO_3-N, provided the enrichment was at the appropriate stoichiometric ratio for each carbon source (1.4:1 C:N for methanol, or 2.0 for glycerin). At the lower level of C enrichment significant amounts of NO_2-N were present in outlet water, signaling incomplete denitrification. Incomplete denitrification was also evidenced by increased N_2O emission, both in gaseous form and dissolved in outlet water. In the unenriched control bioreactors gaseous N_2O release was slight, but N_2O release in outlet water was substantial (when expressed as a percentage of denitrified NO_3-N). A low level of C enrichment led to high gaseous and dissolved N_2O release. However, N_2O release was minimal when C enrichment was sufficient to complete denitrification.

In the field C enrichment was only done using methanol, for two reasons. First, our experience in the laboratory study showed that working with glycerin was problematic, in that it encouraged the growth of bacteria in the supply lines, requiring frequent cleaning. Second, the industrial glycerin we used (obtained from a biodiesel refinery in Watsonville) also contained a low level of impurities (presumably triglycerides) that had to be removed. While a higher purity product could undoubtedly be produced, its added cost would at least partially negate the potential price advantage of glycerin over methanol as a feedstock.

Carbon enrichment of the field bioreactor yielded results similar to the laboratory study. Constant enrichment at approximately 270 PPM C resulted in essentially complete denitrification (Fig. 1a). Over the period 5 May through 17 June inlet NO_3-N varied from 150-193 PPM, averaging 170 PPM. Outlet water NO_3-N was consistently below 1 mg L^{-1}, with no measureable NO_2-N. DOC in outlet water averaged 41 PPM higher than inlet water across 5 sampling dates, supporting the 1.4:1 C:N ratio for methanol determined in the laboratory studies.

The ISUS sensor proved to be consistently accurate, with the mean of 26 daily grab samples analyzed spectrophotometrically in the lab agreeing with ISUS readings within 1 PPM NO_3-N. When the C injection system scaled to inlet NO_3-N load was operating (injecting C at a ratio of approximately 1.4 C:N on a weight basis), outlet NO_3-N was consistently maintained below 1 PPM (Fig. 1b). During this period the DOC in outlet water averaged less than 20 PPM, approximately 10 PPM above inlet DOC, confirming that C enrichment can be managed for essentially complete denitrification without substantially increasing DOC (and the associated increase in biochemical oxygen demand in receiving water bodies). Dissolved N_2O in outlet water during this period represented <0.1% of denitrified N, again emphasizing that essentially complete denitrification was achieved.

Project summary

Given the high N load in tile drainage from coastal vegetable farms, a denitrification bioreactor operated in a passive mode (no C enrichment) would have to be quite large to even come close to meeting environmental target NO_3-N concentration in discharged water. We projected the costs for installation, operation and maintenance of a wood chip bioreactor 200 ft long x 50 ft wide x 6 ft deep. This size was estimated to be adequate to achieve a mean discharge water NO_3-N concentration of 10 PPM during the irrigation season from a 200 acre coastal vegetable farm producing 65,000 gallons of tile drainage daily, based on the very conservative assumption that farm management could limit tile drainage NO_3-N to 60 PPM (substantially lower than observed at either field bioreactors used in this 4-year study). Over a projected 10 year life the total system costs were estimated at approximately $92,000, or about $1.50 per pound of N denitrified. At higher tile drainage NO_3-N concentrations (like those observed at the field bioreactor sites) the bioreactor size would have to increase, and in a passive operation mode there would be no way to effectively treat periodic fluctuations in NO_3-N load.

Carbon enrichment provided a tool for handling fluctuating N loads, and could substantially reduce bioreactor size. Based on this year's results, a bioreactor employing C enrichment could achieve complete denitrification within 1.7 days of HRT, regardless of tile drainage NO_3-N concentration. Therefore, a bioreactor 100 ft x 30 ft x 6 ft should be adequate for a 200 acre farm producing 65,000 gallons of drainage water daily. The cost of methanol fluctuates with oil prices, but at an estimated bulk price of $2.50-3.00 per gallon, methanol would cost approximately $1.40-1.70 per pound of N denitrified. Currently, sensors capable of continuously measuring NO_3-N concentration are expensive; commercial NO_3-N sensors based on the ISUS technology are at least $15,000. Furthermore, more active management would be required to keep a C enrichment system operating efficiently, compared to a passively managed bioreactor. Therefore, C enrichment may be a technology more appropriately employed on a regional basis, rather than on an individual farm. A larger installation would likely achieve an economy of scale that would reduce per acre equipment and management costs.

Table 1. Effect of carbon enrichment on laboratory bioreactor performance.

	Inlet PPM		Outlet PPM[z]		N_2O emission (% of denitrified N[y])	
Treatment	NO_3-N	Carbon	NO_3-N	NO_2-N	Gaseous N_2O	Dissolved N_2O
control	160	unenriched	151	1	0.6	11.9
methanol	160	120	34	8	1.6	6.5
	160	230	<1	<1	1.2	0.1
glycerin	160	160	44	3	1.0	11.9
	160	320	<1	<1	0.2	0.2

[z] NO_3-N and NO_2-N concentrations are the means of 2 replicate columns over 25 days of sampling for each treatment/ C enrichment combination

[y] N_2O values represent the means of 8 replicate measurements across two days of sample collection for each treatment/C enrichment combination

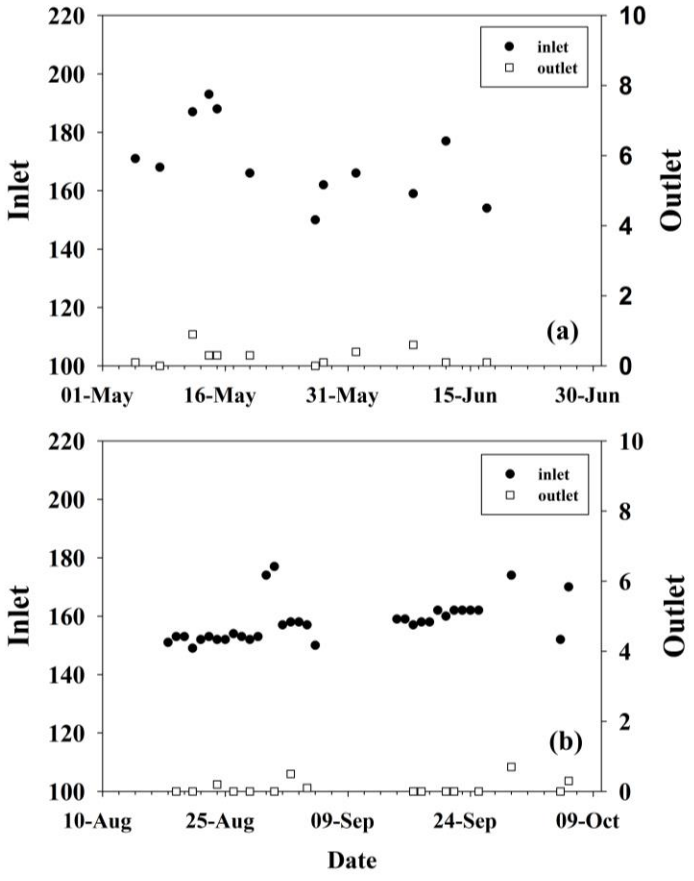

Fig. 1. Performance of carbon enrichment with methanol at the site 1 bioreactor at a constant enrichment of 270 mg L^{-1} C (a), or with proportional enrichment at a ratio of 1.4:1 C:N (b).