Methane Production and Removal in a Denitrifying Stream-bed Bioreactor

Zach Elgood

Grade 10, Cameron Heights Collegiate Institute, Kitchener, ON, Canada

Background, Purpose and Hypothesis

Nitrate (NO_3) is a major contaminant of rivers, lakes and potential drinking water sources[1]. Denitrifying bioreactors are currently being tested for treating NO_3 in agricultural drainage [2]. A bioreactor uses microbes to remove NO_3 in the influent, converting it to nitrogen gas (N_2). Previous research (October 2008-March 2009) at a stream-bed bioreactor indicated that incomplete denitrification results in nitrous oxide production. Data also indicated methane (CH_4) was produced in early fall but not during later winter months (Figure 1).

CH_4 is a potent greenhouse gas (GHG), with a current warming potential of 25 times that of carbon dioxide (CO_2) [3]. If bioreactor use continues to increase, it is important to understand their CH_4 emissions and global warming potential.

The purpose of this project is twofold: to determine seasonal variation in CH_4 production in an operational stream-bed denitrifying bioreactor; and to determine if it is possible to reduce CH_4 emissions from such a woodchip reactor through the implementation of a secondary reactor.

It was hypothesized that CH_4 would be produced in the bioreactor when stream temperatures increased to above 15^oC[4]. It was also hypothesized that CH_4 produced in the primary reactor could be oxidized through the mixing of reactor effluent and original source water in a secondary reactor. A variety of bacteria utilize CH_4 for energy, so it was thought that it would be possible to utilize naturally occurring bacteria to oxidize CH_4 to CO_2, which has a lower warming potential than CH_4.

Materials, Analytical Equipment and Methodology

The materials required for field sampling included: 60 ml glass and 30 ml plastic sample bottles, tape, exetainers, syringes, needles, safety goggles, nitrile gloves, mercuric chloride solution, HACH 40Qd meter, graduated bucket, stopwatch, cooler and ice. Additional materials for the lab experiment included: three-way valves, woodchips, gravel, Plexiglas columns, tin foil, Peristaltic pumps, timers, tubing, tube clamps and graduated cylinders. Analytical equipment included: Balance, Orbital shaker, Varian CP-3800 gas chromatograph, Dionex ICS90 ion chromatograph and a Technicon Auto Analyzer.

Field Methodology: Dissolved gas and anion samples were collected approximately every two weeks from January to October 2009. Dissolved O_2 and temperature were measured in the field. Dissolved gas samples were collected in 60 ml serum bottles and preserved in the field using Mercuric Chloride. 30 ml Anion samples were field filtered to 0.45 um.

Lab Methodology: To simulate the reactor, woodchips were obtained from the field reactor and gravel was purchased for the secondary columns. Three Plexiglas columns were assembled and leak tested prior to the media being added. 60L of stream water was collected from above the field reactor, transferred to the lab and refrigerated (4^oC) until use. Stream water was pumped into the woodchip column and left stagnant to allow the microbial population to cultivate. After a conditioning period (4 days), stream water was pumped through the woodchip and first gravel columns. NO_3, SO_4, temperature, dissolved CH_4 and O_2 were monitored over a period of 18 days. Anions and dissolved gases were sampled from the inflow, 2 ports in the first column

(simulating the bioreactor), and a port near the top of the second column until effluent concentrations from column one and column two remained fairly constant. Following this period, the outflow of column 2 was mixed with source water in a 2nd gravel column in the attempt to remove CH_4. NO_3, SO_4, Temperature, dissolved CH_4 and O_2 was monitored for an additional 16 days. Additional samples were collected from the stream water fed to column three and from ports at the bottom and top of the third column (Appendix 1). Anions and dissolved gases were analyzed using a Dionex ICS90 ion chromatograph and a Varian 3800 gas chromatograph respectively.

Results and Discussion

Results of the field study are presented in Figures 1-3. Seasonal variation in temperature was accompanied by variable NO_3 removal, SO_4 reduction and GHG. Effluent O_2 concentrations were <1mg/L, suggesting denitrification was occurring in all seasons. NO_3 effluent ranged between <0.01-3.9 mg/L, and removal between 18-100%. SO_4 reduction between January and October ranged between in 0.2-5.3 mg/L in the effluent (Figure 2). CH_4 was produced in warmer periods (June-October). Concentrations ranged from 100 - 7800 µg C/L (Figure 1). When CH_4 emissions were calculated as potential emissions per square meter, production ranged between -3 and 1237 mg C m^{-2} d^{-1} (Figure 3).
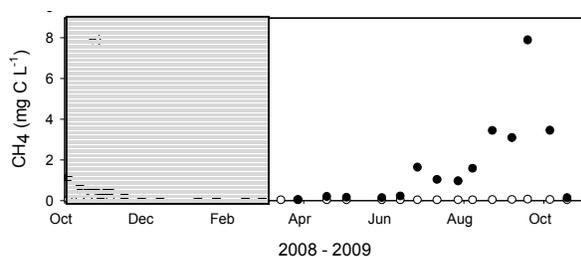

Figure 1. Avon stream-bed reactor, comparison of stream water and reactor effluent; dissolved CH_4 concentrations.
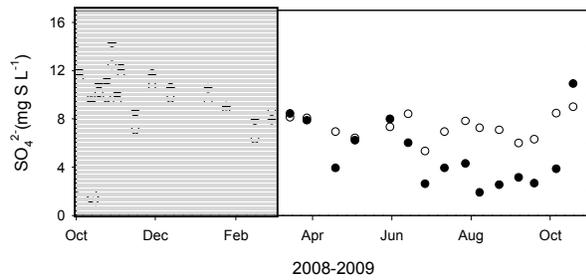
Figure 2. Comparison of Avon Reactor influent and effluent; SO_4^{2-} concentrations.
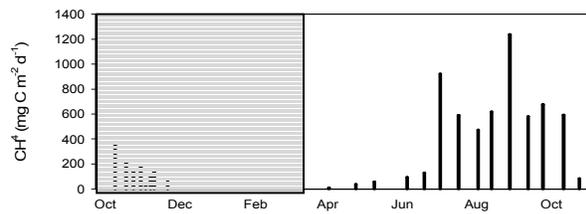

Figure 3. Daily CH_4 production calculated as difference between influent and effluent concentrations multiplied by the reactor flow rate and divided by reactor surface area.

In the lab woodchip column simulation, dissolved oxygen was consumed rapidly. Complete denitrification occurred in the first half of the column and partial denitrification of stream water added to the secondary reactor occurred in the bottom of the reactor (C3). SO_4 reduction occurred in all columns. These conditions were favourable for CH_4 production. (Figure 4b).

When effluent from the woodchip column and first gravel column were mixed in equal proportions with source water in the secondary reactor, O_2 was consumed almost immediately and ~60% of the additional NO_3 was denitrified (C3B). SO_4 reduction in the secondary reactor was coupled with up to 73% CH_4 removal(C2T).

Results of the column experiment suggest the hypothesis, that CH_4 could be removed in a secondary reactor, was correct. O_2 was consumed and CH_4 oxidized during rapid denitrification which occurred as soon as the source water entered the secondary reactor (Figure 4). No oxidation occurred in the top of the final column and concentrations actually increased, suggesting that methanogenesis resumed in that portion of the reactor.
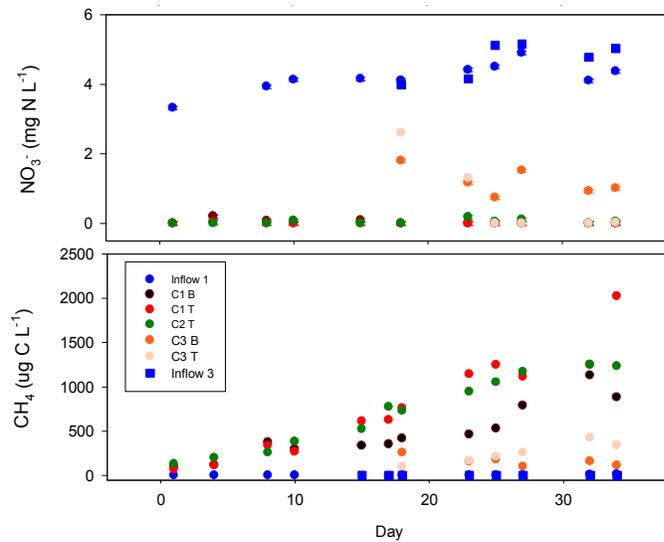
Figure 4. Comparison of column influent and effluent; a) NO_3^- and b) CH_4 concentrations. In most cases error bars are encompassed by the symbols

.

As denitrification continued in the secondary reactor accompanied by CH_4 reduction, it is possible that in addition to SO_4 reduction, denitrification using CH_4 as the carbon source is also responsible for removal of CH_4

Conclusion

Bioreactors are efficient methods of removing NO_3, providing the benefit of improved water quality. This study demonstrates that reactor design and environmental conditions play a role in determining CH_4 production. Careful consideration of flow dynamics and the use of secondary reactors may limit CH_4 production and minimize resulting emissions. With increasing concern over GHG emissions, all attempts must be made to minimize GHG production, including GHG produced by remedial technologies.

Acknowledgments

References

1) Camargo, J.A., Alonso, A., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environ. Inter. 32, 831-849.

2) Ditch This: Wood-chip Trenches Reduce Nitrate Runoff. Marc Hequet. Published 30 Oct. 2008.
<http://www.naturalresourcesnewsservice.org/index.php?option=com_content&view=article&id=43:ditch-this&catid=15:nrns-stories&Itemid=63>

3) Intergovermental Panel on Climate Change: Assessment 4
http://www.ipcc.ch/pdf/assessment-report/ar4/wg1/ar4-wg1-chapter2.pdf

4) Madigan, Michael et al., Brock Biology of Microorganisms: Tenth Edition, Pearson Education Inc, New Jersey, 2003

5) Appelo C.A.J., Postma D., 1994. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam, the Netherlands

Selected Bibliography

Brigmon, R., Methanotrophic Bacteria: Use in Bioremediation, Westinghouse Savannah River Company, Aiken, SC, U.S. Department of Energy, WRSC-MS-2001-00058

Greenan C. et al., Denitrification in Wood Chip Bioreactors at Different Water Flows. Journal of Environmental Quality, 38:1664-1671 (2009)

Raghoebarsing, Ashna et al., A microbial consortium couples anaerobic methane oxidation to denitrification, Nature, 440:918-921, 2006

Robertson, W.D. and L. C. Merkley. 2009. In-Stream Bioreactor for Agricultural Nitrate Treatment. J. Environ. Qual. 38:230-237.

Valentine, David, Biochemistry and microbial ecology of methane oxidation in anoxic environments: a review, Kluwer Academic Publishers, 81: 271-282, 2002

Wetzel, R.G., Limnology: Lake and River Ecosystems: Third Edition, Academic Press, California, 2001

Nitrous oxide emission from agricultural drainage waters. David S. Reay et al. Published 5 February, 2008.
<http://www3.interscience.wiley.com/journal/118895802/abstract?CRETRY=1&SRETRY=0>

Woodchip Bioreactors <http://www.admcoalition.com/Woodbio.pdf>