

*Wood decomposition after five years in anaerobic nitrate rich groundwaters:
Implications for lifetime of Nitrex™ Permeable Reactive Barriers*

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Abstract

Permeable reactive barriers can benefit aquatic ecosystems by using wood chips to remove anthropogenic nitrate from groundwater. However, the barriers can decompose over time. This study compared the fates of nitrogen and carbon in the wood of two permeable reactive barriers on Cape Cod, MA, as well as in fresh wood chips, as a means of understanding the decomposition and lifetime of the barriers. The results showed that the barrier located at Waquoit Bay had decomposed more over the past five years than the barrier at Childs River, possibly due to sulfate reduction at Waquoit Bay. Also, the loss of dissolved organic carbon was an important process in the fresh wood chips, whereas that of dissolved inorganic carbon was more important in the wood from the barriers.

Keywords

Nitrate removal, Permeable Reactive Barriers, estuaries, Cape Cod, anaerobic decomposition

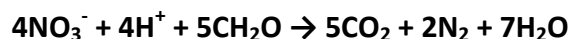
1. Introduction

Anthropogenic nitrogen (N) can cause adverse effects in aquatic ecosystems, such as in the estuaries of Cape Cod, MA (Valiela et al. 1990, 1992). This excessive N, often in the form of nitrate (NO_3^-) and ammonium (NH_4^+), enters watersheds from terrestrial inputs such as waste water and lawn fertilizer and flows through groundwater into estuaries. When it reaches an estuary it can cause eutrophication, resulting in increased algal blooms and depleting the oxygen available to other aquatic organisms (Hecky and Kilham 1988; Rabalais 2010). To reduce the pollution of the ground water, various treatment options are available, with differences in cost and effectiveness. This study considered one such option: permeable reactive barriers (PRBs).

1.1. Nitrex™ permeable reactive barriers

Permeable reactive barriers are relatively affordable waste water treatment devices that provide carbohydrates (CH_2O) to bacteria. If NO_3^- is present at anaerobic depths, denitrifying bacteria will colonize and grow because the energy yield from NO_3^- reduction is high and NO_3^- reducing bacteria are ubiquitous (K. Foreman, pers. comm.). The process of denitrification decreases the N loading to downstream aquatic ecosystems such as estuaries.

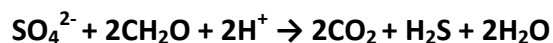
Denitrification:



Specifically, Nitrex™ PRBs use wood chips as the carbon (C) source. In 2005, the Marine Biological Laboratory (MBL) installed PRB systems to intercept NO_3^- rich plumes in groundwater entering the Childs River (CR) and Waquoit Bay (WB). Initial studies suggested that these PRBs could successfully perform denitrification, with NO_3^- removal by the WB barrier at nearly 100% (Moreau 2005; Anderson 2006; Bonsall 2008). However, complications occurred in installing both barriers. The CR barrier was installed at high tide, which allowed sand to cave in, preventing the contractor from burying the barrier deep enough to intercept the most concentrated NO_3^- plume (Moreau 2005). Although the WB barrier was installed at a more

effective depth to intercept NO_3^- , it was located in a position that received significant and continuing saltwater inundation (O’Leary 2010, unpublished; K. Foreman, pers. comm.). This process could allow sulfate (SO_4^{2-}) reduction to occur, causing an increase in the rate of wood decomposition at the WB barrier.

Sulfate reduction:



1.2. Questions addressed

Considerable research of wood has addressed its aerobic decomposition (Weedon 2009), but little is known about its anaerobic decomposition. I excavated wood chips from the CR and WB systems and sought to answer the following questions: How have the chips in these barriers changed over the past five years? How do they compare to fresh wood chips in terms of performance and size? What are the implications for installing barriers in the future?

1.3. Importance of this study

The effectiveness of PRBs is important to study for economic reasons; these barriers may only cost a third as much as centralized wastewater treatment and could therefore save money for towns looking to improve water quality (K. Foreman, pers. comm.). Having better water quality might also reduce downstream algal blooms, allowing the water to support greater biodiversity (Vitousek et al. 1997).

2. Methods

I conducted this study in November and December 2010, collecting samples at two field sites and analyzing them at the Ecosystems Center.

2.1. Site descriptions and woodchip collection

I extracted wood chips from the CR and WB barriers, which are located in the Falmouth region of Cape Cod (Figs. 1-3). This involved removing the overburden of sand to about 0.5 m while using a trench box to prevent the sides from caving in, and then cutting away a layer of geotextile cloth with a knife. I climbed into the trench box and used my hands to extract wood chips and to place them in plastic storage buckets. I also used a pump to collect feed water in a 55-gallon plastic drum from a well away from the beach at Waquoit Bay National Estuarine Research Reserve (WBNERR). I added some of the water to the buckets of wood chips to keep the chips saturated in order to maintain anaerobic conditions for the microbial communities. I also obtained “fresh” wood chips (FW) that had not been buried in a barrier but that came from the same contractor as the barrier chips (Fig. 4).

2.2. Microcosm construction and water flow

The laboratory setup consisted of six microcosms with 20-L plastic carboys, serving as replicates for three categories of data: WB, FW, and CR. Each microcosm employed the Mariotte technique (McCarthy 1934) to drip groundwater through a PVC pipe containing wood chips, ultimately delivering the water to a graduated cylinder (Fig. 5). I stored the microcosms in a temperature-controlled room at 15°C to simulate field conditions for groundwater and allowed

the microbial communities in the wood chips to stabilize for a week. I performed nutrient additions by adding 500 μM NO_3^- to the WB and FW carboys, and 200 μM NO_3^- to the CR carboys. In order to maintain constant flow rates, I measured the cumulative volume of water that collected in the graduated cylinders, finding that the rates ranged from 2.11 to 2.36 L/d among the three treatments (Fig. 6).

2.3. Laboratory procedures

I measured NO_3^- using 25 mm GF/F filters and a Lachat QuickChem, with samples from three days of water that had been flowing into and out of the six microcosms. I used an Aurora autosampler to analyze dissolved organic carbon (DOC) and created a time series from three days' data. Using a Shimadzu GC-14A gas chromatograph, I measured the dissolved inorganic carbon (DIC) flowing into and out of the microcosms after collecting the water in 60 mL glass BOD bottles (Staff 2010).

For 200 individual wood chips from each treatment (a total of 600 chips), I measured wet mass. Then I dried 30 WB chips and 30 CR chips to solve for the dry:wet ratio of 0.2515 (Fig. 7). Using this ratio, I calculated the dry weights of the remaining WB and CR chips and compared them to the weights of 200 dry FW chips.

To measure lignin, I ground wood chip samples with a Wiley Mill and analyzed them using the acid solubility method (Effland 1977). I measured N content by using a WIG-L-BUG amalgamator and running 5-6 mg samples through a Perkin-Elmer elemental analyzer. This yielded % N, from which I obtained lignin : N ratios.

3. Results

3.1 Microcosms

All six of the microcosms removed NO_3^- from the water, with the two WB microcosms removing the greatest percentage of incoming NO_3^- at more than 97 percent and the two FW microcosms removing the least at under 30 percent (Table 1). DOC production was nearly constant for each microcosm and was greatest for FW with a rate of 76 mg C/d (Figs. 8, 9). All of the microcosms produced DIC, with WB producing the most at an average of 30 mg/L and FW producing the least at 4 mg/L (Fig. 10).

3.2 Additional chips

WB had the highest frequency of small wood chips, whereas CR and FW had more chips in the large size classes (Fig. 11). The mean dry mass for WB chips was 0.17 g and that of CR was nearly three times as great (Table 2). The WB chips had significantly higher % N than the CR and FW chips (Fig. 12). WB had a significantly lower % lignin : % N ratio than the other treatments of wood, with a ratio of 92 (Fig. 13).

4. Discussion

The data suggested that the chips in the WB barrier had been decomposing more quickly than the CR and FW chips. These differences may have been due to saltwater input causing SO_4^{2-} reduction at WB, as well as the complications that prevented the CR barrier from intercepting the most concentrated NO_3^- plume.

4.1 Microcosms

The WB and CR microcosms had high NO_3^- removal, suggesting that these chips contained microbial communities that performed denitrification. The FW chips, in contrast, had not had time for the denitrifying communities to develop, so the FW microcosms exhibited relatively low NO_3^- removal. This small amount of NO_3^- removal may have been due to other processes such as N-immobilization.

DOC production was more important in the fresh chips than in the barrier chips, but DIC production was more important in the older chips that had been buried. The DOC results suggested that the FW chips were leaching organic compounds such as sugars, tannins, and phenols. These compounds may have already washed out of the CR and WB chips during their time in the barriers. Since CO_2 is a product of the denitrification reaction, the higher DIC production from the barrier microcosms, particularly WB, corroborated the idea that these systems were performing denitrification.

4.2 Additional chips

The WB chips appeared to have decomposed more than the other chips due to mass, % N, and % lignin : % N ratios. The WB chips seemed to have lost more mass than the CR chips, as evidenced in their smaller mean mass and the differences in size frequency among the three chip types, with more WB chips in the smaller size classes. Also, the high % N and low lignin : N ratio in the WB chips suggested greater decomposition in WB than in the other chips.

4.3 Future studies

I could strengthen this study by increasing the sample size and by calculating the lifetimes of the barriers. Although I analyzed thousands of wood chips, I excavated them from only one hole at each site. It would be valuable to look at chips from holes at different locations along the barriers and at different depths because these variables might affect the characteristics of the chips. To calculate the lifetimes of the barriers, I would need to determine the mass of wood chips in each microcosm. With this information I could use a first order decay equation such as $M_t = M_0 e^{-kt}$ to solve for t , or the time that it would take for a given percentage of the wood to decay.

If the MBL or other organizations install more barriers, I recommend doing so at low tide so that the barriers can be deep enough to intercept the most concentrated NO_3^- plumes. Furthermore, the barriers should be located where they are safe from saltwater inundation in order to avoid excessive decomposition due to SO_4^{2-} reduction, which can remove CH_2O that would otherwise be available for denitrification. These installation techniques would help to optimize NO_3^- removal and barrier lifetime, perhaps resulting in long-term economic savings.

Acknowledgments

I am grateful to Ken Foreman for advising this project and permitting me to extract wood chips from his research sites at CR and WB. I also thank Rich McHorney, Will Daniels, and Stefanie Strebel for assistance in the lab. Thanks to Chris Neill for inspiring me to consider the value of denitrification. Additionally, I appreciate the collaboration with my classmates. Finally, this project would not have been possible without guidance and encouragement from Hamilton College, Friends School of Baltimore, and my family.

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Tables and Figures

Table 1. Average percent nitrate removal by six microcosms, taken from three measurements of nitrate concentration in the water's inflow and outflow.

Microcosm	WB1	WB2	FW1	FW2	CR1	CR2
Average % nitrate removal	97.01	97.33	26.19	29.68	81.70	88.05

Table 2. Mean dry mass of 200 wood chips from the three treatments, with dry masses calculated for WB and CR from the chips' respective wet masses.

Treatment	WB	FW	CR
Mean dry mass (g)	0.17	0.38	0.45



Fig. 1. Maps of Cape Cod, MA, and barrier sites (K. Foreman 2010). Stars estimate the location of PRBs at CR and WB, respectively.



Fig. 2. The first 30 of 200 individual CR chips analyzed.



Fig. 3. Chip samples from the WB barrier.



Fig. 4. Thirty samples of fresh wood chips.



Fig. 5. Microcosm setup including the Mariotte bottle (carboy), tubing into the PVC pipe, the pipe containing wood chips and sand, and tubing from the pipe into a graduated cylinder.

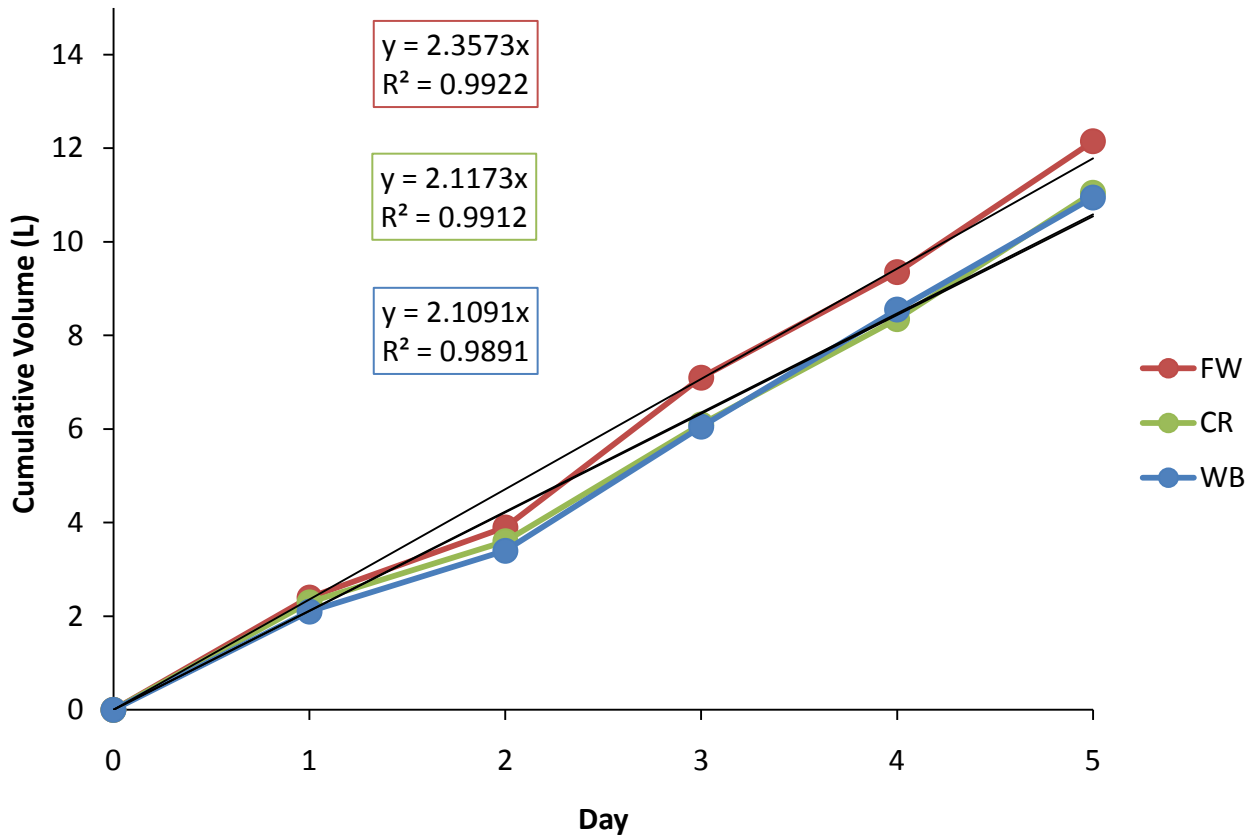


Fig. 6. Cumulative flow of groundwater through three treatments of wood chips.

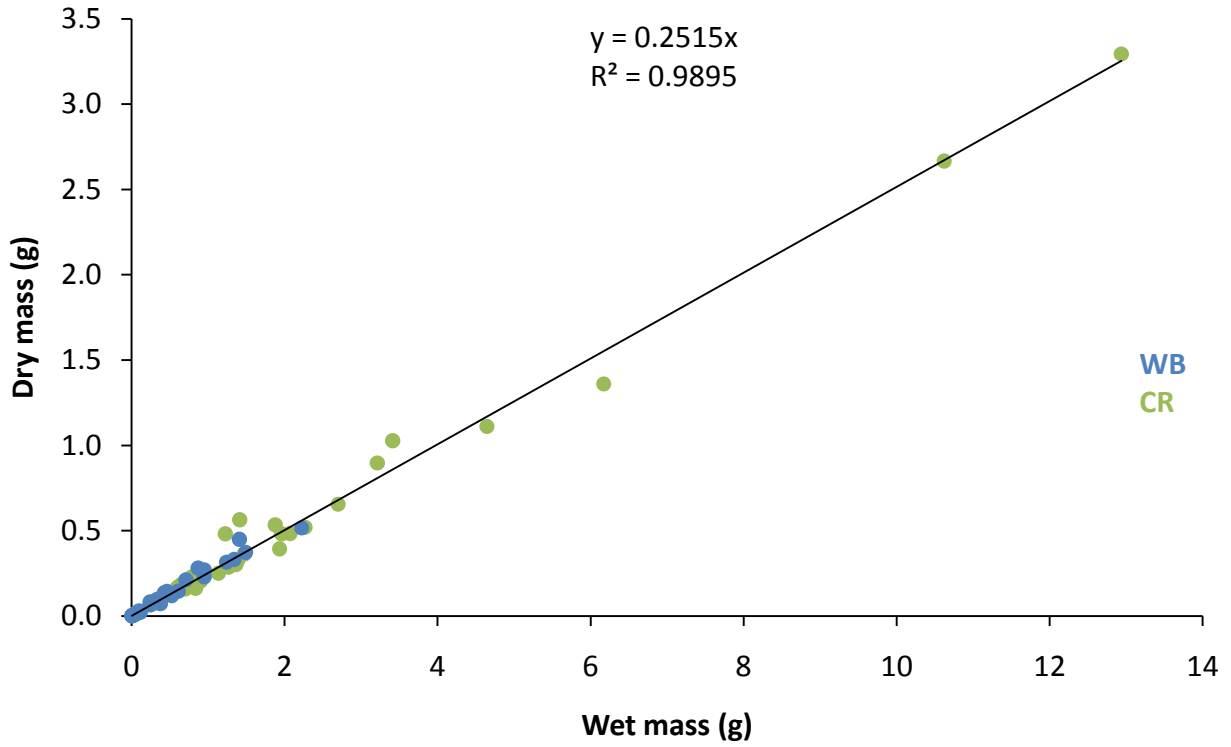


Fig. 7. Dry vs. wet mass in WB and CR chips, yielding the ratio for conversion from wet mass to dry.

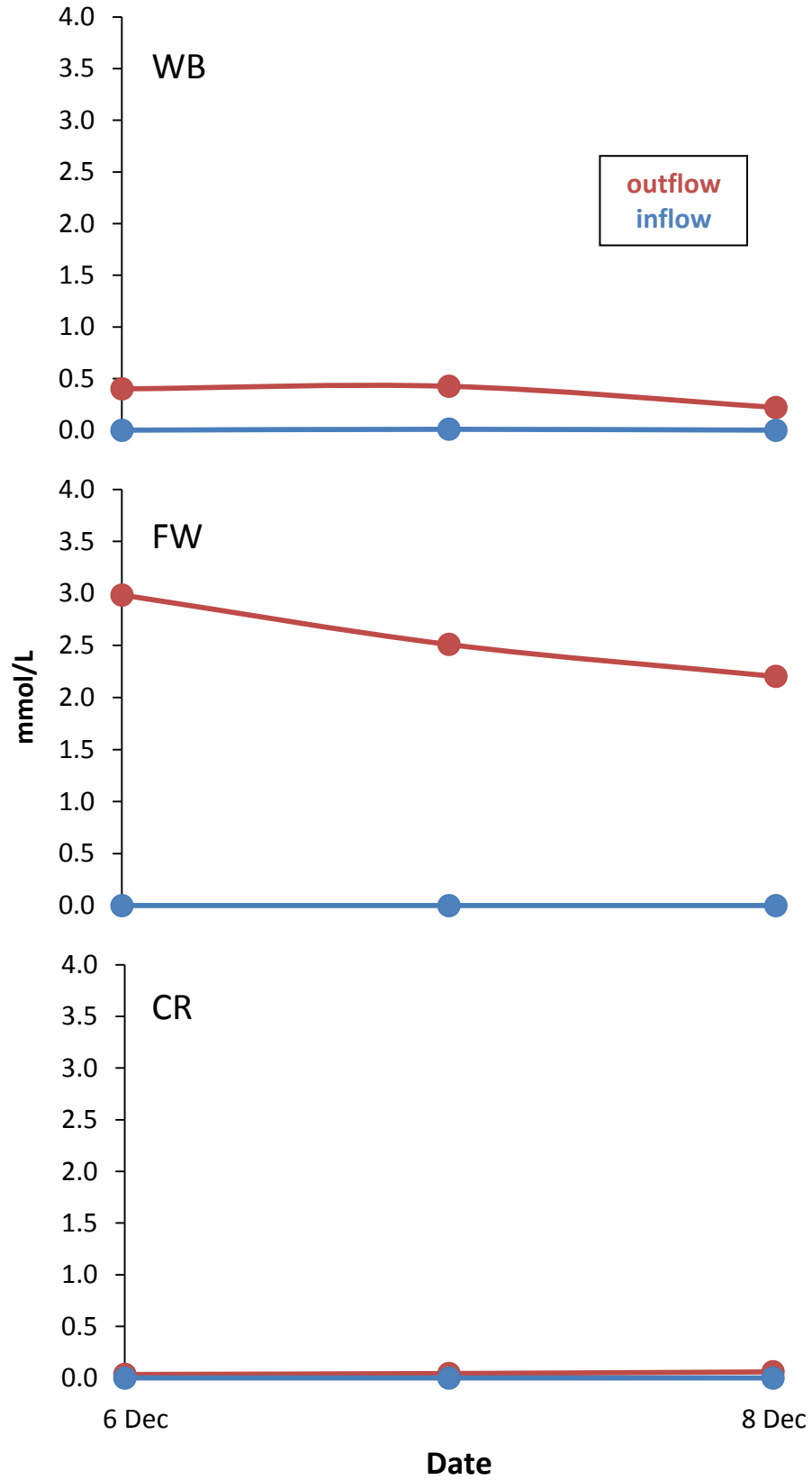


Fig. 8. DOC flowing into and out of each treatment on three separate days.

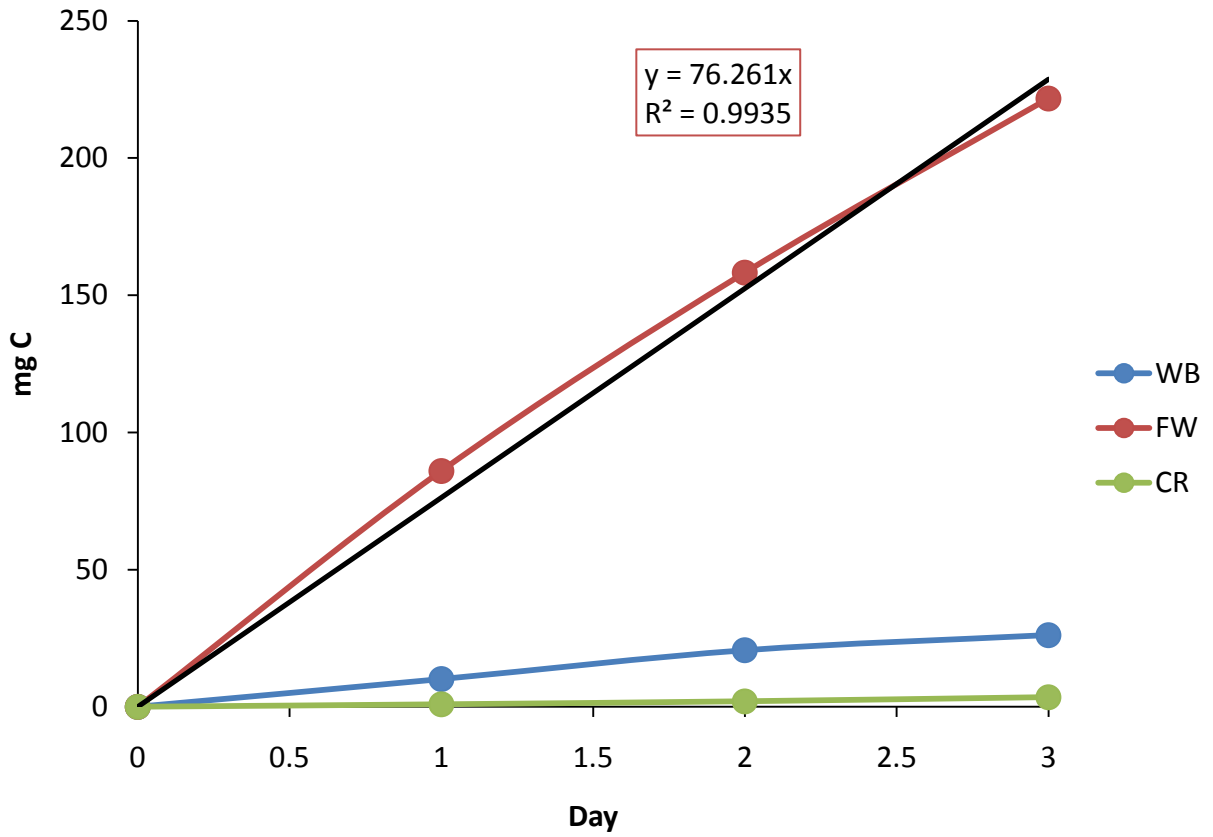


Fig. 9. DOC production by microcosms as calculated by [DOC (out – in)] * cumulative flow.

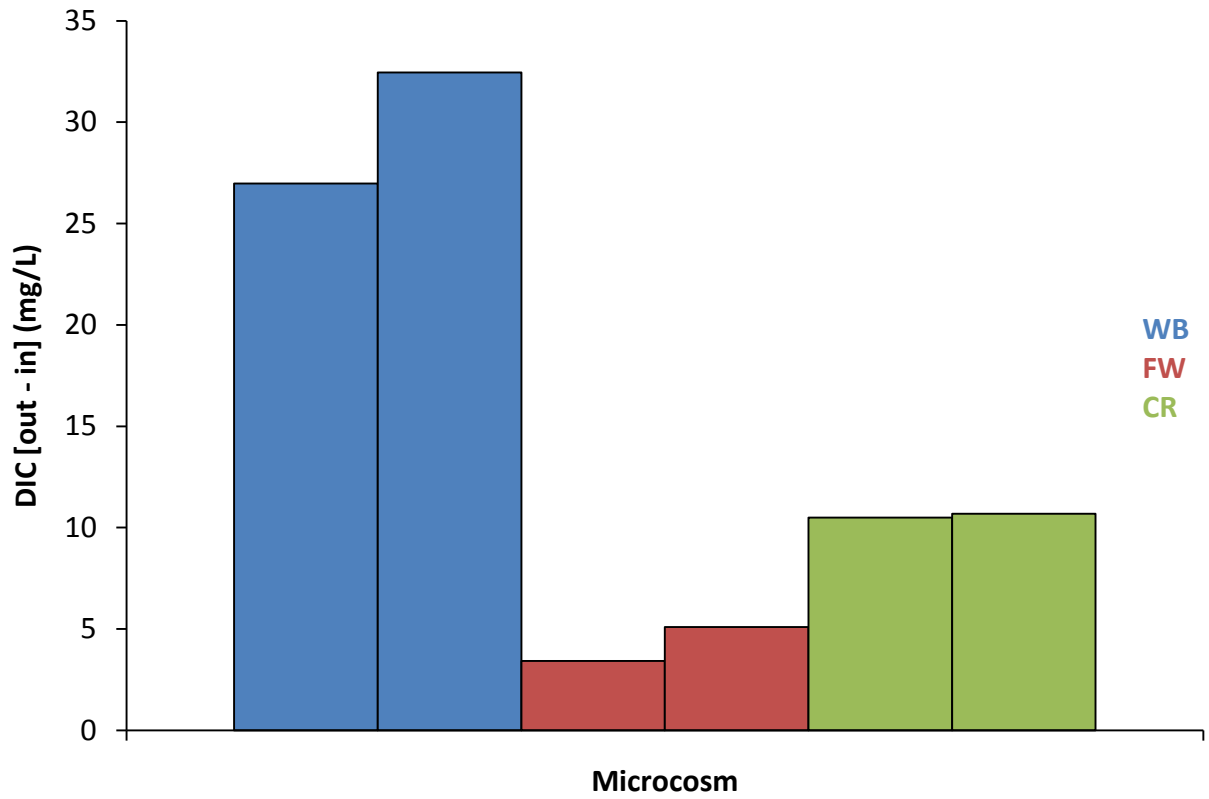


Fig. 10. DIC (out – in) for replicates of three treatments, totaling six microcosms.

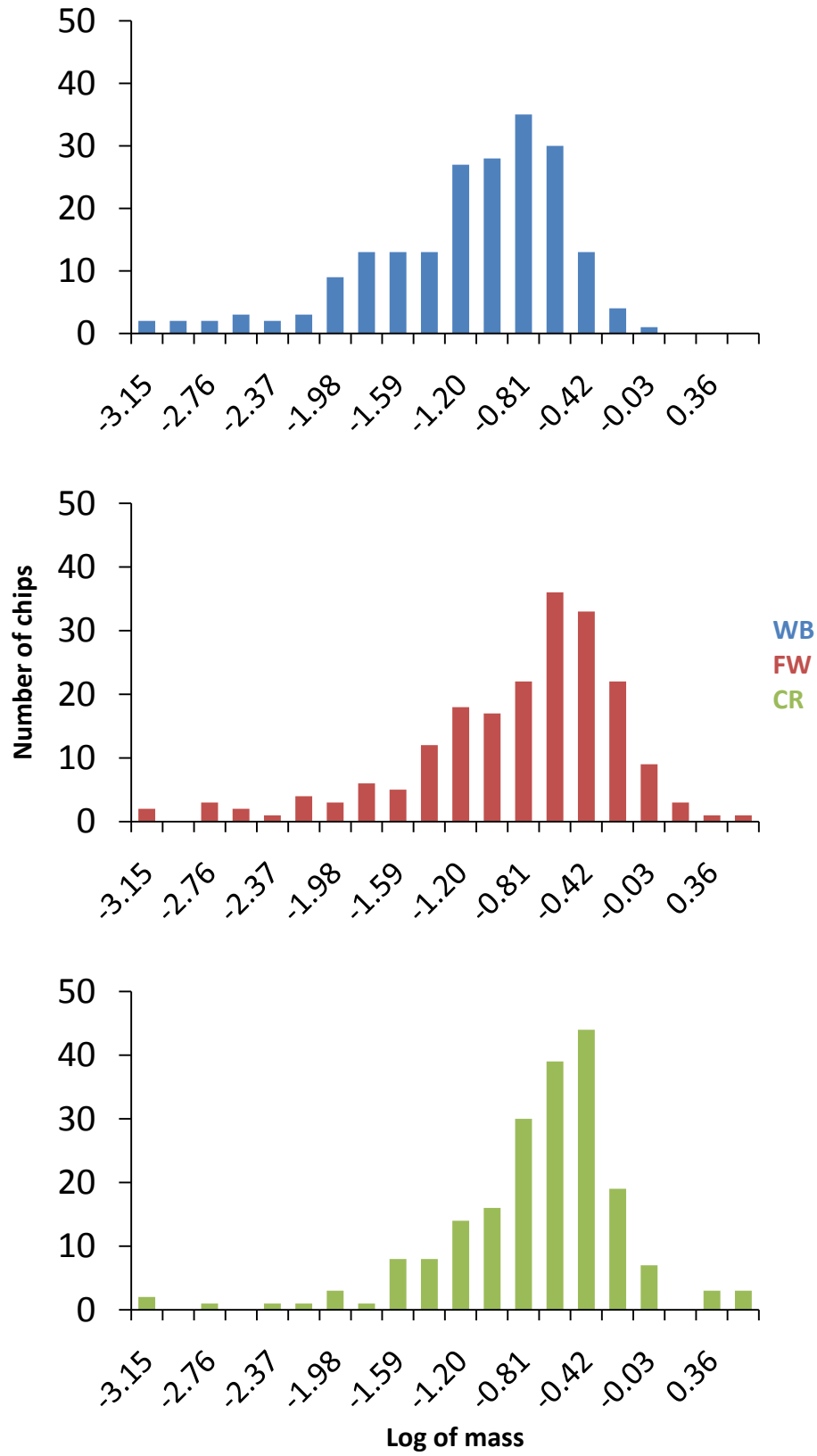


Fig. 11. Size frequency of wood chips in the three treatments, as logarithms of dry mass.

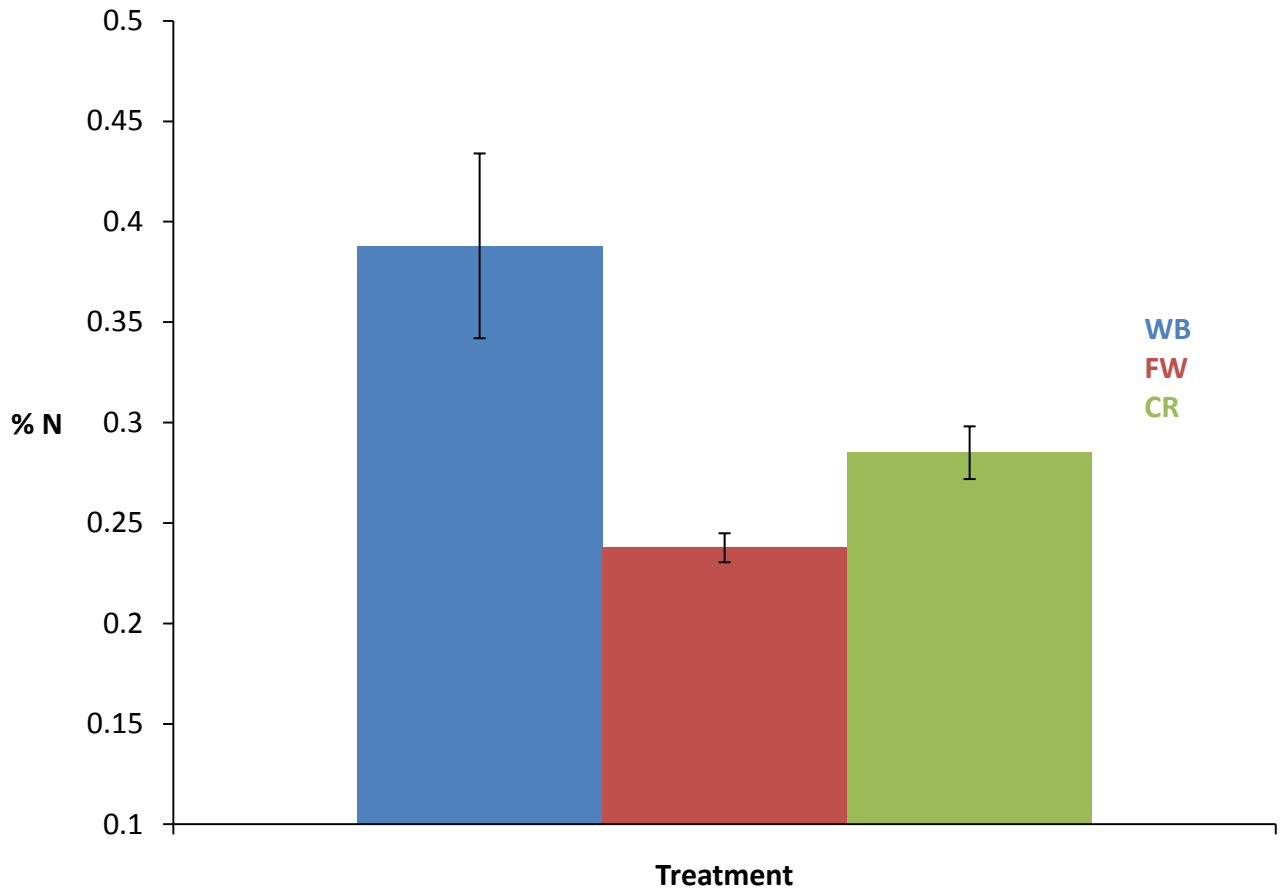


Fig. 12. Percent N in wood chip samples from three treatments.

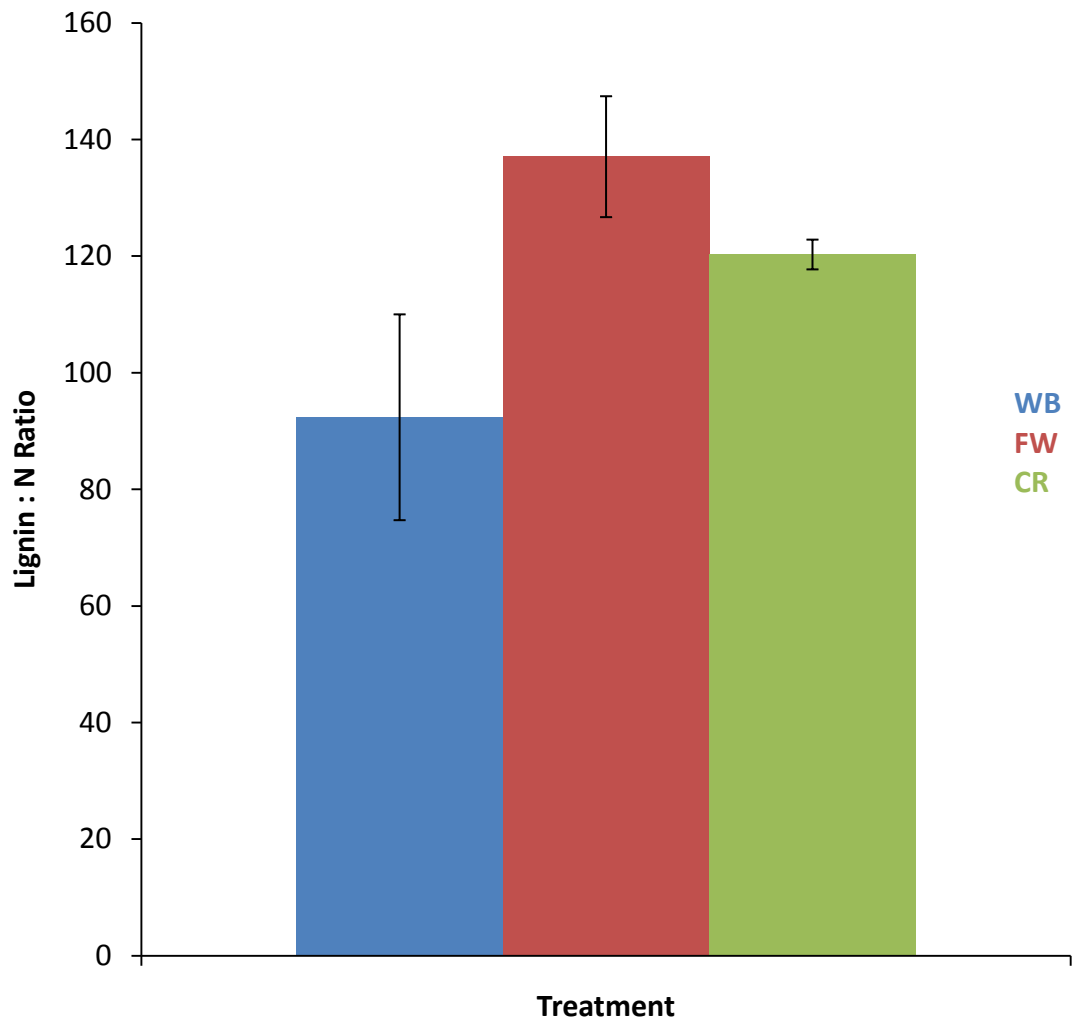


Fig. 13. Percent lignin : percent N ratios for the three wood chip types.