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Integrating Zero-valent Iron and Biochar Amendments in Green Stormwater Management Systems for Enhanced Treatment of Roadway Runoff
2015 Progress Report

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Abstract

In 2015 extensive testing was conducted of a pilot-scale system to evaluate the combination of zero valent iron (ZVI) and biochar as soil amendments for bioinfiltration on the University of Delaware campus. This system collects and “treats” runoff from a University of Delaware parking lot. The system includes a treatment cell with the new media containing biochar and ZVI and a control cell with a standard bioretention mix. Field testing using this well-instrumented system shows that biochar increases the pollutant residence time by ~ 12% while simultaneously *increasing* stormwater infiltration rate by 50%, and biochar/ZVI increases nitrate removal by between 50% and 470% over the standard bioretention mix, depending on the season. Concurrent laboratory experiments elucidated the mechanisms by which biochar/ZVI enhance nitrate removal. These results were presented at the Fall Meeting of the American Geophysical Union and a portion of them were recently published in the *Journal of Environmental Quality* and *Science of the Total Environment*. In March 2016 this work was presented at the Chesapeake Bay Day on Capitol Hill, where PI Imhoff met with congressional staff and discussed the utility of biochar amended bioretention media to reduce the cost of stormwater BMPs for treating nutrient runoff from transportation systems. Finally, a portion of this research was presented in a webinar entitled "Simultaneous Removal of Nitrogen and Phosphorus from Stormwater by Zero-Valent Iron and Biochar in Bioretention Cells” hosted by the Mid-Atlantic Transportation Sustainability Center – Region 3 University Transportation Center.

Research conducted in 2015 was designed around three research tasks. The results from each of these tasks is reported below.

1. Task 1: Pilot-Scale Field Study

The purpose of this task was to complete fabrication and begin testing of the pilot-scale field system to test the utility of biochar and ZVI for amending bioretention media to enhance removal of nitrogen compounds, in particular nitrate. A plan view illustrating the location and drainage area for the field system is shown in Figure 1. A collage of photographs illustrating the construction and completion of the pilot-scale field system is presented in Figure 2.

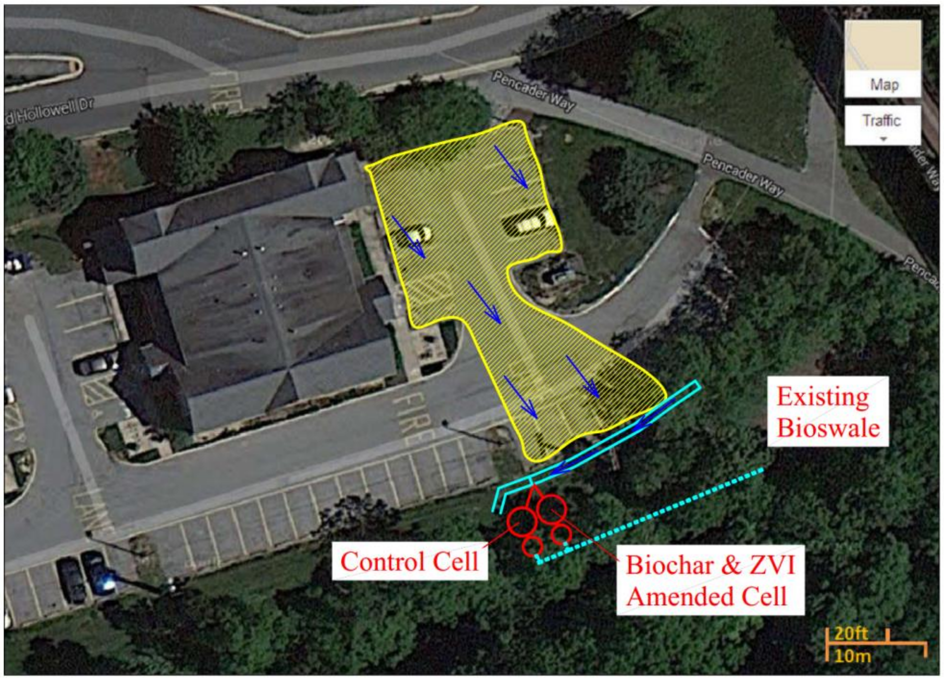

Figure 1. Plan view of pilot-scale field system illustrating (1) drainage area, (2) collection trench for diverting parking lot runoff to side-by-side treatment cells, (3) control and biochar and ZVI amended cells, and (4) drainage pipe from treatment cells to bioswale.

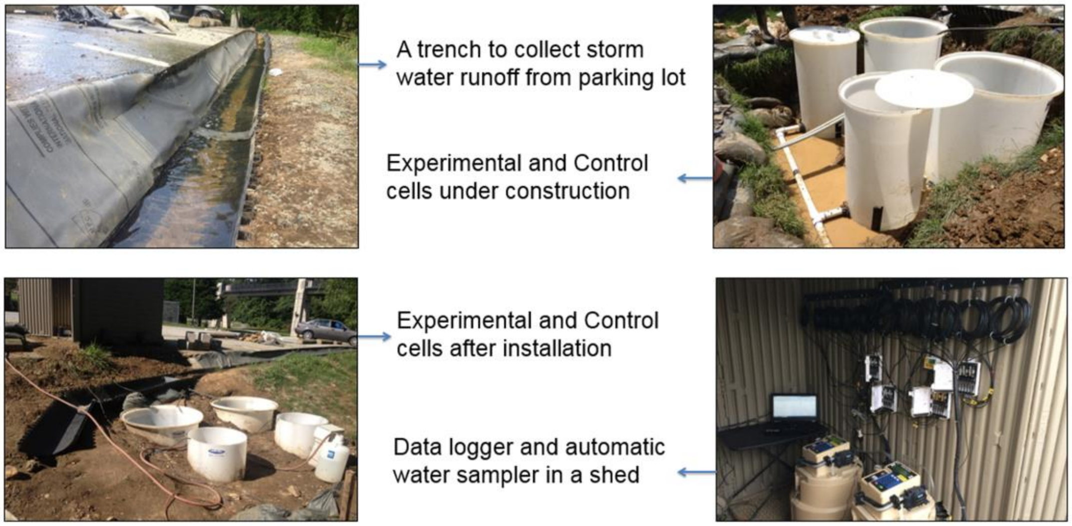

Figure 2. Photos of field construction and instrumentation of pilot-scale field facility.

The test cells, experimental with biochar and ZVI and control with standard bioretention media, were instrumented with sensors to measure in situ volumetric water content, water pressure, and temperature. Pore water sampling ports were inserted at the interface between the biochar and ZVI layers, and at the bottom of the ZVI layer in the experimental cell. Pore water samplers were installed at identical depths in the control cell. Water samples collected from these points were used to determine the amount of treatment occurring in the biochar region versus the ZVI region. A schematic of the instrumented experimental cell is shown in Figure 3.

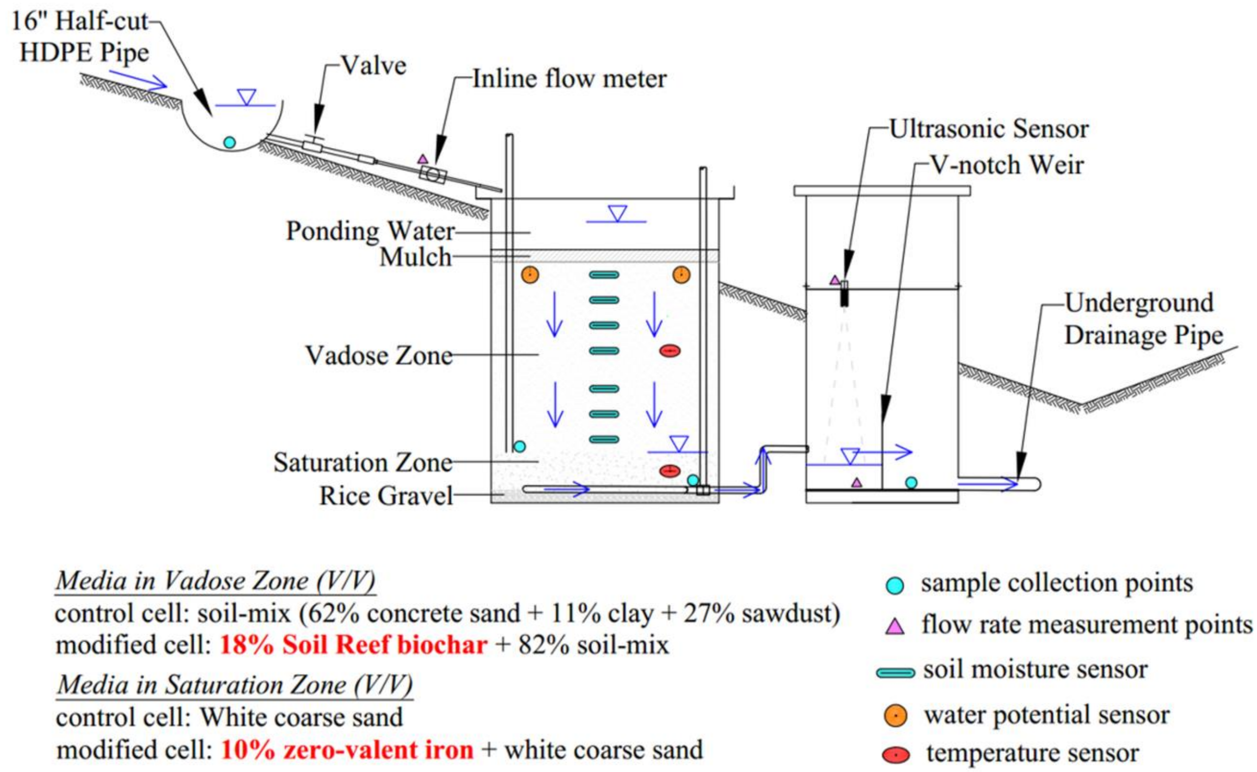

Figure 3. Cross sectional view through experimental test cell containing biochar and ZVI in field. The control cell containing the standard bioretention medium was instrumented similarly. Media content are presented as percent by volume.

A series of field tests were conducted in the control and experimental cells in 2015 to evaluate the performance of the biochar and ZVI amendments. Rather than allow natural storm events to "load" the treatment systems, these experiments used controlled rainfall events. These events mimicked 0.11 in/hr storms of 24 hr duration over the parking lot. Each rainfall event consisted of a synthetic stormwater containing nitrate at a background concentration 2 ppm, with a pulse of 100 ppm Br^- and 10 ppm (or 20 ppm) nitrate injected between times 3.0 and 3.5 hrs. During each storm, samples were collected from the effluent to each treatment cell that complemented a suite of in situ measurements.

Results for the 1st test are presented for illustration. In Figure 4, the profile of volumetric water content is shown for the control (standard bioretention mix) and experimental (biochar and ZVI amended media) cells. The experimental cell holds 27% more water than the control cell during the storm event, which increases the hydraulic residence time by 12%. The increased residence time means there is more time for biological degradation processes to occur.

The removal of nitrate for the 1st test is shown in Figure 5. The control cell has a similar anaerobic zone at the bottom as the experimental cell with biochar and ZVI. Cumulative nitrate removal is 14.2% in the control cell, but 66.2% in the experimental cell: the biochar and ZVI amendments significantly increased nitrate removal. The ability of the control cell to remove nitrate decreases with time, while the ZVI layer in the experimental cell maintains a high removal rate for the duration of this experiment.

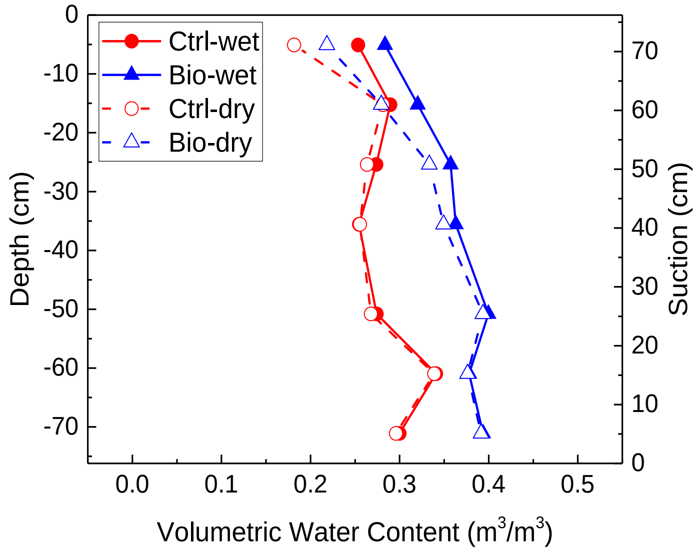

Figure 4. Volumetric water content in the control and experimental cells (biochar and ZVI, labeled Bio) for experiment #1. Dry data are before the onset of stormwater infiltration, while wet data are during the storm.

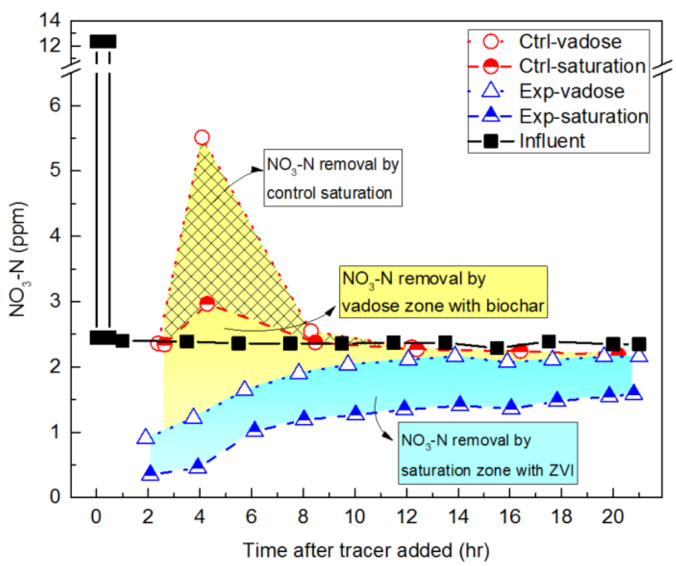

Figure 5. Nitrate concentrations for 1st test. Data in black are influent concentrations, which are identical for the control and experimental cells. Data in red and blue are effluent data from the control and experimental cells, respectively. Shadings indicate the nitrate removed in the biochar zone (yellow) or the ZVI zone (blue).

Results for the three field tests are summarized in Table 1 below. The cumulative nitrate removals for the 1st test are 14.2% and 66.2% in the control and experimental cells, respectively; 58.9% and 92.9% for the 2nd test; and 30.0% and 72.4% for the 3rd test. Overall, biochar/ZVI increases nitrate removal by between 50% and 470% over the standard bioretention mix, depending on the season. The 1st field test was conducted in April, the 2nd test in June/July, and the 3rd test in August.

Table 1. Summary of nitrate removal in control and experimental cells for three field experiments.

Test No.	Temperature (°C)	Experimental Condition	NO_3^- Removal ※ (%)	NO_3^- Overall Removal (%)	[DO]§¶ (ppm)	Redox Potential §¶ (mv)
1st	14	Base Case	30.6 (36.6)	66.2	N/A	N/A
2nd	22	Base Case	84.7 (41.2)	92.9	2.01 (2.15)	-204.9 (229.5)
3rd	22	2*[NO_3-N] x Base Case	71.7 (55.4)	72.4	2.56 (1.13)	-151.5 (142.5)

※ In vadose zone, first number is for experimental cell (biochar region) and number in parenthesis is the difference between experimental and control cells.

§ First number is the value for experimental cell and number in parenthesis is the difference between control and experimental cells.

¶ Results are at water table level.

2. Task 2: Supporting Laboratory Experiments

Laboratory experiments were conducted to evaluate the ability of different biochar to sorb ammonium, a common form of nitrogen. These experiments showed that biochar derived from poultry litter did not perform as well as biochar produced from wood feedstock. The field tests reported above used a wood-based biochar. The results from these experiments were submitted for publication in 2015, and this work is now published in *Science of the Total Environment*. A copy of this manuscript is attached to this report.

Laboratory experiments were also conducted to assess biochar's impact on soil wettability. Wettability affects water movement in biochar-amended media, and we were concerned that this effect would cause biochar to hinder water infiltration in some situations. This work was published in the *Journal of Environmental Quality* in fall 2015.

Additional laboratory and field experiments were performed to determine the impact of biochar on the infiltration rate of stormwater, which can be assessed by the saturated hydraulic conductivity. This work shows that the biochar employed in this study results in an increase in saturated hydraulic conductivity for the tested bioinfiltration medium when added at a 4% mass fraction. The effect of biochar particle size on saturated hydraulic conductivity was measured, and models that predict saturated hydraulic conductivity as a function of particle size were evaluated. This work is summarized in the MS thesis by Jing Jin and will be submitted for publication in a peer-reviewed journal in 2016. A copy of this thesis is attached to this report.

3. Task 3: Development of Specification for the Biochar and ZVI Treatment System

Based on the field and laboratory work to date, we can recommend a biochar and ZVI system that works well in the field for removing nitrate, at least over one season. This system consists of two different media: a standard bioretention medium amended with 4% biochar by mass in the vadose zone, and a mixture of sand and ZVI in the saturated zone. The constituents in these two media and the layer thicknesses in a bioretention system are described in Figure 3. Additional tests in 2016 are needed to confirm the utility of these media over a second season.

4. Conclusions

With support from the Delaware Department of Transportation (DelDOT) and guidance from DelDOT staff, we developed an integrated biochar and ZVI system for treating stormwater contaminated with nitrogen compounds. A pilot-scale system was designed and constructed on the University of Delaware campus, and this system was operated for synthetic stormwater events in 2015. The addition of biochar increases stormwater infiltration rate by 50%, and biochar/ZVI increases nitrate removal by between 50% and 470% over a standard bioretention mix, depending on the season. Concurrent laboratory experiments elucidated the mechanisms by which biochar/ZVI enhance nitrate removal. These results were presented at the Fall Meeting of the American Geophysical Union and a portion of them were recently published in the *Journal of Environmental Quality* and *Science of the Total Environment*. In March 2016 this work was presented at the Chesapeake Bay Day on Capitol Hill, where PI Imhoff met with congressional staff and discussed the utility of biochar amended bioretention media to reduce the cost of stormwater BMPs for treating nutrient runoff from transportation systems. Finally, a portion of this research was presented by PI Imhoff and PI Chiu in a webinar on April 27, 2016 entitled "Simultaneous Removal of Nitrogen and Phosphorus from Stormwater by Zero-Valent Iron and Biochar in Bioretention Cells” hosted by the Mid-Atlantic Transportation Sustainability Center – Region 3 University Transportation Center.

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