National Science Foundation SBIR Phase II

Development of Activated Swelling Organosilica-Metal Composites Filter Media in Bioretention Systems for Enhanced Remediation of Stormwater Runoff

Interim Progress Report #2: 6 – 12 Months August 9, 2013

Project Summary. Stormwater treatment has become an essential component in urban, industrial, and agricultural areas to manage stormwater runoff. Stormwater policies are also increasingly viewed as critical to ensure safer living environments and cleaner waters. Consequently, federal and state regulations in U.S. are becoming much more stringent.

Decentralized approaches to stormwater management, including green infrastructure and low impact development strategies like bioretention systems, are gaining great traction because they cost-effectively reduce the volume of runoff to sewer systems and have potential for protecting surface water from pollution. However, a critical challenge to implementing bioretention systems (including rain gardens, bioswales, and wetlands) is finding effective and persistent treatments for stormwater pollutants such as nutrients, hydrocarbons, herbicides, and pharmaceuticals.

ABSMaterials is creating such a solution to meet this challenge under the trade name: BioMix-Osorb® stormwater systems. We are developing a suite of innovative biofiltration nano-glass media to protect the ecosystem and remediate organic pollutants from stormwater runoff. This nanomaterial called "Osorb" is an engineered sand grain with reactive metal composites encased within. The Osorb-based materials can be viewed as tiny chemical reactors to remediate runoff pollutants such as hydrocarbons, herbicides, endocrine disruptors, and pharmaceuticals. The sand-like grains of Osorb capture runoff pollutants and degrade the pollutants to non-toxic forms, then release to the biofilter media where they are generally mineralized or biologically consumed. These systems are now in place in the United States and are testing for 10+ -year life cycle. The Osorb-based material works in conjunction with biology by helping maintain the health of microorganisms in the filter media due to overexposure to chemicals.

Status of Commercialization Activities. During the first year of the project, significant effort was placed on converting our research and development into profitable client-based projects. ABSMaterials has developed a market ready solution with innovative Osorb®-metal composites filter media which have the highest treatment capacity of any existing stormwater management systems and protect the ecosystem. Constant and excellent results obtained from our demonstration sites have already accelerated the establishment of Osorb-enhanced bioretention systems for a number of client-based projects in 2013. ABSMaterials has successfully built three additional Osorb-enhanced bioretention systems during the first year of the grant (two in OH and one in FL) and won contracts to build several additional units in Q3-Q4 2013 including: one at Ursuline College (OH), one at Izaak Walton League agricultural site (OH), two at Lake County exfiltration trench site (OH), two at Ellwood City watershed sites (PA), one at CostCo parking lot (WI), and 16 freeway runoff sites for the Pennsylvania Department of Transportation projects (PA). Other prospective customers who have requested projects bids and are seeking permits and funding include: Cleveland Hopkins Airport, Cleveland Clinic, Lake County (OH), URS Corp in four US States, Boeing Field in WA State, two parking lots for garbage trucks owned by Waste Management, Inc., and a major runoff concern at Flinders Port (Adelaide Australia). The company has recently closed reseller agreements for our first generation of stormwater solutions with Hanging Gardens

Inc. (A national leader in Green Roof Solutions) and is negotiating a larger agreement pending the CostCo (WI) project with publicly traded building materials Oldcastle, Inc. (http://www.oldcastlematerials.com/company.htm).

Of note, ABSMaterials has undertaken to expand development capital with a business plan based on the success of the stormwater solutions. A first term sheet from a venture capital firm is in hand. The BOD and CEO are undertaking to competitively bid this term sheet. Five venture firms and a number of high net worth individuals are considering the investment with favorable discussions on valuation. The validation and participation of the NSF and the ongoing involvement of ABSMaterials with the scientific community has been a positive element of the value discussion. When a finance expansion partner is chosen in the coming weeks, an SBIR IIB will be filed to address a number of extremely interesting developments the company and PI believe may make the solutions under development even more compelling to prospective users.

The notable integrated effect of Osorb removing toxic contaminants and the extremely visible and positive impact on plant life is worth noting for the NSF. Kathleen Holmok, a Senior Landscape Designer at URS Corp. summed up a compelling commercial reason this system is so effective, she said: "I know I am supposed to be excited about the water quality, but what I really love it your systems have such beautiful, healthy plants. I won't get calls from clients angry about the plants dying." Plant death from toxins in runoff is a real and qualitative reason why many locations have avoided low-energy, low-impact green stormwater designs. The ABS BioMix-Osorb solutions being researched here are demonstrably and visibly reversing this bias.

The demand and interest for improving water quality have been higher than expected in other stormwater low impact development (LID) practices. Osorb amendment concept as filter media in bioretention systems under the trade name BioMix-Osorb has also received great attention from other stormwater management practices such as permeable pavers and exfiltration trench systems. ABSMaterials has been developing standardized methods to use BioMix-Osorb fill media as (1) base filter media underneath permeable paving materials or (2) joint filling media in interlocking concrete paver systems. We have been working with K.B. Industries and Oldcastle Materials, two leaders in permeable pavements during the first year of the project. First Osorb-enhanced permeable pavers were installed on a garbage truck parking lot at Waste Management, Inc. (FL) in this 6 month period of the project. The site has been currently monitoring water quality by a third-party lab to evaluate the effectiveness of BioMix-Osorb filter media in permeable pavers. With great demand and interest for advanced stormwater treatment systems, we expect between 10 – 15 new commercial stormwater projects using Osorb-metal composites systems by 2014, including 5 under contract that are scheduled for construction in the next 6 months.

The following sections summarize the progress made in each key task outlined in the proposal:

Task 1: Field demonstration of Fe-Osorb enhanced bioretention system (70% Completed). In this 6 month period of the project, two field-scale bioretention systems installed at the College of Wooster campus in 2011 have been continuously monitored to evaluate hydraulic performance (i.e. runoff volume and peak flow rate) and pollutant treatment efficiency (Figure 1).

Figure 1. Current site views of the experimental iron (Fe)-Osorb enhanced bioretention system and standard bioretention system installed at the College of Wooster campus (built in summer 2011). Both systems are filled with a 6 inch layer of gravel then a 1.5 ft soil layer. The Fe-Osorb system contains a 6-inch layer of Fe-Osorb enhanced soil (1% *w/w*, a total Fe-Osorb of 36 kg) placed in the middle of the soil layer. The standard system does not contain any Osorb.

No effluent exiting from each system was observed during most rainfall events in this 6 month period which is similar to what we have seen over 2 years, indicating both bioretention systems have high runoff infiltration and groundwater discharge rates. Even during abnormal rainfall months which were 50 percent above the normal rainfall months (i.e. June and July, 2013), effluent exiting from each system was very minimal, achieving 90 – 99% reduction of runoff volume and 95 – 99% reduction of peak flow rate. Limited effluent water samples obtained from the iron (Fe)-Osorb enhanced bioretention system during the abnormal rainfall months indicated that the Fe-Osorb system significantly reduced nutrient and metal runoff generated from parking lots and rooftops (Figure 2). Both water quantity and quality will be continuously monitored in a long-term study to evaluate the ongoing effectiveness of the Fe-Osorb bioretention system.

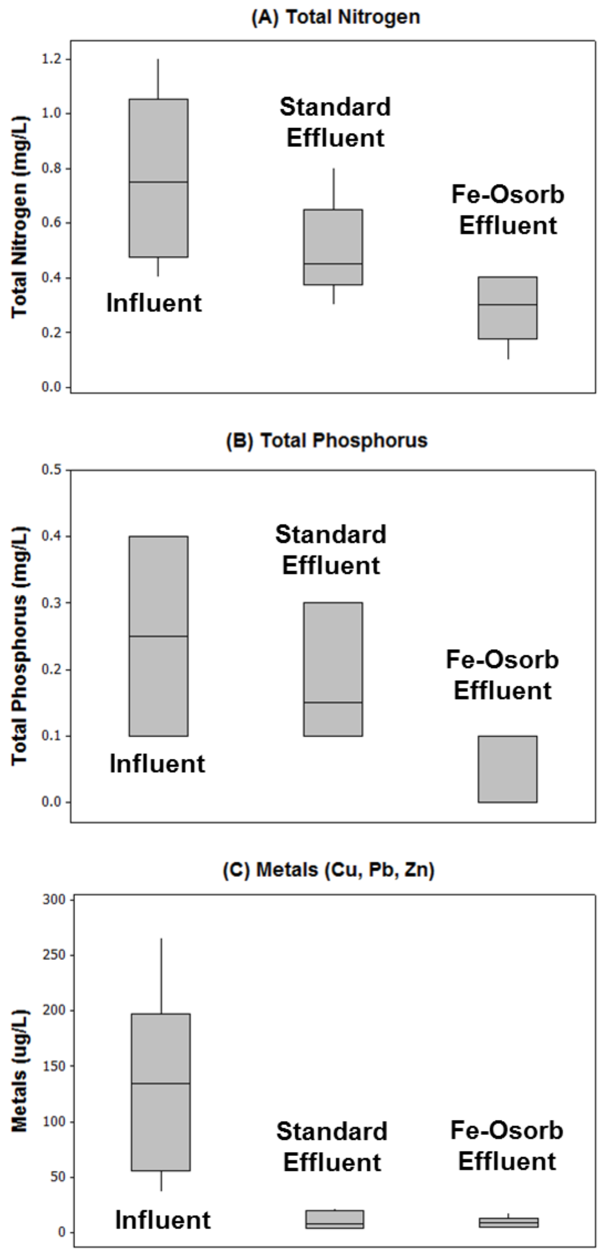

Figure 2. Influent and effluent concentrations of total nitrogen (A), total phosphorus (B), and metals (Cu, Pb, and Zn) (C) obtained from both standard and Fe-Osorb bioretention system at the College of Wooster campus. The water samples were taken from three rainfall events occurred during July, 2013. Sample size, n = 8 for each influent and effluent. All statistical analyses were conducted using MINITAB v.16. Both influent and effluent concentrations were compared between treatments (e.g. standard (control) vs. Fe-Osorb) using one-way analysis of variance and followed by pair-wise comparison using Tukey's honestly significant differences at an alpha level of 0.05

Task 2: Long-term field demonstration of Fe-Osorb enhanced bioretention systems for clients (50% Completed). Two field-scale bioretention systems were built at a former Bell and Howell plant in Ohio during the first 6 months of the project and have been continuously tested to examine the effectiveness of the Fe-Osorb amendments under various runoff conditions generated from the parking lot and rooftop (Figure 3).

Figure 3. Current site views of Fe-Osorb enhanced bioretention systems installed at an industrial site in Wooster, Ohio to treat parking lot runoff (A) and rooftop runoff (B).

Spiked concentrations of runoff pollutants, including nutrients (N and P), herbicides (atrazine and 2, 4-D), and metals (Cu, Pb, and Zn) were also added during selected runoff events to assess pollutant removal capacity under various runoff conditions. Both water quantity (i.e. peak flow and runoff volume) and water quality (i.e. removal efficiency) have been monitored from the systems since summer 2012. The data collected in this 6 month period show that: (1) the Fe-Osorb enhanced bioretention systems have been constant and effective in reducing both peak flow rate and runoff volume while maintaining a high infiltration rate (Table 1 and Figure 4), (2) the Fe-Osorb enhanced systems have been highly effective in removing nutrients (70 – 99%) and herbicides (~ 99%) under high levels of pollution loading (Table 2), and (3) the Fe-Osorb enhanced systems have also effectively removed heavy metals, achieving up to 99% removal efficiency (data not shown). Both water quantity and quality from these systems will be continuously monitored in a long-term study.

Table 1. Summary of monitored storm events from Fe-Osorb enhanced bioretention system in Wooster, Ohio during 6-12 months of the project

Storm ID	Date	Total Precipitation (inch)	Rainfall Duration (hour)	Peak Flow Reduction (%)	Runoff Volume Reduction (%)	Runoff Volume Reduction [a] (gallons)	Reference
6	03-11-13	0.71	5	88	60	13,980	
7	04-10-13	1.13	6	81	53	19,654	
8	04-19-13	0.31	1	89	88	8,952	Spiked [b]
9	04-24-13	0.68	8	92	72	16,067	
10	05-23-13	0.12	2	99	99	3,898	
11	06-10-13	0.42	4	90	81	11,164	
12	07-03-13	1.06	72	87	63	21,916	Spiked [b]

[a] Monitored both influent and effluent rates over time and calculated. Maximum (initial design) water storage capacity of the system is approximately 10,600 gallons. The data indicates that some of the captured runoff in the system is further reduced via groundwater recharge and/or evapotranspiration. The water storage capacity for each rainfall event was affected by rainfall intervals and intensity, ambient temperature, and initial soil water content.
[b] Spiked solution consisted of nitrate (50 g N), phosphate (50 g P), atrazine (500 mg), 2,4-D (500 mg), Cu (20 g), Pb (20 g), and Zn (60 g) were added into the bioretention system during a rainfall event.

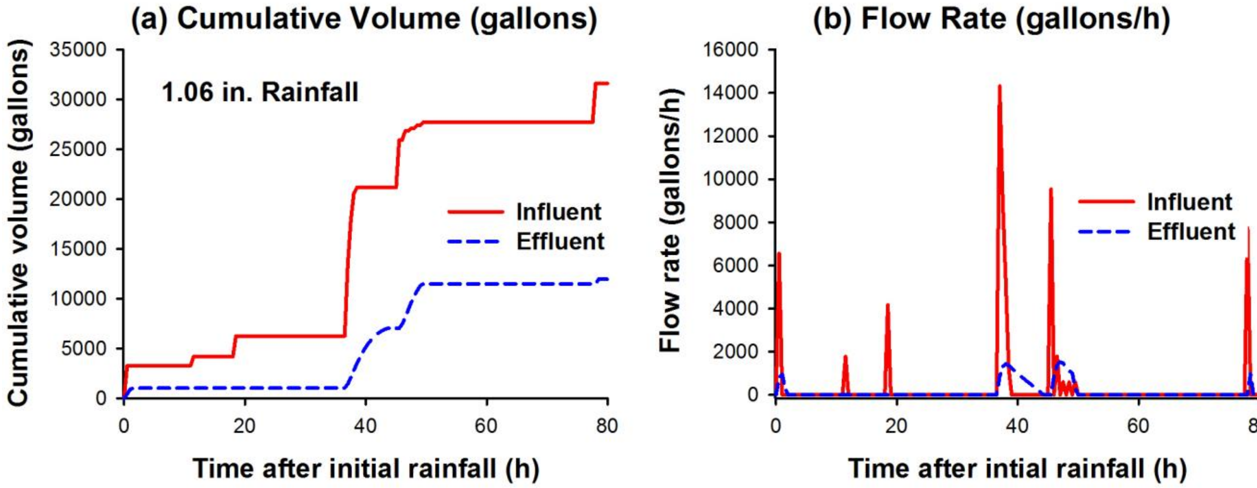

Figure 4. Cumulative volume (a) and flow rate (b) of influent and effluent from the Fe-Osorb enhanced bioretention system, built in Wooster, Ohio for a 1.09 in. rainfall event. Values are recorded using a rainfall gauge and portable flow meter.

Table 2. Pollutant loads and removal efficiencies via Fe-Osorb enhanced bioretention system in Wooster, Ohio during 6-12 months of the project

Storm ID	Date	Peak Nitrate-N Concentration (mg/L)		Net Mass Removal [a] (%)	Peak Phosphate-P Concentration (mg/L)		Net Mass Removal [a] (%)	Reference
		Inlet	Outlet		Inlet	Outlet		
6	03-11-13	1	0.4	78	0.3	0	99	
7	04-10-13	1	0.4	70	0.2	0	99	
8	04-19-13	865	9.3	82	788	5.3	92	Spiked [b]
9	04-24-13	0.8	0.1	86	0.2	0	99	
10	05-23-13	1.3	0.2	95	0.4	0	99	
11	06-10-13	1.8	0.2	91	0.1	0	99	
12	07-03-13	903	3.5	86	811	1.3	97	Spiked [b]

Storm ID	Date	Peak Atrazine Concentration (mg/L)		Net Mass Removal [a] (%)	Peak 2,4-D Concentration (mg/L)		Net Mass Removal [a] (%)	Reference
		Inlet	Outlet		Inlet	Outlet		
6	03-11-13	-	-	-	-	-	-	
7	04-10-13	-	-	-	-	-	-	
8	04-19-13	7.0	0.001	99	7.3	0.002	99	Spiked [b]
9	04-24-13	-	-	-	-	-	-	
10	05-23-13	-	-	-	-	-	-	
11	06-10-13	-	-	-	-	-	-	
12	07-03-13	9.1	0.003	99	8.6	0.002	99	Spiked [b]

[a] Net mass removal (%) for each runoff event performed by integrating hourly flow rate and concentration data collected from influent and effluent.
[b] Spiked solution consisted of nitrate (50 g N), phosphate (50 g P), atrazine (500 mg), 2,4-D (500 mg), Cu (20 g), Pb (20 g), and Zn (60 g) were added into the bioretention system during a rainfall event

Constant and excellent results obtained from this site for the first year of the project have already accelerated the establishment of Osorb-metal composites bioretention systems for a number of client-based projects in 2013. ABSMaterials successfully built one additional Fe-Osorb bioretention system at Arc Tech Academy (Lyndhurst, OH) in summer 2013 (Figure 5) and has initiated water quantity/quality monitoring program in collaboration with the high school faculty and students.

Several Fe-Osorb enhanced systems have been also scheduled to build in Q3-Q4 2013 that include one at Ursuline College (OH), one at Izaak Walton League agricultural site (OH), two at Lake County exfiltration trench site (OH), two at Ellwood City watershed sites (PA), one at CostCo Parking lot (WI), and 16 freeway runoff sites for the Pennsylvania Department of Transportation projects (PA). In addition, we have been actively seeking other potential sites for demonstration projects. Pending projects for approval include Cleveland Hopkins Airport, Cleveland Clinic, Lake County (OH), URS Corp in four US States, Boeing Field in WA State, two parking lots for garbage trucks owned by Waste Management, Inc., and a major runoff concern at Flinders Port (Adelaide Australia).

Figure 5. Newly installed Fe-Osorb enhanced bioretention at Arc Tech Academy in Lyndhurst, Ohio to receive and treat runoff generated from rooftop and parking lot.

The demand and interest for improving water quality have been higher than expected in other stormwater low impact development (LID) practices. Fe-Osorb amendment concept as filter media in bioretention systems (BioMix-Osorb) has received great attention from other stormwater management practices such as permeable pavers and exfiltration trench systems. ABSMaterials has been developing standardized methods to use Fe-Osorb fill media as (1) base filter media underneath permeable paving materials or (2) joint filling media in interlocking concrete paver systems. We have been working with K.B. Industries and Oldcastle Materials, two leaders in permeable pavements during the first year of the project. First Fe-Osorb enhanced permeable pavers were installed on a garbage truck parking lot at Waste Management, Inc. (FL) on April, 2013 (Figure 6). The site has been currently monitoring water quality by a third-party lab to evaluate the effectiveness of Fe-Osorb filter media in permeable pavers.

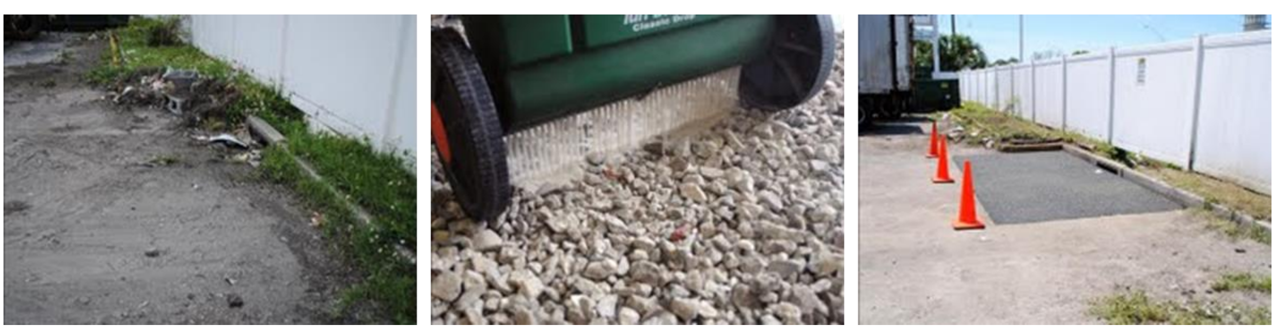

Figure 6. Fe-Osorb enhanced permeable pavers installed on a garage truck parking lot at Waste Management, Inc. (FL).

Task 3: Monitor microbial community and plant health in bioretention systems (40% Completed).
One of the most interesting observations during this 6 month period of the project is that the use of Osorb-metal composites as a soil amendment in bioretention systems improves plant growth. One of the bioretention systems installed at an industrial site in 2012 consists of two distinct soil zones: (1) Fe-Osorb (1% w/w) enhanced soil and (2) standard soil. This site has been monitored for plant growth over time to evaluate the effect of Fe-Osorb amendment on plant growth and health (Figure 7). The observation during spring and summer of 2013 indicates that plant growth and health appear better in the Fe-Osorb enhanced soil zone compared to the standard zone while the Fe-Osorb enhanced soil zone has received higher contaminant loads (Figure 7). This also agrees with findings observed in another demonstration site that the Fe-Osorb enhanced bioretention system produced more plant biomass (31 g biomass/ft^2) compared to the standard bioretention system (27 g biomass/ft^2), indicating the addition of Fe-Osorb in bioretention fill media facilitates plant growth. The results provide limited information on the effect of Fe-Osorb on plant growth and health because the data only show one-year period of the plant growth. The ongoing effectiveness of the Fe-Osorb amendments on plant growth and health will be continuously monitored in a long-term study.

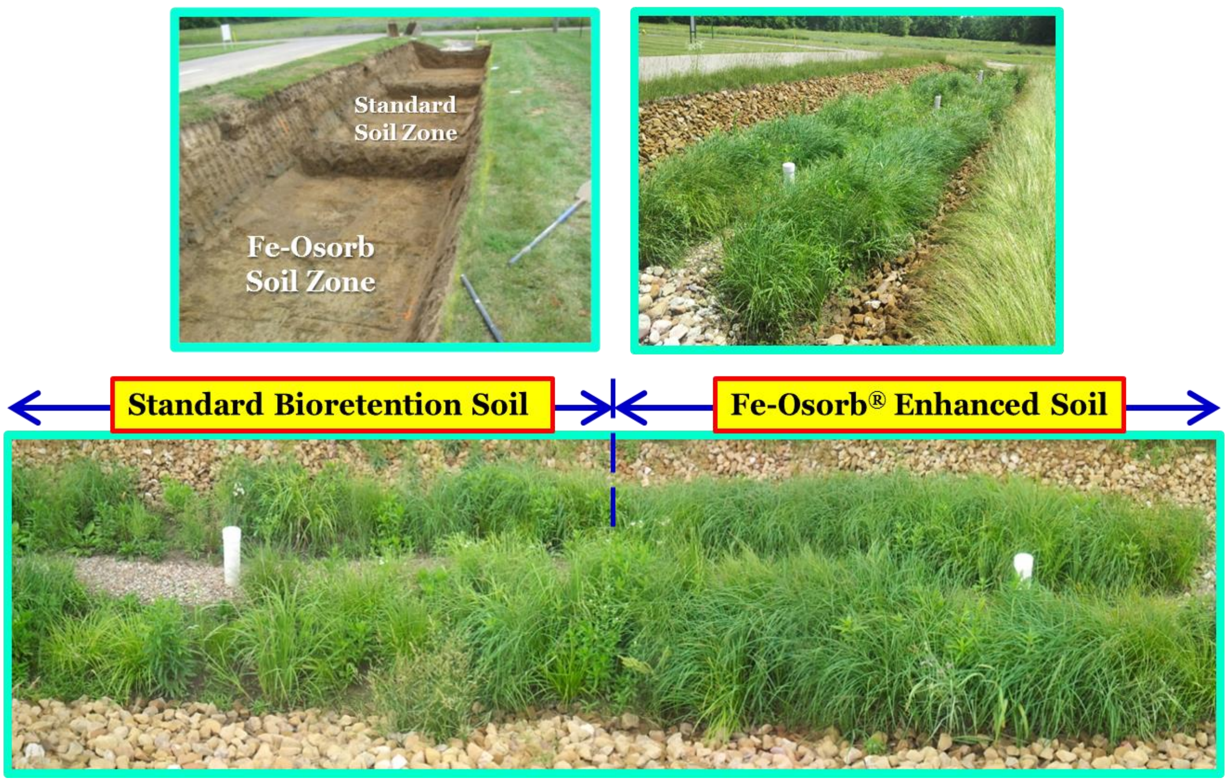

Figure 7. Field-scale bioretention system installed at an industrial site (Wooster, Ohio) where left half has regular bioretention soil and right half contains Fe-Osorb enhanced soil. Runoff generated from parking lot enters from the right so contaminant loads are theoretically higher on the right. Despite higher contaminant loads, plant health appears better in the Fe-Osorb enhanced soil zone.

Since the importance of better understanding the effects of Osorb-metal composites on plant growth and health becomes commercially apparent, extensive growth testing has been initiated in collaboration with Dr. Warren Dick at the Ohio State University – Ohio Agricultural Research and Development Center (OARDC). It was hypothesized that Osorb-metal composites protect plants by capturing and inactivating toxic pollutants from runoff. To test this hypothesis, germination and plant growth experiments have been started in the OARDC greenhouse facility using 120 different experimental set-ups containing 2 different soil media, 3 plant species, and 5 different mixing ratios of Osorb-metal composites with 4 different contaminant loads. The ongoing greenhouse plant testing has been scheduled for next 6 months and field data (i.e. above-ground plant biomass) will be continuously collected from the demonstration sites in a long-term study to confirm beneficial effects of Osorb-metal composites on plant growth and health.

In parallel with evaluating the effects of Osorb-metal composites on plant growth and health, monitoring changes in soil microbial community by adding Osorb-metal composites has been another important research topic for ABSMaterials because the roles of microbial community in bioretention systems are substantial for pollutant removal and significantly affect overall treatment performance. The initial work during Phase I showed that bacterial communities were more diverse and more abundant in Osorb-metal composite amended sand media compared to standard sand media, indicating Osorb-metal composites have the potential to protect and facilitate bacterial community from toxic runoff pollutants. To confirm and better understand this observation, changes in diversity and abundance of microbial community due to the addition of Osorb-metal composites have been continuously investigated at field-scale projects using molecular fingerprinting (T-RFLP) and microscopy (SEM) methods. Soil samples have been taken from the field demonstration sites once every 6 months and SEM and T-RFLP analyses are currently underway at Dr. McSpadden Gardener's lab and the Molecular Cellular Imaging Center (Ohio State University-OARDC, Wooster, OH). We expect that this long-term evaluation will be completed in Q1-Q2 2014.

Task 4: Understanding reduction mechanisms and refinement of Fe-Osorb (60% Completed).
Extensive efforts have been continuously made to understand pollutant removal mechanisms and longevity of the Osorb-metal composites (i.e. Fe-Osorb) during this 6 month period of the grant. It was hypothesized that Osorb immediately acts as a buffer by capturing toxic pollutants from runoff. The captured pollutants and/or their breakdown compounds in the Osorb-metal composites will be slowly released back to soil environment in trace amounts that can be used as nutrient source for both soil microbes and plants without any adverse effects. To better understand absorption-desorption mechanisms of contaminants by Osorb, the back diffusion rate of pollutants from Osorb has been measured. Regular Osorb (without embedded metals) was used for the study to minimize variables caused by chemical reduction via reactive metals. Osorb was preloaded with a model herbicide, atrazine with a very high concentration (5% *w/w*). Aliquots of the atrazine laden Osorb were sealed in packets and buried in the bioretention system at the College of Wooster campus. At various time intervals over multiple rainfall events, an individual packet was removed from the site, the Osorb removed and dried, and the atrazine recovered by rinsing the sorbent with a 30X volume of dichloromethane. The solvent extraction is sufficient to recover atrazine from the Osorb and samples were then analyzed by using a GC-MS. The results show that the back diffusion rate of atrazine from Osorb is slow, but measurable over multiple rainfall events (Figure 8). This agrees with our hypothesis that the captured atrazine in Osorb can be slowly released back into the soil environment in trace amounts that can be further utilized by biological processes.

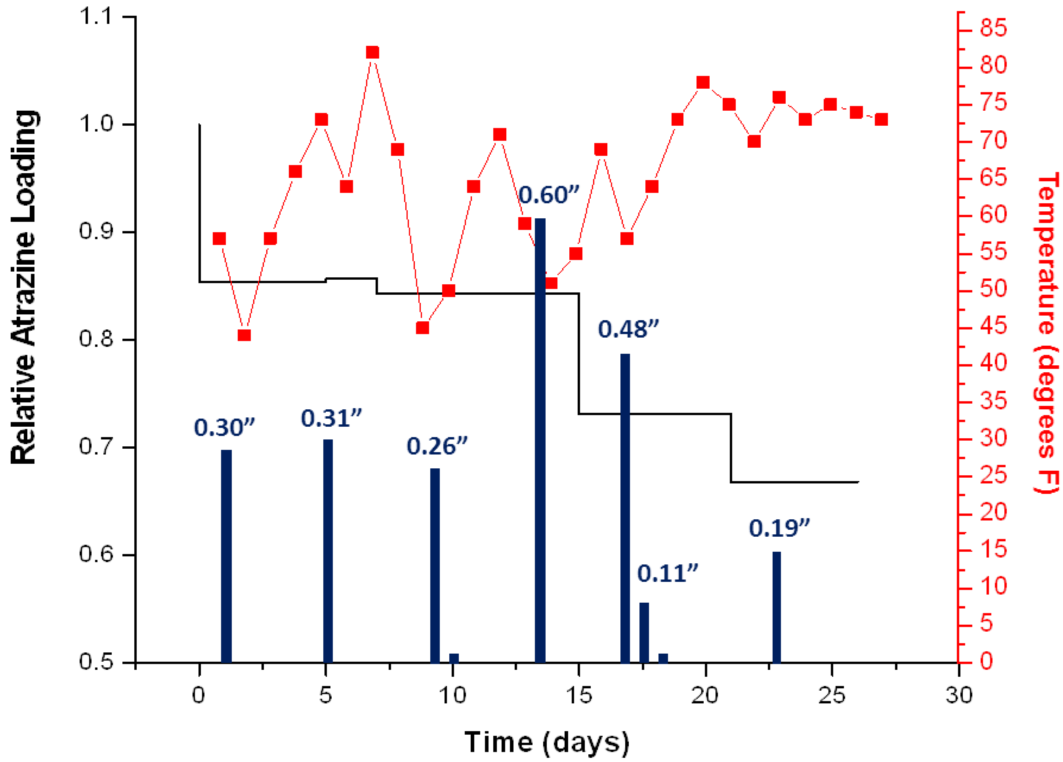

Figure 8. Back diffusion rate of atrazine from Osorb during multiple rainfall events. Aliquots of the atrazine laden Osorb were sealed in packets and buried in the bioretention system at the College of Wooster campus and measured the residual atrazine from the Osorb over time.

In this 6 month period of the project, the focus has also been to understand the roles of reactive zero-valent metals embedded in the Osorb on pollutant removal. Degradation of triclosan, an antibacterial chemical was measured by sealing either µ-Fe (25 mg), Fe-Osorb (50 mg), or Osorb (50 mg) in jars containing 50 mL of 1.0 mg/L triclosan. Glassware was autoclaved prior to use. After each time point the contents of an individual jar was extracted with dichloromethane to recover residual triclosan from both the aqueous solution and captured triclosan from the Osorb. The recovered triclosan was analyzed by GC-MS and compared with the initial concentration. The results show that substantial decreases in triclosan concentration were observed for both µ-Fe and Fe-Osorb while no decrease was observed for the Osorb, indicating iron (Fe) involves in degrading triclosan (Figure 9). However, Oxidation of µ-Fe was noticeable over time. A majority of the free µ-Fe had been converted to Fe-oxide after 1-2 months. In contrast, the Fe embedded in the Osorb appeared to be less oxidized over the same period of time, indicating Fe was protected by the Osorb matrix while substantial degradation of triclosan occurred. This also agrees with the findings from scanning electron microscopic (SEM) images of the Fe-Osorb, showing zero-valent iron particles are well trapped within the Osorb matrix that prevents a short-term metal exhaustion caused by direct exposure to organic compounds in water (Figure 10).

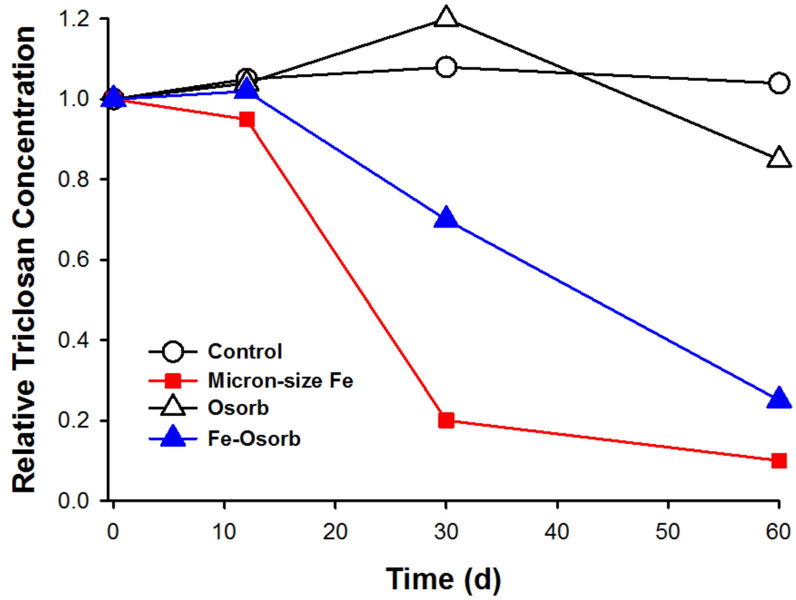

Figure 9. Triclosan degradation treated with either μ-Fe (25 mg), Fe-Osorb (50 mg), or Osorb (50 mg). Both residual triclosan from the aqueous solution and captured triclosan from the Osorb were extracted with dichloromethane over time.

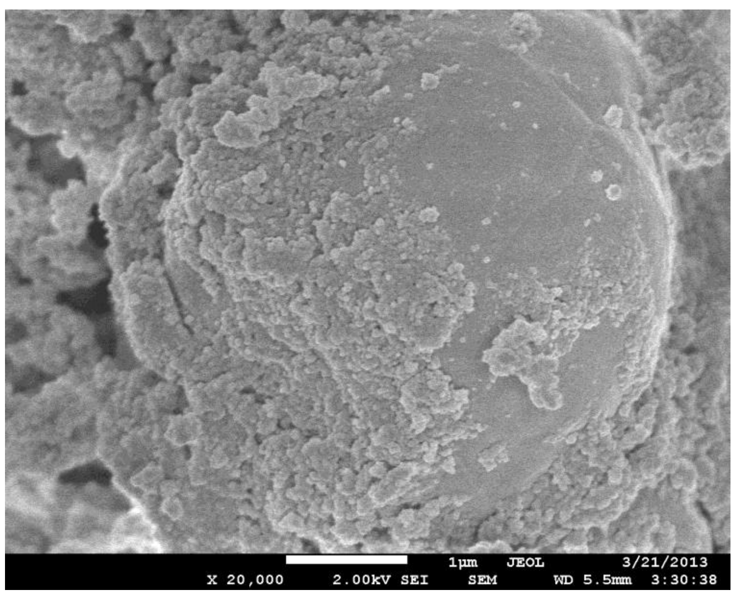

Figure 10. Scanning electron microscopic (SEM) image of the Osorb-metal composites, Iron (Fe)-Osorb. (Photo taken by Dr. Paul Edmiston). The image shows that zero-valent iron (Fe) particle is well trapped within the Osorb matrix that prevents a short-term metal exhaustion caused by direct exposure to organic compounds in water.

Partial degradation products of triclosan were also assayed for each sample to determine degradation pathway. One of the most interesting results in this study is that a decrease in triclosan concentration did not correspond with the appearance of molar equivalent amounts of degradation products, indicating complete or near complete breakdown of triclosan. If reductive transformation (i.e. dechlorination) by the Fe is primary degradation pathway then degradation products such as phenolic species should be only observed. The lack of the degradation products (i.e. diphenylether compounds) in samples where triclosan concentrations decreased (i.e. μ-Fe and Fe-Osorb) suggests a secondary route of degradation, presumably biodegradation. The results also indicate that reactive zero-valent Fe can break down toxic biocide and their degradation products can be further degraded by biological processes. Further testing is scheduled for next 6 months to evaluate the reduction mechanisms of other pollutants such as atrazine and pharmaceuticals by Fe-Osorb.

The importance of determining long-term effectiveness of Fe-Osorb in bioretention systems has commercially become apparent. In the first 6 months of the grant, column testing over 20 sequential runoff events with spiked concentrations of runoff pollutants showed that a 1% addition of the Fe-Osorb in bioretention fill media can significantly improve pollutant removal efficiency over time. However, the results did not show breakthrough points that can be used for estimating maximum removal capacity of the Fe-Osorb enhanced media in bioretention systems. We have initiated a new column testing that includes excessive runoff volume and extremely high pollutant loadings, creating an exaggeration of real conditions (Figure 11). However, it was necessary to provide an assessment of pollutant removal capacity of the Fe-Osorb enhanced media under extreme conditions and to determine breakthrough points in a short-term.

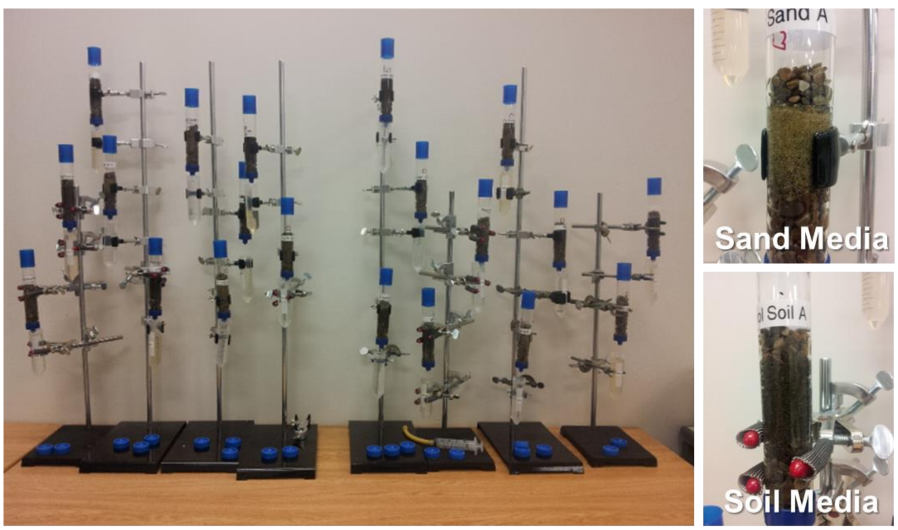

Figure 11. Column-scale bioretention systems amended with micron-size iron (μ-Fe), Osorb, or Fe-Osorb. Two different base media: (a) sand and (b) soil mix were used in the study with high pollutant loadings, including nutrients (TN and TP), herbicides (atrazine and 2,4-D), and metals (Cu, Pb, and Zn).

The ongoing column testing over the first 6 sequential runoff events shows that a 1% (*w/w*) addition of the Fe-Osorb in bioretention fill media can significantly improve pollutant removal performance of bioretention systems under extreme conditions (Figures 12 and 13). This finding is consistent with the results obtained from previous column and field tests. Addition of the micron-size iron (μ-Fe) in the bioretention fill media also significantly improved nutrient removal efficiency and some metals (Figure 12 and 13). However, substantial iron concentrations were observed in the effluent from the μ-Fe enhanced bioretention fill media, indicating potential leaching and metal exhaustion in a short-term. All soil mix media showed excellent removal efficiency of metals (80-99%) compared to the sand base media (20-90%) (Figure 13). We are continuously evaluating ongoing effectiveness of the Fe-Osorb and μ-Fe in the bioretention fill media to determine pollutant removal capacity over time.

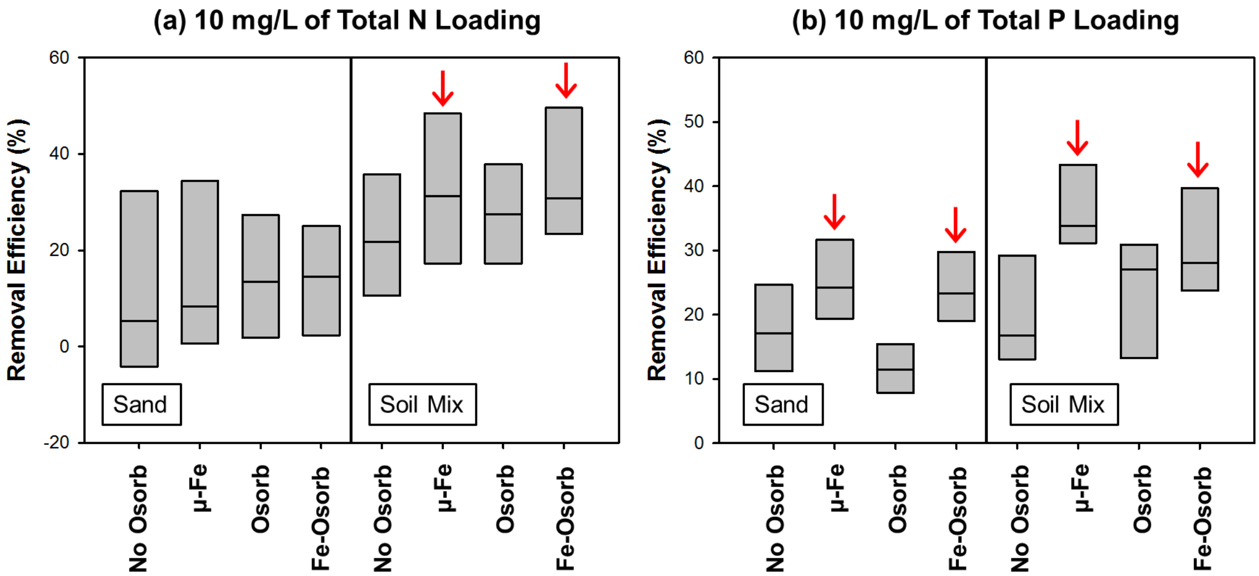

Figure 12. Removal efficiency of total nitrogen (TN) (a) and phosphorus (TP) (b) via column-scale bioretention systems among different soil amendments from the first 6 sequential runoff events. The column testing is currently ongoing for a long-term study. Each box contains the middle 50%of the data. The Upper edge (hinge) of each box indicates the 75th percentile of the data set. The lower hinge indicates the 25th percentile of the data set. Red arrows indicate substantial difference between treatments.

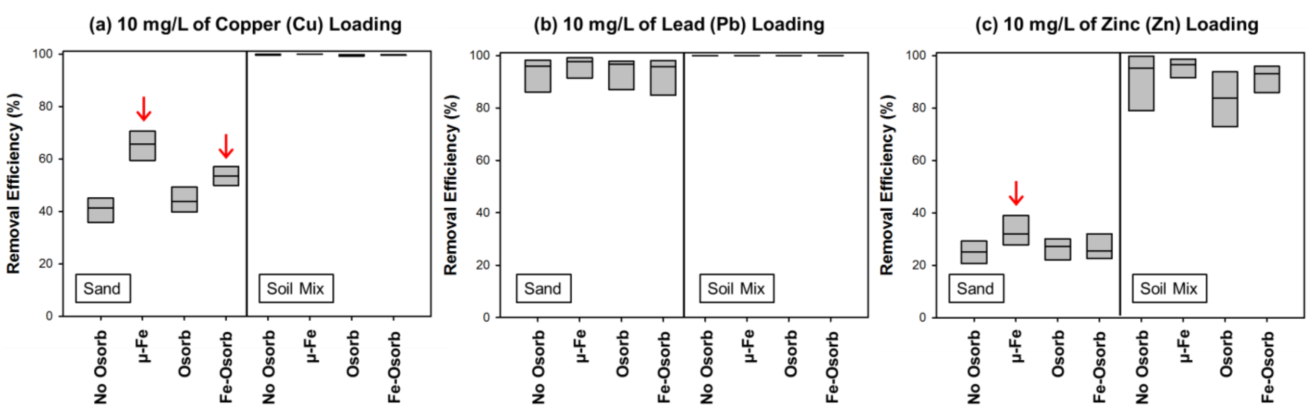

Figure 13. Removal efficiency of copper (a), lead (b), and zinc (c) via column-scale bioretention systems among different soil amendments from the first 6 sequential runoff events. The column testing is currently ongoing for a long-term study. Each box contains the middle 50%of the data. The Upper edge (hinge) of each box indicates the 75th percentile of the data set. The lower hinge indicates the 25th percentile of the data set. Red arrows indicate substantial difference between treatments.

Fundamental work has also been initiated to determine abiotic treatment (i.e. absorption) capacity of Fe-Osorb for various runoff pollutants. Batch absorption isotherm testing is currently ongoing with herbicides (atrazine and 2,4-D) and pharmaceuticals (i.e. triclosan and estradiol). One of the most unusual observations in the preliminary testing with atrazine is that overall absorption capacity of Fe-Osorb for atrazine (mg atrazine sorbed per kg Fe-Osorb) increased as initial concentration of atrazine increased, achieving same percent absorption (95%) regardless of different initial concentrations of atrazine (Figure 14). Such behavior of Fe-Osorb does not follow the standard paradigm of absorbents in that there is a fixed amount or maximum amount of generally equivalent absorption sites that become saturated. The absorption characteristics of Fe-Osorb suggest that there appears to be an equilibrium state that exists between atrazine captured in Fe-Osorb and in solution. Similar non-saturating behavior has been achieved for the absorption of toluene and perchloroethylene by Osorb previously (see PL Edmiston, LA Underwood, Absorption of dissolved organic species from water using organically modified silica that swells, Separation and Purification Technology, Volume 66, 2009, Pages 532-540). We attribute the lack of saturation to swelling where initial absorption events serve to open the nanoporous matrix. Osorb can be thought of a "solid solvent" since the nanoporous silica is similar to a liquid solvent as it can expand volumetrically to accept large amounts contaminants. Osorb extraction, like liquid-liquid extraction, is appears to be governed by partition equilibrium as opposed to surface adsorption equilibrium. We are further investigating this behavior under extremely high concentration of atrazine to further understand the absorption characteristics of Fe-Osorb.

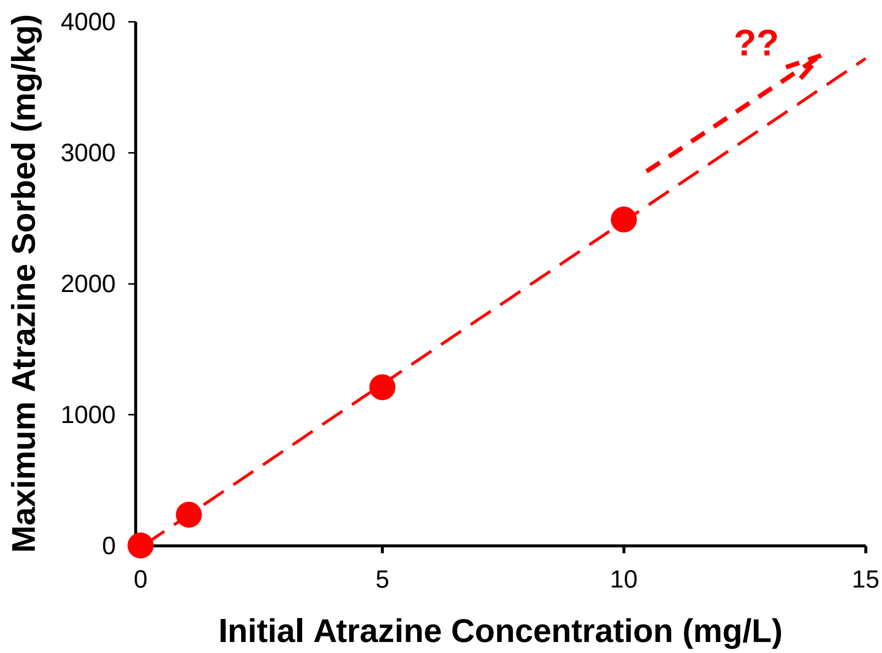

Figure 14. Linear regression analysis of maximum atrazine absorption capacity of the Fe-Osorb among different initial concentrations of the atrazine.

Task 5: Development of modeling tools and a total design package (20% Completed). Although tasks for the development of modeling tools have been originally scheduled on Q1-Q2 2014, fundamental work has been initiated ahead of schedule to estimate hydraulic performance of bioretention systems. In this 6 month period, ABSMaterials has made significant progress in the development of a hydraulic model that can compute water balance terms, including inflow, outflow, evaporation, underdrain flow, soil moisture, ponding times, and number of overflow events based on bioretention system characteristics, user-specified precipitation, and evaporation data using a MATLAB® program (Figure 15). Significant effort will be placed on developing a modeling tool that can estimate both hydraulic and pollutant treatment performance and modifying this model with data obtained from our field-scale testing for next 12 month period.

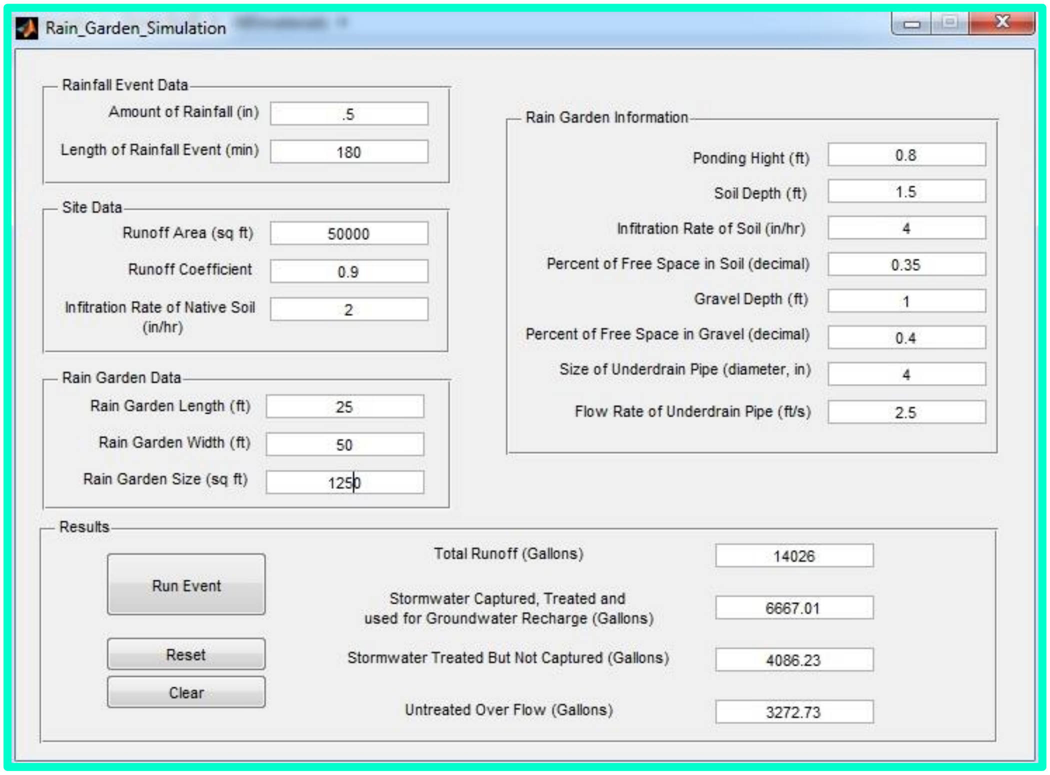

Figure 15. A hydraulic model currently being developed for bioretention design and performance. MATLAB program is used to create a graphical user interface (GUI) for the model that input design parameters and estimate hydraulic performance of bioretention systems.