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 #1: 0 – 6 Months January 30, 2013

Project Summary. Stormwater runoff quantity and quality is an immediate and growing concern in the U.S. Stormwater is often laden with nutrients, hydrocarbons, herbicides, and pharmaceuticals, damaging surface water and carrying persistent chemicals that impact humans, groundwater, and ecosystems. In recent years, stormwater quantity and quality control began to be addressed together. Federal and state regulations are becoming much more stringent, and stormwater policies are increasingly viewed as critical to ensure safer living environments and cleaner waters.

Green, LID (low impact design), and decentralized approaches to stormwater management are gaining traction. These approaches are very cost-effective for reducing bulk loading of runoff. However, this decentralized approach has caused significant challenges in finding effective treatments for stormwater pollutants and nutrients.

ABSMaterials' Osorb® stormwater systems are meeting this challenge. We are developing new filter media to remediate multiple pollutants from stormwater runoff by integrating a novel absorbent material, Osorb®, with embedded reactive metal composites in bioretention systems. Osorb is a patented, chemically inert, silica-based material that physically absorbs a wide range of organic pollutants from water. Reactive, non-leaching micro-metals embedded in the Osorb can chemically reduce and/or degrade the captured pollutants. Our overarching goal is to develop sustainable and commercially viable onsite runoff remediation practices by integrating novel Osorb-metal composites into new or existing bioretention systems that enhance the economic, social, and environmental health of urban, industrial, and agricultural areas.

ABSMaterials is demonstrating that distributed, green, LID stormwater systems can be more cost-effective, durable and resilient than any old-line centralized system, and we do it by building aesthetic features that add value to the landscapes where they are developed.

Status of Commercialization Activities. During the first 6 months of the project, we have begun to convert our research and development into profitable client-based projects. ABSMaterials is meeting a market ready of a solution with the Osorb-metal composites filter media which have the highest treatment capacity of any existing stormwater management system. The company has designed and completed two large systems at a former Bell and Howell plant in Ohio and has been asked to bid or been paid to design 22 additional projects. One of these projects, constructed at the College of Wooster in 2011, is the site of our first installed system under the NSF SBIR Phase I. The site has become a magnet of study for the campus and a focus of alumni interest. A keystone member of the board of trustees and the president of the college hired ABS to redesign the entire campus stormwater system with the goal of having a green-capstone, STAR-rated campus with no stormwater discharge and no negative water quality impacts. The system, now in phase one of design, will incorporate as many as 30 distributed Osorb stormwater bioswales over a 200 acre area.

Other prospective customers who have requested project bids include: Cleveland Clinic, Ursuline College, the City of Euclid, Ohio, Brush High School (Cleveland, Ohio), the Pennsylvania Department of Transportation, and URS Corp.

The market is demanding systems capable of meeting water quality standards using low impact development and green infrastructure strategies made possible with Osorb-metal composites to improve plant survival with minimal maintenance, which are two top priorities for this market. We are marketing such a solution under the trade name BioMix-Osorb®, providing (1) site-specific design and construction service and/or (2) a pre-bagged material that can be easily mixed on-site by a contractor. With great demand and interest for advanced stormwater treatment systems, we have already built two Osorb-metal composites enhanced bioretention systems in the first 6 months of this grant. We expect between 5 and 10 new commercial stormwater projects using Osorb-metal composites systems in 2013, including 2 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 (20% Completed). Two field-scale bioretention systems built in June, 2011 during the Phase I project have been continuously tested to examine the on-going effectiveness of the Fe-Osorb enhanced bioretention system over the standard system for runoff pollutant removal (Figure 1).

Figure 1. Site views of field-scale bioretention systems (rain gardens) installed at the campus of the College of Wooster, Ohio. One standard model and one version enhanced with Fe-Osorb.

Further field evaluation under natural runoff conditions during the first 6-month period confirmed that existing experimental Fe-Osorb enhanced bioretention system demonstrates as much as a 99.9% reduction in runoff volume and a 99.6% reduction on runoff pollutants such as petroleum hydrocarbons and other organic pollutants (Figure 2). However, no effluent exiting from each system was observed during most rainfall events, indicating both systems have high runoff infiltration and groundwater discharge rates. This is ideal for real application by reducing discharge runoff, but new installation and/or modification of sampling ports in both systems are scheduled within next few months to overcome a limited sample size for monitoring water quality.

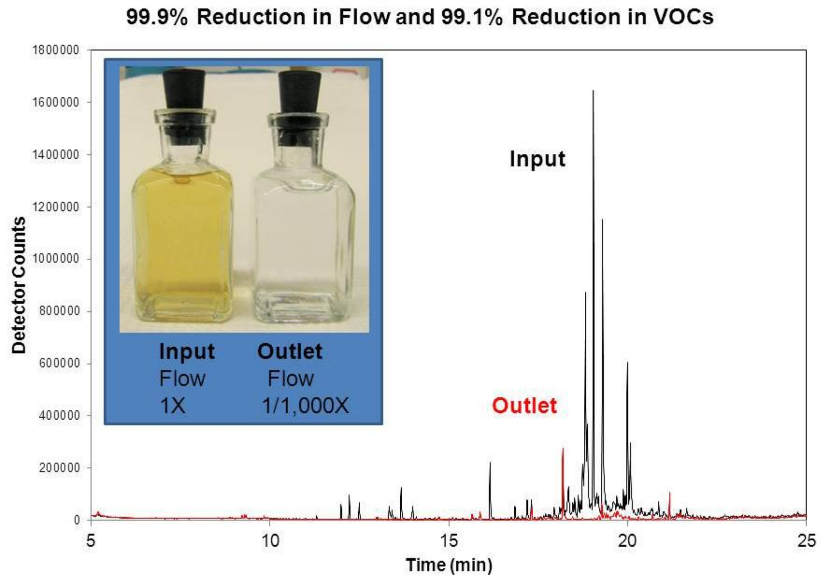

Figure 2. A comparison of input and outlet volume and quality from the experimental Fe-Osorb bioretention system as measured by gas chromatography-mass spectrometry from a rain event Nov. 21, 2012. Peaks in the chromatogram are essentially derivatives of petroleum hydrocarbons and other organic pollutants. Insert: inlet and outlet water samples, where X-factors refer to the relative volume of the input and outlet flow from the rain event.

Task 2: Long-term field demonstration of Fe-Osorb and Zn-Osorb enhanced bioretention systems for clients (20% Completed). Extensive efforts have been made to find additional demonstration sites that represent a majority of the range of site and runoff conditions in which stormwater volumes and pollutants are being addressed by prospective clients. ABSMaterials has successfully built two more Fe-Osorb enhanced bioretention systems at an industrial site (Wooster, OH) in summer 2012 to remediate pollutants associated with stormwater runoff generated from the parking lot and rooftop (Figure 3).

Figure 3. Fe-Osorb enhanced bioretention systems at an industrial site (Wooster, OH) built in summer 2012. The systems remediate pollutants associated with stormwater runoff generated from parking lot (A) and rooftop (B).

The systems have been monitored and tested to examine the effectiveness of the Fe-Osorb amendments under natural runoff conditions. Spiked concentrations of runoff pollutants, including nutrients and herbicides, were also added during selected runoff events to assess pollutant removal capacity under extreme 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 the summer 2012. The data show that: (1) Fe-Osorb enhanced bioretention systems have effectively reduced both peak flow rate and runoff volume (Table 1), (2) the Fe-Osorb enhanced systems have been highly effective in removing nutrients (41 – 99%) and herbicides (77 – 99%) under high levels of pollution loading, even with an extreme rainfall condition such as Superstorm Sandy (Table 2), and (3) the Fe-Osorb amendment has not altered hydrodynamics of runoff in the fill media while maintaining a high infiltration rate. 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

Storm ID	Date	Total Precipitation (inch)	Rainfall Duration (hour)	Peak Flow Reduction (%)	Runoff Volume Reduction (%)	Reference
1	09-26-12	0.3	2	91	91	
2	10-18-12	0.11	0.5	98	98	Spiked [b]
3	10-27-12 [a]	4.63	96	78	11	Spiked [b]
4	11-12-12	0.72	9.5	85	56	
5	12-04-12	0.42	5	88	85	

[a] Superstorm Sandy
[b] Spiked solution consisted of nitrate (50 g N), phosphate (50 g P), atrazine (300 mg), and 2,4-D (300 mg) were added into the bioretention system during a rainfall event.

Table 2. Pollutant loads and removal efficiencies via Fe-Osorb enhanced bioretention system in Wooster, Ohio

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		
1	09-26-12	0.6	0.1	72	0.2	0.1	82	
2	10-18-12	877	4.6	94	800	1.9	98	Spiked [c]
3	10-27-12 [b]	840	19.9	41	746	8.9	52	Spiked [c]
4	11-12-12	0.5	0.1	78	0.2	0	99	
5	12-04-12	0.4	0.1	81	0.2	0	99	
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		
1	09-26-12	-	-	-	-	-	-	
2	10-18-12	8.8	0.003	99	8.4	0.001	99	Spiked [c]
3	10-27-12 [b]	7.4	0.008	98	7.6	0.015	77	Spiked [c]
4	11-12-12	-	-	-	-	-	-	
5	12-04-12	-	-	-	-	-	-	

[a] Net mass removal (%) for each runoff event performed by integrating hourly flow rate and concentration data collected from influent and effluent.
[b] Superstorm sandy
[c] Spiked solution consisted of nitrate (50 g N), phosphate (50 g P), atrazine (300 mg), and 2,4-D (300 mg) were added into the bioretention system during a rainfall event

ABSMaterials expects that the promising results obtained from this site during the first 6 months will accelerate establishment of Osorb-metal composites bioretention systems for a number of client-based projects in 2013. Several Fe-Osorb bioretention systems have been already scheduled to build in Spring 2013 that include one at ArcTech Academy (OH) and four at the College of Wooster (OH). In addition, we have been actively seeking other potential sites for demonstration projects. Pending projects for approval include Cleveland Clinic parking lot sites (OH), St. John's High School parking lot site (OH), Izaak Walton League agricultural site (OH), Euclid City parking lot sites (OH), and Cleveland Metro Park street sites (OH).

Task 3: Monitor microbial community and plant health in bioretention systems (20% Completed). The importance of better understanding the effects of Osorb-metal composites on soil microbial community and plant health in bioretention systems became commercially apparent. 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 sand controls. It was hypothesized that Osorb immediately acts as a buffer by capturing toxic pollutants from runoff while reactive metals embedded in the Osorb increase available nutrient sources for both soil microbes and plants by breaking down the captured pollutants. To test this hypothesis, 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. First, soil samples were taken from the field demonstration sites during this period, and SEM and T-RFLP analyses are currently underway at Dr. McSpadden Gardener's lab and the Molecular Cellular Imaging Center (Ohio State University, Wooster, OH). Soil samplings are currently scheduled once every 6 months.

In addition, extra efforts have been made to evaluate the effects of Osorb-metal composites on bacterial growth under the presence of a toxic biocide, triclosan, which is commonly detected in stormwater runoff. Ampicillin-resistant DH5 (alpha) *E. coli* grown in LB media were used and tested at three different conditions: (1) control LB media, (2) LB media + 100 ppb of triclosan, and (3) LB media + 100 ppb of triclosan + 1g (0.3% *w/v*) of Fe-Osorb which was pre-sterilized using ethanol. Bacterial cell density was measured over time using OD600 method. The results show that the bacteria grew well with Osorb-metal composites even with triclosan added (Figure 4). Without Osorb-metal composites, all the bacteria died (no growth) in the presence of 100 ppb triclosan. The results indicate that Osorb-metal composites protect bacteria by capturing and inactivating biocides from the media. Since the roles of microbial community in bioretention systems are substantial for pollutant removal, the results of bacterial growth suggest that the Osorb-metal composites have the potential to protect and facilitate bacterial community from toxic biocides and improve overall soil health and treatment performance of bioretention systems.

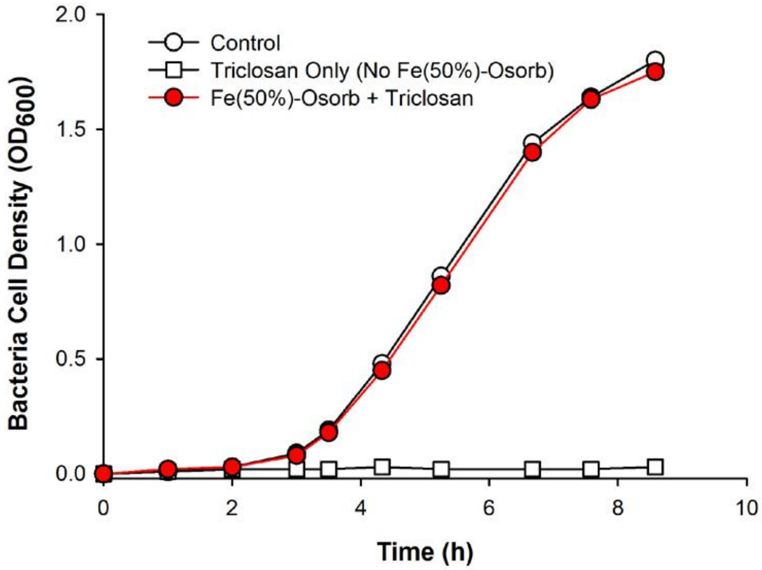

Figure 4. Bacterial cell (Ampicillin-resistant DH5 (alpha) *E. coli*) growth over time at three different conditions: (1) control LB media, (2) LB media + 100 ppb of triclosan, and (3) LB media + 100 ppb of triclosan + 1g (0.1% *w/v*) of Fe(50%)-Osorb.

The first-year above-ground plant biomass was also measured from two field-scale bioretention systems to evaluate the effects of Osorb-metal composites on plant growth. The result shows 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. We are planning to take the measurement every year to evaluate the long-term effects of Osorb-metal composites. The demand and interest for healthy plant growth along with water quality improvement in the green infrastructure industry have been higher than expected that have led us to reconsider the business model for the use of Osorb-metal composites in bioretention systems. Since aligning research to commercial activity has been a priority at ABSMaterials, extensive plant growth testing including both laboratory- and field-scales is scheduled for next 12 months to obtain more accurate data and to confirm beneficial effects of Osorb-metal composites on plant growth and health.

Task 4: Understanding reduction mechanisms and refinement of Fe-Osorb and Zn-Osorb (30% Completed). During the first 6 months of the grant, the focus has been to understand pollutant removal mechanisms and to refine Osorb-metal composites for maximizing longevity of remediation. Nutrients such as nitrate and phosphate have been tested with both Osorb-metal composites and with Osorb without metals as a control at a laboratory scale. The preliminary lab testing showed that significant removal of nutrients was observed in the Osorb-metal composites while no substantial removal of nutrients was observed in the Osorb without metals. This indicates that reactive metals (i.e. Fe^0 and Zn^0) and their products embedded in the Osorb matrix can potentially increase reductive transformation and adsorption of nutrients. Since biological nutrient removal processes play an important role in bioretention systems, we are currently investigating the effect of Osorb-metal composites on biological process in column-scale bioretention systems.

To maximize longevity of remediation capacity over time, different amounts (i.e. 10%, 30%, and 50% *w/w*) of zero-valent iron (Fe^0) and zinc (Zn^0) were added during the Osorb synthesis. The modified types of Osorb-metal composites have been tested at a column scale (Figure 5) with spiked concentrations of runoff pollutants, including nutrients (i.e. nitrate and phosphate), metals (i.e. copper, lead, and zinc), and herbicides (i.e. atrazine and 2,4-D). All experiments consisted of applying 20 sequential simulated runoff events to the columns at 3-day intervals. For each event, 500-mL of spiked solution was applied and effluent was collected and analyzed for each pollutant using a GC-FID, LC-MS, and IC.

Figure 5. Column-scale bioretention systems amended with modified types of Osorb-metal composites. Two different base fill media: (a) sand and (b) soil mix (a mixture of 60% sand, 20% soil, and 20% compost) were used in the study.

Our column testing over 20 sequential runoff events shows that a 1% addition of Osorb-metal composites in bioretention fill media can significantly improve pollutant removal performance of bioretention systems, achieving average 70 – 99% removal for nitrate (Figure 6a), 40 – 60% removal for phosphate (Figure 6b), and 95 – 99% removal for both atrazine (Figure 7a) and 2,4-D (Figure 7b) over time. It was hypothesized that the treatment capacity of Osorb-metal composites increased as the amount of zero-valent metal embedded in the Osorb matrix increased. However, no significant increase in the treatment capacity was observed as the amount of metals increased. This is most likely due to the fact that a limited amount (~1% *w/w*) of Osorb-metal composites was applied in the bioretention fill media that hindered the effect of different amount of metals on the performance. Addition of micron-size zero-valent iron (10 – 20% *w/w*) in the bioretention fill media significantly improved phosphate removal efficiency while the effect of additional metals on herbicide removal was less significant, indicating that additional micron-size reactive metals in fill media may facilitate phosphate adsorption. However, there should be a balance since too much metal in fill media may cause potential leaching. All soil amendments showed excellent removal efficiency of metals (90 – 99%) over time (data not shown). We are continuously evaluating the ongoing effectiveness of Osorb-metal composites in the bioretention fill media and higher pollutant loadings are scheduled for next 6 months to evaluate their long-term performance.

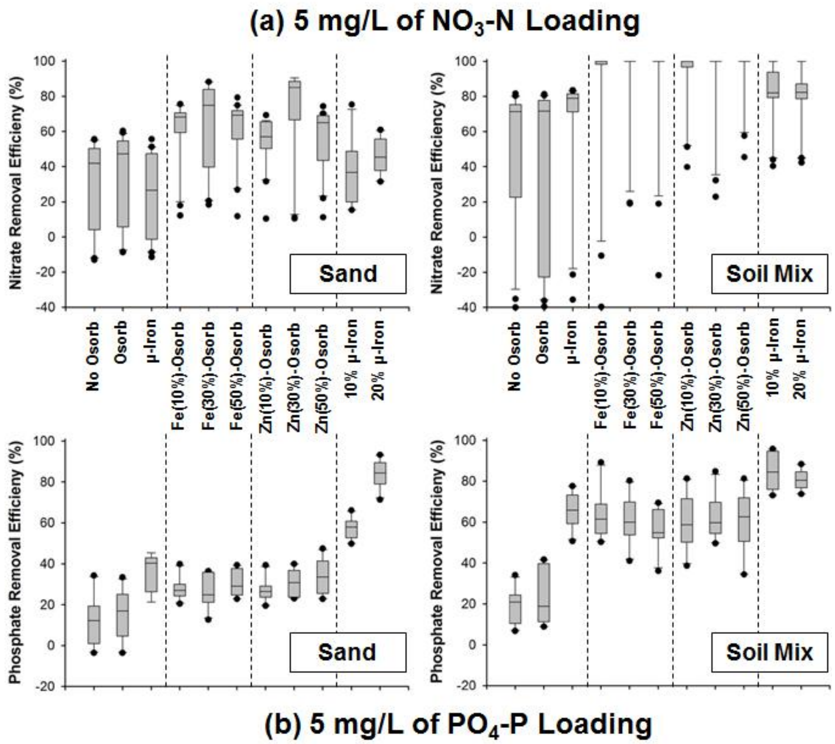

Figure 6. Removal efficiency of NO_3 (a) and PO_4 (b) via bioretention systems among different soil amendments from 20 sequential runoff events. Each box contains the middle 50% of the data. The upper edge (hinge) of each box indicates the 75th percentile of the data set. The lower hinge indicates the 25th percentile of the data set.

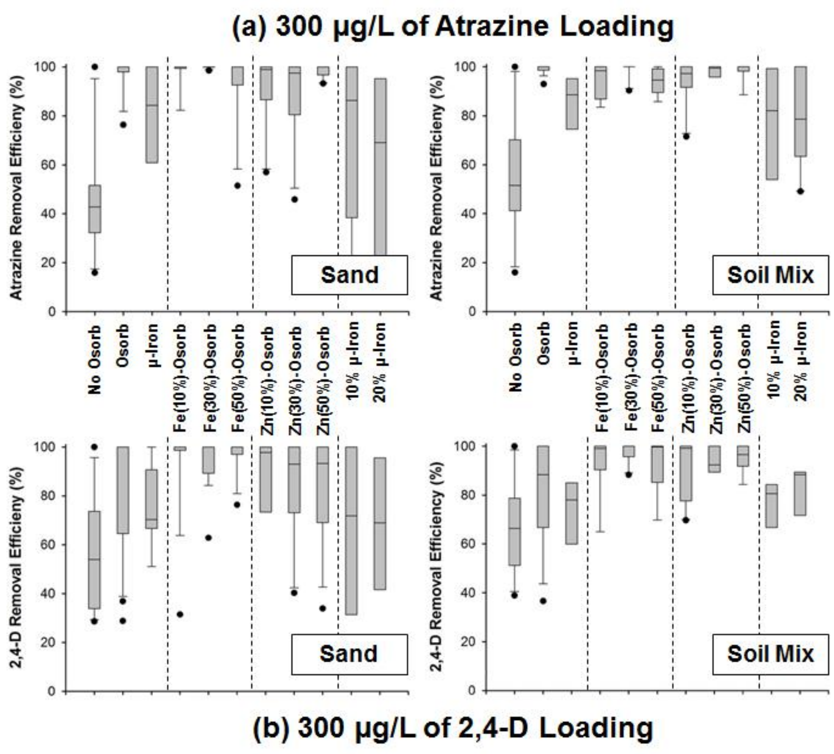

Figure 7. Removal efficiency of atrazine (a) and 2,4-D (b) via bioretention systems among different soil amendments from 20 sequential runoff events. Each box contains the middle 50% of the data. The upper edge (hinge) of each box indicates the 75th percentile of the data set. The lower hinge indicates the 25th percentile of the data set.

Task 5: Development of modeling tools and a total design package (0% Completed). No efforts have been made for the development of modeling tools in the first 6 months of the grant. Extensive efforts for this task have been scheduled on Q1-Q2 2014.