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Stormwater Runoff Treatment Using Bioswales Augmented with Advanced Nanoengineered Materials

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1.1 Introduction

Bioretention systems have the potential for managing stormwater by reducing peak runoff flow and improving surface water quality in a natural and aesthetically pleasing manner (Dietz, 2007; Davis et al., 2009). Most bioretention systems such as vegetated buffers, rain gardens, and stormwater wetlands are designed to treat runoff by employing filtration, deposition, adsorption, and infiltration through porous media (USEPA, 2004). However, pollutant treatment performance of these systems is highly variable and often less effective in the long-term due to the limited treatment capacity of filter media (Davis et al., 2001; Hsieh and Davis, 2005; Maurakami et al., 2008; Cho et al., 2009; Yang et al., 2010). Since bioretention media compositions greatly affect pollutant removal mechanisms, development of different media compositions is critical to determining bioretention performance.

ABSMaterials, Inc. developed new filter media to remediate multiple pollutants from stormwater runoff by integrating a novel absorbent nanomaterial, 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 (Burkett and Edmiston, 2005; Edmiston and Underwood, 2009; Edmiston, 2010). Osorb has the significant ability to absorb organic contaminants because swelling ability of the material allows for an unmatched absorption capacity when compared to current alternate absorbents. Osorb-metal composites combine two advanced remediation materials: (1) a high-capacity organosilica sorbent, Osorb, and (2) embedded reactive metals. The captured pollutants by Osorb such as petroleum hydrocarbons, nitrate, biocides, endocrine-like volatiles and chlorinated organic compounds including herbicides will be further transformed and detoxified by reactive metals via various chemical reactions including hydrogenation, dehydrogenation, and dehalogenation (Edmiston et al., 2011). Breakdown products can be biologically mineralized in bioretention systems.

This work is part of broader project on the development of new bioretention filter media that can be used to remediate various organic pollutants in addition to removal of nutrients by adding Osorb-metal composites in bioretention systems. The objective of the work presented here was to determine remediative effectiveness of various Osorb-metal composites to remove a wide range of runoff pollutants. We tested five different Osorb-metal composites as an amendment to two common soil bioretention base media; (1) sand and (2) sand-soil-compost mix among two different bioretention design configurations; (1) internal water saturated design and (2) water unsaturated design.

This chapter will be divided into two distinct sections. The authors will first examine the business case and market that make nano-glass materials useful in stormwater remediation. Later, we will discuss in a limited fashion the science of the Osorb nano-glass materials.



Figure 1.1

A tour group observes the nano-glass Osorb stormwater system at the College of Wooster. This is Study Site #1 for a National Science Foundation study of Osorb nano-glass enabled stormwater treatment. Note: Extremely robust plant has been observed, here shown at only 12 months after initial planting. All plants are far larger and more robust than either a control bed or what would normally be expected for plants being fed waters directly from an urban parking lot and dumpster storage area.

1.2 Key Market Drivers

There are three key drivers of the water-energy nexus as it impacts global stormwater usage. They are as follows.

First, in 2010, 97% of the drinking waters tested by the United Nations during the World Water Survey tested positive for volatile organic compounds associated with cancer, infertility, transgendering, birth defects and numerous other health concerns. In advanced and developing nations, the problem was generally more pronounced than in underdeveloped nations. Many of these compounds, including estradiol, antidepressants and polyaromatic hydrocarbons, increase in number and concentration in the most heavily developed nations. There are a number of technologies which are moderately effective in removing these compounds, but they require energy intensive inputs and often high degrees of consumables. Advanced materials capable of removing these compounds from water is in demand.

Second, today, 14% of the electricity generated globally is used to move and manage water and about 1/3 is used for each of three types of water: agricultural, industrial and human direct usage. Water is second only to industrial systems in this regard and globally consumes far more energy than lighting. Many nations have created goals to specifically address reducing the electrical costs of water. Global firms, including IBM, GE, Siemens and CH2M Hill have created complete business units to capture what McKinsey project to be a \$3T global investment in water electrical infrastructure development by 2050.

Third, commercial chemicals, pharmaceuticals and agrochemicals are becoming both more complex and more powerful. Many of these highly engineered chemicals elude removal by 19th and 20th century water technologies.

These three drivers confront the water treatment engineers, managers and operators, who tend to be technology-conservative and change-resistant. They are however very aware they lack the treatment tools needed to address increasingly complex chemistry, with lower electrical loads and costs, at the same time public awareness and regulatory pressures are becoming less tolerant of these trace chemicals in both drinking and natural surface waters.

This awareness is high or growing for 1) municipalities, 2) developers, 3) universities and schools and 4) ag-soil professionals. Stormwater control issues stem primarily from customers with impervious surfaces (e.g. parking lots, sports complex, high production ag-sites, construction sites, golf courses) and insufficient management for high volumes of stormwater. High volumes of contaminated stormwater runoff are common and costly, often causing eutrophication of lakes, fishkills, erosion, sedimentation of wetlands and fish breeding sites, contamination of aquifers and degradation of drinking water sources.

To address these issues, a growing focus is being placed on addressing both volume of stormwater flow and stormwater quality protection as far upgradient as possible. But while a number of very good solutions are capable of high quantity diversion of water into detention and aquifer recharge systems, there are no effective systems for long-term runoff pollutants from modern chemistry, fuels from motor vehicles and nutrients from fertilizers. Stormwater runoff quality management is a pointed, immediate and global issue seeking new solutions.

ABSMaterials, Inc.'s nano-functional material, Osorb[®], which was initially developed to remove toxins at superfund sites and industrial waste water processes, fills this need. When added to

“green” stormwater systems such as enviroswales, bioswales, rain gardens, retention zones and stormwater swales, Osorb removes and destroys nearly all persistent industrial pollutants it was designed to manage at industrial sites. Unexpectedly, the addition of Osorb to green stormwater systems also encourages more robust rizome communities, increased genetic complexity and a resulting biomass increase and nutrient consumption within the systems.

1.3 Functionality of Osorb Materials and Outcomes in Stormwater Systems



Figure 1.2

At NSF Study Site #2, an Osorb stormwater system is estimated to treat apx. 6.5M gallons/year of industrial stormwater runoff. Note: The foaming is associated with trace surfactants and industrial agents historically used at this site, including halons from chemical fires in 1974 and twice in the 1980s. The water has also picked up contaminants from parking lots and loading docks. This image was taken during a heavy rainfall event shortly after system was constructed in July 2012.

Impacted stormwater runoff is making some waters unusable, polluting drinking water sources, surface water features and groundwater. Adding Osorb media fill far upgradient in a system greatly improves the removal efficiency of herbicides, drugs, fuels and other components of runoff and provides a method for capturing high concentration pollutants after heavy rainfall or snowmelt. Osorb media is shown to be durable and long-lasting and have a high loading capacity to remove large amounts of pollutants at any given time.

Beginning in 2011, ABSMaterials began National Science Foundation SBIR-funded research to document how various types of Osorb material improved efficiency in removal of pollutants at three indicative stormwater locations. Two additional long term study sites will be selected in the coming months. The research, still ongoing, is measuring the functionality, durability and cost effectiveness of different Osorbs with reactive metal components at each study site.

Site 1 (*figure 1.1*), built in July 2011, is a twin chamber system. Chamber 1 contains Fe-Osorb fill media. The second is a control chamber that does not contain Osorb. The unit is located at the College of Wooster in Wooster, Ohio and drains 3.5 acres, including 80 parking spaces, a dumpster parking pad and 4 buildings.

Site 2 (*figure 1.2*), built in July 2012, drains apx 6.5 acres of industrial site runoff, including 220 parking spaces, 6 loading docks, 120,000 sq. ft. of industrial rooftops. The site has been an active industrial site for over 50 years with legacy chemical residues, including fuels, halons, solvents and various chemicals associated with the site's 30-year use as a photography and microfiche processing facility.

Site 3, now in the engineering and permit phase, will drain 8.2 acres of parking roadways and rooftops at an active hospital complex.

Over the first 16 months of testing at site 1 and five months at site 2, testing has validated substantial advantages to using nano-glass Osorbs in the runoff systems, and in most cases the field results are exceeding the results predicted from column tests conducted in a lab setting. The possible reasons for results are examined in the science review below, but in summary:

1 – Osorb added to stormwater systems removes at least 90% and often 99.9% of industrial and urban pollutants in the runoff. Concentration of volatile organic contaminants in runoff at times exceeds 400ppm, and the Osorb nano-glass consistently reduces the concentration to below 1ppm.

2 - Osorb in the stormwater system removes volatile organics directly, but has the “knock-on” effect of creating extremely robust and healthy rizome and soil communities. These healthy communities result in extremely vigorous plant life and substantial and unpredicted reductions in nutrient loading associated with algae blooms and other water quality issues. This effect was not observed in the column lab testing conducted from 2009-2011.

3 – Osorb nano-materials are extremely durable and continue to perform with no degradation of performance in stormwater systems measured to date. Accelerated lab testing indicates 12-20+ year durability should be seen in the field.

4 – These systems are passive and require no power, and they are thusly extremely cost effective. The price-per-gallon treatment of stormwater from these systems is presently \$0.0008 to \$0.0013 per gallon over the projected lifespan of the system. This is less than 50% of any comparable treatment system capable of this volume and quality of stormwater management.

5 – Commercially interested parties, including civil engineers, LEED architects, campus planners and stormwater management agencies, are particularly excited to find a system this effective at treating stormwater, but many of the them simply cite the extreme healthiness of the plants in the system as the primary reason for interest. Many of them have moved away from other “green” stormwater systems because the urban runoff regularly kills off the plants in the system. Osorb captures the same pollutants and in turn chemically reacts with them, reducing them to foods accessible to the plantings, as will be discussed below.

1.4 The Stormwater Industry

The runoff control industry is driven by civil engineering firms, who have a very long history with the subject, and regulations set by federal, state and local agencies. Until today, 99% of spending on stormwater management went to systems that have pipes or tunnels to move stormwater runoff away from human development and into local waterways or to central processing plants.

Regulations and incentives have recently and somewhat radically changed in some locations where officials are attempting to restore natural systems, a process in the design community broadly called “biomimicry.” Municipalities, large campus locations and developers are now seeking runoff control for quality as well as quantity upgradient, but are finding the need to deal with industrial chemicals a challenge. These cultural forces and regulations can be seen as marketplace “sticks.” At the same time, many architects are finding their design bonus payments attached to “carrots” in the

form of LEED (Leadership in Energy and Environmental Design) certifications. LEED certification incorporates green stormwater management as a critical aspect of building design.

Domestically, the U.S. market for relieving non-point source pollution and stormwater volume is estimated to be \$6 billion annually. The Seattle area alone has announced an initiative to build 12,000 green stormwater sites over five years with a goal to reduce urban runoff by 16,000,000 gallons annually. Boston, Philadelphia and the Chesapeake Watershed Joint Management Group are completing scoping documents and plan to announce targets for this market in 2012, which will be on scale with the Seattle initiative.

Internationally, especially in areas with lack of access to easy fresh water, the carrot of the marketplace is in capturing and safely harvesting urban runoff for human usage. Areas of the Mideast and West Africa have deep and acute needs for stormwater harvesting, while increasingly toxic urbanized environments and the extraction industry make the challenge of cleaning the water more difficult.

1.5 Osorb and the Need for Innovations in Stormwater Technology

Raingardens and bioswales are very effective at reducing runoff volumes, but have generally failed to improve runoff quality from impacted urban locations. They are generally useful only as small systems capturing stormwater from single residential locations or small groups of residential properties and make up far less than 1% of the total amount spent on stormwater management in the U.S.

Osorb stormwater systems incorporate blends of Osorb nano-materials and bioretention soils to capture and reduce organic pollutants. Osorb is a highly ordered and mechanically functionalized silica material capable of hinge-like unfolding of individual and functionalized nano-pores. The material has been further engineered to include embedded nano- and micro-metals inside the Osorb glass, which causes chemical species captured by the Osorb to undergo a chemical reduction.

Table 1.1 The chemical species captured and/or reduced by Osorb materials. “Osorb reduction” refers to the chemical reduction of the compound due to non-leaching reactive metals embedded in the Osorb.

Product	Osorb Absorption	Osorb Reduction
Chlorinated Solvents		
Trichloroethylene (TCE)	>99%	Yes
Perchloroethylene (PCE)	>99%	Yes
Dichloroethylene (DCE)	>75%	Yes
Vinyl Chloride (VC)	>75%	Yes
Trichloromethane (Chloroform)	>75%	Yes
Carbon Tetrachloride	>99%	Yes
Dichloromethane	>30%	No
Aromatic Compounds		
Toluene	>99%	No
Naphthalene	>99%	No
Phenol	>75%	No
Benzene	>99%	No
Ethylbenzene	>99%	No

Nitrobenzene	>99%	No
Trinitrotoluene	>99%	Yes
Chlorobenzene	>99%	Yes
Phthalate Esters	>75%	No
Polychlorinated Biphenyl (PCB)	>99%	Yes
Bisphenol A	>75%	No
Xylene	>99%	No
Atrazine (herbicide)	>99%	Yes
Pharmaceuticals		
Triclosan (antibacterial)	>99%	No
Fluoxetine (antidepressant)	>99%	No
Ibuprofen (anti-inflammatory)	>75%	No
Diphenhydramine (antihistamine)	>75%	No
Estradiol (birth control)	>99%	No
Imipramine (antidepressant)	>99%	No
Alcohols		
Methanol	>30%	No
Ethanol	>30%	No
Butanol	>75%	No
Hexanol	>75%	No
Solvents		
Octane	>99%	No
Hexane	>99%	No
MTBE	>75%	No
Dioxane	>75%	No
Acetone	>30%	No

The challenge with all the species of pollutants above is that they are commonly found on hard, impervious surfaces in urban or industrial settings. These chemicals are persistent, bio-active and easily entrained in stormwater runoff. Previous systems could capture the stormwater but frequently suffered from mass plant die-offs or soil biological collapse. Often the pollutants would pass into the water table to create further problems in groundwater and well water, as well as down gradient re-emergence.

Adding nano-glass allows the stormwater system to address both water volume and quality in an effective and energy efficient manner. Further, most stormwater processed through an Osorb nano-glass system will meet or need only trivial secondary treatment to meet drinking water standards. Planning is now underway with United Nations-funded development agencies in West Africa to develop and deploy modular eight ton units capable of treating 400 gallons per day of surface waters impacted by industrial pollutants into potable waters. Previously, no systems existed that were durable, effective and could be operated power-free for years, perhaps decades.

Besides the potable water solutions, discussions are now underway to offer packaged specialty soil amendments for removal of nitrates, phosphates, herbicides, fuels, pharmaceuticals and other common runoff pollutants for first world customers placing a premium on removing all or nearly all volatile organics from their food supply. These same volatiles are often a cause of great concern to waste and stormwater treatment plants which often have compliance requirements with EPA consent decrees and/or other discharge requirements.

Testing results to date indicate that Osorb bioretention soil blends will remove over 90% of stormwater volume and over 95% of contaminants coming into the stormwater system. The addition

of Osorb media up-stream also reduces the cost for water treatment plants downstream to remove these contaminants. Twentieth century technology to remove these contaminants is focused on central waste water treatment plants, which pay \$6.00-12.00/lb for phosphate removal due to electrical energy, labor and chemical consumables needed to treat phosphate laden waters. The cost to remove phosphate with Osorb nano-glass is lower by an order of magnitude, at only \$0.60-1.90/lb using Osorb stormwater systems up-gradient. This cost savings is further compounded by the nutrients having a valuable potential impact up-gradient if the plants grown with the Osorb stormwater system have commercial value.

To address this growing demand to treat these waters, substantial incentives for building up-gradient and passive systems are becoming commonplace in the U.S. Seattle, Portland and Philadelphia are three cities leading a movement to manage stormwater quality and quantity up-gradient in a distributed manner. Further public interest and architect/developer/contractor interest in designing to achieve LEED certifications have created a further financial and public awareness driver for green stormwater management.

LEED certification, and similar programs like STARS, Living-Machines and BioBuilt, all place a very high value on installing smart methods for energy saving, water recycling and stormwater savings integrated into a building or campus design. There are five categories in the LEED program where integrating Osorb nano-glass materials into a stormwater system on site can score points toward certification, with up to 13 points achieved as a result. 13 LEED points for the use of any system is a relatively large number and has been driving a substantial interest in the use of the material.

Osorb nano-glass materials are enabling LEED certification points from: lower operating costs, waste reduction, water quality improvement, on-site water management and reuse, native habitat restoration, technology innovation and energy efficient construction due to the small footprint and vastly reduced need for concrete piping. In addition, LEED-enabled tax rebates, zoning allowances and other financial and structural incentives are benefits of integrating Osorb stormwater systems into building design. Some cities offer tax credits up to \$1 million over a ten year period (% tax credit per year depends on certification level). Los Angeles, CA, requires LEED certification for all new structural buildings over 50,000 ft². Including rain gardens that provide water reuse will help many of the companies rebuilding to attain points to become LEED certified, as well as meet requirements in cities where LEED certification is mandatory.

1.6 Legacy Stormwater Technologies Replaced by Nanoengineered Glass

Currently, there are no twentieth century technologies fully capable of distributed removal of volatile organics, nitrates and phosphates. Osorb nano-glass as a soil media is truly breakthrough media that in many cases removes 99%+ of pollutants from stormwater runoff. Osorb materials are replacing legacy systems that at best remove 50% of the pollutants. These legacy materials are, in large part, various mixtures of mulch and biochar (or granulated charcoal) soils.

A few non-nano commercial products compete with nano-glass media. One is produced by Filtrexx International, LLC. This “natural absorbent” (Filtrexx® Nutrient Control, Filtrexx® Petroleum Hydrocarbon Removal) is a soy-polymer matting that removes most petroleum products from runoff and is often specified for use on parking lot runoff next to or near sensitive natural water systems. Filtrexx’s advertised retail price is approximately the same as Osorb and explicitly notes it is not as effective with biocides, pharma-products or nutrients.

Most distributed stormwater infrastructures utilize mulch and biochar soil to remove heavy oils and fuels that come with parking and roadway runoff. These systems generally demonstrate about 50% effectiveness on these species and substantial enhancement effects on plants, but almost no effect on water soluble or molecular level contamination. One firm, Hydro International LLC, sells Up-Flo® Filter Mix to remove “sediments and hydrocarbons from stormwater.” These sand-mulch-biochar box-filter systems require frequent replacement and do not remove pesticides, herbicides, excess pharmaceuticals, pharma-agents (including endocrine disruptors) or nutrients from runoff. Hydro-Flo claims to remove 50% of the fuels in runoff, far short of the 90-99% that Osorb nanomaterials remove.

Table 1.2 Osorb nanoengineered glass media vs. alternative technologies

Product	Remove % Nutrients (NPK)	Remove % Pharma Agents and Biocides	Remove % Hydrocarbon	\$Cost/yd3	Lifetime
Osorb - Soils	>80%	>90%	>95%	175-275	10+ yr
Filtrex	<10%	<25%	>80%	200 -250	2-5 yr
BioChar Soils	<10%	<25%	<50%	25-35	5-10 yr

1.7 Estimation of Markets, Entry, and Product Reception

The customers for Osorb Stormwater products have been identified as: 1) professional landscape architects, LEED architects and green developers, 2) municipal prospects, schools, community and organizations and 3) Individual land owners/organic farmers with a high interest in no biocide agents.

Professional architects and developers may require stormwater management to obtain LEED certification, especially in the circumstance where the client may want to hold their water in a cistern to reuse for landscaping. Community groups and universities are drawn toward sustainability in stormwater because of their larger campus goals and missions. These “green” flagship projects also provide an educational aspect to the community or students involved.

Green stormwater systems for single family homes can be built for as little as a few hundred dollars, while tens of thousands of dollars are spent to address rain gardens for major parking lots, sports stadiums or other large hard surface sites. Subsurface retention basins can cost several hundred thousand dollars. By comparison, a catchment remediation system with added Osorb would be a fraction of that cost at \$25,000-\$55,000.

The estimated pricing for systems to be built by ABSMaterials using Osorb nano-glass to remediate pollutants in the runoff range from \$4,000 to \$155,000 with 20-50% of the cost of the system being the Osorb engineered soil media.

1.8 The Acceptance of Engineered Materials to Assist Distributed Stormwater Systems

One may argue that the nano-materials industry has suffered from two obstacles in the marketplace. The first is the perception that nano-materials are solely of interest to lab-coat-wearing propeller heads. The second is a failure to communicate to a larger public that all chemistry is a molecular-surface or “nano-scale.” ABSMaterials has made a concerted effort to make this communication a key element of the introduction of this nano-material for stormwater management.

After column testing in 2010-2011 and a first fielded pilot in summer 2011, ABSMaterials employees began to contact potential customers and gauge interest. 386 people from stormwater or ecological interests were contacted between November 2011 and February 2012 in Ohio and western Pennsylvania. The people ranged from civil engineers to sustainability activists. The goal of the calls was to explain the fundamentals of the materials and explore the commercial acceptability of engineered nano-glass for stormwater usage/treatments. Those who expressed interest to the point of requesting a proposal included: URS Engineering, Forest City Ratner Development, Wayne County Civil Engineering, Killbuck Watershed Authority, Mahoning County Combined Sewer Authority, The University of Akron Dept. of Civil Engineering, Wright State University, College of Wooster, City of Euclid Ohio, Westminster College, Oberlin College and the Nature Conservancy.

This wide ranging and generally positive market prospecting effort was followed with efforts to convert some portion of these prospects into customers. Systems have now been built in Killbuck Watershed Authority and are in engineering-permit phase at the College of Wooster and Westminster College. 11 additional proposals for solutions are now in consideration for sites in four U.S. states and two Canadian provinces. This conversion rate of prospects at over 3% of market is a very good conversion rate for an introductory and novel product.

Beyond direct customer contacts, initial awareness relationships have already been established with a number of federal agencies, developers and regulatory bodies who can impact what materials are specified by a building process. Soil and water conservation districts (SWCDs) in both Franklin (Columbus, OH) and Cuyahoga (Cleveland, OH) counties have expressed interest in incorporating Osorb materials in future rain garden projects. Mr. Todd Houser is the stormwater manager of Cuyahoga SWCD has become a key advocate on ABS and has been pushing projects under his permit authority to closely examine the material. Likewise, the Ohio EPA SWIF program that funds stormwater improvement products has informed application parties that proposals which include Osorb-based materials to improve water quality will be favorably reviewed.

While a macro effort to introduce a product is important, it is each individual response that makes or breaks the introduction of any product. Mr. John Veney is a resident who lives next door to the twin chamber Osorb stormwater system built at the College of Wooster in 2011. This system replaced a rather ugly ditch, which had gathered rain water from several locations for years and was well known for overflowing into the street and being a low-grade eyesore. ABS was not aware of how bad the situation had been until Mr. Veney sent letters to both the College of Wooster and ABSMaterials expressing gratitude for the Osorb stormwater system addition to the street and for solving this long standing problem, which included a regular flooding into his garage. He also noted the amazing native plant garden which had replaced the former mud-trench and asked to be updated on how the system was working. Mr. Veney, a retiree, has since become a reference point and public advocate for systems.

1.9 Introduction in Lab

The following section provides a brief summary of research project on the development of new bio-retention filter media to enhance pollutant removal by adding Osorb nanomaterials in bioretention systems. The research results presented here are based upon work supported by the National Science Foundation Small Business Innovation Research Program under Grant No. 1113260.

1.10 Development of Osorb[®]-Metal Composites

Five nanoscale zero-valent metals including aluminum (Al^0), iron (Fe^0), magnesium (Mg^0), nickel (Ni^0), and zinc (Zn^0) were used to create Osorb-metal composites. Osorb was used to entrap the metals to create composites. Five different Osorb-metal composites (Figure 1) were created by adding each metal during the synthesis of the Osorb to embed each metal within the Osorb matrix. Manufacturing was accomplished by adding 10% w/w of each metal during the manufacture of the Osorb. Each Osorb-metal composite was grinded and three particles sizes (0.2-2.0, 0.125-0.2, and < 0.125 mm) were prepared for further evaluation.



Figure 1.3

Five types of Osorb-metal composites include: (1) Al-Osorb, (2) Fe-Osorb, (3) Mg-Osorb, (4) Ni-Osorb, and (5) Zn-Osorb.

1.11 Batch- and Column-Scale Testing

All tests were carried out with simulated runoff solution with spiked concentrations of five contaminant categories (Table 1). Pollutant removal efficiency, hydraulic performance, and metal leaching were all studied before Fe-Osorb and Zn-Osorb were selected for field-scale testing and commercial development because of the combination of their relatively low production costs, low toxicity, long-term reactivity, and stability.

Table 1.3 Composition of simulated runoff

Parameter	Pollutants	Concentration (mg L^{-1})
Petroleum hydrocarbons	Motor oil	1000
Nutrients	Nitrate ($\text{NO}_3\text{-N}$)	10-20
	Phosphate ($\text{PO}_4\text{-P}$)	10
Herbicide	Atrazine ($\text{C}_8\text{H}_{14}\text{ClN}_5$)	0.5-1.0
Pharmaceuticals	Ethinylestradiol ($\text{C}_{20}\text{H}_{24}\text{O}_2$)	0.5-1.0
	Triclosan ($\text{C}_{12}\text{H}_7\text{Cl}_3\text{O}_2$)	0.5-1.0

In batch tests, results showed that all five Osorb-metal composites were successful in removing a significant percentage of most tested contaminants from water. Observed results included ~99% removal of both petroleum hydrocarbons and pharmaceuticals (Table 2), 96% removal of pesticides (Figure 2), and 30-50% removal of nutrients. No significant removal of antifreeze was observed.

Column-scale testing confirmed that the Osorb-metal composites do not negatively affect the hydraulic performance of a bioretention system, and removal results were consistent to batch-scale results with one notable exception: as the amount of Osorb-metal increased in both base sand and soil mix media (a mixture of 60% sand, 20% compost, and 20% topsoil), significantly higher removal efficiency of nutrients was observed, achieving 99% removal with Fe-Osorb and Zn-Osorb amended media (Figures 3 and 4). The results indicate that zero-valent metals in the Osorb matrix likely increased reductive transformation and adsorption capacity for nutrient during intermittent wetting and drying conditions created in the bioretention systems.

Table 1.4 Residual concentrations of runoff pollutants after 1-min treatment with Osorb[®] composites (1% w/v)

Osorb-metal composites	Motor oil (mg/L)			Ethinylestradiol (µg/L)			Triclosan (µg/L)		
	Particle Size (mm)			Particle Size (mm)			Particle Size (mm)		
	> 0.2	0.125 – 0.2	< 0.125	> 0.2	0.125 – 0.2	< 0.125	> 0.2	0.125 – 0.2	< 0.125
Al-Osorb	3.8	2.5	0.6	10.3	3.1	0.1	50.1	10.3	3.1
Fe-Osorb	4.1	3.6	0.5	8.2	1.8	0.1	42.6	3.1	0.9
Mg-Osorb	3.7	2.8	0.9	7.8	2.0	0.1	48.5	8.5	4.2
Ni-Osorb	3.6	3.0	0.1	7.6	3.8	0.1	32.9	7.8	5.1
Zn-Osorb	2.8	2.0	0.5	10.0	2.4	0.1	31.4	8.8	4.5

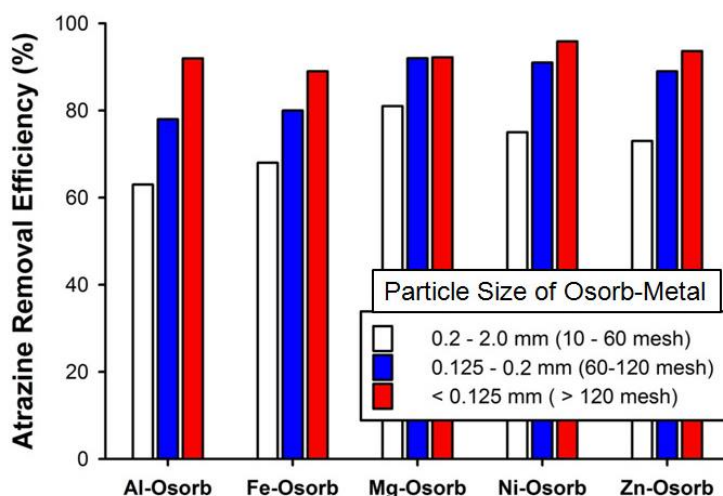


Figure 1.4

Removal efficiency of atrazine treated with different particle sizes of Osorb[®]-metal composites (1% w/v) for 1 min. Initial concentration of atrazine was 1000 µg/L.

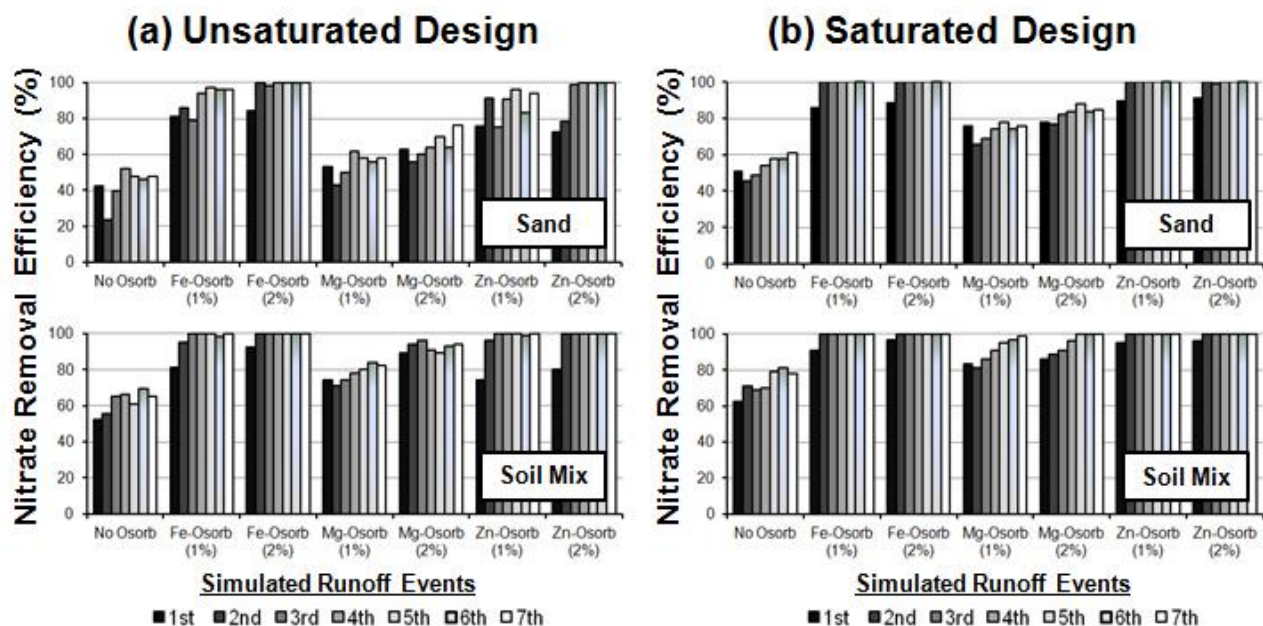


Figure 1.5
Removal efficiency of nitrate via unsaturated (a) and saturated (b) bioretention systems among Fe-Osorb, Mg-Osorb, and Zn-Osorb with three staggered concentrations (0, 1, and 2%) in two bioretention base media (sand and soil mix) from seven sequential runoff events. Loading for each event was 10 mg of nitrate-N in 1 L (10 ppm).

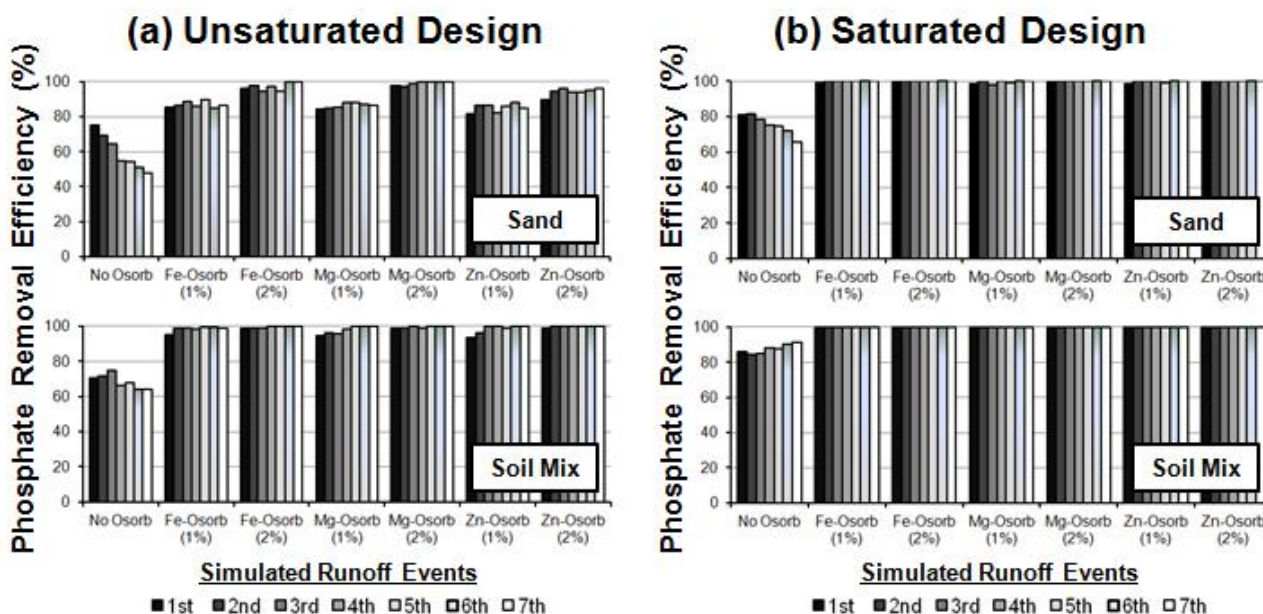


Figure 1.6
Removal efficiency of phosphate via unsaturated (a) and saturated (b) bioretention systems among three different Osorb®-metal composites amendments (Fe-Osorb, Mg-Osorb, and Zn-Osorb) with three different amounts (0, 1, and 2%) in two bioretention base media (sand and soil mix) from seven sequential runoff events. Loading for each event was 10 mg of phosphate-P in 1 L (10 ppm).

Removal of atrazine was also significantly improved in the Osorb-metal composites amended media (Figure 5), in average 45% increase at the unsaturated design and 35% increase at the

saturated design, indicating that the Osorb-metal composites amended media effectively capture and remove atrazine, even in the sand.

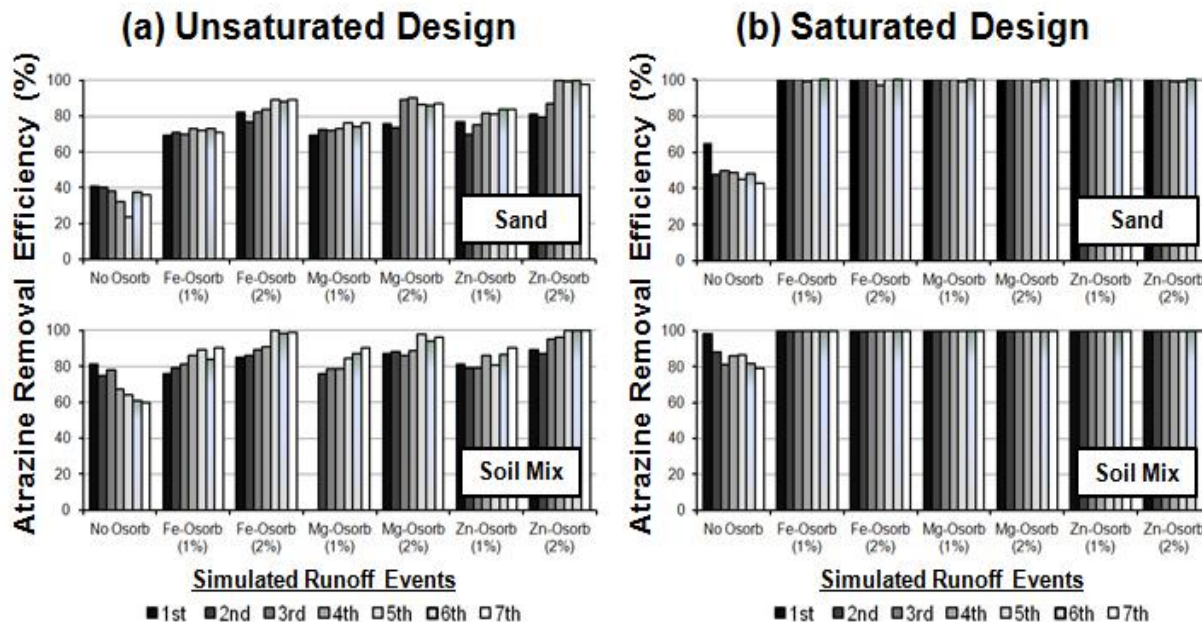


Figure 1.7
Removal efficiency of atrazine via unsaturated (a) and saturated (b) bioretention systems among three different Osorb-metal composites amendments (Fe-Osorb, Mg-Osorb, and Zn-Osorb) with three different amounts (0, 1, and 2%) in two bioretention base media (sand and soil mix) from seven sequential runoff events. Loading for each event was 0.5 mg of atrazine in 1 L (500 ppb).

1.12 Field-Scale Testing

Two field-scale bioretention systems (rain gardens), one with standard bioretention media and one with Fe-Osorb enhanced media, were constructed at the campus of the College of Wooster, OH (Figure 1.7). The systems were tested to examine the effectiveness of the Fe-Osorb enhanced bioretention system over the standard system for runoff pollutant removal. The source of runoff was the two parking lots adjacent to the systems. The first bioretention system has a traditional underdrainage design with typical bioretention fill media that consists of 60% sand, 20% soil, and 20% compost, used as a standard (control). Fill media of the second bioretention system, however, have been mixed with 1% (w/w) of Fe-Osorb to improve treatment performance. Each bioretention system has a depth of 2.5 ft with surface area of 10 ft by 15 ft (150 ft²) to handle a 2.54 cm/h (1 in./h) rainfall.

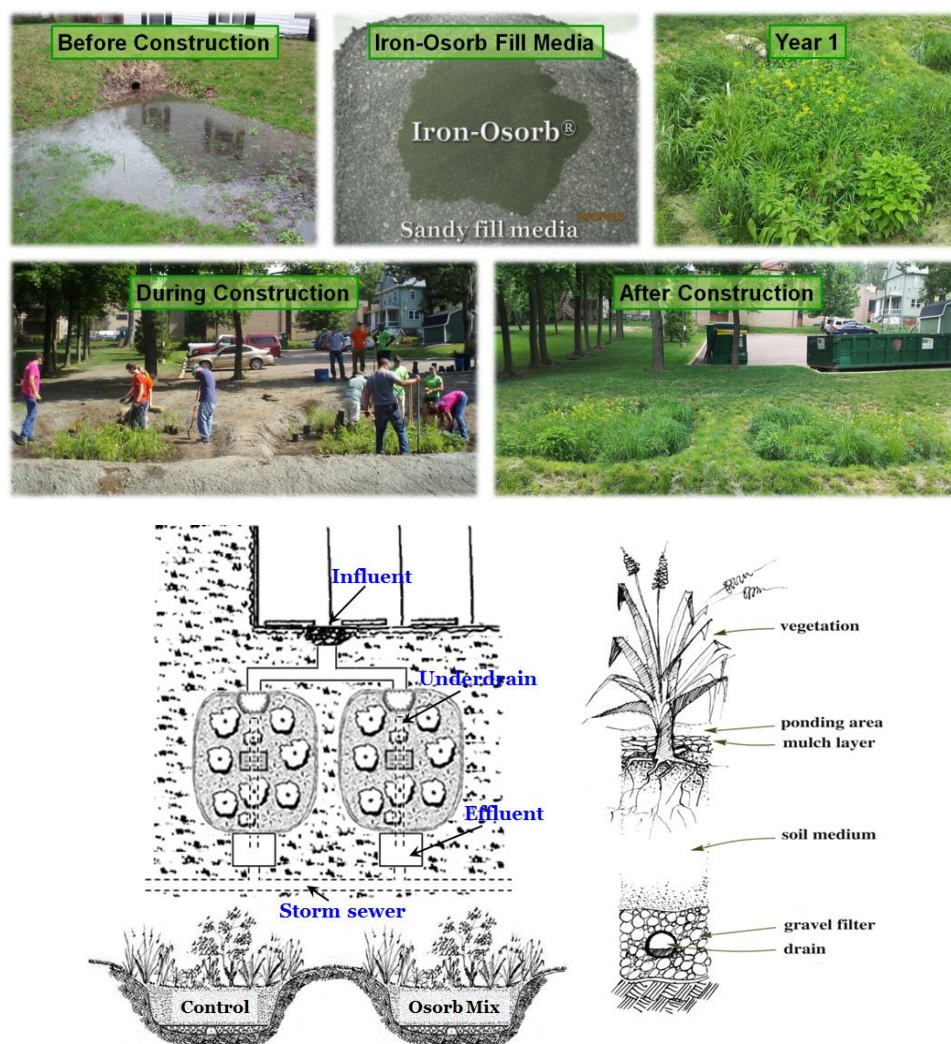


Figure 1.7

Site, plan, and cross-section 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.

In 2011 field-scale experiments were conducted under natural and simulated runoff events. The data show that: (1) Fe-Osorb enhanced bioretention system improved removal efficiency of fertilizer runoff (i.e. nitrate and phosphate) more than 40% compared to the standard bioretention system (Figure 7), (2) significantly lower concentration of leaching nutrients was also observed in the Fe-Osorb enhanced bioretention system compared to the standard system (Figure 7), (3) both bioretention systems significantly reduced runoff volume (~95%) and peak flow (~97%) during natural runoff events, and (4) Fe-Osorb amendment did not alter hydrodynamics of runoff in the fill media while maintaining a high infiltration rate. Further field tests will be continued to evaluate both hydraulic and treatment performance of the standard and Fe-Osorb enhanced bioretention systems with a wide range of other runoff pollutants.

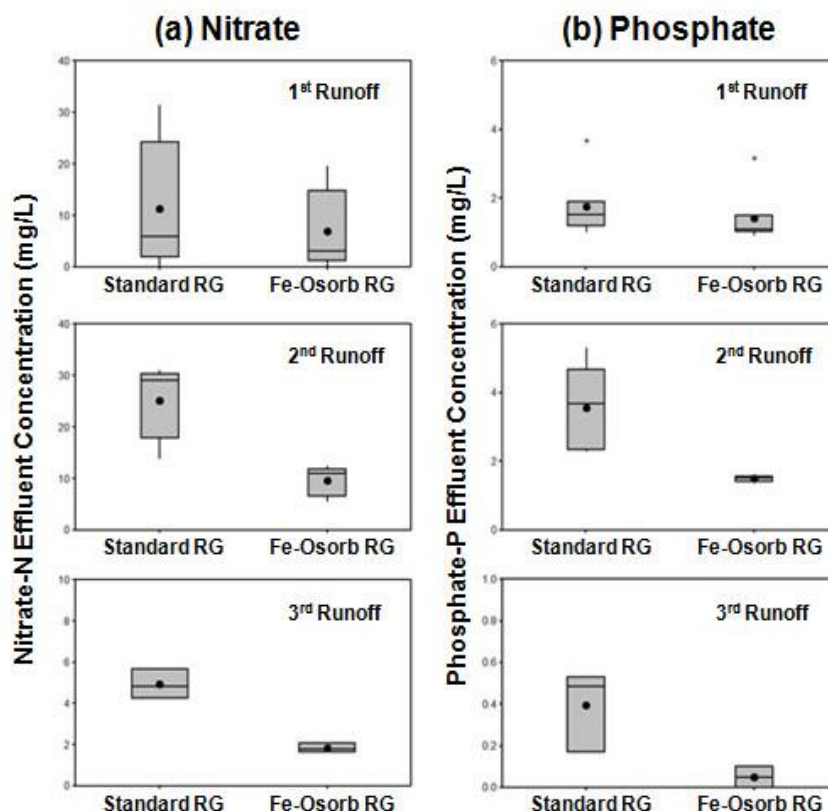


Figure 1.8

Nitrate (a) and phosphate (b) concentrations in effluent of standard and Fe-Osorb enhanced bioretention systems (rain garden, RG) during three simulated runoff events. The first two runoff events (3.0 in. total rainfall) were applied to each bioretention system using tap water 2 d apart with spiked concentrations of nitrate (34g for each) and phosphate (34g for each). No pollutants were applied for the third simulated runoff to evaluate potential leaching of nutrients.

1.13 Bacterial Growth Testing

Effects of Osorb on bacterial growth were evaluated under the presence of a biocide, triclosan. 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 + 3g (0.3% w/v) of Osorb which was pre-sterilized using ethanol. Each experiment was performed by first growing a starter culture of bacteria. 1.00 mL of the starter culture was added to 1.0 L of sterile LB media. Bacteria were grown in ampicillin (1 µg/mL) to ensure selection of only the experimental strain. Bacterial cell density was measured over time using OD600 method.

The results show that the bacteria grew the best with Osorb even with triclosan added (Figure 1.9). Without Osorb all the bacteria died (no growth) in the presence of 100 ppb triclosan (Figure 1.9). The results indicate that Osorb protects 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 performance of bioretention systems.

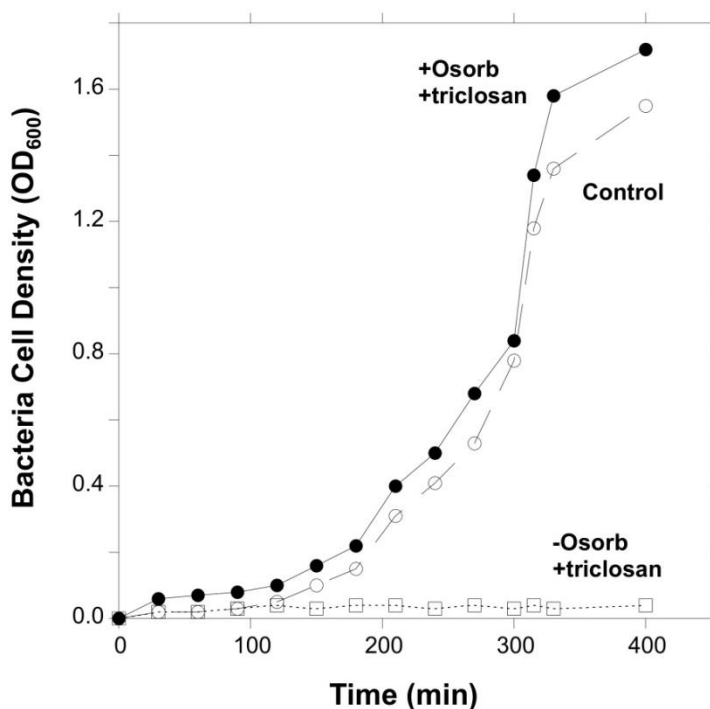


Figure 1.9

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 + 3g (0.3% w/v) of Osorb.

1.13 Conclusions

New Osorb-metal composites have been initially batch-, column-, and field-scales for enhanced remediation of runoff pollutants in bioretention systems with good, consistent, and commercially viable results. The materials are highly effective at removing multiple runoff pollutants including nutrients (i.e. nitrate and phosphate), herbicide (i.e. atrazine), and pharmaceuticals (i.e. ethinylestradiol and triclosan).

One of the key factors to successful remediation of runoff pollutants in bioretention systems is maintaining consistent hydraulic and pollutant removal performance in the long-term due to the excessive runoff volume and pollutant loads over time. Results obtained from column- and field-scale experiments have shown that the use of Osorb-metal composites in bioretention systems has the potential to simultaneously capture and remove multiple runoff pollutants such as motor oil, nitrate, phosphate, atrazine, and estradiol through enhanced physico-chemical absorption and reductive transformation with excellent hydraulic performance. Ongoing effectiveness of Osorb-metal composites in field-scale bioretention systems is currently being evaluated in the long-term. Future work is also focused on modification of Osorb-metal composites to maximize longevity of remediation capacity over time.

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