Additives for Stormwater Filters:
What Works, What Doesn't, and What Is Still To Be Learned

Glenn Brown & Jason Vogel
Oklahoma State University

Stormwater Filters

- Various stormwater filters are being built to improve stormwater runoff quality, including bioretention, tree boxes, bioswales, and filter boxes.
- There has also been considerable work on filters for agricultural drainage.
- Size and appearance differ, but their goal for influent treatment are the similar.
- Many additives have been proposed and tested to improve filter performance with respect to one or more pollutants.

Issues to address

- Pollutants of concern.
- Treatment processes.
- What makes a good filter additive?
- Additive categories.
- Level of testing.
- Recommendations.

Pollutants of Concern

- Phosphorous (usually cation)
- Nitrogen (usually NO^{-3})
- Heavy metals (usually cation)
  - Zinc
  - Lead
  - Copper
  - Cadmium
- Organics (carbon chains or rings, charge variable)
  - Ag chemicals, including pesticides and herbicides
  - Emerging contaminants including PAH
- Biologic
  - Bacteria
  - Viruses

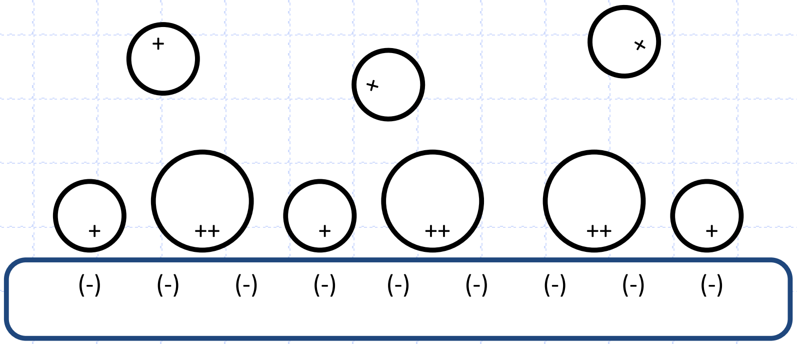
www.gizmodo.com.au

Treatment Processes

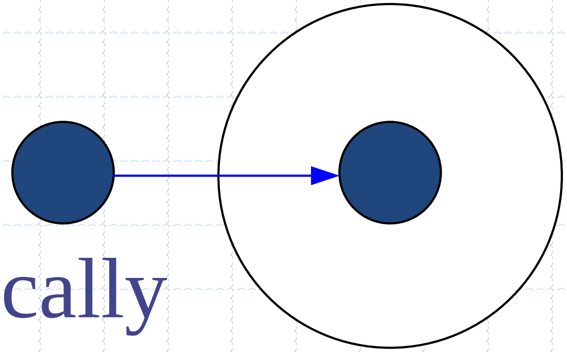
- Effluent properties, filter design and filter operation will determine the effectiveness of treatment in a given application.
- Processes in filters that remove pollutants include:
  - Physical filtration of particulates,
  - Biological uptake and degradation,
  - Biological sequestration,
  - Surface a**d**sorption,
  - Physical a**b**sorption and
  - Chemical precipitation.

Surface adsorption

- Primarily electrostatic exchange of cations.
- Heavy metal adsorption on soil is an example.
- The cation is not transformed, it is just stuck to the surface.
- Strong function of:
  - Surface area, and
  - Cation charge.
- Usually reversible. If clean water is introduced, the cations will desorb from the solid and go back into solution.



Physical absorption



- Occurs when a solute is physically incorporated into a solid particle.
- An example is when an hydrocarbon dissolves into an organic mass, such as a piece of wood.
- Sometimes, but not always, associated with a chemical transformation.
- Usually relatively irreversible.
- Not as common as most assume.

Chemical precipitation

www.umich.edu

- Occurs when an ion binds with an oppositely charged ion and forms a relatively insoluble mineral.
- A simple example is when calcium binds with carbonate and precipitates in your shower. (Other examples get into metal-ligand chemistry.)
- Usually relatively irreversible, except if aqueous chemistry changes, such as with fluctuating pH.

Three points to keep in mind

- It is usually difficult and impractical to determine which process is retaining a solute in a porous media. In many cases, it may be a combination of two or three.
- There will be different a**d**sorption and a**b**sorption properties for each mineral or material in the porous media.
- All of these processes are limited and can be "used up". Only a fixed amount of pollutant solutes can be expected to be retained.

What makes a good additive?

- Almost from the first applications, various additives have been tested to improve filter performance.
- A bewildering number of potential additive materials have been tested and reported.
- A common additive, mulch, is specified in many bioretention cell standards, to aid plant growth.

A mad scientist from www.pinterest.com

Good additive characteristics

- Not be a pollutant in its own right,
- Low cost,
- Readily available,
- Permeable,
- Effective for multiple pollutants, and
- Easily discarded or recycled after use.

Activated Carbon

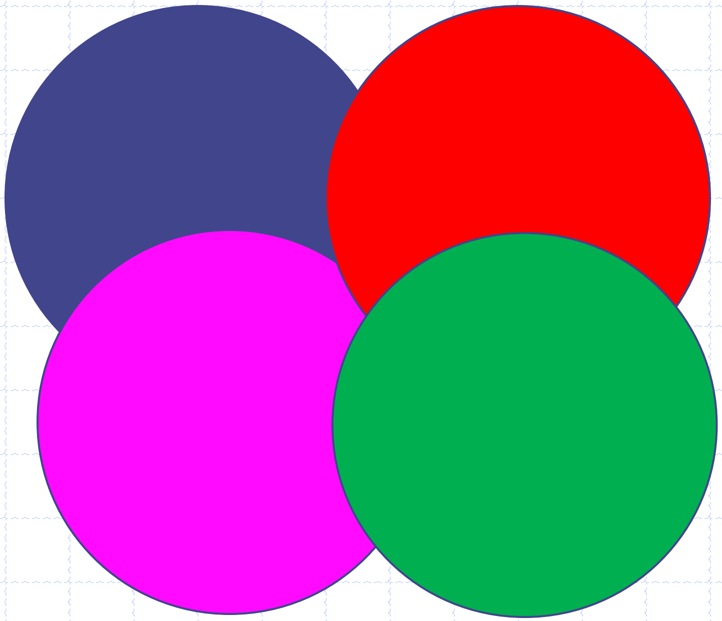
www.avellobioenergy.com

Fly Ash

www.us-concrete.com

Additive Categories

- Additives may be categorized into these four broad groups.
  - High Carbon
  - High Iron
  - High Aluminum
  - High Calcium



  - Note that some additives may fall into more than one group.

High Carbon

- Plant material
  - Fresh
  - Compost or decayed
- Animal waste
  - Chicken Litter
  - Manure
  - Sewer Sludge
- Coal/Coke
- Activated carbon
- Biochar (every kind imaginable)

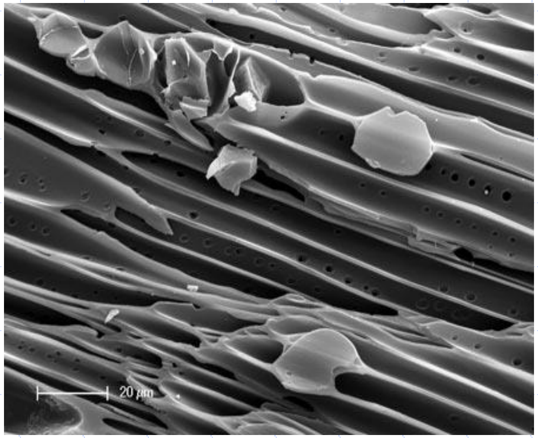
Compost from recyclenation.com

High Carbon: *Works on*

- Any carbon source is effective for a**d**sorption and a**b**sorption of organic hydrocarbons:
  - Oil and grease,
  - Pesticides, and
  - Most chain or ring carbon compounds.
- Plant and animal waste, if the filter is design correctly, can provide carbon for biological denitrification and biodegradation of organics.
- Activated carbon and biochar, *with molecular sieves*, may be effective to a**d**sorb heavy metals and nitrate.

High Carbon: *Problems*

- Plant and animal waste will decay. When they do, they will release nitrogen, phosphorous and humus (soluble organics). *If you load your filters with mulch, expect that the water quality leaving the cells will be worst than that entering.*
- Biochars are a form of activated carbon. To be effective, they must be produced by pyrolysis with the correct method and temperature for the feedstock to produce a molecular sieve. *There can a big difference between 500 and 600^{o} C.*



environmentalresearchweb.org

High Iron

- Zero valent iron (filings, etc)
- Iron slag
- Iron oxide
- Acid mine drainage residuals
- Sulfur modified iron

Iron slag from Chad Penn

High Iron: *Works on*

- All high iron additives will provided adsorption of phosphorous, heavy metals and hydrocarbons.
- Zero valent iron and sulfur modified iron will act as a reactive media (electron donor) on,
  - Chlorinated hydrocarbons,
  - Nitrate, and
  - Hexavalent chromium.

Chad Penn

High Iron: *Problems*

- Will probably increase dissolved iron in effluent.
- Removal process are very dependent on:
  - Aqueous chemistry,
  - pH, and
  - Retention time.

Iron Enhance Sand Filtration for Agricultural Tile Drainage. Stormwater.safl.umn.edu

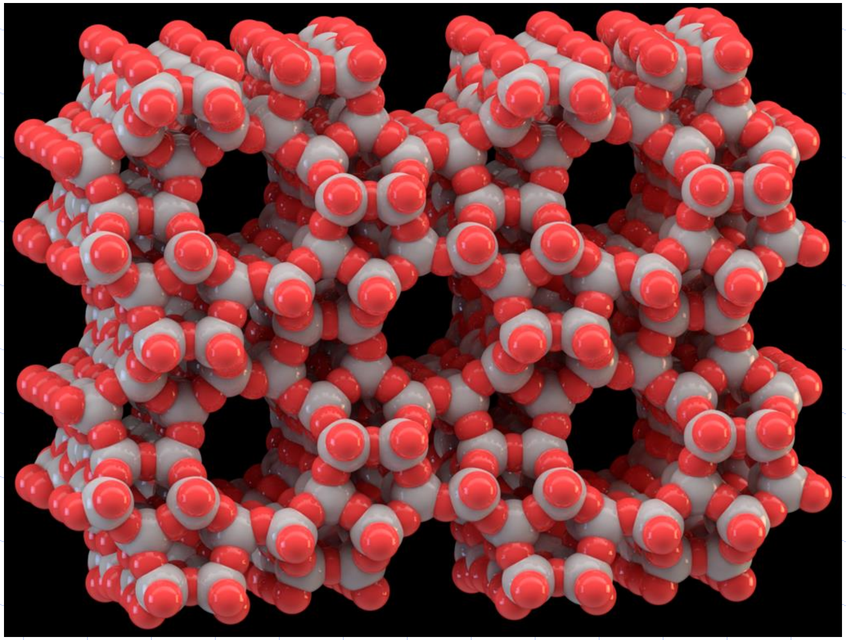
High Aluminum

- Alum (aluminum sulfates)
- Bauxite (aluminum ores)
- Acid Mine Drainage Residuals (AMDR)
- Water Treatment Residuals (WTR)
- Zeolite

Water Treatment Residuals,
from Chad Penn

High Aluminum: *Zeolite*

- Zeolites are a mircoporous aluminoslicate clay minerals.
- Used in some cat litters.
- Can be very effective adsorbing metals and other cations



En.wikipedia.org

High Aluminum: *Works on*

- Adsorbs and precipitates heavy metals and phosphorous.

A phosphorous removal structure, Penn, et. al., 2016.

High Aluminum: *Problems*

- High Al materials trend to have less bang for the kilogram than other additives.
- Zeolites and WTR have low permeability.

Acid Mine Drainage Residuals
from Sibrell, USGS

High Calcium

- Calcite/Limestone ($CaCO_3$)
- Fly ash
- Shale
- Expanded Shale (heat treated to increase porosity)
- Recycled Concrete

Limestone

www.yurtopic.com

High Calcium: *Works on*

- Adsorbs and precipitates heavy metals and phosphorous.

Recycled Concrete

www.concretethinker.com

High Calcium: *Problems*

- Limestone has low surface area for exchange.
- Shale and recycled concrete not that effective.
- Expanded Shale is very variable in adsorption properties.
- Fly ash is very basic and can cement the filter.

Expanded Shale
www.yurtopic.com

Level of Testing

- Many materials have been tested
- The range of testing has been:
  - Lab screening – simple batch adsorption tests
  - Lab bench scale – column leaching
  - Initial field scale – new filter performance
  - Aged field scale – old filter performance

wwe-co.com

Batch Testing

- Batch (test tube) testing of material
  - Small amount of test material.
  - A lot of water and pollutant of interest.
  - Shake for a day, more or less.
  - Measure how much pollutant is still in solution.
  - Results usually fit to isotherm curve.
- Great for rapid screening.
- Poor for predicting field performance.

Batch shakers in use,
from Barry Allred

Laboratory Column Testing

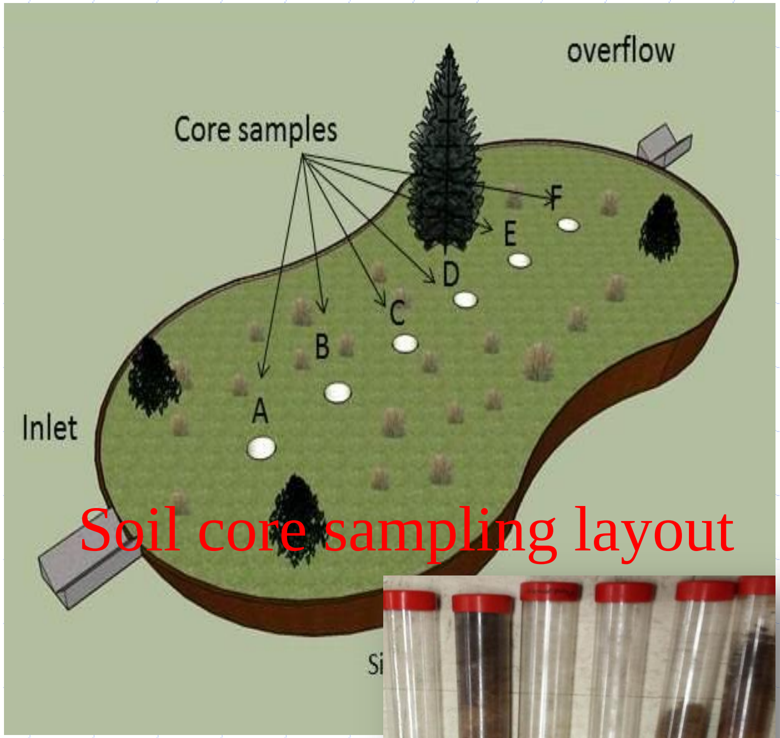
- Column testing procedures,
  - Pack column with test material.
  - Pump solution with pollutant of interest for a few days or less.
  - Measure pollutant concentration of effluent.
  - Results usually fit to retardation coefficient.
- Better predictor of field performance.
- Unable to replicate full complexity of field.

New filter performance

- Some researchers have monitored filters for a brief period after installation.
- Usually only influent and effluent concentrations are measured.
- A direct measure of initial performance.
- A poor measure of long term performance.
- Does not quantify the capacity of the filter to continue removing pollutants.

Aged filter performance

- A few researchers have monitored filters that are more than one year old.
- Influent and effluent concentrations are measured.
- Sampling the filter media provides a measure of the pollutants held in the filter.



Soil core sampling layout

Recommendations

- Any recommendation must be placed into context. Specifically, the objective of the party acting on it should be of primary concern. As such these recommendations are directed at the following two communities:
  - Agencies and consultants looking to implement proven designs with an expectation of success.
  - Agencies and researchers looking for proof of concept leading to widen use.

Recommendations

- Any recommendation should also provide a basis of its foundation. These recommendations are based on[1],
  - 35 years in groundwater contaminant transport,
    - PhD in Civil Engineering, PE, F.EWRI, F.ASABE
    - Three years of field experience in environmental studies, and numerous consulting contracts through the years,
    - Graduate teaching of “Flow in Porous Media”, “Groundwater Contaminant Transport”, and “Groundwater Laboratory Methods”,
    - Extensive funded research on transport and fate of pollutants, and
    - 11 years in the LID field, including building and testing more than a dozen bioretention cells.
  - A recent literature search of the literature.
  - Communicating with researchers in the field.

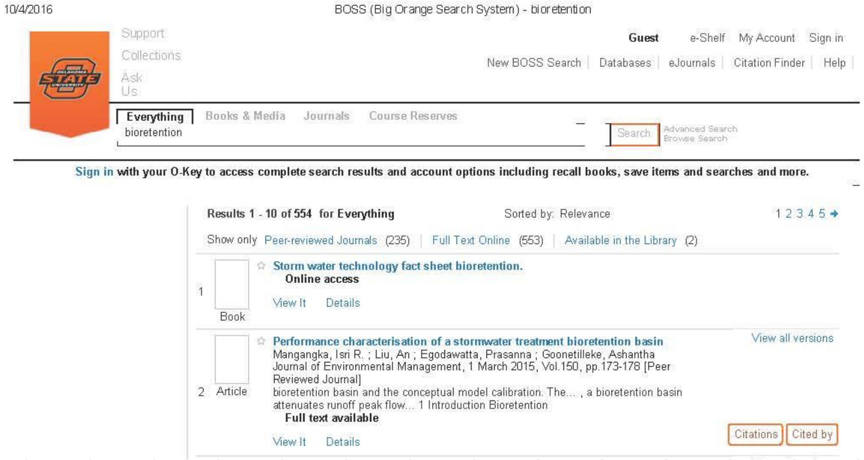
[1]Senior author

Recommendations

- One big qualification,
  - Every day, there are more groups working in this area, some of who are not publishing, or are only publishing in the gray literature. Thus,
  - We may well have missed something.

Recent Literature on Additives

- A search in the last month of the refereed and proceedings literature (2016-2000) specific to additives found
  - 43 Studies with laboratory results
  - 12 Studies with field results
  - 1 Study with long-term field results (The authors')



Recommendation: *Expectation of success*

- For an *expectation of success*, there should be at least one long duration field test that substantiate the performance of an additive at the conditions relevant to the user. There are none at this time.
- Thus, we cannot recommend any specific additive for general users at this time.

thedepression.org.au

Recommendation: *Proof of concept*

- For agencies and researchers who want to evaluate *proof of concept designs*, the following seems to have the best potential
  - *Iron blast furnace slag* for nitrate, phosphorous, and Zn (Li, et al., 2016)
  - *Acid mine drainage residuals* for phosphorus (Penn, et al., 2016)
  - *Zero valent iron* for metals, for nitrate, metals, phosphorous, and organics (various)
  - *Biochar* for metals and nitrate (various)
  - *Fly ash* for metals and phosphorous (Brown, et al., 2016)

Closing comments

- Additive in stormwater filters have potential, but have not been proven.
- If you consider an additive remember:
  - Cost
  - Availability
  - Permeablity
  - Material specifications
    - Source material
    - Composition (major and trace elements)
    - Preparation

Review Articles

- The following review articles are available for those who wish to look deeper into the subject.
  - LeFevre, G., Paus, K., Natarajan, P., Gulliver, J., Novak, P., and Hozalski, R. (2014). "Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells." J. Environ. Eng., 141(1): 04014050 1-23.
  - Bhatnagar, A., Vilar, V., Botelho, C., and Boaventura, R., (2010). “Coconut-based biosorbents for water treatment — A review of the recent literature.” Adv in Colloid and Interface Sci., 160 (1-2): 1-15.
  - Roy-Poirier, A., Champagne, P., and Filion, Y., (2010). “Review of Bioretention System Research and Design: Past, Present, and Future.” J. Environ. Eng., 136(9): 878-889.
  - Bailey, S, Olin, T., Bricka, R. and Adrian, D., (1999). “A Review of Potentially Low-Cost Sorbents for Heavy Metals.” Water Research, 33(11): 2469-2479.