Selection of Bioinfiltration Media for Stormwater Treatment, an example for a site having Restrictive Numeric Effluent Limits

Robert Pitt, Ph.D., P.E., BCEE
Emeritus Cudworth Professor of Urban Water Systems
University of Alabama

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Presentation Topics

- Numeric effluent limits
- Critical site constituents
- Treatability of critical constituents
- Media alternatives
- Testing protocols
- Column tests vs. batch tests
- Clogging, flow, and breakthrough column tests
- Recommended media for treatment targets
- Conclusions

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Numeric Effluent Limits (NELs)

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Stormwater Control Performance Optimization; an Example for a site having Numeric Effluent Limits

- Some locations are subject to specific numeric effluent discharge limits. For example, one site has permit limits including:
  - Cadmium: 4 µg/L
  - Copper: 14 µg/L
  - Lead: 5.2 µg/L
  - Mercury: 0.13 µg/L
- Many of the permit limits would likely be exceeded for most stormwater discharges, including residential and open space areas.

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Stormwater Control Performance Optimization

- Study site is a large RCRA (*Resource Conservation Recovery Act*) regulated field lab located in Southern California with low NPDES numeric effluent limits for stormwater (all outfalls and all events are monitored for compliance). Historical use of site was for rocket engine and energy research and testing. Some permit limits for organics and radioactive contaminants include:

	Numeric Effluent Limit (NELs)	Historical Maximum Observed Concentration on Site
Perchlorate	6 µg/L	<1.5 µg/L
Oil and Grease	15 mg/L	16 mg/L
TCDD	2.8 X 10^{-8} µg/L	10^{-3} µg/L
Gross alpha radioactivity	15 pCi/L	16 pCi/L
Gross beta radioactivity	50 pCi/L	24 pCi/L
Radium 226+228	5 pCi/L	2 pCi/L

- Many other numeric effluent limits also exist for the site, including heavy metals that cause exceedances (especially lead at 5.2 µg/L).
- Dioxin and lead are the most critical constituents, but also important that treatment methods (media) do not increase concentrations of any regulated contaminants.

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Critical Site Constituents

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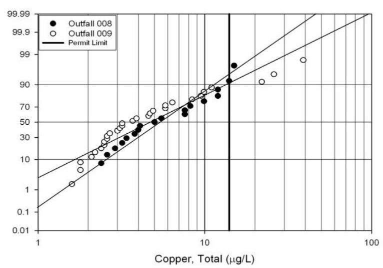
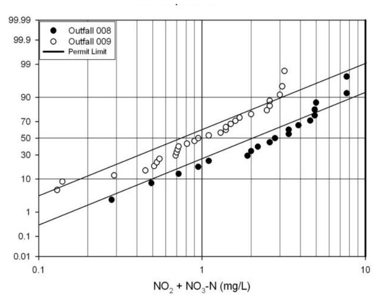
Introduction: On a Permit with Many Numeric Limits, Which Limits Should Drive Stormwater Control Design?



Probability plots of site data can be used to predict which pollutants are likely to exceed permit limits.

Copper likely to have periodic permit exceedences (> 14 µg/L effluent concentration).



Nitrite+Nitrate not likely to have many permit exceedences (> 10 mg/L effluent concentration).

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Site Stormwater Characteristics and Permit Limits

Analytes on Permit	90th percentile historical conc.	Permit Limit	Exp. Exceedence (% > limit if untreated)
Oil and grease (mg/L)	3	15	**5**
Chloride (mg/L)	30	150	0.1
Sulfate (mg/L)	100	250	<<0.01
Ammonia (mg/L as N)	NA	10.1	SMALL
NO_2+NO_3 (mg/L as N)	8	8	**10**
Total Zinc (µg/L)	140	159	**10**
Total Copper (µg/L)	15	14	**10**
Total Mercury (µg/L)	0.15	0.13	**15**
Total Lead (µg/L)	25	5.2	**40**
Total Thallium (µg/L)	ND	2	UNK
TCDD (µg/L)	5x10^{-6}	2.8x10^{-8}	**40**
Perchlorate (µg/L)	1.5	6	0.1

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Pollutants Used to Guide Media Selection

(exceedances shown are before current treatment at site)

- Potential for Exceedence in 40% of Storms
  - Dioxin (TCDD)
  - Total Lead
- Potential for Exceedence in 15% of Storms
  - Total Mercury
- Potential for Exceedence in 10% of Storms
  - Total Copper
  - Total Zinc
  - NO2+NO3
- Potential for Exceedence in 5% of Storms
  - Oil and Grease

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Treatability of Critical Constituents

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Introduction

- Predicting the pollutant removal potential of (bio)(in)filtration media requires understanding soil AND water chemistry, including influent runoff chemistry.
- But … guidance documents typically have very generic media specifications and do not provide guidance regarding media that address the active processes occurring in device (physical straining plus potentially biogeochemical processes).

2. **Planting Soil** should be a loam soil capable of supporting a healthy vegetative cover. Soils should be amended with a composted organic material. A typical organic amended soil is combined with 20-30% organic material (compost), and 70-80% soil base (preferably topsoil). Planting soil should be approximately 4 inches deeper than the bottom of the largest root ball.

3. **Volume Storage Soils** should also have a pH of between 5.5 and 6.5 (better pollutant adsorption and microbial activity), a clay content less than 10% (a small amount of clay is beneficial to adsorb pollutants and retain water), be free of toxic substances and unwanted plant material and have a 5 –10% organic matter content. Additional organic matter can be added to the soil to increase water holding capacity (tests should be conducted to determine volume storage capacity of amended soils).

Unfortunately, both of these guidance points have been shown to cause effluent water quality or operational problems.

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Influent Water Chemistry: Our Historical Classifications

- Solids
  - Wide range of sizes from colloidal to sands/gravels
- Pollutants (fraction of total load) that are associated with, or attached, to solids
  - Metals, Phosphorus, Organics, Bacteria
- Pollutants that are “dissolved” or “unbound” to solids
  - Remainder of total load metals, phosphorus, organics, bacteria
  - Nitrates, Nitrites, Ammonia, Chloride, etc.

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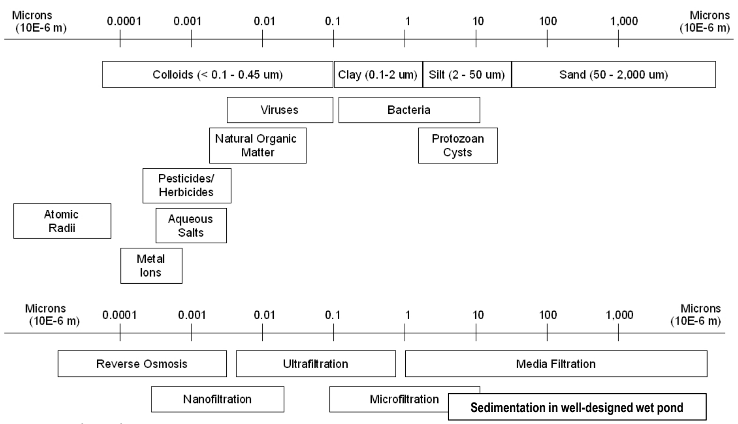
Anticipated Physical Filtration Performance (after a sediment forebay)



Need (bio)chemically-active media to remove some pollutants

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Example Pollutant Size Associations

	Percent Pollutant Reductions after Removing all Particulates Greater than Size Shown			
	20 µm	5 µm	1 µm	0.45 µm
Suspended Solids	76	81	98	100
Turbidity	43	55	92	96
Total-P	68	82	89	92
Nitrate	0	0	12	17
Cadmium	20	22	22	22
Copper	26	34	34	37
Lead	41	62	76	82
Zinc	64	70	70	72

Reference: Morquecho 2005

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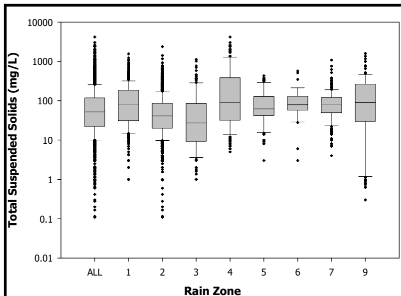
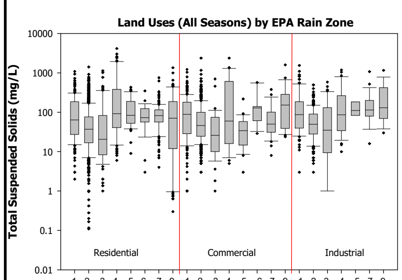
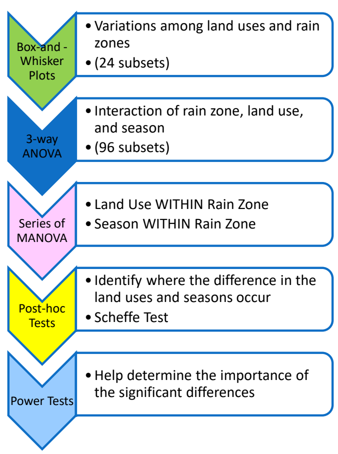




TSS at National Level using NSQD (Bochis 2010)



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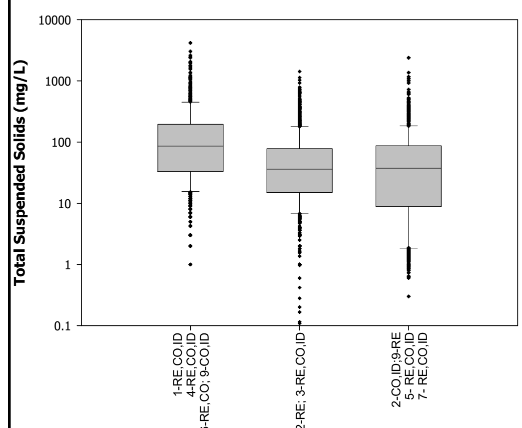
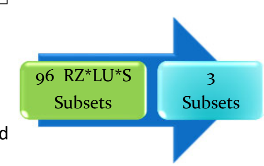
National Level: TSS Final Groups (Bochis 2010)



Groups	N	Avg. (COV)
1-RE,CO,ID 4-RE,CO,ID 6-RE,CO 9-CO,ID	748	199 *(1.9)*
2-RE 3-RE,CO,ID	1139	76 *(1.6)*
2-CO,ID 5- RE,CO,ID 7- RE,CO,ID 9-RE	972	78 *(1.9)*



For each rain zone, the land uses and seasons were grouped based on their significance

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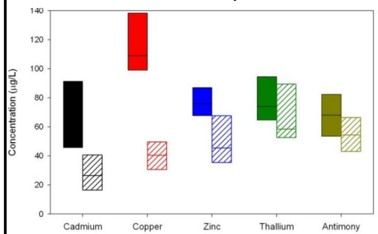
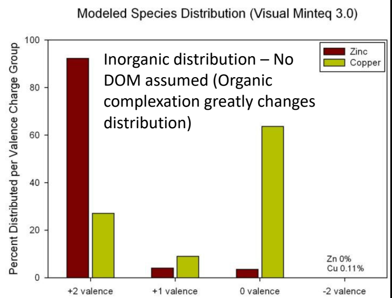
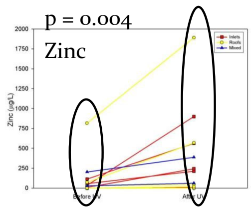
Influent Water Quality and Treatability of Stormwater Metals (total and filtered concentrations)





What form are those compounds that pass through a 0.45-µm filter?



	% Ionic	% Bound
Zinc	15	85
Copper	70	30
Cadmium	10	90
Lead	12	88

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Soil Chemistry Effects on Design to Be Considered

- Remove pollutants in the upper layers of the media in a biofilter. The deeper into the soil profile that the pollutants penetrate, the greater the likelihood of groundwater contamination or transport out of the device through an underdrain.
- Potential properties of interest in predicting removal (based on literature and batch-testing in the lab):
  - Soil and water pH
  - Pollutant forms (relationship to solids loading and PSD)
  - CEC (and AEC)
  - Mineral matter
  - Organic content
  - Phosphorus content
  - Oxidizing or reducing environment
  - Salinity and SAR

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Can permit limits be reached? Select media to improve pollutant removal and reduce permit violations.

Total zinc permit limits are usually about 120 µg/L. Total zinc may be at least four times the dissolved zinc concentrations. Most of these controls are therefore expected to meet the total zinc limit, but dissolved zinc may still cause receiving water problems.

BMP Category

DB	Detention Basin
GS	Biofilter
HD	Hydrodynamic Device
MF	Media Filter
RP	Retention Pond
WB	Wetland Basin
WC	Wetland Channel

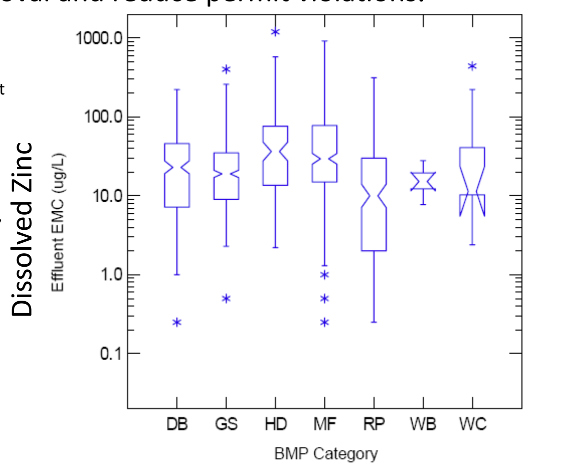

Figure 4. Individual effluent Dissolved Zinc EMCs by BMP category

Source: International BMP Database

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NO_3+NO_2 permit limits are usually 5 or 10 mg/L; only few effluent samples likely to exceed these values (but these provide little control also)

BMP Category

DB	Detention Basin
GS	Biofilter
HD	Hydrodynamic Device
MF	Media Filter
RP	Retention Pond
WB	Wetland Basin
WC	Wetland Channel

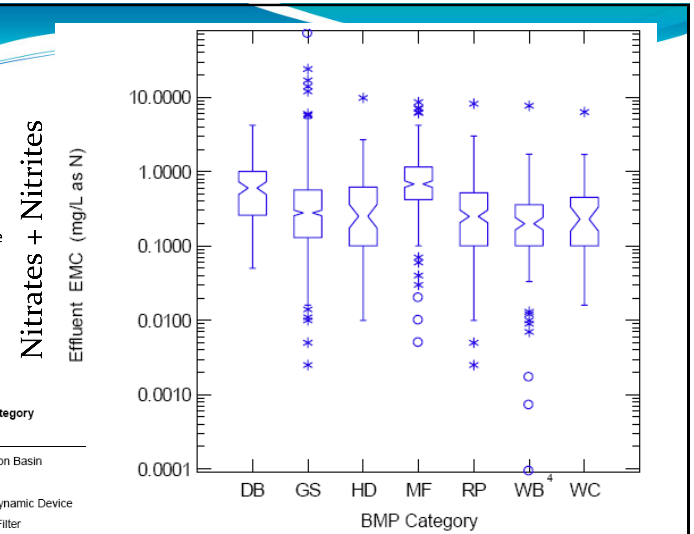

Figure 6. Individual effluent Nitrate Nitrogen EMCs by BMP category

Source: International BMP Database

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Treating Cations and Anions (NH_4^+, NO_3^-, PO_4^{3-}, Cl^-, Metals)

- Nitrogen removal:
  - Ammonia (NH_3) – uncharged
  - Ammonium (NH_4^+) – positively charged (+1)
  - Ammonia pKa = 9.3; at runoff pH, ammonia typically charged ion if an ion and not complexed with metals.
    - Charged positive ion able to be removed by ion exchange resin, although not bound as tightly as ions with higher valence charge (+2 or greater).
    - Ammonia/ammonium is small molecule and can be removed by ion-exchange resins acting as molecular sieves
  - Nitrate (NO_3^-) – negatively charged (-1)
    - Need media with higher anion exchange capacity or uptake with vegetation
    - Because of small valence charge, not strongly held and can leach out from organic media

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- Phosphorus Removal:
  - If in root zone of media, uptake by plants possible
  - Higher valence charge than nitrogen anion; more likely to be attracted to cations on surface of media
  - Reacts and forms stable compounds with iron and aluminum oxides.
  - Can form precipitates with some metals. (measure using Ksp).
  - Some media (especially compost and soil) are sources of phosphorus and underdrain phosphorus effluent concentrations can be high.
- Chloride Removal:
  - Similar problems for removal as nitrate, but limited uptake by plants.
  - For non-salt tolerant plants, can cause plant stress.
  - Main problem in areas using salts for ice control resulting in very high chlorides in snowmelt (and sodium causes severe SAR (sodium adsorption ratio) problems, especially if clays in media or soil).

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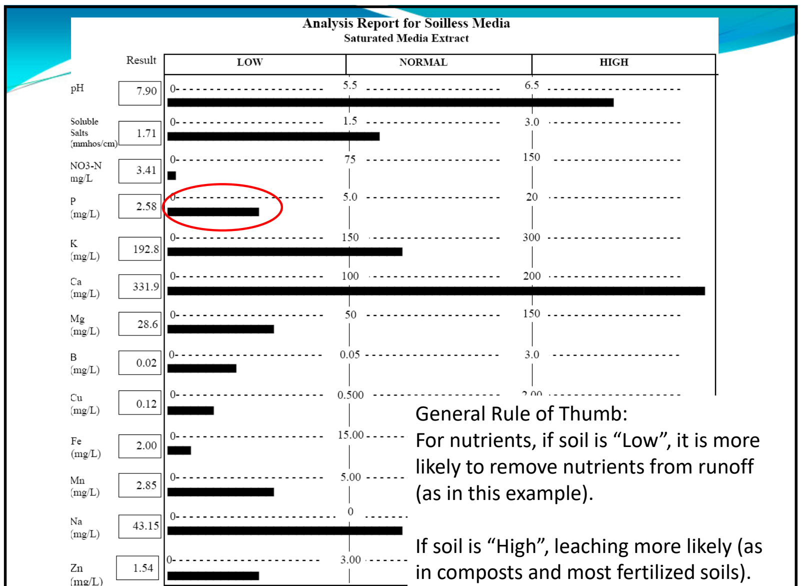

General Rule of Thumb:
For nutrients, if soil is "Low", it is more likely to remove nutrients from runoff (as in this example).

If soil is "High", leaching more likely (as in composts and most fertilized soils).

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Treatability of Organics (example: Pesticides, PAHs)

- Compounds with high Log Kow (preferentially partition to organic phase) typically better removed by organic based media(GAC, peat moss, compost). Limited removal by sand filters and ion exchange resin.
- Compounds with high solubility (Log S) have variable removal by media; likely tied to whether they are negatively or positively charged in solution. Limited removal in ion-exchange resins such as zeolite because of molecular size.
  - Zeolites are called molecular sieves because the lattice openings will "screen out" larger molecules.
  - These molecules are removed in organic-based media because of variety of removal sites. Plus media that support microbial growth (organic content) encourage degradation.

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Media Alternatives

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Types of Media

- Sand – relatively inert (without modification)
  - Common modifications are iron oxide and manganese oxide coatings.
- Ion-exchangers/Zeolites – molecular sieves
  - Exchanges out ions with stronger attractive forces and correct size
- Activated carbon
  - Hydrogen bonding and van der Waals forces through dipole interactions
- Organic Non-Activated Media (soil, peat, compost, biosolids) – Function of base material
  - Soils – mixture of organic matter from organic debris and weathering of parent material (rock)
  - Organic fraction reservoir for plant nutrients, nitrogen, phosphorus, and sulfur; increases soil water holding and cation exchange capacities; and enhances soil aggregation and structure.
  - Most chemically active: colloidal clays and organic matter. Clays: very large surface area per unit weight, generally net negative charge and high adsorptive capacity.
  - Organic colloids greater cation exchange capacity than silicate clays.
  - Soil pH affects nutrient transformations and the solubility of nutrients and metals.
    - Phosphorus most available in slightly acid to slightly alkaline soils, while all essential micronutrients, except molybdenum, become more available with decreasing pH.
    - Aluminum, manganese, and even iron can become sufficiently soluble at pH < 5.5 to become toxic to plants.
    - Bacteria generally tend to be most active in slightly acid to alkaline conditions.

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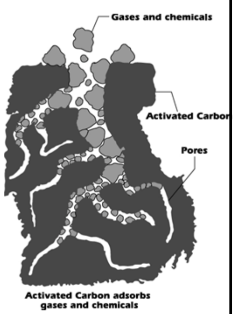
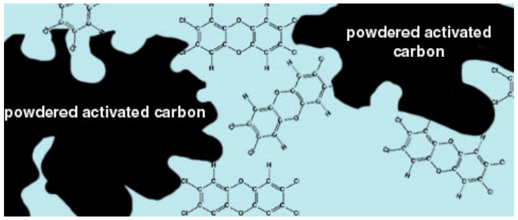
Activated Carbon Media

- Activated carbon – made from a variety of carbon sources
  - Reacts with chemicals through hydrogen bonding and van der Waals forces
  - Typical attraction through dipole interactions

  Biochar (an uncontrolled charcoal made from agricultural wastes, has some properties as activated carbon)



Peakpureair.com



http://www.chemistry.wustl.edu/~courses/genchem/Tutorials/Water/Adsorption.htm

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Soils as Media

- Soils – mixture of organic matter from organic debris and weathering of parent material (rock)
  - Less weathering products (Ca, Mg, Na, K) and more relatively insoluble elements such as Fe and Al than original rock.
  - Most chemically active: colloidal clays and organic matter.
  - Organic fraction < 10% of soil mass by weight.
    - Reservoir for plant nutrients, nitrogen, phosphorus, and sulfur
    - Increases soil water holding and cation exchange capacities
    - Enhances soil aggregation and structure.

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Soil Chemistry Effects on Design to Be Considered

- Remove pollutants in the upper layers of the media. The deeper into the soil profile that the pollutants penetrate, the greater the likelihood of groundwater contamination or transport out of the device through an underdrain.
- Potential properties of interest in predicting removal (based on literature and batch-testing in the lab):
  - Soil and water pH
  - **Pollutant forms (relationship to solids loading and PSD)**
  - CEC, cation exchange capacity (and also AEC, anion exchange capacity)
  - Mineral matter
  - Organic content
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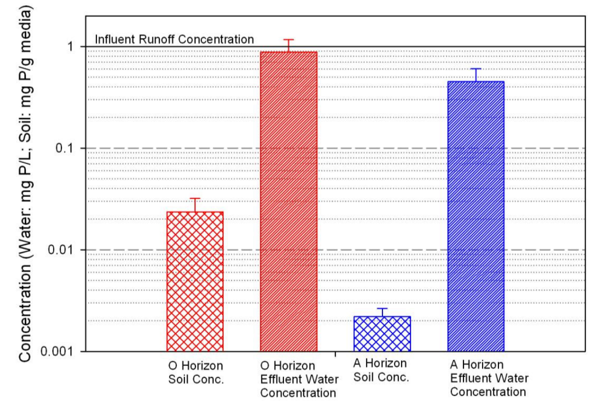
Impact of Initial Soil P Content



- Organic horizon has higher P content and minimal P removal.
- Mineral horizon has lower initial P content and thus P retention occurs.

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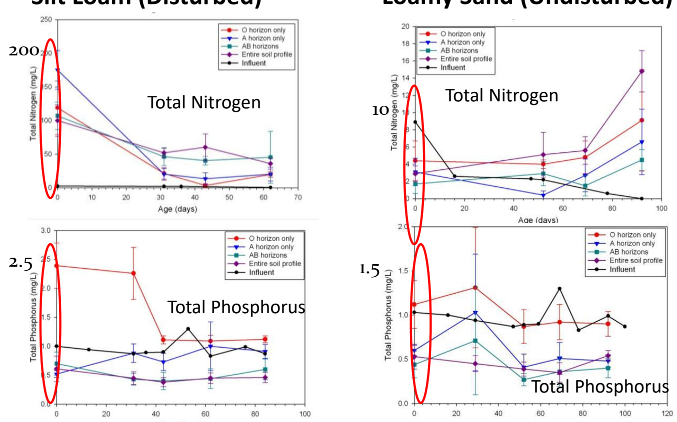
Impact of Soil Disturbance on Nutrient Release Immediately after Construction

Silt Loam (Disturbed) **Loamy Sand (Undisturbed)**



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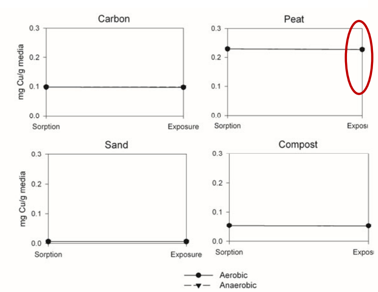
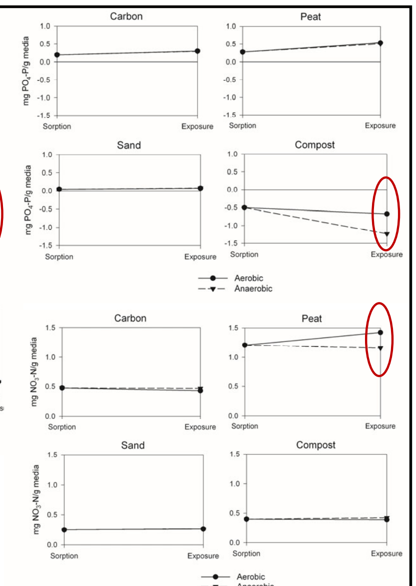
Additional Considerations: Changes in Soil and Porewater Chemistry between Storms





Heavy metals mostly retained.

Release of nutrients (N from peat [release captured N], P from compost [increased release]) under anaerobic conditions.

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Media Testing Goals

- To provide information for design (e.g., optimal media components, depths, and contact times).
- To maximize the likelihood that filtration-based treatment controls will achieve performance objectives.
- To optimize design considering the large investment ($0.10 to $1.00 per lb of media and many tons needed) and to ensure long-life before clogging or break-through.

- Bench-scale lab experiments performed by Penn State – Harrisburg and the University of Alabama
- Full-scale installations at Southern California site.

Media (from left to right): GAC, Rhyolite Sand, Site Zeolite, Surface Modified Zeolite, Sphagnum Peat Moss 33

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Testing Protocols

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Testing Protocol

- A thorough evaluation of biofiltration media was conducted to predict removal ability as a function of time, effects of clogging and maintenance, optimization of contact time, and changes in pore water chemistry in the filters between storms.
- The bench-scale testing protocol had four phases:
  - Long-term column testing – pollutant removal as a function of water and pollutant loading; highlights breakthrough/pollutant saturation, and maintenance (including recovery of media functionality and length of maintenance periods)
  - Media depth testing – pollutant removal as a function of media depth (function of contact time of the runoff water with the media
  - Batch kinetics testing – pollutant removal as a function of contact time; highlights optimal contact time, trade-offs with ion-exchange
  - Aerobic/anaerobic testing – retention of pollutants by the media as it relates to pore-water chemistry

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Constituents Evaluated during Laboratory Media Tests

- Critical site constituents (possible periodic permit exceedences if untreated): cadmium, copper, lead, zinc, oil and grease, mercury, and TCDD (2,3,7,8-Tetrachlorodibenzo-p-Dioxin).
- Some of the other constituents listed on permit (rarely, if ever, expected to exceed permit limits if untreated): pH, TDS, sulfate, chloride, nitrates plus nitrites, fluoride, ammonia, nickel, antimony, boron, thallium, perchlorate, tritium, uranium, gross alpha, gross beta, radium, and strontium-90.

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- Other constituents that affect performance of media in removal of contaminants: flow rate, suspended solids, suspended sediment, particle size distribution, turbidity, sodium, calcium, magnesium, potassium, conductivity, oxidation-reduction potential, filtered aluminum, and filtered iron.
- Other constituents that help in understanding removal mechanisms of media: COD, UV-254, phosphate, nitrate, *E. coli* bacteria, alkalinity, hardness, and other filtered metals (Cd, Cr, Cu, Pb, Zn).

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Design for Treatment Contact Time

- Starting off with conflicting requirements:
  - Rapid infiltration to prevent flooding, protect against standing water, etc.
  - Slow infiltration to allow for sufficient time for pollutants to be removed from the water and adhered to the media.
  - These requirements are balanced by using depth filtration (sufficient media depth to ensure adequate contact).
- Soil physical characteristics that affect infiltration rate and contact time:
  - Texture, which affects the following (some states dictate soil texture class for infiltration devices):
    - Porosity
    - Bulk density
    - Permeability
  - Degree of compaction during and after construction (affects porosity, bulk density, permeability).
  - Degree of clogging (affects porosity, permeability)
- Choice of soil texture components to meet drain down time affects pollutant removals (chemical composition of media components).

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Column Tests vs. Batch Tests

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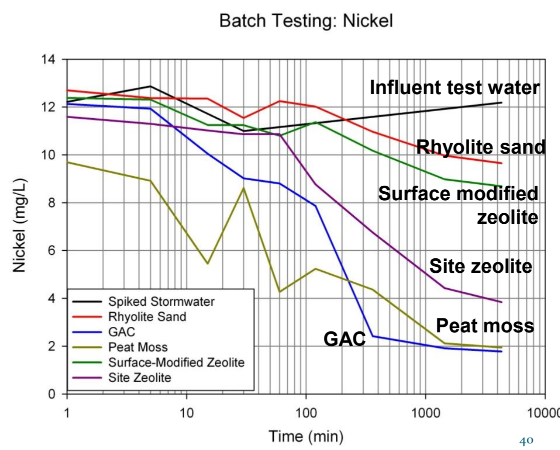
Contact Time for Filtered Metals

- Minimal filtered metal removal when contact time <10 minutes (except peat).
- Optimal contact times removal ranged from 10 to 1,000 minutes, depending on metal and media type.



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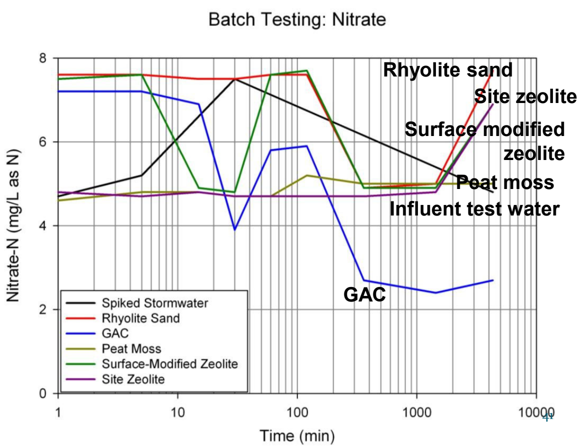
Contact Time for Nitrate

- Only removal by GAC column.
- GAC removal required > 20 minutes and fluctuated. Consistent removal after 100 minutes contact time.



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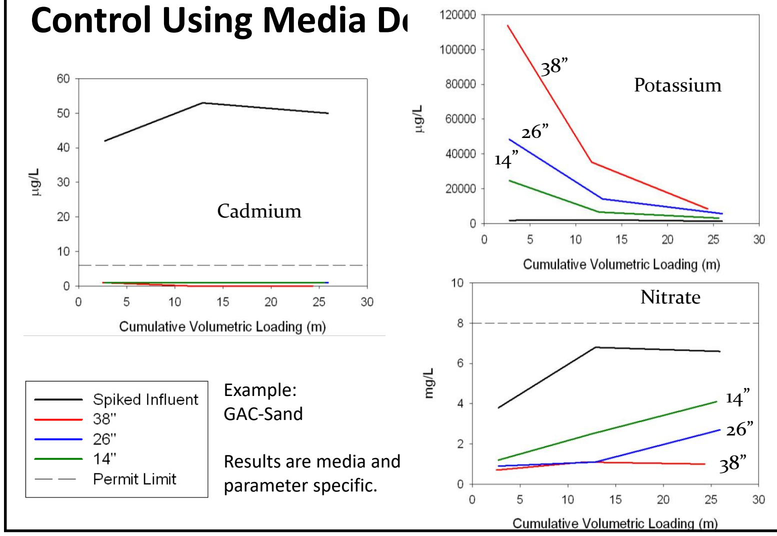
Initial Design Question: Contact Time Control Using Media De



Example:
GAC-Sand

Results are media and parameter specific.

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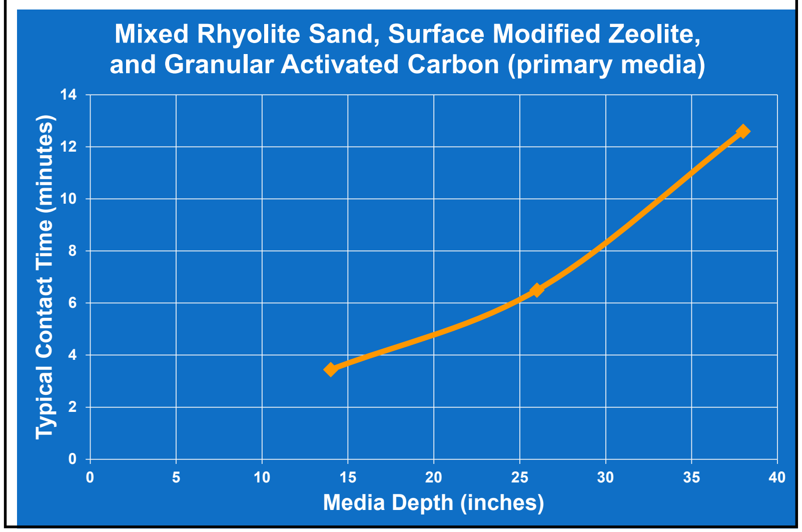
Column Contact Time



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Clogging, Flow, and Breakthrough Column Tests

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Flow as a Function of Solids Loading

- Infiltration rates typically decrease over a device's life due to solids capture on the surface of and in the media.
- Most media typically fail when the total solids loading is about 10 to 25 kg/m^2 of media surface (flow rate < 1 m/d, generally).

Tried potential maintenance options once flow rate < 5 m/d (effects of disturbing media vs. removing media from filter).

Deep media removal generally more effective than simple surface scrapping. Need to remove at least 10 to 15 cm because clogging solids are captured deep in the media (deeper than visible solids buildup).

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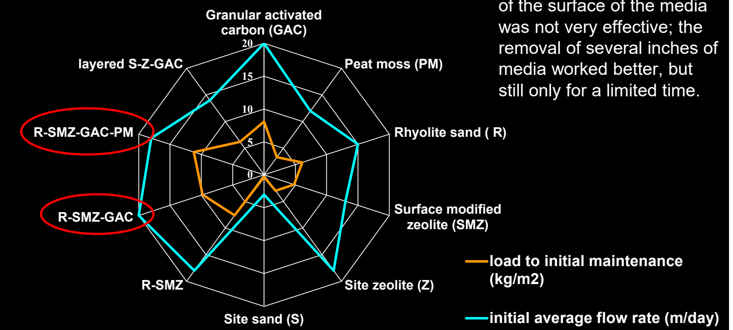
Hydraulics and Clogging



Maintenance with scraping of the surface of the media was not very effective; the removal of several inches of media worked better, but still only for a limited time.

1. Site sand clogged first and had the lowest flow rate
2. Site zeolite and peat alone were next to clog
3. Mixing media and taking advantage of mixed pore spaces performed better than current site layered media combination; better depth filtration

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Mixed Rhyolite Sand - Surface Modified Zeolite - Granular Activated Carbon (R-SMZ-GAC) Removals by Particle Size Range

Particle Size (µm)	Mean Influent Concentration (mg/L) (approximate range)	Mean Effluent Concentration (mg/L)	Reduction (%)
< 0.45	199 (80 to 250)	225	0
0.45 to 3	9.9 (3 to 22)	7.2	0
3 to 12	54.9 (22 to 90)	2.9	95
12 to 30	54.5 (18 to 90)	0.67	99
30 to 60	37.4 (3 to 80)	1.0	97
60 to 120	20.0 (2 to 58)	0.76	96
120 to 250	5.1 (0 to 17)	0.08	98
>250	13.9 (3 to 45)	4.1 (likely media washout)	71
SSC	206 (50 to 400)	13.6	93

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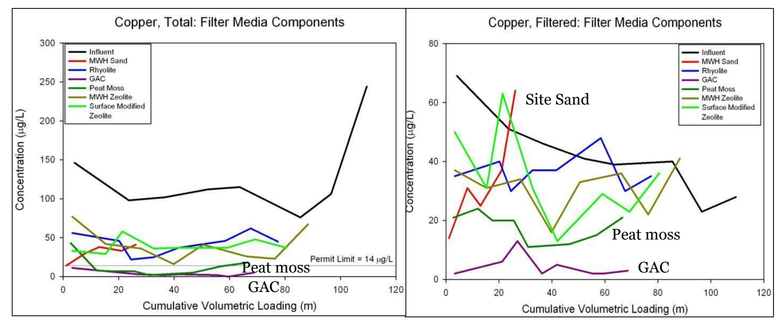
Initial Design Question: Pollutant Form – Particulate Associated or Dissolved/Colloidal?



- Good overall removal of total copper, but much poorer removal of filtered copper – function of particulate associations.
- For dissolved copper, removal greatest in GAC and peat moss, likely resulting from multiple types of binding sites available in media. Note poorer performance comparatively of zeolites, indicating ion exchange occurs, but not only removal mechanism.

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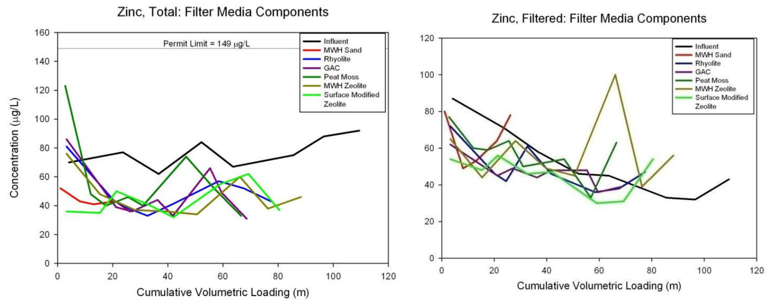

- Poor removal of total and filtered components – likely because most of the zinc was dissolved/colloidal for this challenge water.
- Model predicted mostly ionic +2 form, likely because OM effects ignored in model.
- Historical data has shown zinc 85% bound by organic matter (particulate-bound).
- Zinc likely to form many complexes with Cl, OH, Cu, etc.

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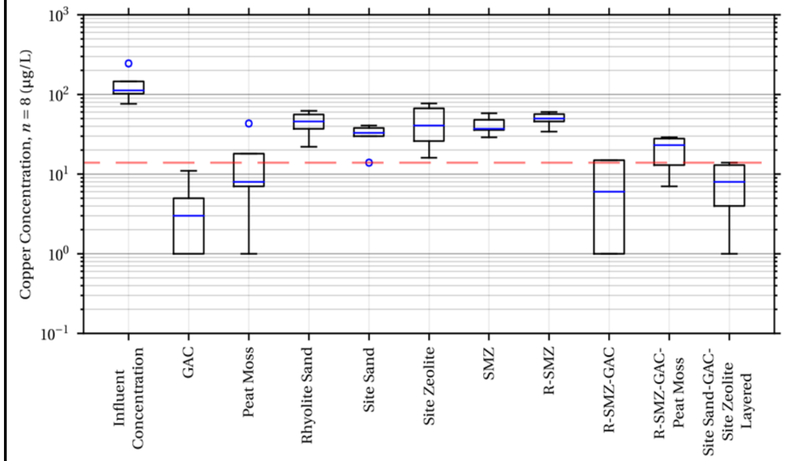
Media Performance Plots for Copper, Full-Depth Long-Term Column Tests



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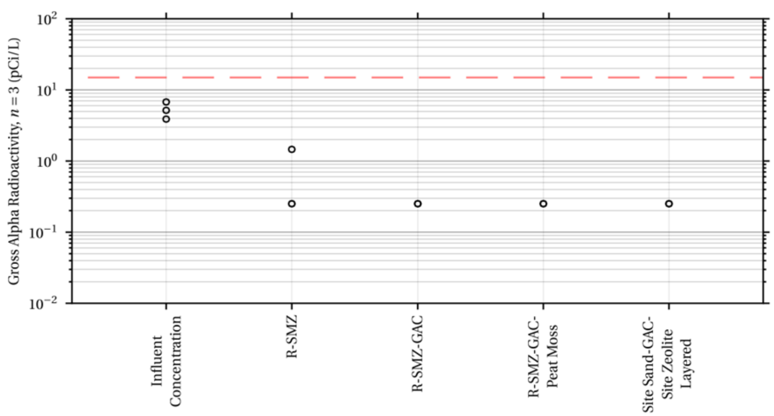
Gross Alpha Radioactivity Control Observations



At least 90% reductions for effective media (influent and effluent samples were all below the numeric effluent limit)

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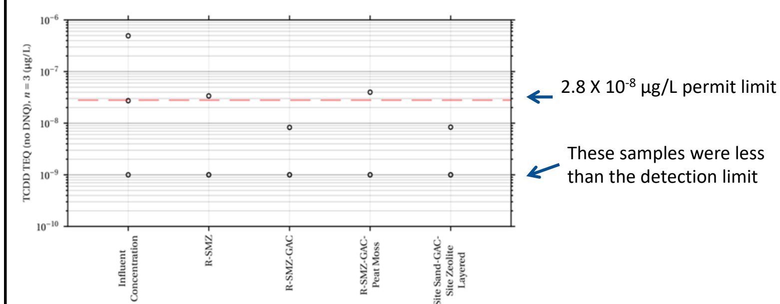
Dioxin Control Observations



- Dioxin results indicate good control; however, cannot be definitive since few data available (complexities and costs of the analyses limited samples).
- Two of the three effluent observations for each media were below the detection limit. The R-SMZ-GAC and layered media column each had a single detected effluent dioxin value at about 1/3 of the permit limit.
- The detected effluent concentrations were at least an order of magnitude less than the observed influent concentrations for these two media mixtures, showing good removals to close to, or below, the extremely low site permit limit.

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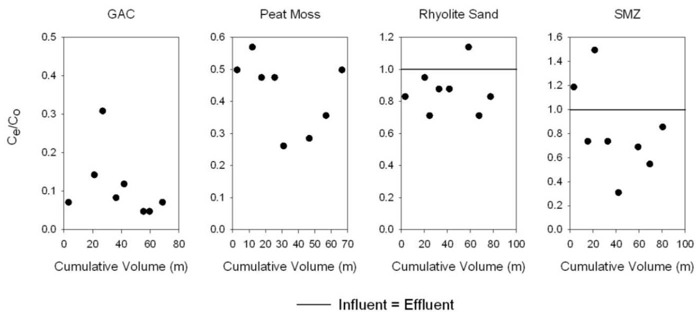
Selecting the Media Mixture from a Set of Potential Components: "Dissolved" Copper Example



- Model prediction: 25% +2 valence, 10% +1 valence, 65% 0 valence charge.
- Sand with modification: prefers ion exchange (+2 charge)
- Zeolite (SMZ) ion exchange resin (+2 charge)
- GAC and peat moss have multiple types of exchange/adsorption sites – good for all valence charges; GAC performing better for filtered copper but EXPENSIVE

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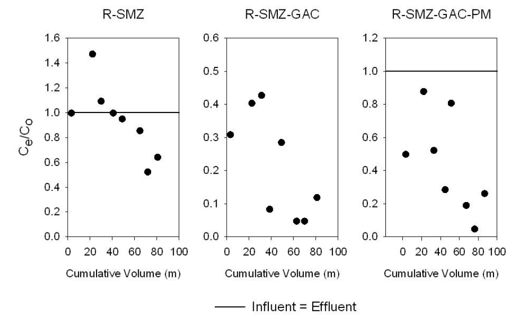
Selecting the Media Mixture from a Set of Potential Components: "Dissolved" Copper Example (continued)



- Modified sand and zeolite mixture – best removal 50%, but generally poor removal.
- GAC and peat moss were better than sand and zeolite; GAC performing better for filtered copper, but may not support plant life
- Adding small amount of peat moss as organic matter for plant life support only slightly reduced performance.

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Column Test Results: Pollutant Removal

(paired sign test: influent vs. effluent; independent observations)

Media Type	Cr, Cu, Sb, Al	Pb	Zn	Cd, Ni, Tl, Fe	Hg	NO_3	TCDD	
R-SMZ-GAC	**T**, F	**T**	T	**T**, F	T	T	**T**	**Preferred mixed media combination**

R = rhyolite; SMZ = surface modified zeolite; GAC = granular activated carbon; PM = peat moss; S = site sand; Z = site zeolite
T = removal for total form (unfiltered); F = removal for filtered form (passed through 0.45-µm membrane filter)

Other findings (data not shown here; specific example of tested media and permit limits shown earlier, but analysis type can be used in other situations):

- Extensive modification of zeolite unneeded; simple ion exchange not primary removal mechanisms even for filtered metals.
- Mixed media combination met all current site permit limits, except Cu & Hg during peak conditions (not expected to occur); significant removals for all constituents measured, except for phosphorus and gross beta radioactivity.

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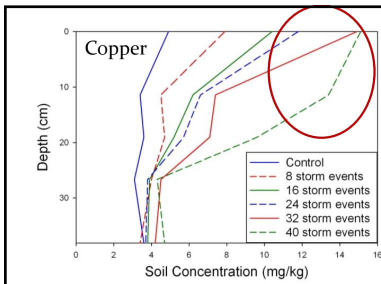
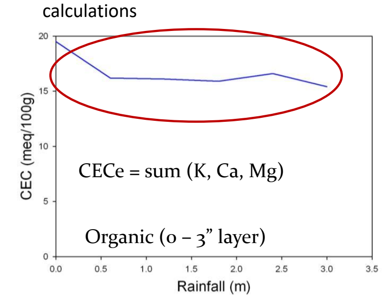
Breakthrough



- Copper Accumulation in Upper Layers of Soil with Subsequent Downward Migration
- Limited Release of CEC Cations or Decrease in CECe (sum of K, Ca, Mg)
- May also be complexation/chelation / exchange with organic compounds, which is not measured in CECe calculations



- Column testing breakthrough capacity about 15 mg/kg
- Bench-scale batch capacity testing about 45 mg/kg
- Difference potentially due to inability of/insufficient time for metal ions to migrate to inner pore spaces during flow-through operation and therefore, total removal ability of media not used.

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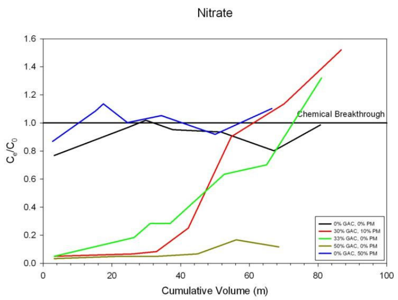
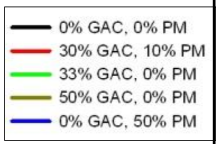
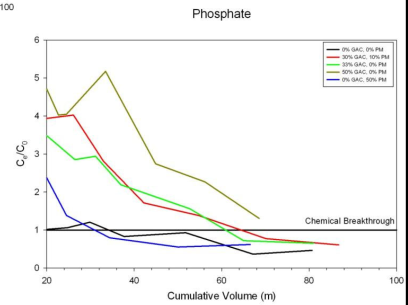


Trade-Offs in Media Mix Components and Ion-Exchange





Inverse removal behavior of nitrate and phosphate.

Reducing GAC content reduces nitrate removal life, but decreases amount of phosphate released.

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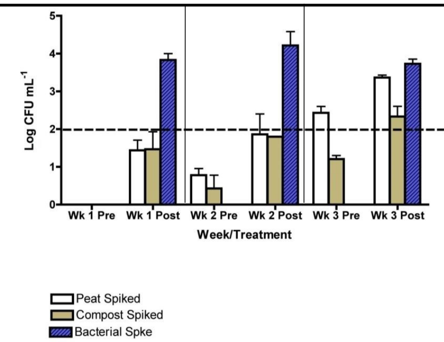

Bacteria Removal

Little difference between peat and compost.

Impact of organic matter (OM) content on retention and regrowth with little impact of pH change.

Initially, no coliform flush from peat (30% v/v) or compost (equivalent amount of OM). Retention after spiked stormwater passage approximately 2-log.

Weeks 2 and 3 pre-spike flush indicate a flushing out of captured bacteria (likely due to growth on media during inter-event period). Post-spike filtering showed concentrations near recreational water quality standards.

Week 3 first flush near WQS; after filtering, above WQS.

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Breakthrough Capacity Compared to Clogging Period: Analyzing Combined Data Sets

Ratios of Media Capacity to Clogging Period	R-SMZ	R-SMZ-GAC	R-SMZ-GAC-PM	Site Sand-GAC-Site Zeolite Layered
Cadmium, Total	>230	>170	>130	>150
Copper, Total	>2.2	>3.4	>1.7	>2.2
Gross Alpha radioactivity	>0.3	>0.3	>0.2	>0.2
Lead, Total	>2.1	>1.6	>0.9	>0.9
Mercury	>250	>230	>130	>140
Oil and Grease	0.1	>0.1	>0.1	<0.1
TCDD	>3.1	>2.5	>1.3	>1.5

Green: will clog before breakthrough for example permit limits and media
Red: breakthrough before clogging for example permit limits and media

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Recommended Media for Treatment Targets

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Analytes on Permit	Treatment Technology Options
NO_2+NO_3	Ion-exchange or plant uptake (potential denitrification? Other problems with denitrification)
Total Zinc and Total Copper	Chemically-active filtration (organic media sorption/ion-exchange) after pre-settling
Total Lead	Physical filtration of larger particulate-associated lead after pre-settling. Chemically-active filtration (organic media sorption and potential ion-exchange)
TCDD	Chemically-active filtration with strong organic sorption (GAC) after pre-settling. Other organics potential elevated parent material contamination.
Total Mercury	Chemically-active filtration with sorption for organic methyl mercury (MeHg) and ion-exchange for inorganic mercury and complexes.
Oil and grease	Chemically-active filtration with strong organic sorption component (GAC) after capture of free-floating material if concentrations are high and visible. Peat and compost also possible.

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Conclusions

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Stormwater Control Performance Optimization

- With numeric effluent limits, site requires designs refined to a much higher degree than in typical practice
- Need to optimize stormwater control performance through various design factors:
  - Treatment trains using combinations of sedimentation and media filtration
  - Long sedimentation pre-treatment drainage time
  - Sufficient media contact time to increase control of critical constituents
  - Specially-selected filtration media
- Bench-scale laboratory and pilot-scale media testing was therefore conducted to provide needed performance and design information.

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Capacity of Biofilters for Retention of Radioactive and Organic Contaminants (per unit of filter surface area) (0.5 m layer of mixed media)

Constituent	R-SMZ-GAC	Units
Gross Alpha	> 337,000	pCi/m^2
Gross Beta	38,300	pCi/m^2
Radium-228	12,600	pCi/m^2
Alpha Radium	> 40,700	pCi/m^2
Uranium	> 87,300	pCi/m^2
Oil and Grease	>32,400	mg/m^2
TCDD	>1.35E-5	mg/m^2

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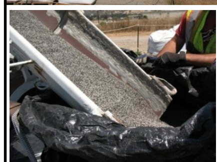
Preparing Recommended Media for Large Biofilters

1. Filling individual media bags prior to mixing

2. Loading Rhyolite sand media bags into mixer

3. Loading surface modified zeolite media bags into mixer

4. Loading granular activated carbon media bags into mixer



5. Finished mixed media loaded into final bags

6. Mixed media ready for placement into biofilters

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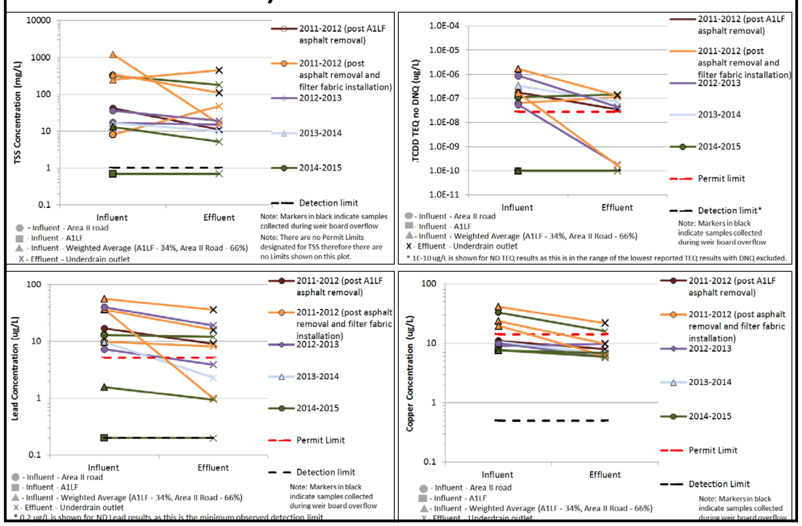
CM-9 (culvert modification, under-sized with high treatment flow rate)



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CM-1, CM-9, and B-1 Culvert Modifications

Influent to Effluent, 2011-2015	TSS (mg/L)	Dioxins (µg/L)	Copper (µg/L)	Lead (µg/L)
Total pairs of observations	47	40	37	47
Number of influent samples having larger concentrations than effluent samples	30	28	32	35
p by paired nonparametric 1-tailed sign test	0.018	0.0003	0.000004	0.0003
Average influent concentrations	87	5.7E-06	7.3	7.9
Average effluent concentrations	37	2.9E-07	5.0	4.4
Average percent change	**57%**	**95%**	**32%**	**45%**

Statistically significant removals for these critical constituents (32 to 95% removals), some exceedances still occur due to being under-sized.

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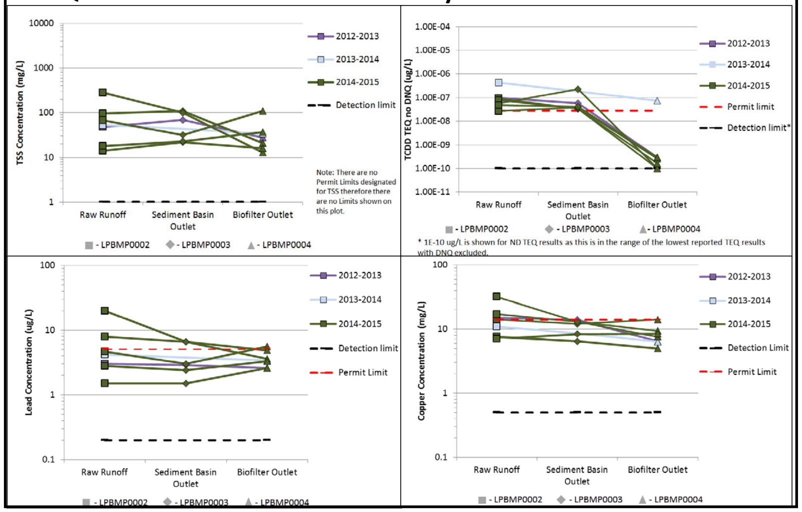
Lower Lot Biofilter (a recent fully-designed treatment train having detention bioswale, sediment pond, and biofilter). Was awarded the CASQA best stormwater control of the year in 2014 for California.



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Lower Lot Biofilter

Runoff to Outlet, 2012 - 2015	TSS (mg/L)	Dioxin (µg/L)	Copper (µg/L)	Lead (µg/L)
Total pairs of observations	7	7	7	7
Number of influent samples having larger concentrations than effluent samples	4	7	5	4
p by paired nonparametric sign test	0.50	0.0078	0.11	0.50
Average (and COV) influent concentrations	82	1.20E-07	145	6.3
Average (and COV) effluent concentrations	37	1.08E-08	8.2	3.7
Average percent change	55%	91%	45%	41%

Only dioxin had significant removals due to few events occurring during recent drought years. However, no exceedances have been observed from this treatment train.

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Conclusions and Questions

- Conclusion: Media can be tailored to address specific pollutant problems.
- Conclusion: Removal function of both water and media chemistry
  - Knowledge rich and data poor on water quality chemistry and speciation.
  - Media specifications beginning to address fundamental media characteristics.
  - Limited understanding of bacterial effect on pollutant removal.
- Question: How to improve media specifications to reduce variability in treated water concentrations?
- Question: Improve/develop models for predicting media effectiveness and lifespan for filtered metals removal?
- Question: And many more…….

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- Most devices fail because of clogging.
  - Design for clogging first (assume with vegetation, solids loading for most media mixes approximately 25 kg/m^2).
  - Maintenance has limited effectiveness. Vegetation likely will extend lifespan because of biological disturbance of soil helping deeper penetration of solids and pollutants.
- Evaluation of potential chemical removal.
  - Physical removal primary mechanism, even in media with “good” sorption/ion-exchange potential.
  - Removal based on influent quality (including “speciation” or “association” of pollutants with particulates of all sizes).
  - Evaluate media choices (either individually or as part of a mix) based on both adequate removal of pollutants and ensuring that the exchanged ions are not causing degradation.
    - CEC, AEC, OM, P-content, SAR, soil pH predict, but may not be able to quantify, removal efficiency or effluent quality. Also not precise measurements of lifespan.
    - Increasing OM and P content has an unquantified maximum effect. Above a certain amount, the media releases nutrients, color compounds, and colloids that may have associated pollutants.

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Conclusions on Media Selection

- Bioretention media can be selected/designed based on needed pollutant removals. See recent article, for example: Clark. S. and R. Pitt. "Targeting treatment technologies to address specific stormwater pollutants and numeric discharge limits." *Water Research*. Vol. 46, pp. 6715-6730. July 2012: http://www.sciencedirect.com/science/article/pii/S0043135412004915
- Soil testing for nutrients can indicate whether media likely to capture or leach nutrients.
- Must match media chemistry to chemistry of pollutants.
  - Complexation of metals
  - Organic polarity vs. non-polarity
- Tradeoffs (most media act as ion exchange resins and therefore release materials as they capture targeted constituents)
- Sorption more important than usually thought (and ion exchange probably less important)
- Direct translation of laboratory tests to field conditions problematic.
  - Capacity less than predicted by lab testing, for example;
  - Isotherms cannot be extrapolated to low stormwater concentrations from saturated test solutions;
  - Complex interactions occur with stormwater compared to simple test mixtures.

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- Radionuclide, mercury and TCDD had significant and large removals (75 to 90+% reductions) by most of the media mixtures tested when detectable influent concentrations were seen.
- Critical that the media be kept aerobic as anaerobic conditions accelerated degradation of the media and losses of previously captured material (especially nutrients)
- The GAC was the most important component in these mixtures (but most costly at about $500/m^3), while the addition of either of the zeolites (at about $100/m^3) was also needed.
- The sand is critical to moderate the flow rates and to increase the contact times with the coarser media, unless other flow controls were used in the filter designs.

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- The Rhyolite sand added some removal benefits compared to the filter sand.
- A small amount of peat added to the mixture increased metal removals during high flow rates (good removals even during short contact times).
- Therefore, the best mixture for removal of the large variety of pollutants to levels that met the very low numeric effluent limits was the mixture of Rhyolite sand (30%), surface modified zeolite (30%), GAC (30%), and 10% peat.
- The treatment flow rate was high, the particulate removal was excellent, and the clogging potential was low with this mixture, resulting in a long and effective operational life.

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