Designing Treatment Media for Emerging Stormwater Contaminants Based on Water and Soil Chemistry

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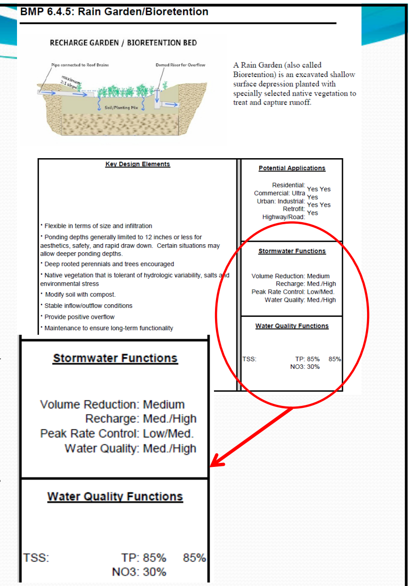
Current PA Guidance

- Many guidance documents apply expected pollutant removals based on literature.
  - However, typically presented as efficiencies of removal and have been misinterpreted and misapplied.
  - Also difficult to remove 85% of pollutants in "clean" water.
  - Do not address metals or problematic organics.



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TMDL needs concentrations

Total Nitrate-Nitrogen (TN)

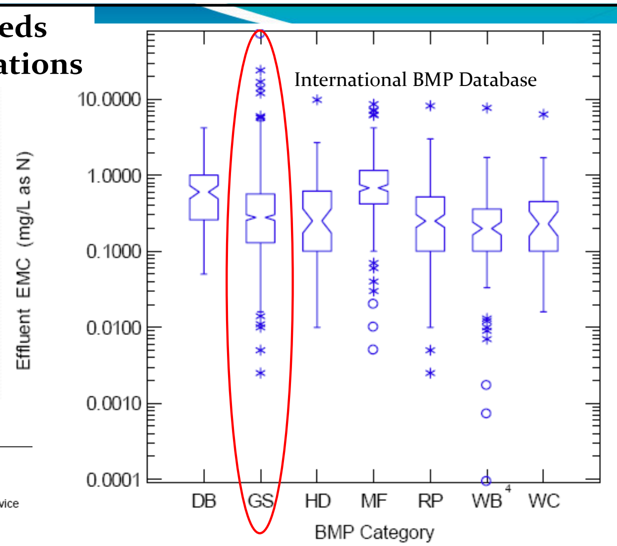

Figure 6. Individual effluent Nitrate Nitrogen EMCs by BMP category

BMP Category

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

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Why Does the Literature Report Widely Different Efficiencies for Bioretention?

FACTORS
- Influent Water Chemistry
- GeoChemical Reaction Equilibrium
- GeoChemical Reaction Kinetics
- Microbiogeochemical Interactions
- Vegetation

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Influent Water Chemistry

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

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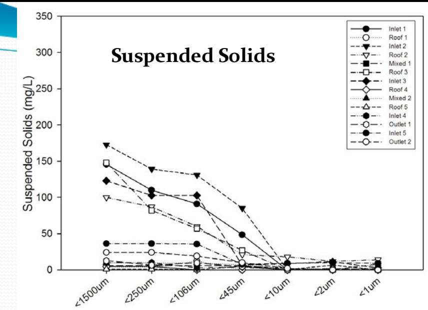
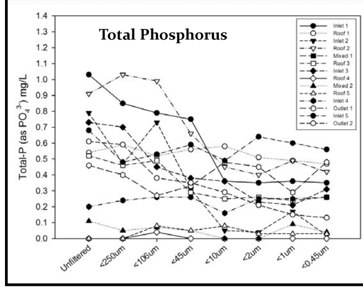
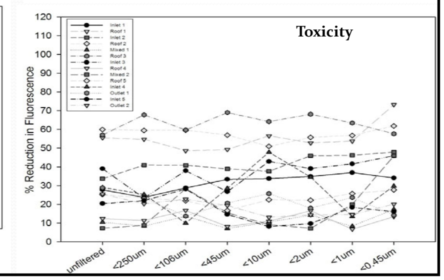
Associations of Pollutants with Specific Particle Sizes

From: Morquecho 2005







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Influent Water Chemistry

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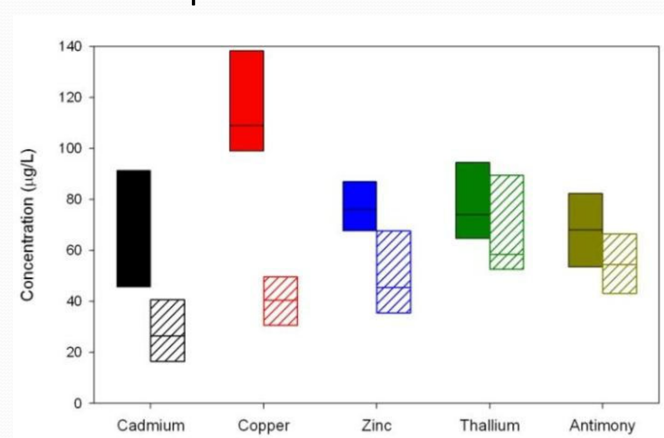
Metals Partitioning – Why Different for Representative Metals?



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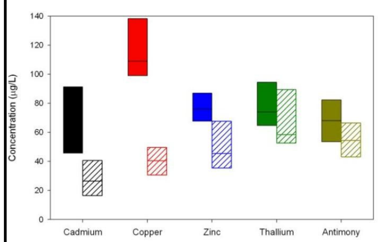
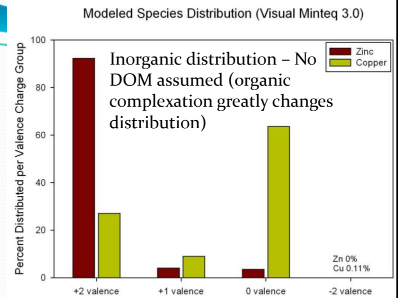
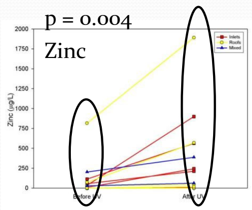
INFLUENT WATER QUALITY AND TREATABILITY





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

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SOIL STRUCTURE

O-horizon: leaf litter, organic material

A-horizon: plough zone, rich in organic matter

B-horizon: zone of accumulation

C-horizon: weathering soil; little organic material or life

R-horizon: unweathered parent material

www.seafriends.org.nz/enviro/ soil/geosoil.htm

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Soil Chemistry Effects

- GOAL: Remove pollutants in the upper layers of the media (deeper penetration into the soil profile, greater likelihood of groundwater contamination or transport out of the device through an underdrain).
- Potential properties of interest in predicting removal:
  - Soil and water pH
  - Pollutant forms (relationship to solids loading and PSD)
  - Cation Exchange Capacity (CEC) [and Anion Exchange Capacity (AEC)]
  - Mineral matter
  - Organic content
  - Phosphorus content
  - Oxidizing or reducing environment
  - Salinity and Sodium Adsorption Ratio (SAR)

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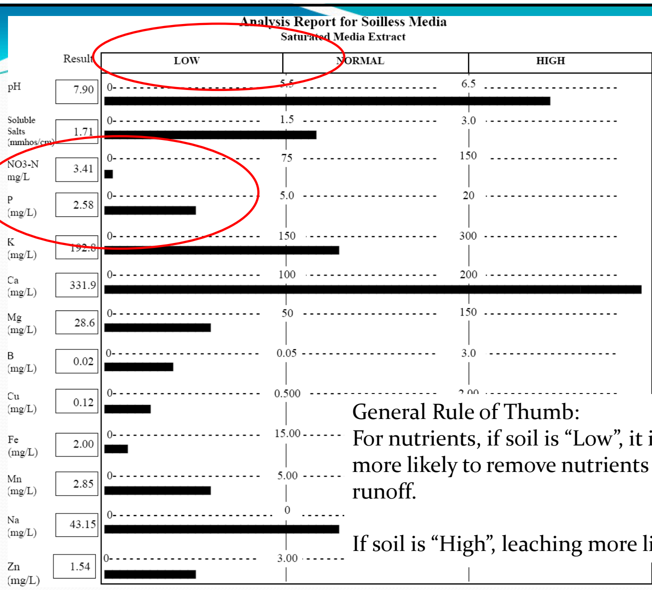

General Rule of Thumb:
For nutrients, if soil is “Low”, it is more likely to remove nutrients from runoff.

If soil is “High”, leaching more likely.

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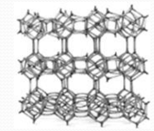
Example Media Types

- Sand – relatively inert (without modification)
  - Common modifications are iron oxide and manganese oxide coatings to improve pollutant retention.
- Ion-exchangers/Zeolites – lattice structure
  - Interested in exchanging out ions with stronger attractive forces (particularly ones that have a higher valence/charge state)



Zeogarden.com

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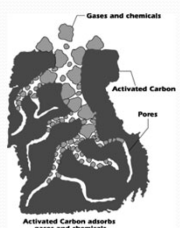
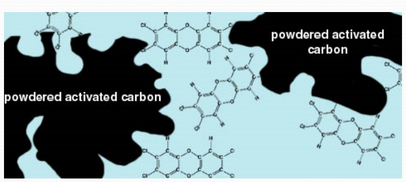
Example Media Types

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



Peakpureair.com



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

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Example Media Types

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)
  - Less weathering products (Ca, Mg, Na, K) & more relatively insoluble elements such as Fe & Al than original rock.
  - Most chemically active: colloidal clays & 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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Summarizing Types of Media

Organic Non-Activated Media (soil, peat, compost, biosolids)

- Soils – mixture of organic matter from organic debris and weathering of parent material (rock)
  - Soil pH affects nutrient transformations and the solubility of nutrients.
    - 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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Design Considerations

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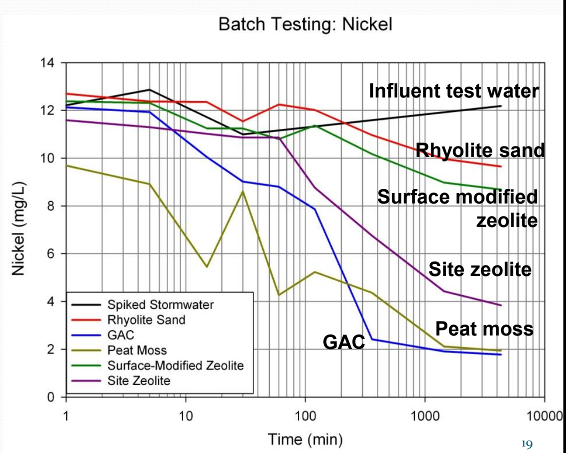
Contact Time → Reaction Kinetics

- 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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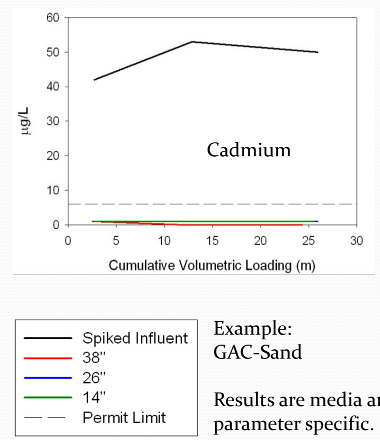
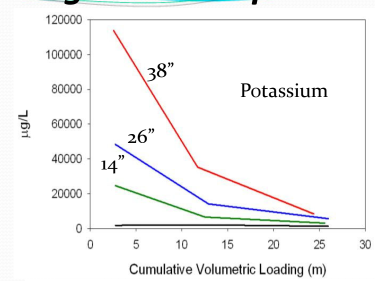
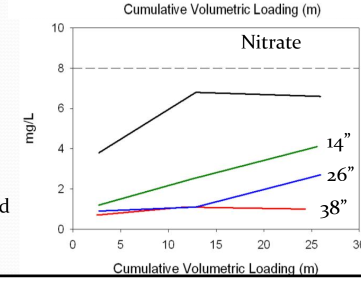
Contact Time Control Using Media Depth





Example: GAC-Sand

Results are media and parameter specific.



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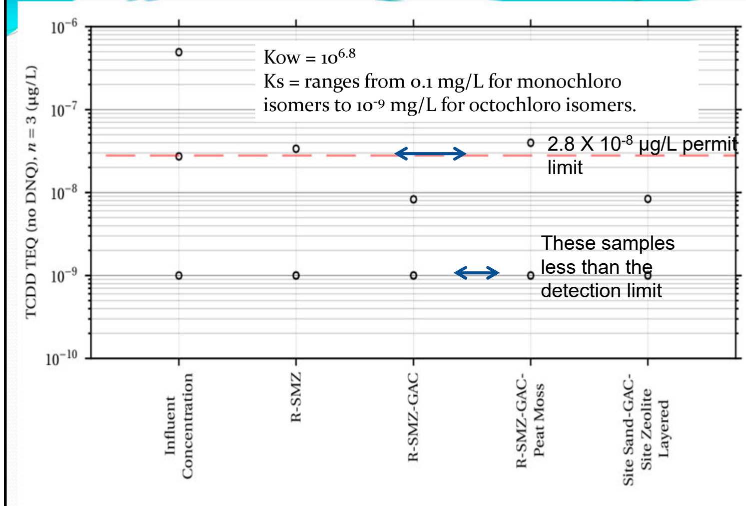
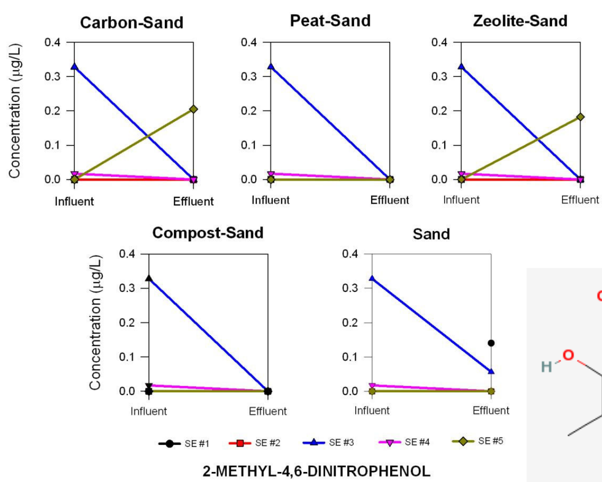
Treatability of Organics (example: Pesticides, PAHs)

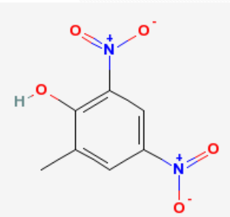
- Compounds with high Log Kow (preferentially partition to organic phase) typically better removed by organic based media(GAC, peat moss, compost).
- Compounds with high solubility (Log S) variable removal by media; likely tied to whether they are negatively or positively charged in solution. Limited removal in ion-exchange resins such as zeolite because of molecular size.

Dioxin Control Observations





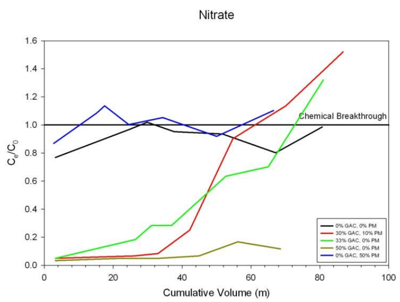
Clark and Pitt (1999). *Stormwater Runoff Treatment: Evaluation of Filtration Media.* EPA 600/R-00/010. U.S. Environmental Protection Agency. 405 pages.



Log Kow = 2.1; pKa = 4.3 – 4.5; Log S ~ 2
Some organic media removal, plus weak ionic potential

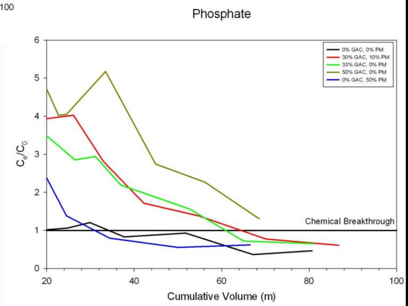
Urban Runoff Quality and Treatability

Pollutants	Media Treatment Notes
NH3-N	NH_4^+ removed by organic media with variety of removal sites. May be removed by ion-exchange resins/zeolites if limited competition from +2 ions.
NO3-N	Uptake by plants. Limited removal below root zone. Leaches. (AEC)
PO4-P	Removed in high AEC or high Al/Fe media. Leaches if excess P in soil. (use soil test for preliminary determination) (low P; low OM)
TSS	Removal excellent for particles greater than 1 – 2 µm.
Cu, Total	Particulate fraction removed to some extent; Limited physical removals for Cu bound to particles smaller than 1 – 2 µm.
Cu, Dissolved	Valence charges range from +3 to -2. Cations potentially removed in ion-exchange resin. Anions and small positive charges likely removed in organic media with variety of removal sites. (CEC/OM)
Zn, Total	Particulate fraction removed to some extent; Limited physical removals for Zn bound to particles smaller than 1 – 2 µm.
Zn, Dissolved	Valence charges range from +3 to -2. Cations potentially removed in ion-exchange resin. Anions and small positive charges likely removed in organic media with variety of removal sites. (CEC/OM)



Selecting Media Mix Components

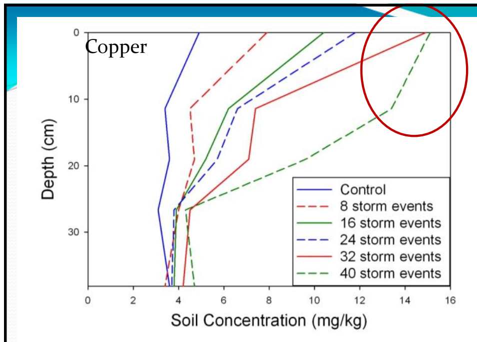
- 0% GAC, 0% PM
- 30% GAC, 10% PM
- 33% GAC, 0% PM
- 50% GAC, 0% PM
- 0% GAC, 50% PM



Inverse removal behavior of nitrate and phosphate.

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

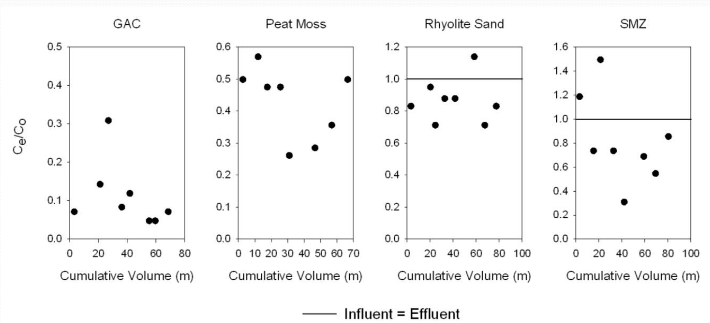
Breakthrough



Copper Accumulation in Upper Layers of Soil with Subsequent Downward Migration

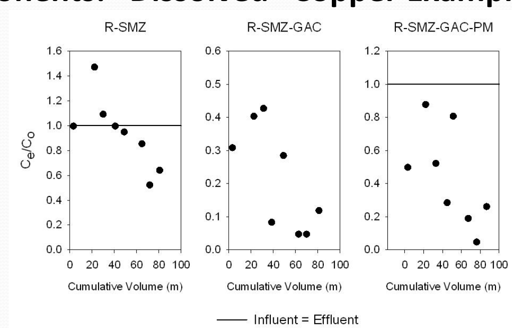
- Column testing breakthrough capacity = ~ 15 mg/kg
- Bench-scale batch capacity testing = ~ 45 mg/kg
- Difference potentially due to inability of/insufficient time for metal ions to migrate to inner pore spaces during flow-through operation and therefore, total removal ability of media not used.
- Transfer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

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 "dissolved" copper

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



- 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.

Conclusions

- Bioretention media can be selected/designed based on needed pollutant removals.
- Soil testing for nutrients can indicate whether media likely to capture or leach nutrients.
- Must match soil/media chemistry to chemistry of pollutants.
  - Complexation of metals
  - Organic polarity vs non-polarity
- Tradeoffs (most media act as ion exchange resins)
- Direct translation of laboratory tests to field conditions problematic.
  - Capacity less than predicted by lab testing, for example.