Treatability of Organic and Radioactive Emerging Contaminants in Stormwater Runoff


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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). Some permit limits for organics and radioactive contaminants include:

	Numeric Effluent Limit (NELs)	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 larger numbers of exceedences.
- 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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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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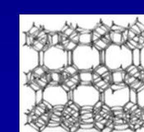
Example Media Types

- Sand – relatively inert (without modification), but effective for particulate removal
  - 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 those having a higher valence/charge state)



Zeogarden.com

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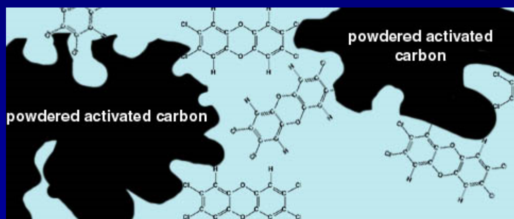
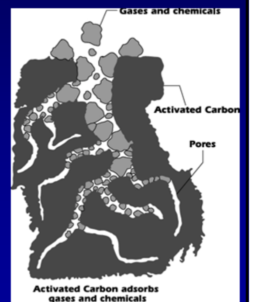
Example Media Types (continued)

- 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





Peakpureair.com

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

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Example Media Types (continued)

- 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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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

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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

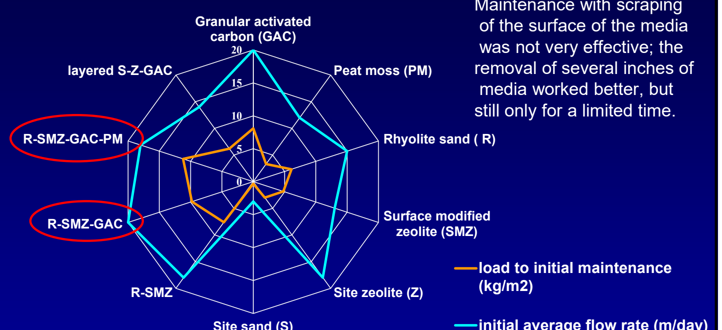
- Critical site constituents (possible periodic permit exceedences if untreated): cadmium, copper, lead, zinc, oil and grease, mercury, and TCDD (2,3,7,8-Tetrachlorodibenzo-p-Dioxin).
- Other constituents listed on permit (rarely, if ever, expected to exceed permit limits if untreated): pH, TDS, sulfate,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

Constituents Evaluated during Laboratory Media Tests (Cont.)

- 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).

Column test results: 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.

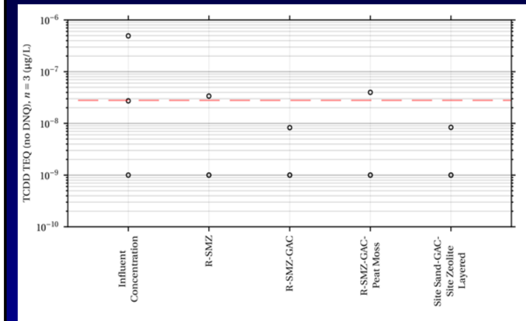


1. Site sand clogged first and had the lowest flow rate
2. Site zeolite and peat alone were next to clog
3. Biofiltration mixed media combination performed better than current site layered media combination

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	71
SSC	206 (50 to 400)	13.6	93
TSS (0.45 to 75 µm)	171 (50 to 310)	10.2	94

Dioxin Control Observations



2.8 X 10^{-8} µg/L permit limit

These samples were less than the detection limit

- The dioxin results indicate good control. However, few data are available due to the complexities and costs of the analyses.
- Two of the three effluent observations for each media were below the detection limit. The R-SMZ-GAC media 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 this media mixture, showing good removals to close to, or below, the extremely low site permit limit.

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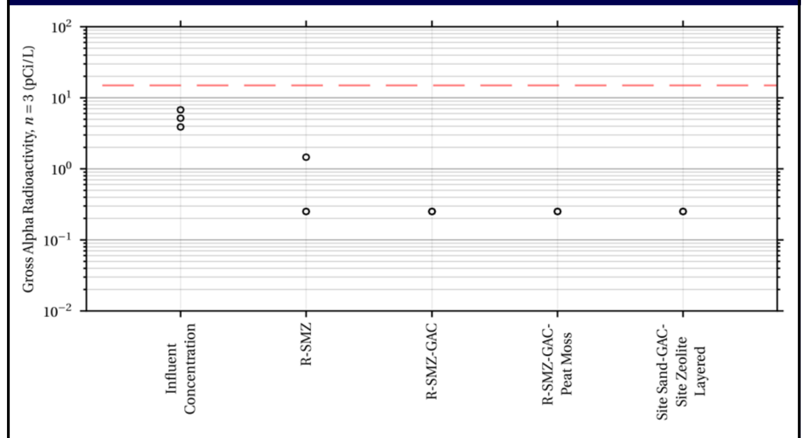
Gross Alpha Radioactivity Control Observations



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

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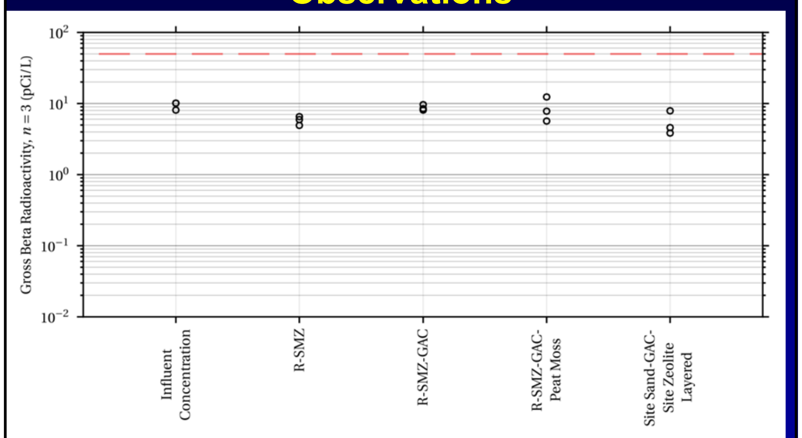
Gross Beta Radioactivity Control Observations



Gross beta and combined radium did not indicate any significant reductions with the media (all were below the numeric discharge limit)

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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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Breakthrough Capacity Compared to Clogging Period

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
Red: breakthrough before clogging

Treatability of Organics (example: Pesticides, PAHs)

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

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

Conclusions

- 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/yd^3), while the addition of either of the zeolites (at about $100/yd^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.

Conclusions, continued

- 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.

Acknowledgements

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