Biochar for Enhanced Trace Organic Contaminant Retention in Stormwater Biofilters

Bridget Ulrich, David Werner, Christopher Higgins

US Biochar Initiative Conference 2016

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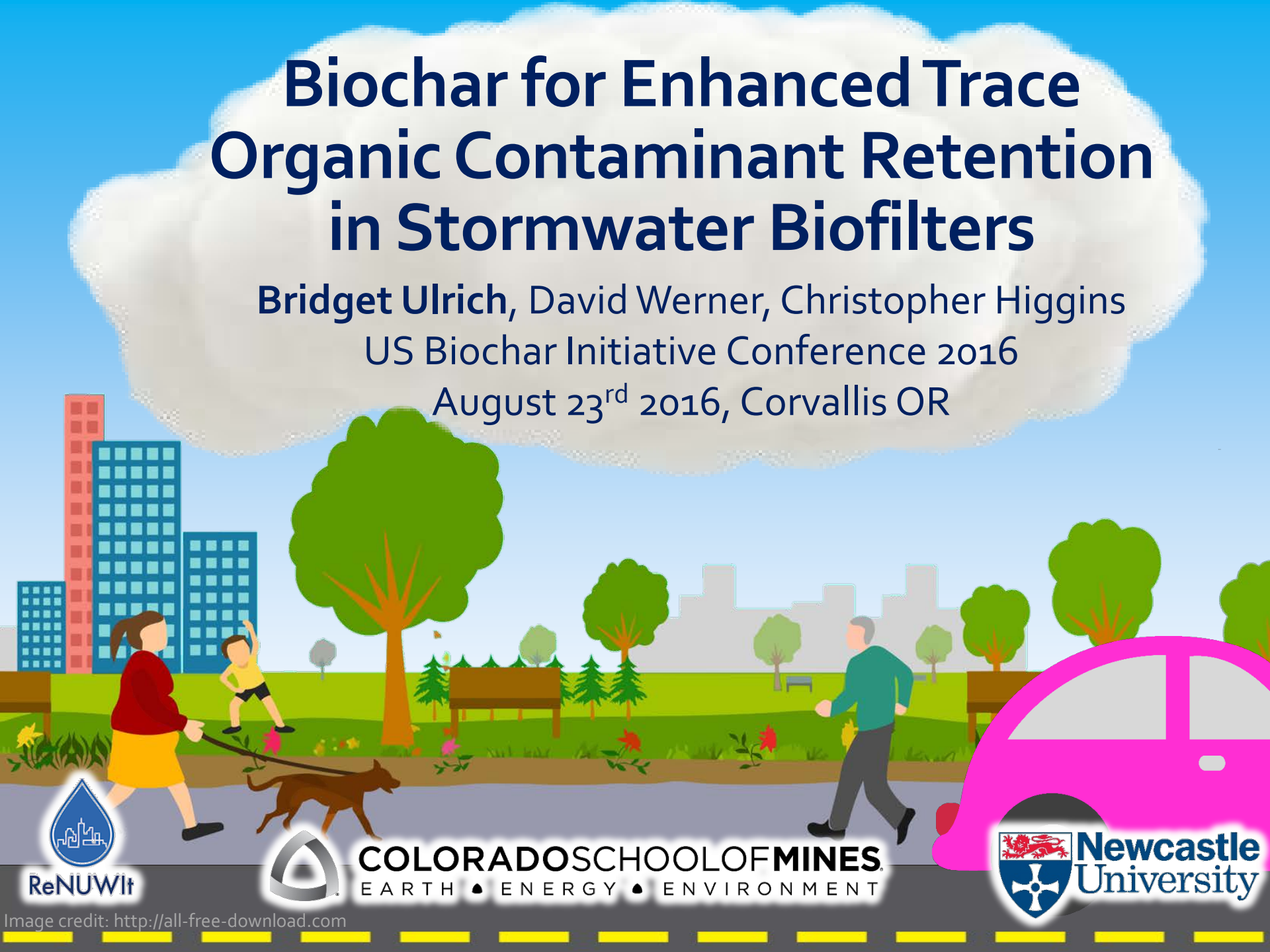

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Urban Sources of Trace Organic Contaminants

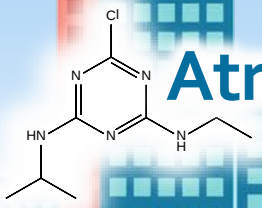
Construction Materials

Lawn Care

Atmospheric Deposition

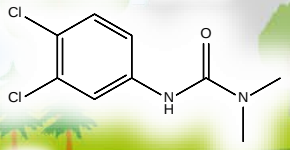
Pest Control

Automobile Fluids

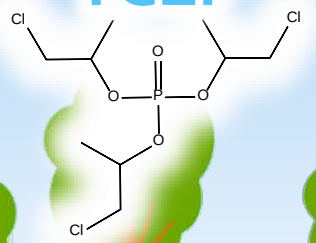


Atrazine

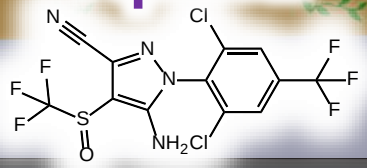
Diuron



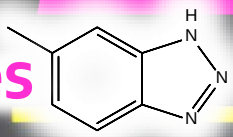
TCEP



Fipronil



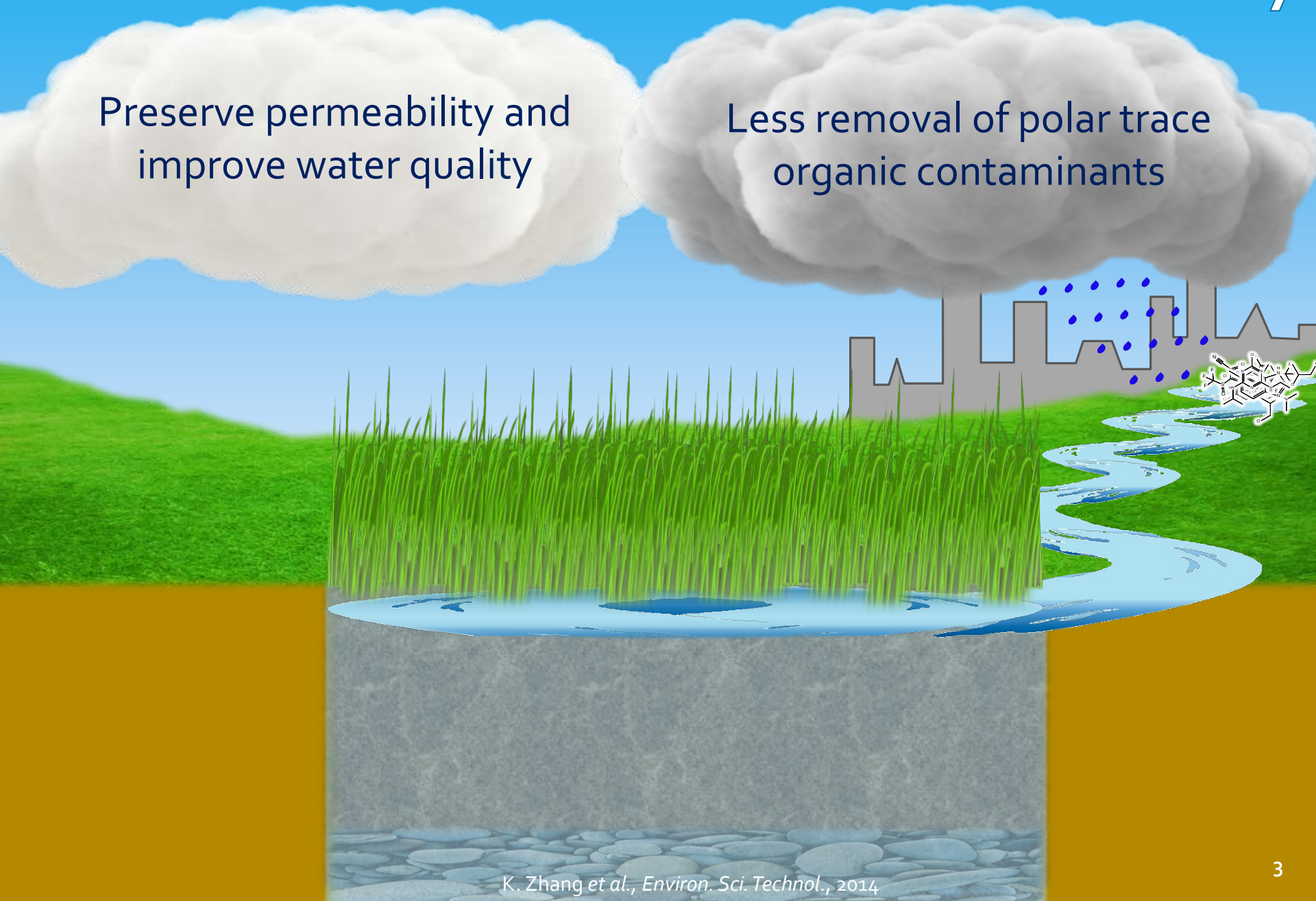
Benzotriazoles



Biofilters & Urban Stormwater Quality

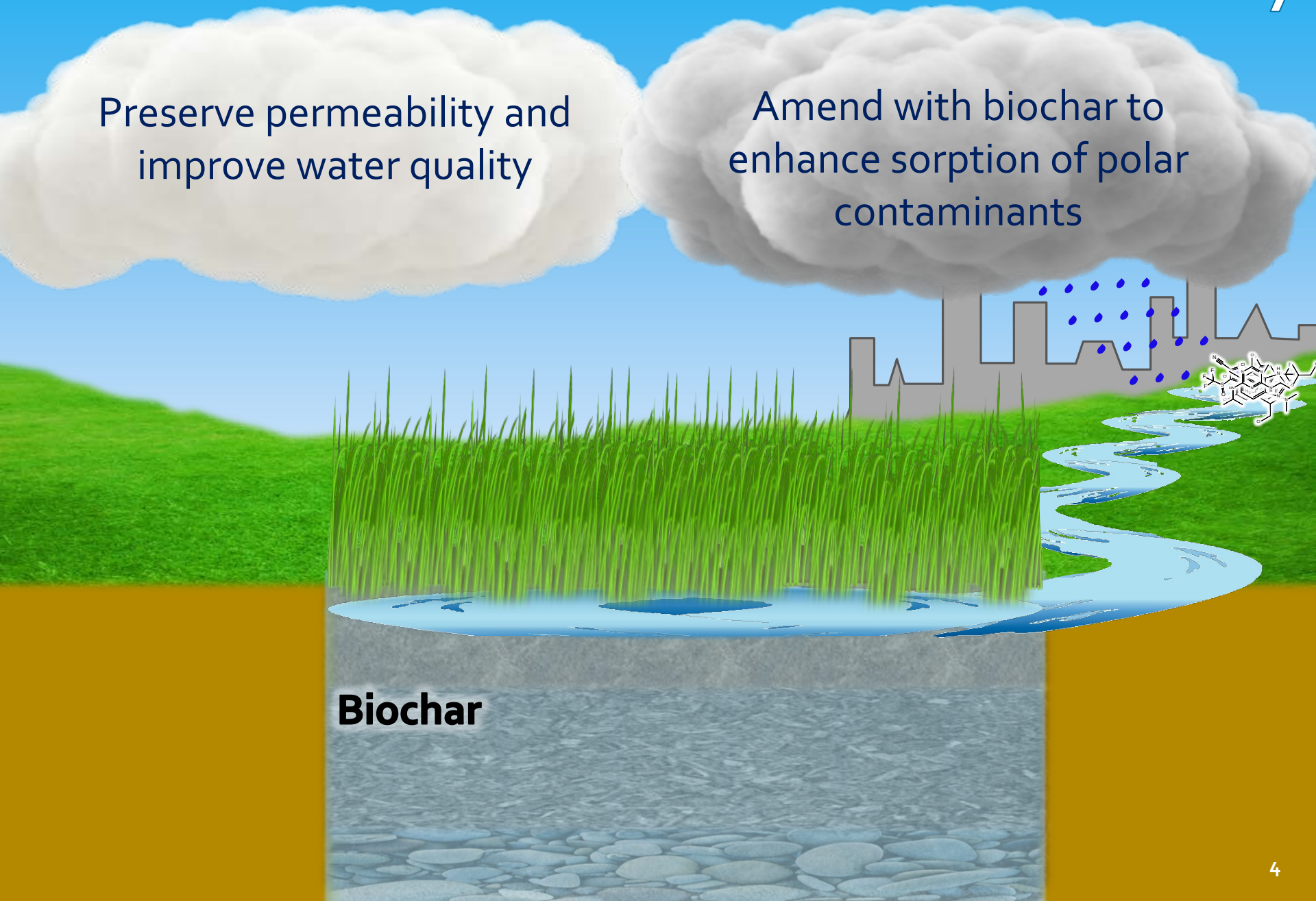
Preserve permeability and improve water quality

Less removal of polar trace organic contaminants



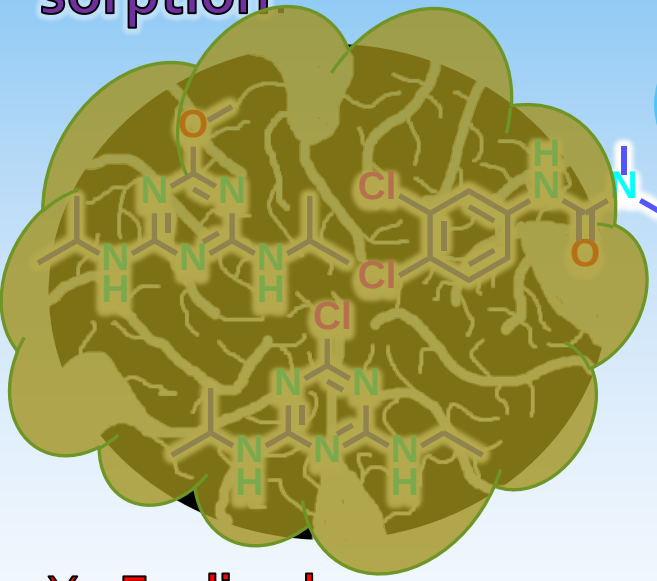
K. Zhang *et al.*, *Environ. Sci. Technol.*, 2014

Biofilters & Urban Stormwater Quality



Research Questions

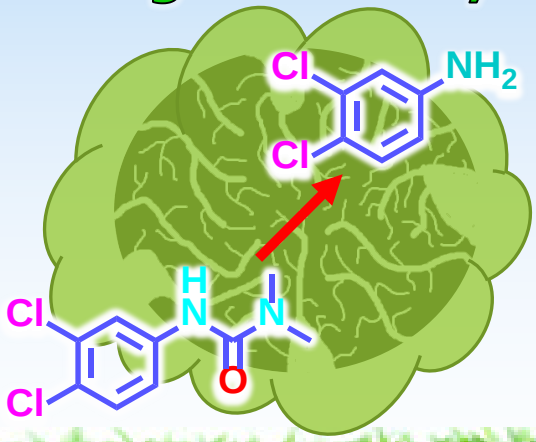
Question 1:
How long can contaminants be retained by **sorption**?



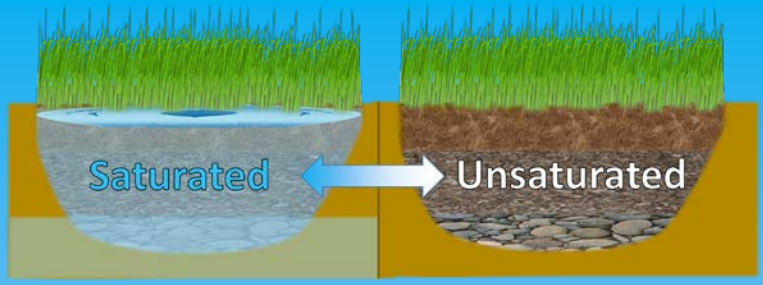
X **Fouling by dissolved organic carbon (DOC)?**

Question 2:
Can contaminant retention be maintained in presence of **biological activity?**

✓ **Biodegradation**
✓ **Sorption to biofilm**
X **Biological Fouling**



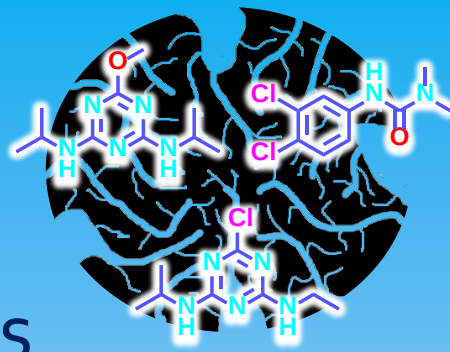
Question 3:
Can contaminant retention be maintained under **intermittent flow?**



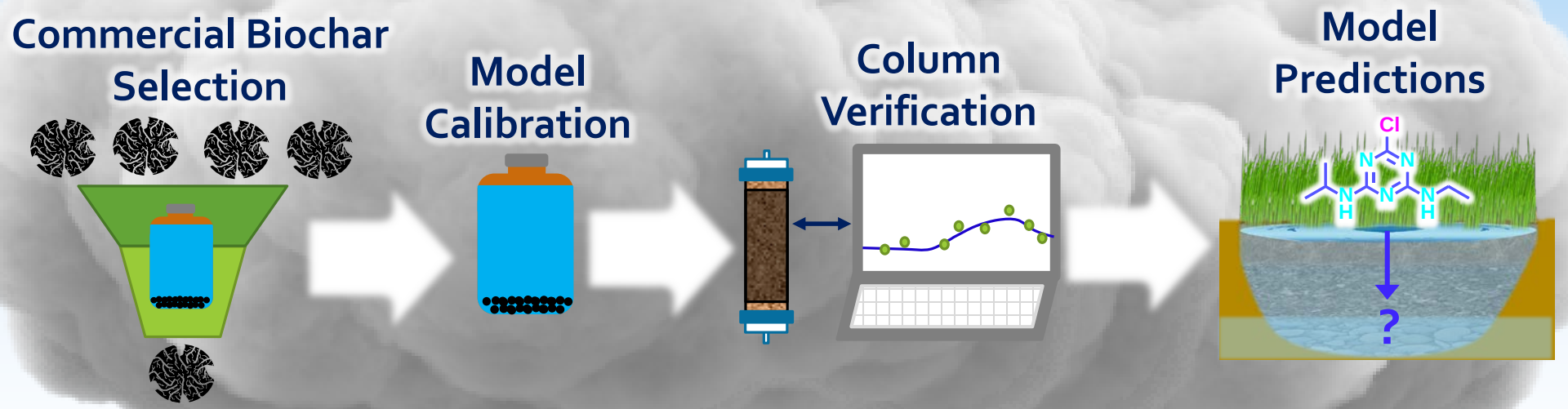
✓ **Stagnant periods**

X **Clogging, channeling**

Question 1: How long can contaminants be retained by sorption?



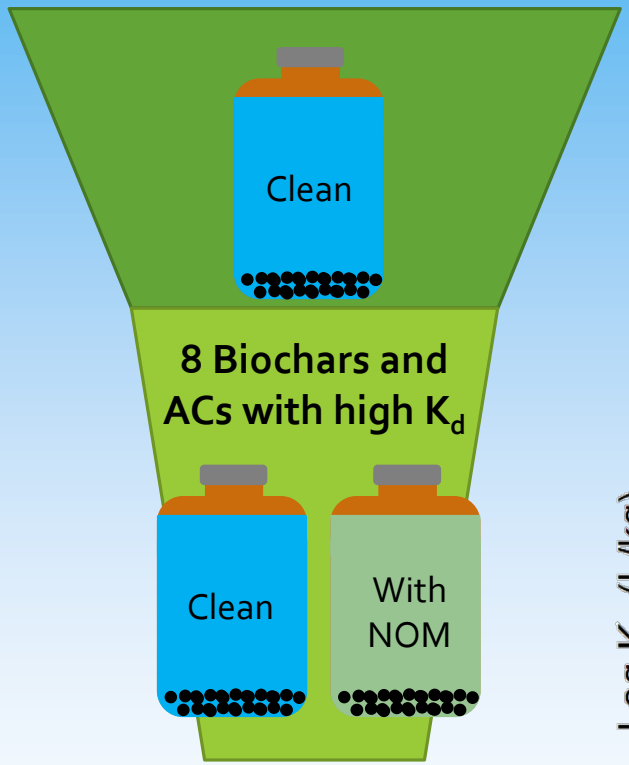
Approach: Predict breakthrough times with forward transport model accounting for intra-particle diffusion-limited sorption kinetics



B. Ulrich et al., *Environ. Sci. Technol.*, 2015, 49, 6222-6230

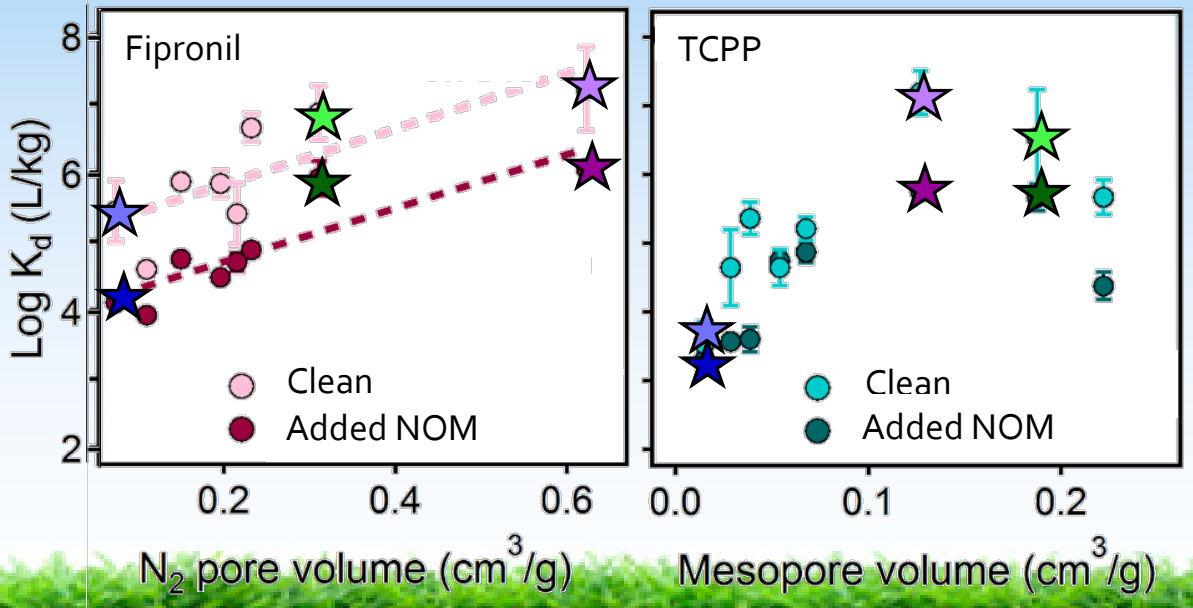
Screening Commercial Biochars

20 Commercial Biochars and ACs



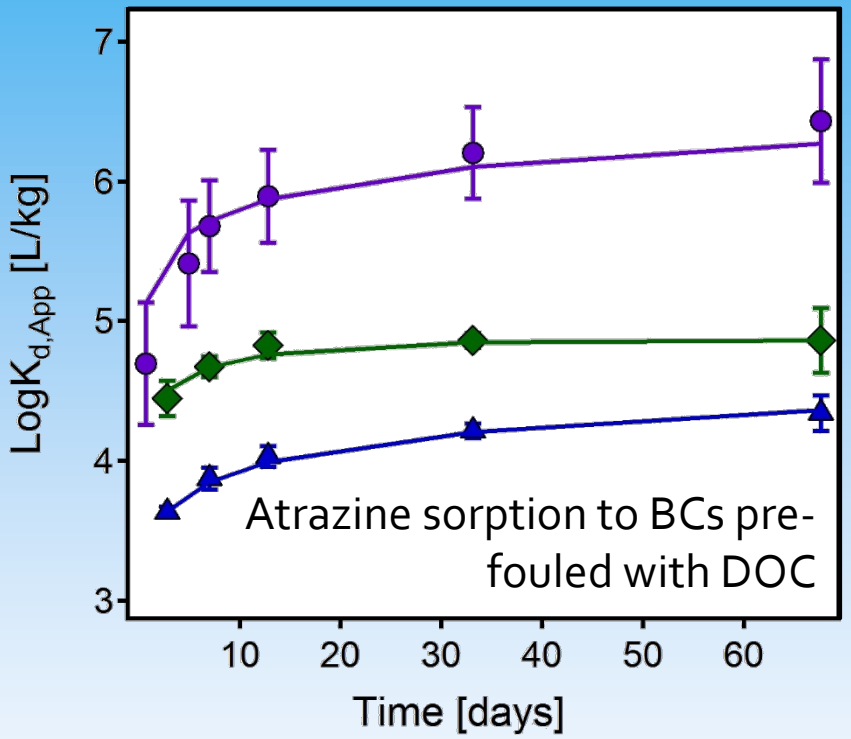
2 Biochars
1 AC as performance reference

Producer	Type	Process	Peak T (°C)	SA (m^2/g)
Calgon, PA	AC	-	-	997
Mountain Crest Gardens, CA	Biochar	Gasification	>1000	351
Aquacarb, CA	Regenerated AC	-	-	350
Sonoma Compost, CA	Biochar	Fast pyrolysis	>1000	330
Biochar Supreme, WA	Biochar	Flash pyrolysis	>1000	202
NREL, CO	Biochar	Gasification	800	178
Biochar Engineering Corp., CO	Biochar	Fast pyrolysis	700	176
Biochar Now, CO	Biochar	Slow pyrolysis	600	118

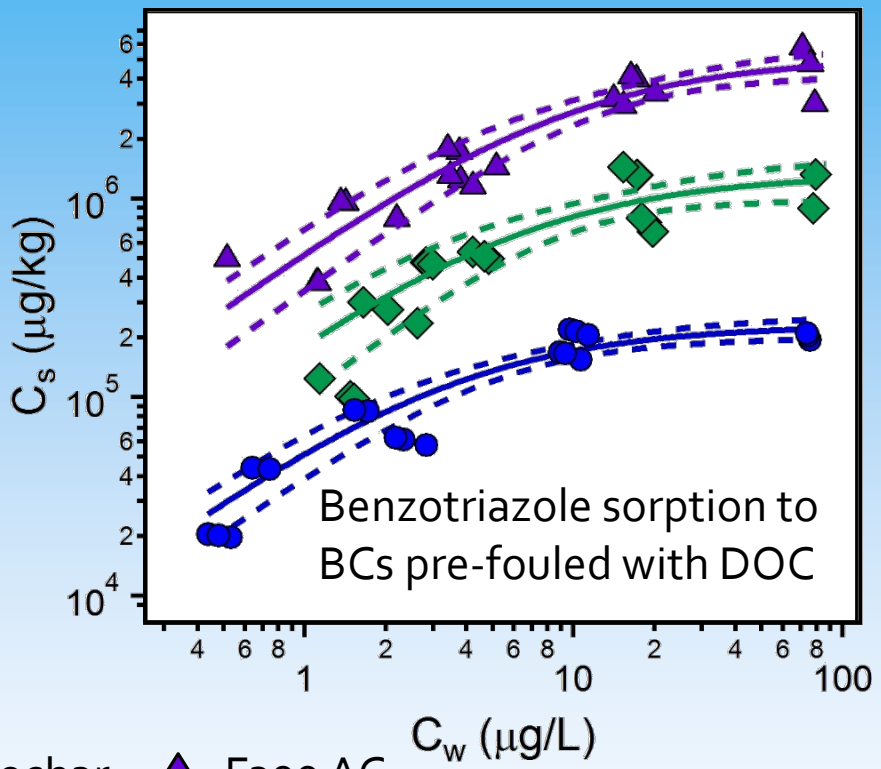


Model Calibration to Batch Results

1. Intraparticle Diffusion Kinetics



2. Equilibrium Sorption Capacity



Batch results: ◇ MCG Biochar ○ BN Biochar ▲ F300 AC

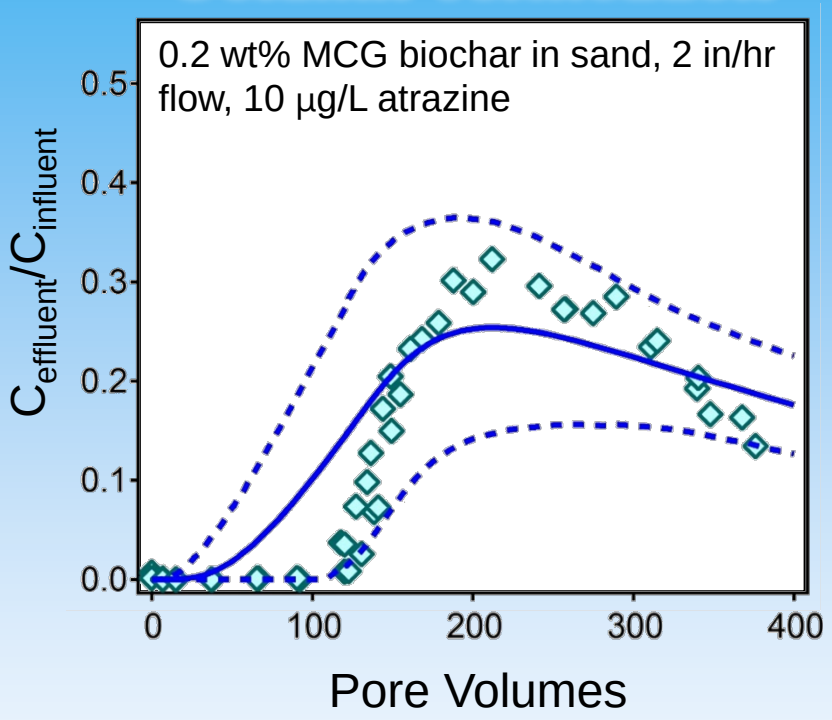
Kinetic equation: $$D_{app} = \frac{pD_w}{\tau[(1-p)\rho_s K_{d,Eq} + p]}$$

Langmuir Isotherm: $$C_s = \frac{C_{s,max} K_L C_w}{1 + K_L C_w}$$

B. Ulrich et al., *Environ. Sci. Technol.*, 2015, 49, 6222-6230

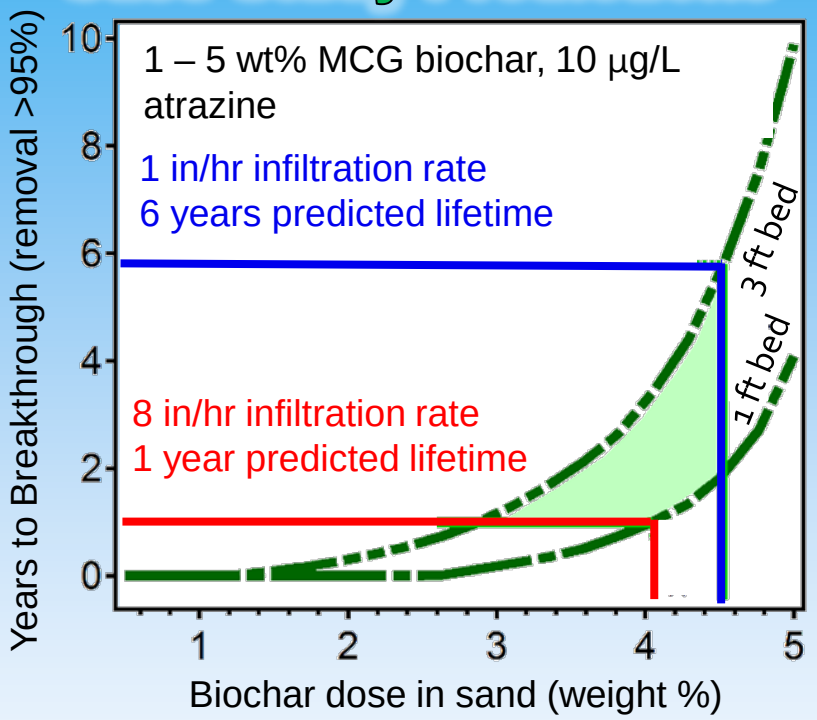
Model Verification and Predictions

Column Verification



- Compared results from pulsed column experiments (markers) to model predictions (solid line)
- Monte Carlo uncertainty analysis (dotted lines)

Case Study Predictions

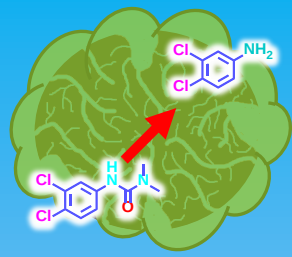


- Simulated as continuous input of 10 µg/L atrazine, converted runoff volume to years
  - Basin 1% of catchment area, receiving 17 in rain/yr, treating 50% of runoff

B. Ulrich et al., *Environ. Sci. Technol.*, 2015, 49, 6222-6230

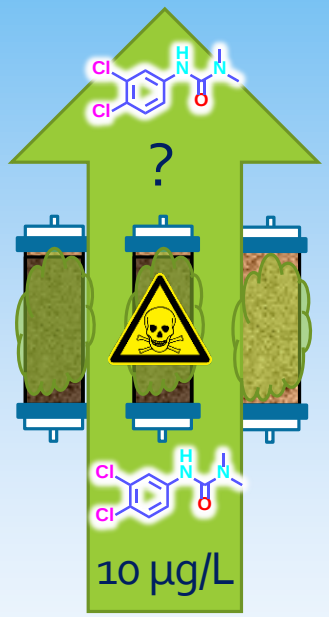
✓ **Sorption-controlled contaminant retention times on the order of years**

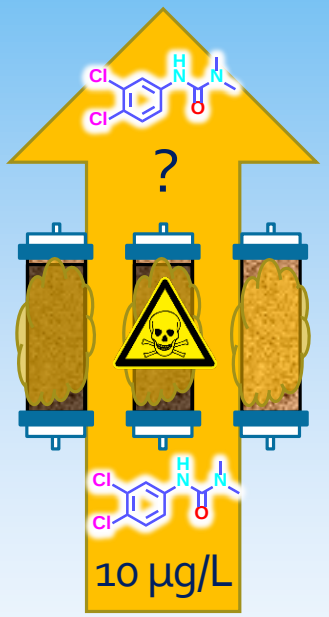
Question 2: Can contaminant retention be maintained in presence of biological activity?



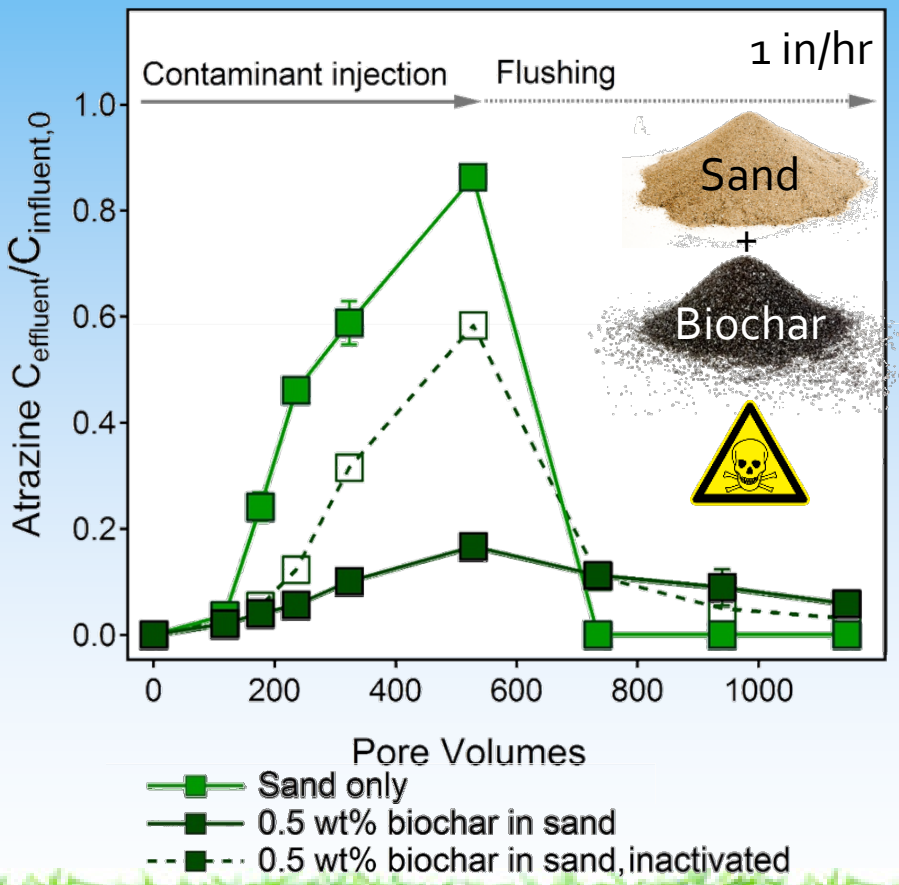
Approach: Biologically active column experiments

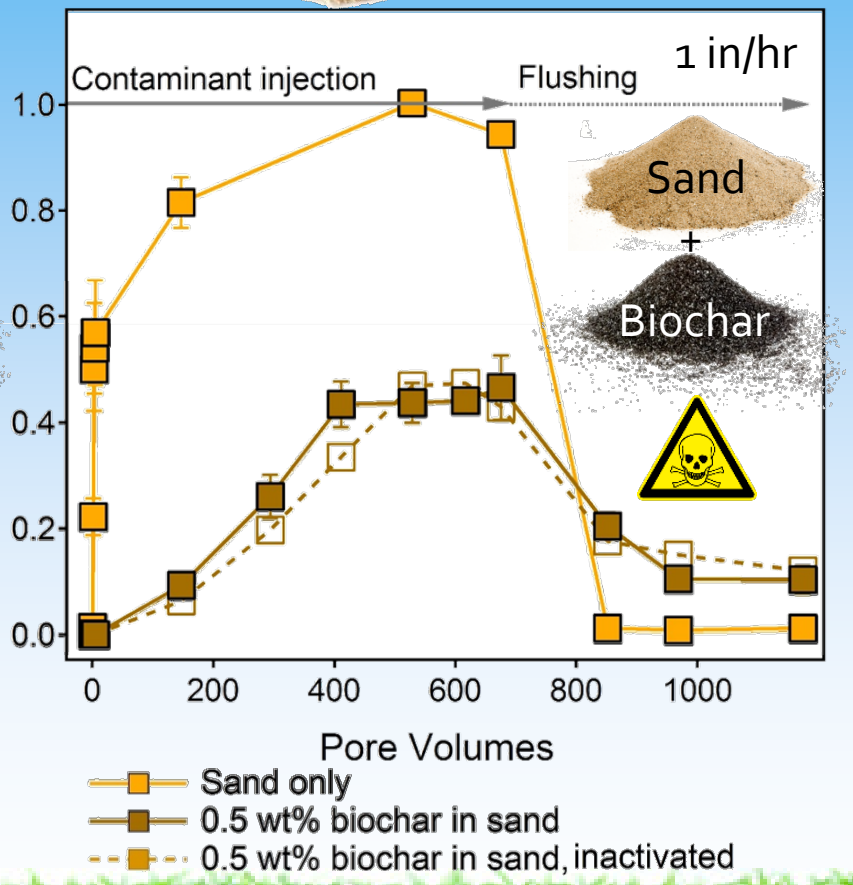
1. Cultivated microbial consortium from runoff with DOC
2. Seeded biofilms on columns (sand, sand + 0.5 wt% MCG-biochar)
3. Biologically inactivated controls
4. Injected with 10 µg/L contaminants at 1 in/hr
5. Flushed at 1 in/hr





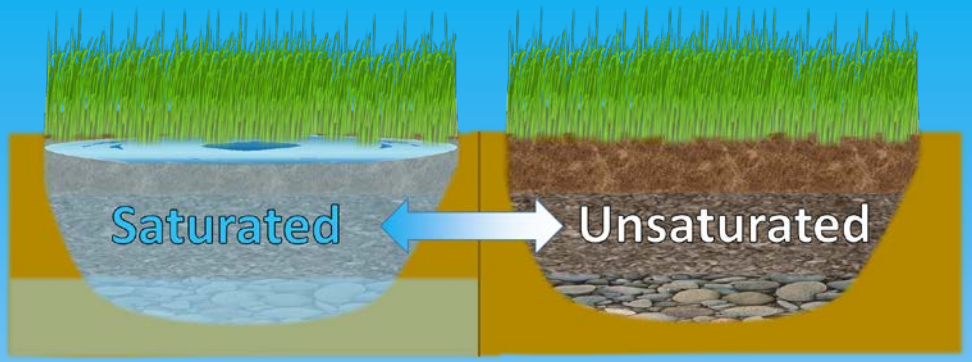
Biologically Aged Columns



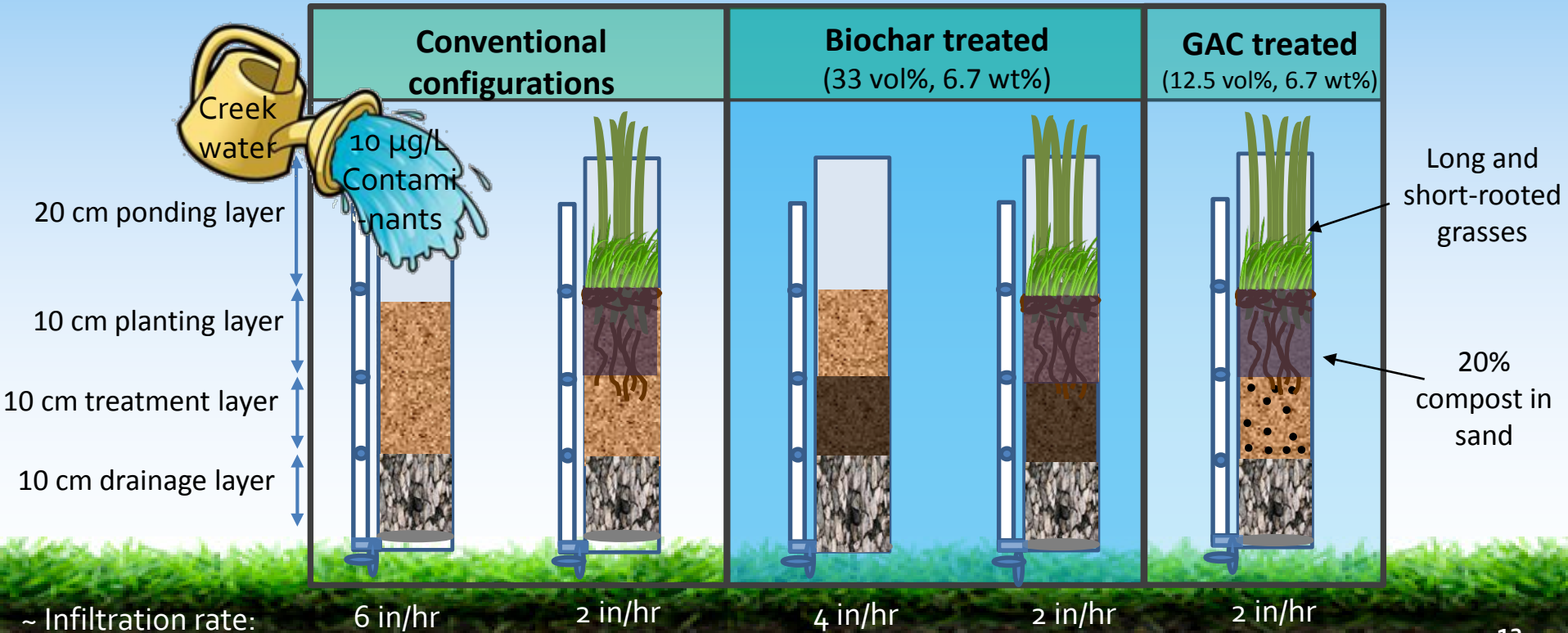


✓ **Biochar and biological activity enhance contaminant retention**

Question 3: Can contaminant retention be maintained under **intermittent flow**?



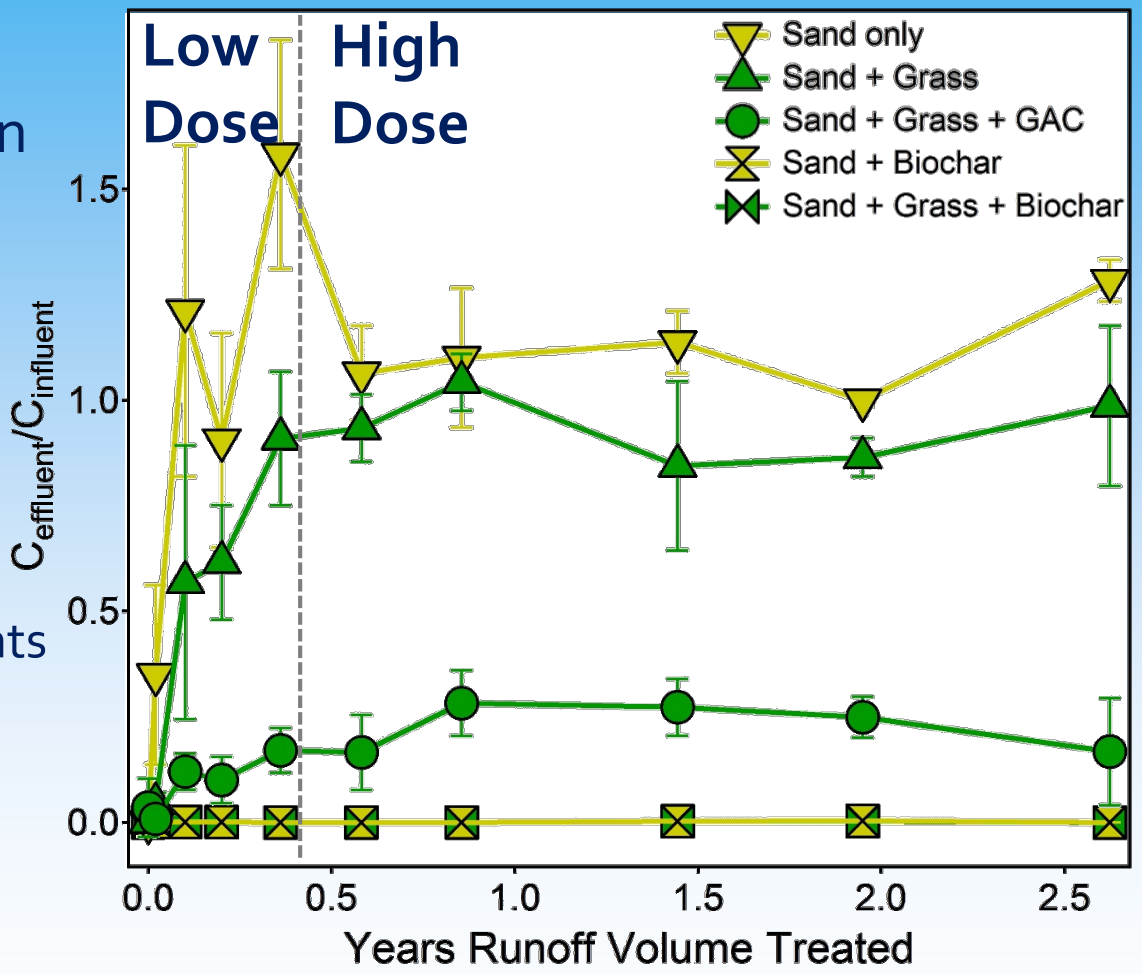
Approach: Intermittently dose pilot columns



Unsaturated Column Challenge Tests

Low Dose:
1 year, 15 min storm, simulated biweekly

- 2 L/dose
- 15 weeks
- 10 µg/L contaminants



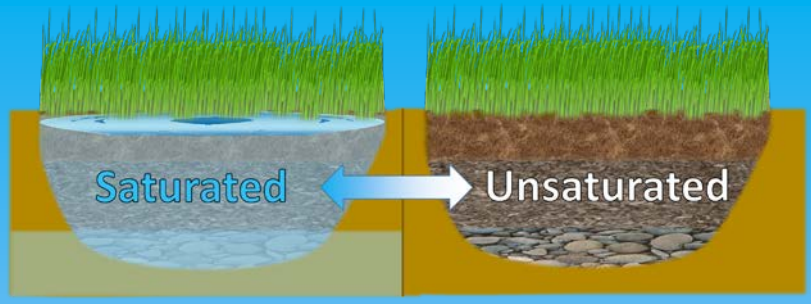
High Dose:
10 year, 1 hr storm, simulated 4x weekly

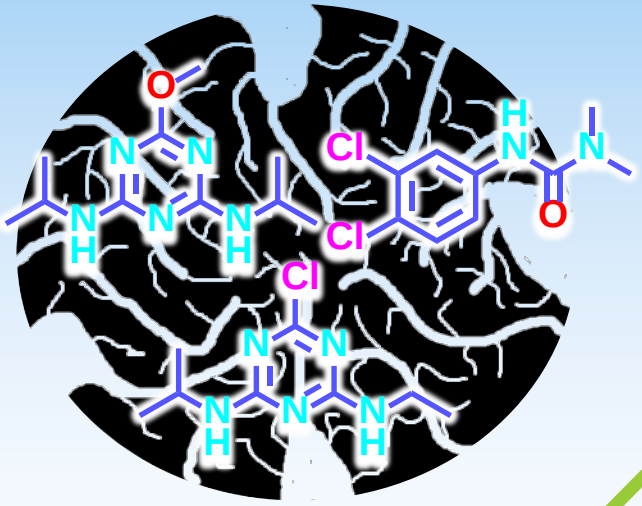
- 8.4 L/dose
- 7 weeks
- 10 µg/L contaminants

✓ Contaminant retention maintained under intermittent flow

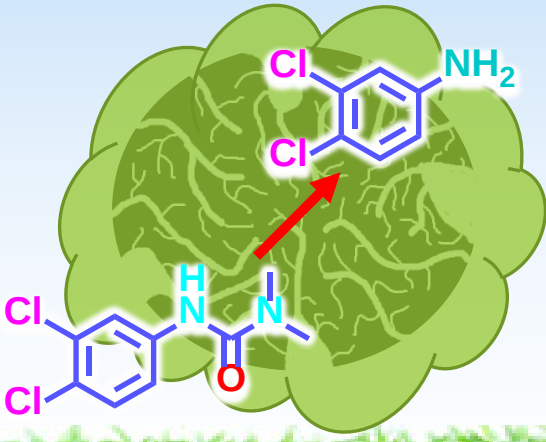
Conclusions

- ✓ **Sorption**-controlled contaminant retention times on the order of years
- ✓ Significant contaminant retention can be maintained under **intermittent flow**





- ✓ Biochar enhances retention in presence of **biological activity**
- ✓ Compost DOC enhances **biological** contaminant removal

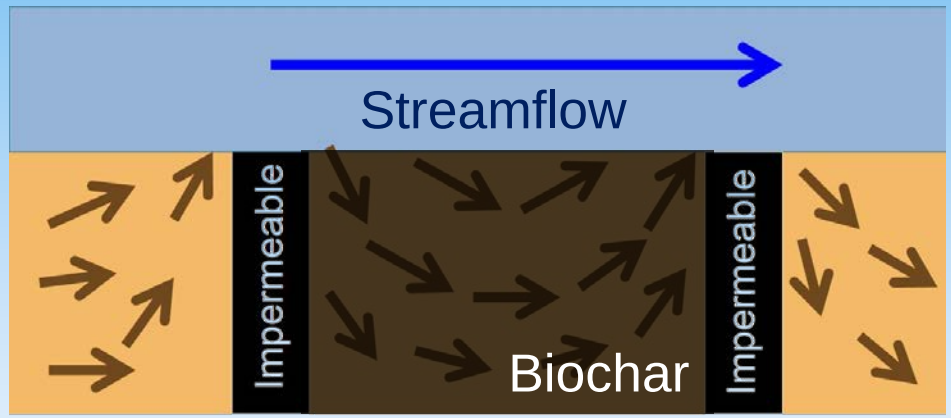


Ongoing Work

Cuernavaca Park

- Biochar-sand infiltration basin in initial design phases, in collaboration with the City of Denver
- Dry weather outfall (continuous discharge to South Platte River)

BEST: Biohydrochemical Enhancements for Streamwater Treatment



- Impermeable barriers to enhance exchange in hyporheic zone
- Biochar amendment for contaminant removal
- Potential agricultural applications

S. Herzog et al., *J. Environ. Eng.*, 2016, 142, 04015053

Acknowledgements

Principal Investigators

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Daniel McMahon

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Questions?

Biochar and AC Characteristics

		Mountain Crest Gardens (MCG-biochar)	Biochar Now (BN-Biochar)	Calgon F300 (F300-AC)
Process characteristics	Process Peak T Feedstock	Slow pyrolysis 600 °C Pine wood	Gasification 900 °C Pine wood	Steam activation - Bituminous coal
Physical characteristics	Surface area Solid density Porosity µPore volume	114 m^2/g 1.5 g/cm^3 0.60 v/v 0.045 cm^3/g	317 m^2/g 1.7 g/cm^3 0.56 v/v 0.110 cm^3/g	884 m^2/g 2.0 g/cm^3 0.70 v/v 0.417 cm^3/g
Elemental composition	C O C:O Ash	83.4% 9.9% 8.4 4.3%	78.2% 5.4% 14.5 15.7%	87.4% 4.6% 19.0 6.4%

Model Equations

Equilibrium transport

$$\frac{dC_{aq}}{dt} = f_{BC} E_{disp} \frac{\partial^2 C_{aq}}{\partial x^2} - f_{BC} u_x \frac{\partial C_{aq}}{\partial x}$$

$$f_{BC} = \frac{1}{\left[1 + \frac{1-\theta_{aq}}{\theta_{aq}}(1-p_{BC})(d_{BC}K_d + p_{BC})\right]}$$

First order kinetic limitations

$$\frac{dC_{aq}}{dt} = E_{disp} \frac{\partial^2 C_{aq}}{\partial x^2} - u_x \frac{\partial C_{aq}}{\partial x} - \frac{\beta}{\theta_{aq}}\left[C_{aq} - \frac{C_{BC}}{K_d}\right]$$

Diffusion limitations

$$\frac{dC_{aq}}{dt} = E_{disp} \frac{\partial^2 C_{aq}}{\partial x^2} - u_x \frac{\partial C_{aq}}{\partial x} - \frac{1-\theta_{aq}}{\theta_{aq}} \frac{d}{dt}\left[3\int_0^R \left(\frac{r}{R}\right)^2 S dr\right]$$

$$\frac{\partial S}{\partial t} = \frac{D_{app}}{R^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial S}{\partial r}\right)$$

Linear

$$D_{app} = \frac{D_{aq} p_{BC}}{\tau[(1-p_{BC})d_{BC}K_d + p_{BC}]}$$

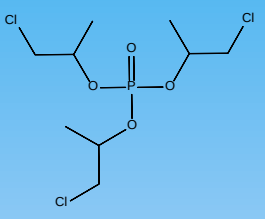
Langmuir

$$D_{app} = \frac{D_{aq} p_{BC}}{\tau\left[(1-p_{BC})d_{BC}\left(\frac{K_l C_{s,max}}{1+K_l C_{aq}}\right) + p_{BC}\right]}$$

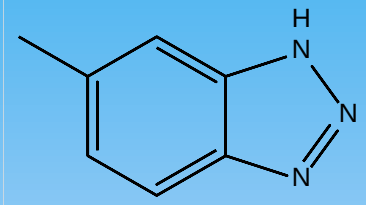
D. Werner et al, *J. Contamin. Hydrol.*, 2012 Wu and Gschwend, *Wat. Resour. Res.*, 1988

Unsaturated Column Challenge Tests

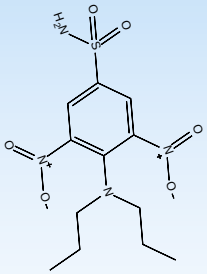
TCEP



Methylbenzotriazole



Oryzalin



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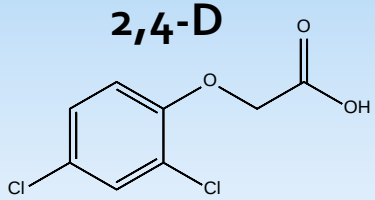

✓ Contaminant retention maintained under intermittent flow