# Modeling Organic Contaminant Removal in Stormwater Runoff by Biochar-Amended Rapid-Flow Filters

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## Highlights

- 1-d advection dispersion with intraparticle diffusion-limited sorption contaminant transport model predicts TrOCs removal in stormwater runoff treated by biochar-amended filters.
- A transport model was fit to laboratory column data by optimizing contaminant sorption parameters and tortuosity, and validated at higher flow rates.
- The predictive transport model illustrates effects of filter carbon content, influent concentration, and filter flow rate on contaminant breakthrough and filter lifetime.

## Introduction

Stormwater runoff is a well-documented carrier of urban contaminants into receiving water bodies, potentially compromising aquatic and human health (Spahr et al., 2020). Recently, stormwater runoff has received attention as a potential source of drinking water supply in drought-prone areas through stormwater capture and recharge (Luthy et al., 2019). However, it is important that captured and recharged urban stormwater does not inadvertently contaminate aquifers. A diverse group of contaminants are carried by urban stormwater runoff in both the particulate-bound and dissolved phase, including trace organic compounds (TrOCs) such as pesticides, herbicides, and corrosion inhibitors among many others. Unfortunately, historical and current stormwater control measures are generally poorly-suited for removing dissolved TrOCs.

Previous work has investigated amending stormwater control measures with biochar and other inexpensive, environmentally-friendly sorbents to better target dissolved contaminants. However, recent studies have been limited in scope and have investigated niche materials that may be difficult to scale up. This paper is part of a larger study that provides a scalable proof-of-concept for a rapid-flow engineered media filter that is capable of effectively treating stormwater at face velocities as high as 60 cm/hr with a wide suite of co-contaminants present. The goal of this paper is to better understand and model TrOCs transport in biochar-amended filters operated under high-flow conditions and in the presence of many co-contaminants. This paper demonstrates the use of an intraparticle diffusion-limited sorption model to accurately predict experimental results under various conditions. These findings are intended to aid stormwater practitioners in designing and sizing stormwater control measures to adequately remove dissolved TrOCs from stormwater runoff.

## Methodology

**Column Experiments**

A series of large (3-inch, 4-ft) column experiments were conducted in the laboratory to assess various engineered media mixtures including biochar (Biochar Supreme, WA) using a synthetic stormwater representative of the Naval Weapons Station in Seal Beach, CA. Catch basin material from NWSSB, straw-derived dissolved organic carbon, and salts were blended to achieve a consistent synthetic stormwater matrix for use in long-term tests. A suite of contaminants containing metals, hydrophobic and hydrophilic TrOCs, and PFAS were spiked and their removal was assessed. Column experiments were conducted in a down-flow gravity-driven configuration at face velocities of 20, 40, and 60 cm/hr. Samples were taken periodically to assess contaminant transport and removal. Samples ports spaced at 25% and 50 % along the 60cm engineered media bed provided data on the intra-bed contaminant transport.

**Contaminant Transport Modeling**

Results from the column experiments were fit to a 1-d advection dispersion model with intraparticle diffusion-limited sorption (equation 1). This model assumes that the sorption is kinetically limited and a function of the intraparticle diffusion of the contaminant into the biochar grain (equation 2). The apparent diffusivity in biochar pores is represented by sorption-retarded diffusion and tortuosity (equation 3). Sorption is described using the Freundlich isotherm.

$$\frac{\partial C_{aq}}{\partial t} = -u_x \frac{\partial C_{aq}}{\partial x} + E_{disp} \frac{\partial^2 C_{aq}}{\partial x^2} - \frac{\theta_{bc}}{\theta_{aq}} \frac{d}{dt}\left[3 \int_0^1 y^2 S dy\right] \qquad (1) \qquad \text{(Werner et al., 2012)}$$

$$\frac{\partial S(r)}{\partial t} = \frac{D_{app}}{R^2} \frac{\partial}{\partial r}\left(r^2, \frac{\partial S(r)}{\partial r}\right) \qquad (2) \qquad \text{(Werner et al., 2012)}$$

$$D_{app} = \frac{D_w p_{aq}}{(d_s K_f N C_{aq}^{N-1} + p_{aq})\tau} \qquad (3) \qquad \text{(Werner et al., 2012)}$$

This model has been used previously to predict contaminant sorption in biochar-amended filter (Ashoori et al., 2019; Ulrich et al., 2015). In this study, we further advanced the model to incorporate input data fluctuation (e.g. real-time flow and influent concentration), so to provide more accurate predictions of contaminant transport.

**Parameter Fitting**

The transport model was fit to data from the column experiments by optimizing Freundlich sorption parameters and tortuosity. The parameters were fit to data from the 25% port from the 20 cm/hr experiment and validated by predicting contaminant breakthrough at the 50% and effluent for the 20 cm/hr and at each sampling location for the 40 and 60 cm/hr experiments (Figure 1). The sorption parameters and tortuosity were then used for predictive modeling in which the filter biochar content, flow rate, and influent concentration were varied.

# Results and discussion

The model fitting generated sorption parameters and tortuosity values that produced accurate predictions of contaminant breakthrough in the model validation of the 50% port and effluent in the 20 cm/hr experiment and at each sampling location in the 40 and 60 cm/hr experiments (Figure 1). Predictive modeling shows that increasing the influent loading and decreasing the biochar content will both substantially decrease filter lifetime, though by differing magnitudes (Figure 2). Additionally, the incorporation of real-time influent concentration and flow rate into the model allow for predicting filter performance across more realistic conditions with fluctuations in contaminant loading and filter throughput. These fluctuations are likely to influence filter performance and lifetime. This modification will allow for modeling biochar-amended filter performance during real storm events for which contaminant loading and flow rate over time are known and for capturing the impact of specific storm phenomena (e.g. first-flush) on filter performance.

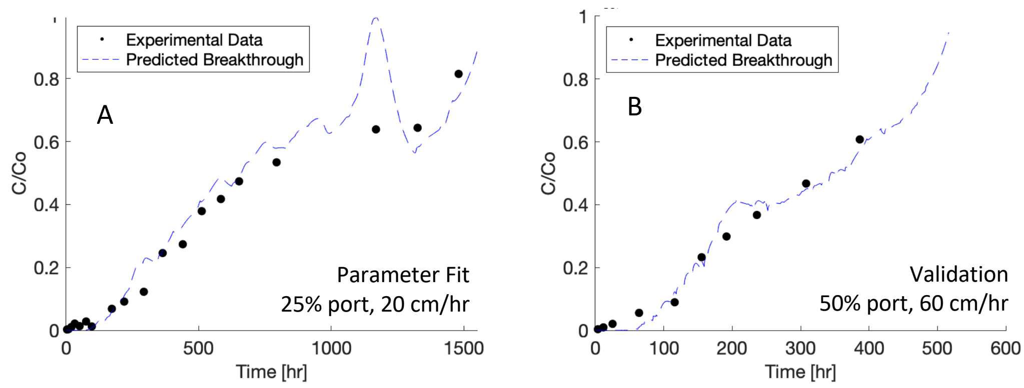


**Figure 1. (A)** Model fit to breakthrough data for Atrazine at the 25% sample port for the 20cm/hr experiment. **(B)** Model prediction validation for Atrazine at the 50% sample port for the 60 cm/hr experiment.

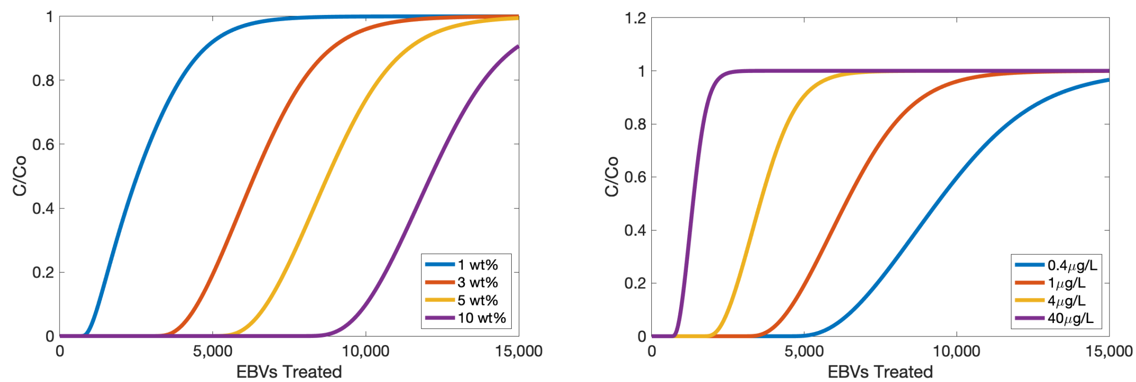


**Figure 2.** Predicted Atrazine breakthrough in 1-meter biochar-amended columns operated at 20 cm/hr with (unless specified otherwise) 3% wt biochar and an influent concentration of 1 µg/L.

## Conclusions and future work

The culmination of this work will be the production of filter performance curves that estimate lifetime based on design considerations and site conditions. These tools are envisioned to help stormwater practitioners better design and size stormwater filters. Future work will assess the accuracy of the transport model to predict breakthrough under dynamic conditions and at the field scale. Key findings:

- The transport model accurately predicts TrOCs contaminant transport in laboratory column experiments across various elevated flow rates with a suite of co-contaminants.
- Flow rate, influent concentration, and carbon content affect filter lifetime to differing degrees.

## References

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