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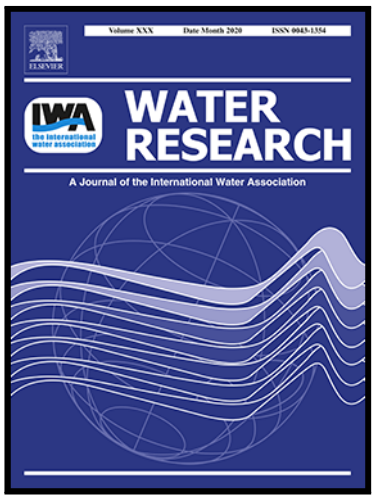

Combined UV/H_2O_2 and Biochar Processes for Enhanced Removal of Contaminants of Emerging Concern in Dry Wells

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HIGHLIGHT:

- Existing dry wells with bioswales are ineffective for hydrophilic CECs
- UV in combination with biochar efficiently removes hydrophilic CECs in runoff
- Estimated field lifespan in Los Angeles is more than four years with 10 wt% biochar
- The insecticide imidacloprid was the limiting contaminant for the system's lifespan
- The UV/biochar design supports stormwater reuse via dry well recharge

Combined UV/H_2O_2 and Biochar Processes for Enhanced Removal of Contaminants of Emerging Concern in Dry Wells

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ABSTRACT

Dry wells are neighborhood-scale stormwater infiltration systems increasingly used in drought-prone areas for stormwater capture and groundwater recharge. These systems bypass the low permeability surface soil to maximize infiltration rates. However, hydrophilic contaminants of emerging concern (CECs) in urban runoff pose potential groundwater contamination risks. Field monitoring in this study confirmed the presence of CECs and the inability of current dry wells to remove these compounds. To address this, we explored stormwater treatment systems that: (1) can be easily operated in dry wells; (2) effectively remove hydrophilic CECs under realistic infiltration rates; and (3) offer multi-year field lifespan. Batch isotherm and kinetic studies were conducted on a large-grain biochar (d_{50} = 2.24 mm) to assess removal efficiency for seven hydrophilic CECs ($\log K_{ow} \leq 4$). Two column experiments evaluated biochar filters (5 wt%) with and without UV/H_2O_2 pre-treatment under continuous high-throughput conditions. Results showed that biochar filters effectively removed five of seven CECs, with reduced efficiency for anionic compounds. The UV/H_2O_2 process with approximately 1500 mJ/cm^2 UV dose degraded all CECs by more than 50%, except dicamba, with direct photolysis as the dominant mechanism due to strong hydroxyl radical scavenging by dissolved organic carbon (DOC). Combining UV and biochar reduced CEC breakthrough concentration by 4 – 92%. Based on the results, a contaminant transport model was calibrated and used to estimate the system lifespan in dry wells in Los Angeles. Findings showed that the insecticide, imidacloprid, is the limiting contaminant for the system's lifespan. Without UV/H_2O_2 pre-treatment, the system could last about four years with 10 wt% biochar in the filter. With pre-treatment, the lifespan will

be determined by other operational factors rather than CEC removal. This study developed effective stormwater treatment systems for dry wells, supporting future local stormwater capture projects while safeguarding groundwater quality.

Keywords: Stormwater Capture, Groundwater Recharge, Stormwater Treatment, Biochar, Advanced Oxidation Process, Field Lifespan

1. Introduction

Drought is a recurring issue in California, highlighting the need for sustainable water supplies through stormwater capture for aquifer recharge (Luthy et al., 2019; Natural Resources Defense Council, 2014). One increasingly adopted solution is dry wells (Ashoor et al., 2016; Graf, 2015), which are vadose zone infiltration wells that are deeper than their widest surface dimension (United States Environmental Protection Agency, 2008). Dry wells bypass the relatively low permeability surface soil and transport urban runoff into the vadose zone at high flow rates. Dry wells are especially promising because of their high infiltration capacity, low costs, and small footprint (California Water Resources Control Board, 2020; Los Angeles Department of Water and Power, 2015; Sasidharan et al., 2021). Figure S1 illustrates a typical dry well design in Los Angeles, where stormwater passes through a vegetated swale, detained in a primary chamber, and infiltrated from a secondary chamber. This process significantly reduces suspended solids and particle-associated contaminants, but is less effective for hydrophilic contaminants of emerging concern (CECs, log K_{ow} values ≤ 4), which are commonly detected in urban runoff (Edwards et al., 2022; Mutzner et al., 2023; Okaikue-Woodi et al., 2020). As a result, concerns have been raised about the potential groundwater contamination through stormwater infiltration by dry wells.

Engineered media filters are widely studied for removing hydrophilic CECs from stormwater. Tested materials include woodchips, straw, compost, and carbonaceous media (Ashoori et al., 2019; Ulrich et al., 2017). Woodchips and straw are generally ineffective for hydrophilic CEC removal unless they are highly biodegradable (Ashoori et al., 2019; Tseng et al., 2020). Compost, while it aids in CEC degradation, poses challenges for field maintenance (Portmann et al., 2022; Ulrich et al., 2017). Carbonaceous materials generally show high adsorption capacity for hydrophilic CECs, with biochar being a cost-effective, energy-efficient, and low-emission option (Alhashimi and Aktas, 2017; Pritchard et al., 2022). Past studies on biochar mainly focused on powdered and fine-grain biochar filters (i.e., maximum diameter < 1 mm, Table S1) because of their high exterior surface area (Portmann et al., 2022; Ulrich et al., 2015), but these filters are prone to clogging and reduced hydraulic conductivity, limiting their field applicability in dry wells. Larger grain biochar may offer better hydraulic conductivity, but its effectiveness in dry wells, where contact time is minimal (less than 5 minutes for the highest 10% flow rate), remains unknown due to the kinetic-limited removal of hydrophilic CECs (Pritchard et al., 2023; Pritchard et al., 2022).

Another technique that has potential for CEC degradation is advanced oxidation processes (AOPs) (Kanakaraju et al., 2018). Ultraviolet light with hydrogen peroxide (UV/H_2O_2) has been adopted for the removal of CECs in wastewater treatment and water reuse (Chuang et al., 2017; Huang et al., 2020). A recent study conducted by Duan and Sedlak tested a modular UV/H_2O_2 device for possible decentralized stormwater treatment (Duan and Sedlak, 2021). They reported that when the UV dose was around 1500 mJ/cm^2, the surrogate compound, carbamazepine (log K_{ow} = 2.45), was removed by more than 90% in stormwater containing 5 mg C/L dissolved organic carbon (DOC) prepared with a synthetic humic acid sodium salt (Duan and Sedlak,

2021). However, this technique has not been tested for the abatement of hydrophilic CECs that are more commonly detected in urban runoff or with stormwater having a more representative level or source of DOC (i.e., ~ 10 mg C/L, DOC from natural sources) (Kalev and Toor, 2020).

Various contaminant transport models have been previously fit to laboratory experimental results and used to estimate biochar performance in the field (Ulrich et al., 2015; Werner et al., 2012). One such model that has shown promise is a 1-d advection dispersion model with sorption-retarded intraparticle pore diffusion, coupled with Freundlich isotherm parameters (Portmann et al., 2022; Pritchard et al., 2023). Intraparticle tortuosity and Freundlich sorption parameters have been estimated either from observed batch isotherms or by fitting column breakthrough curves (Portmann et al., 2022; Pritchard et al., 2023; Spahr et al., 2022). This modeling approach has been validated for various experimental flow rates. Pritchard et al. recently used this model to predict performance in biochar filters (0.4-1.68mm, d_{50}=0.8mm) operated at 40 and 60 cm/hr using parameters generated at 20 cm/hr (Pritchard et al., 2024). However, it has not yet been tested with larger media, where a greater proportion of surface area is internal, and accurate simulation of solute intraparticle diffusion is more critical. Additionally, it remains uncertain whether a model calibrated under specific inflow conditions can accurately predict the performance of biochar when influent concentrations differ significantly, such as when UV/H_2O_2 is utilized as a pretreatment step.

This study investigates retrofitting drywells with AOP pre-treatment and biochar filter to remove hydrophilic CECs in urban runoff. First, a field monitoring program was conducted to understand the current performance of dry wells. Next, a large-grain Douglas fir-sourced biochar (1.7 – 5.6 mm, d_{50} = 2.24 mm) was tested in isotherm and kinetic batch studies, and in continuous flow gravity-driven column studies with and without UV/H_2O_2 pre-treatment.

Finally, a forward stepping predictive transport model was calibrated and applied to estimate the field lifespan of the proposed systems. This study is the first to investigate the performance of dry wells in removing hydrophilic CECs and to combine UV/AOP with carbon adsorption, enabling the removal of a wider range of CECs. Additionally, this work demonstrates the novel application of a previously developed contaminant transport model in large-grain biochar filters across varied influent concentrations. Results from this study inform the adoption of treatment systems in dry wells to safely recharge stormwater without risking groundwater quality.

2. Material and Methods

2.1 Field Monitoring

Stormwater samples were collected from two rainfall events (Table S2) in the 2022-23 wet season at dry well demonstration sites along Laurel Canyon Boulevard, Los Angeles. During each event, samples were taken from three dry well sites, and at each site, grab samples were collected at three locations (inflow, primary chamber, outflow) to illustrate the variation of stormwater quality from curb to dry well infiltration chambers (Figure S2). Comparing inflow and outflow water quality provides insight into the contaminant removal efficiency of vegetated swales. Because there is no further water treatment between the primary and secondary chamber in a dry well, stormwater quality in the primary chamber represents the quality of water percolated into the groundwater. At each location, 1 L samples were collected in pre-cleaned amber glass bottles with 2 mL of 6 N hydrogen chloride as preservative (EPA Method 525.2) for CEC analysis, and additional 40 mL samples was collected during the first rainfall event for DOC analysis. Details on CEC extraction from field samples are provided in the supporting information (SI, S.3.2) and analytical methods are described below in section 2.6. Samples were stored at 4 °C for under 24 hours prior to analysis.

2.2 Chemicals, Media, Synthetic Stormwater

The suite of representative stormwater hydrophilic CECs analyzed in this study include atrazine, benzotriazole, dicamba, diuron, fipronil, imidacloprid, mecoprop, tris(2-chloroethyl)phosphate (TCEP), and 2,4-dichlorophenoxyacetic acid (2,4-D). These compounds were selected for their widespread use, frequent detection in urban runoff (Spahr et al., 2020), and diverse physicochemical properties (e.g., K_{ow} and ionic character). All compounds were quantified in the field samples and the first seven compounds were evaluated in the batch and column studies. Chemical sources and properties are listed in Table S4 and S6. The preparation of the CEC stock solutions is described in the SI (S.4.2).

Three biochar sources from agriculture waste were screened at the beginning of the experiment and Environmental Ultra Biochar™ (Biochar Supreme, Everson, WA) was selected because of its higher adsorption kinetics and capacity (SI, S.4). The biochar and mixing sand (La Paz, Lyngso Garden Material, San Carlos, CA) were sieved to a size range of 5.6–1.7 mm (#3-1/2 – #12 mesh) using a horizontal sieve shaker (Humboldt H-4330, Elgin, IL, USA) before use. The biochar was produced from Douglas fir gasification at 900–1000°C for 1-10 seconds (Karunanayake et al., 2017) and the BET surface area was measured as 499 m^2/g (Particle Technology Laboratory, Downers Grove, IL), with intra-particle and inter-particle porosities of 0.93 and 0.43, respectively. The average grain diameters (d_{50}) of the biochar and mixing sand are 2.24 mm and 3.78 mm. Detailed measurements are provided in the SI (S.5), and additional material characteristics are in Table S7. Pami Pebbles (0.95 cm, Lyngso Garden Material, San Carlos, CA) were used as received as the barrier sand. All materials are commercially available at scale.

Synthetic stormwater was prepared by adding 1 g/L of catch-basin sediment (Los Angeles) and salts into deionized water to replicate the ionic composition of Los Angeles stormwater (Grebel et al., 2016). The sediment was screened with a 3 mm mesh before use. The water was vigorously mixed, passed through a sedimentation tank with a 40-min hydraulic retention time (HRT), and spiked with straw-derived DOC concentrate and CEC stock solution. The straw-derived DOC was added to supplement the existing DOC in the synthetic stormwater, raising its level to match that of observed stormwater. Straw was selected because it is commonly found along the curb and in catch basins in Los Angeles, it releases high amounts of DOC (Pritchard et al., 2022), and the preparation of straw-derived DOC concentrate is easily reproducible. The final DOC concentration in the synthetic stormwater was approximately 8 mg C/L. Concentrations of other constituents are provided in Table S8, with DOC concentrate preparation details in the SI (S.7.1).

2.3 Batch Kinetic and Isotherm Studies

The batch kinetic studies were conducted in triplicate by adding 40 or 400 mg of biochar to 1 L amber bottles containing synthetic stormwater with 40 or 100 µg/L of all compounds. The bottles were placed on a horizontal shaker at 90 rpm for 40 days or until CEC concentration was below the limit of quantification. The performance of the biochar was quantified by calculating the distribution coefficient K_d (Equation 1) at different time points.

$$K_d = C_i^{solid} \left[\frac{g\ i\ sorbed}{kg\ dry\ solid}\right] / C_i^{aq} \left[\frac{g\ i\ sorbed}{L\ solution}\right] \ (Equation\ 1)$$

The batch isotherm study was conducted by adding 30 – 400 mg biochar to 1 L amber bottles containing synthetic stormwater with 25 – 600 µg/L of all CECs. The bottles were mixed for 93 days and samples were collected at the beginning and end of the experiment. In both studies, 500 mg/L sodium azide was added to prevent biological growth.

2.4 Advanced Oxidation Process

The effectiveness of UV/H_2O_2 for the removal of hydrophilic CECs was first investigated separately before it was coupled with the biochar filters. Two different dosages of H_2O_2 (i.e., 0.1 mM and 0.15 mM) were tested (Duan and Sedlak, 2021). During each experiment, the UV reactor was operated at 915 mL/min for one hour. Influent and effluent H_2O_2 and CEC samples were collected every five minutes. H_2O_2 was analyzed within 20 minutes of sampling to avoid unexpected decomposition. Further details on the experimental setup are available in the SI (S.9.1). The reaction parameters of the studied CECs are summarized in Table S10.

For the column experiments with AOP, H_2O_2 (30%, stabilized with sodium stannate/certified, Fisher Chemical) stock solution was added to the synthetic stormwater during the CEC and DOC concentrate addition. The flow-through UV reactor used in the study was designed by Gadgil and Garud (Gadgil and Garud, 1998). The UV reactor is equipped with a gravity driven feed water delivery system and an air-suspended 60-watt low-pressure UV lamp (Philips, Andover, MA). The treatment tray of the reactor is 5.5 L and the applied UV dose was around 1500 mJ/cm^2.

2.5 Column Experiments

Column experiments were conducted using biochar-amended sand filters with and without UV/H_2O_2 pretreatment. The experimental setup was designed to mimic retrofitting dry wells by which UV lamps can be hung on the grate of the primary chamber and the carbon filter can be installed in the secondary chamber. The experimental setup of the two systems is shown in Figure 1 and S10.

Columns for biochar filters were constructed of clear PVC pipe ($122\ \text{cm} \times Ø15.2\ \text{cm}$; McMaster-Carr, Los Angeles, CA). Column inner diameter was sized to be greater than 40 times the d_{50} of the media to ensure proper fluid hydraulic conditions (Gilbert et al., 2014). In each

column, a 20-cm barrier sand layer was placed at the bottom, then pre-measured biochar and mixing sand were gently mixed by hand and added in uniform 15-mm layers until the total length of the filter reached 60 cm, and lastly a 11-cm barrier sand layer was put on the top to keep the filter in place under high flow rates and evenly distribute the influent flow. The final content of biochar and mixing sand in the filters is summarized in Table S11. The hydraulic conductivity of the filter was measured to be 9.51 cm/s and is within the range of well-sorted sand and gravel (Bear and Braester, 1972). This indicates that the hydraulic performance of the proposed biochar filter is adequate for use in dry wells and will not impair the infiltration capacity of these systems.

Upon packing, the biochar filters were saturated in an up-flow configuration with carbon dioxide at 1 L/min for one hour then with DI water at 5 mL/min for 15 hours. Next, the columns were flushed with DI water for one day in downflow configuration at 220 mL/min to remove remaining fines. A tracer test was conducted to assess the HRT and mixing regime of the filter using potassium bromide tracer (SI; S.10.2). The hydraulic dispersivity of each column was calculated from the tracer test and used in the contaminant transport modeling. Subsequently, the biochar filters were conditioned with synthetic stormwater without CECs for 80 empty bed volumes (EBVs; ~3 days) and challenged with CECs for 280 EBVs (~10 days) at 70 cm/hr Darcy velocity. The flow rate was controlled using a needle valve at the column outlet and was checked at least three times a day (Figure S12). This face velocity simulated the 60th percentile infiltration rate in a dry well with a 60-acre catchment area in Los Angeles (Li et al., 2024). A detailed description of system operation, sampling scheme, and observed influent and effluent water quality is included in the SI (S.10).

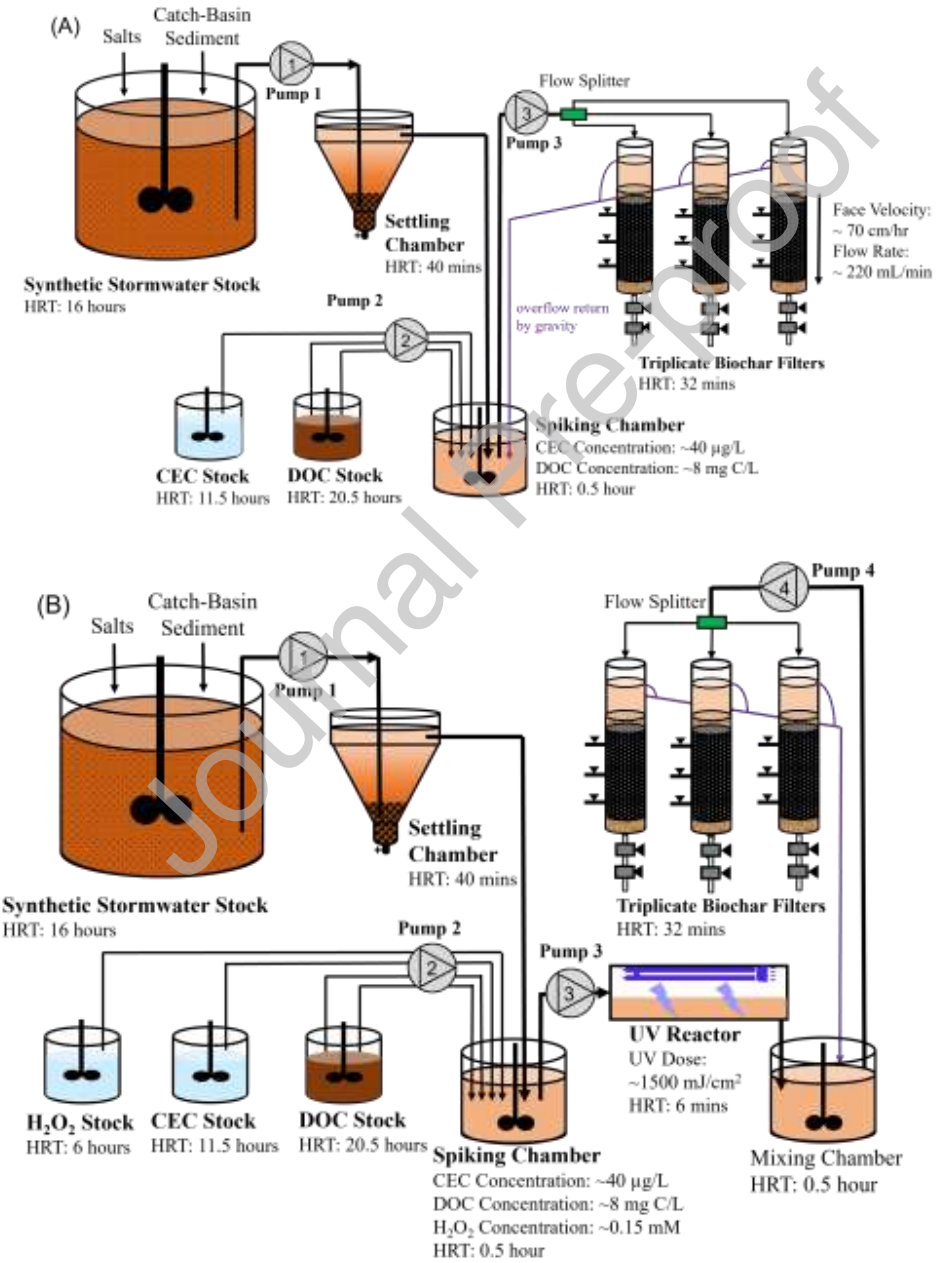
2.6 Analytical Methods

CEC-containing samples were centrifuged at 16000 relative centrifugal force for 25 minutes (Microfuge I8 Centrifuge, Beckman Coulter), spiked with 20 µg/L isotopically labeled internal standards, and analyzed using liquid chromatography with tandem mass spectrometry (LC-MS/MS; SI, S.5.3). DOC in field samples was analyzed by Eurofins (West Sacramento, CA), while DOC in synthetic stormwater samples was measured using a TOC-TN Autoanalyzer

(Shimadzu TOC-LCPN) after filtration through 0.45 µm polyethersulfone filters (SF14501, Tisch Scientific, Cleves, OH). H_2O_2 was quantified using ultraviolet-visible spectroscopy based on its oxidation of DPD dye catalyzed by peroxidase enzyme (Bader et al., 1988). Water quality parameters were assessed with a multi-parameter probe (HI98195, HANNA Instruments), a turbidimeter (HI98713, HANNA Instruments), and a digital optical dissolved oxygen meter

(ProODO, YSI Inc., Yellow Springs, OH). The total suspended solids (TSS) were measured using a vacuum filter assembly with 1.6 µm glass fiber filters (WHA1820-047, Whatman, Maidstone, UK). Detailed analytical methods are provided in the SI (S.4 and S.9).

Figure 1. Experimental setup of biochar-amended sand filters without (A) and with (B) UV-AOP pretreatment. Synthetic stormwater flows by gravity from the settling chamber to the



spiking chamber, and from the UV reactor to the mixing chamber.

2.7 Contaminant Sorption Equilibrium and Transport Model

The Freundlich isotherm model was used to describe the equilibrium sorption of CECs on biochar. CEC transport was modeled using a 1-D sorption-retarded intraparticle pore diffusion model, applying Fick's first law for intraparticle diffusion (Grathwohl, 2012), as used in previous studies to predict CEC concentrations in biochar filters (Pritchard et al., 2023; Spahr et al., 2022). The model's mathematical equations are detailed in the SI (Equations S6–S9). Each biochar particle was divided into concentric spherical shells, with CECs diffusing inward while continuously sorbing and desorbing from the biochar surface. In the batch studies, all biochar particles were modeled as a single group, while in the column study, the biochar filter was divided into segments, each acting as a completely mixed flow reactor, with CECs transporting between segments via advection and dispersion.

In the model, time-dependent influent concentrations, flow rates, and batch/column-specific parameters (e.g., biochar mass, reactor volume) were input directly, while dispersity, Freundlich sorption coefficients, and intraparticle tortuosity were fit from experimental data. For the batch studies, sorption coefficients were obtained from the isotherm study, and intraparticle tortuosity was fitted from kinetic data. In the column study, dispersivity was obtained from the tracer test, and sorption parameters and intraparticle tortuosity were jointly fitted against CEC breakthrough curves at the sample ports 15 cm and 30 cm from the inlet of the biochar filters without UV/H_2O_2 pre-treatment. The model was verified using transport data from the 45-cm sample port and effluent (60 cm) and then used to predict biochar filter performance with UV/H_2O_2 pre-treatment at all sampling locations. The fitting process minimized the normalized mean squared error

(NMSE, Equation S11), and predictions were averaged across the three models developed from column triplicates, following previous recommendations (Pritchard et al., 2023). More details on the model training are provided in the SI (S.11). Finally, sorption parameters and tortuosity from batch and column studies were compared to assess the influence of DOC on CEC removal, considering that sodium azide was used in batch studies to prevent DOC biodegradation, while the column study simulated real dry well conditions where DOC levels dropped due to bacterial activities.

2.8 Field Lifespan Prediction

The field lifespan of the proposed stormwater treatment systems in a hypothetical case study for dry wells installed in Los Angeles was estimated using the model trained with experimental data. The biochar filter was designed to be 183 cm×Ø122 cm to fit a secondary chamber and the UV lamps were assumed to be installed on the grate of the primary chamber (City of Los Angeles Department of Public Works, 2015). The primary chamber's HRT was set at 40 minutes, with an infiltration rate in the filter of 500 cm/hr, corresponding to the 75th percentile infiltration rate for a dry well with a 60-acre catchment area (Li et al., 2024). The highest observed CEC concentrations from this study and previous research (Spahr et al., 2020) were used as influent levels. The lowest environmental quality standards among the US EPA (US EPA), EU Water Framework Directive (European Commission, 2013), and Swiss Ecotox Center (Ecotox Centre Switzerland) were used to define CEC breakthrough. If the observed dry well influent concentrations were below these standards, a minimum of 50% removal was used to estimate system lifespan. The influent and breakthrough concentrations of the studied CECs are summarized in Table S15. When UV/H_2O_2 pretreatment was involved, direct photolysis in the primary chamber was modeled as a 1st-order reaction whose reaction rate was calculated by

Equation S4. UV/H_2O_2 performance was estimated by assuming the Peclet number (Pe) of the primary chamber of 1, 10, or 100 to represent the possible range of its mixing regime.

3. Results and Discussion

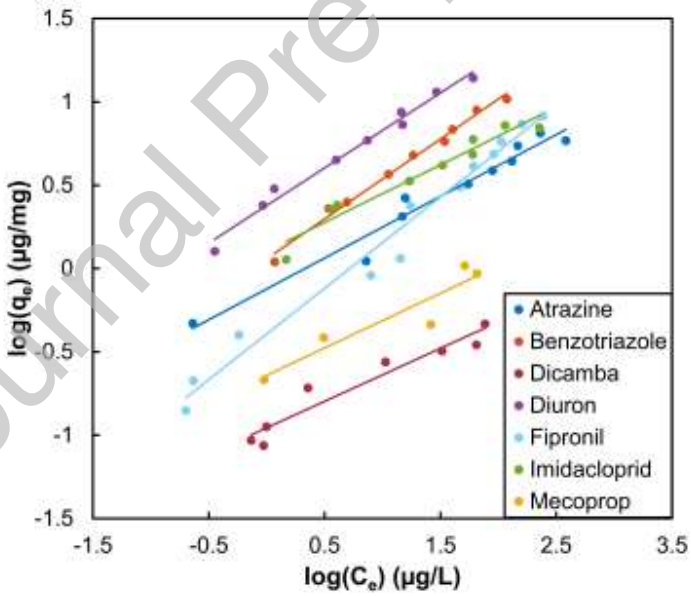
3.1 Field Monitoring

Field monitoring results are presented in Figures S3–S5. The DOC concentration of stormwater was 11.6 ± 1.3 mg C/L, with minimal variation across sampling locations (Figure S3). All studied CECs were detected, with concentrations primarily ranging from 10 to 500 ng/L. CEC levels were generally higher during the first rainfall event compared to the second at the same monitoring locations. No significant difference of CEC concentrations at three monitoring locations for each dry well site was observed, suggesting that the treatment provided by vegetated swales and primary chambers was insufficient to remove hydrophilic CECs because of their high aqueous solubility.

3.2 Batch Isotherm and Kinetic Study

The Freundlich isotherms measured in the batch study are plotted in Figure 2, with sorption parameters and correlation coefficients (R^2) summarized in Table S9. The observed affinity of compounds to biochar followed the order: diuron > benzotriazole > imidacloprid > atrazine > fipronil > mecoprop > dicamba. This order does not correlate with the compounds' hydrophobicity, as noted in previous research (Ulrich et al., 2015). For instance, although fipronil is the most hydrophobic, its affinity on the studied biochar was lower than that of diuron and benzotriazole. Hydrophilic CECs generally interact with biochar through π-π interactions, hydrogen bonds, and electrostatic interactions (De Ridder et al., 2010; Margot et al., 2013). In this study, all compounds formed H-bonds with the biochar, and benzotriazole, dicamba, diuron, fipronil, and mecoprop also engaged in π-π interactions. However, mecoprop and dicamba,

which are negatively charged at pH 7, showed low affinity due to repulsion by the negatively charged biochar surface. The equilibrium adsorption capacity of biochar was comparable to that of commercial activated carbons for hydrophobic organic compounds (Urano et al., 1991), indicating high surface area biochar's potential for removing hydrophilic CECs. Figure 3 presents the batch kinetic study results, showing adsorption kinetics in the order: fipronil > mecoprop > diuron > benzotriazole > imidacloprid > dicamba > atrazine. There was no observed correlation between adsorption rates and CEC molecular size or biochar affinity. K_d values increased by more than three orders of magnitude within the first two days for all compounds. After 40 days, the K_d values for all compounds, except for atrazine, exceeded 10^5 L/kg while atrazine reached about $10^{4.5}$ L/kg. Overall, large-grain biochar demonstrated rapid adsorption kinetics for all



investigated CECs.

Figure 2. Batch isotherm study results.

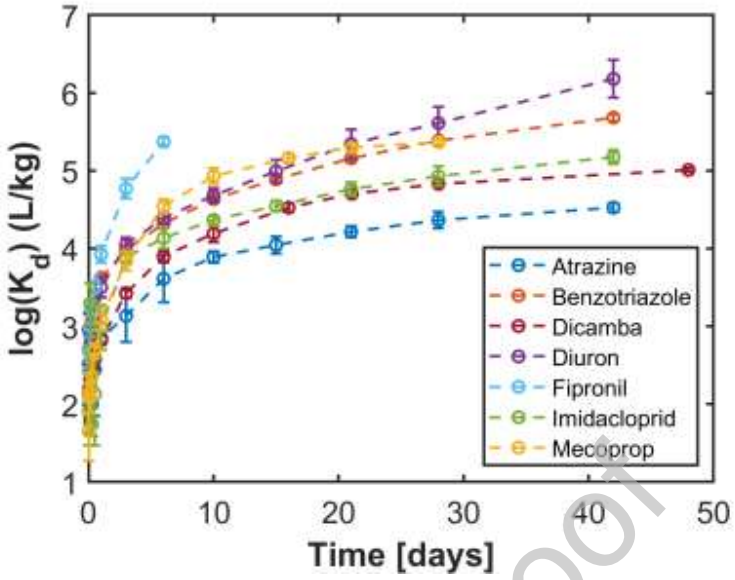


Figure 3. Batch adsorption kinetics with the biochar. The results for fipronil and mecoprop are shown for a shorter time of period than other compounds because they become non-detectable after the last data point on the plot. Error bars indicate one standard deviation above and below the mean (n=3).

3.3 Column Experiment Results

3.3.1 Water Quality and DOC Removal

The water quality parameters measured in the column experiments are shown in Figure S13. The biochar filters significantly reduced total suspended solids (TSS) and dissolved oxygen (DO), slightly lowered pH, moderately increased ORP, and had no effect on conductivity. Specifically, TSS decreased from 6.5 ± 3.9 mg/L to 1.5 ± 1.0 mg/L, and turbidity dropped from 5.2 ± 1.4 FNU to 1.1 ± 0.4 FNU, as fine particles not removed by the sedimentation tank were captured by the top barrier sand and media filter. This effect may reduce the long-term performance of the treatment system in the field. Influent DO saturation was 86.8 ± 6.9%, while

effluent DO fell consistently below 5% after 80 EBVs. The UV reactor had little impact on TSS, DO, pH, ORP, or conductivity.

Influent DOC was maintained at around 8 mg C/L in both systems. As shown in Figure 4, the UV reactor did not reduce DOC. The biochar filter removed 3.5 ± 0.9 mg C/L DOC in the first 25% of the column, with minimal further reduction along the depth of the column, resulting in an effluent DOC of 3.7 ± 0.6 mg C/L. The DOC breakthrough profiles suggest that biodegradation was the primary removal mechanism, as significant DOC adsorption by biochar would have caused a continued decrease in DOC concentration along the filter. Bacterial communities responsible for DOC degradation mainly developed in the top layer of the filter, where conditions were aerobic. As a result, replacing the top layer more frequently in the field can potentially mitigate the problems of filter clogging and fouling.

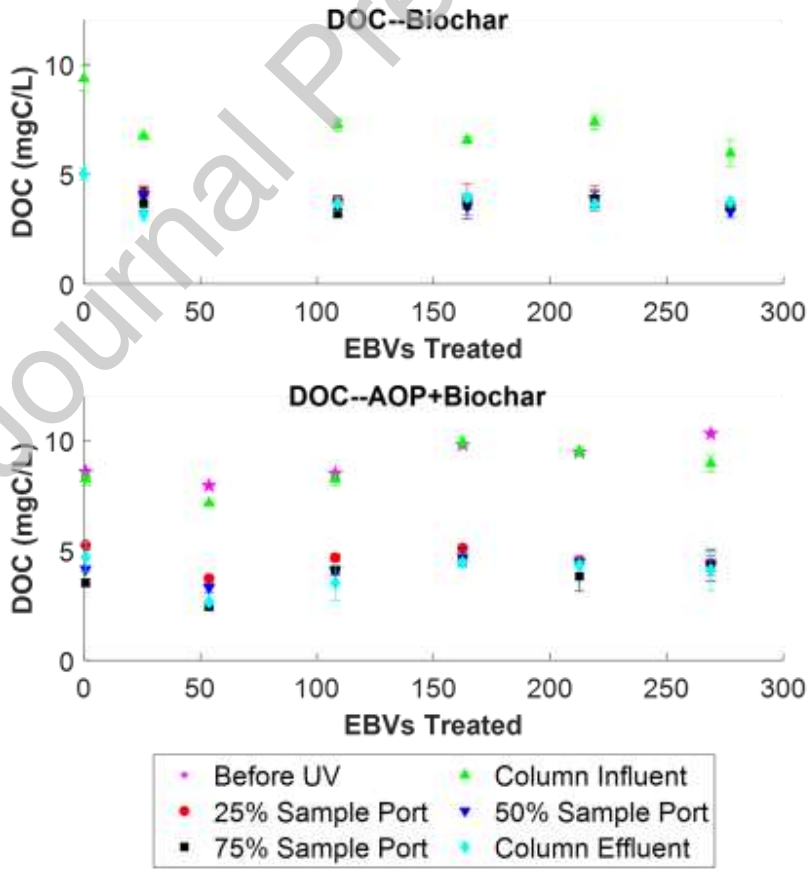


Figure 4. Concentration profile of DOC in the column studies.

3.3.2 CEC Removal in Biochar Columns and Comparison to Batch Studies

In the column study, the initial hydrophilic CEC concentrations were around 40 µg/L. The breakthrough curves of CECs in the two treatment systems are shown as points in Figure 6(A). The most mobile CECs in the biochar columns are: dicamba > mecoprop > fipronil > atrazine > imidacloprid > diuron > benzotriazole. This order is consistent with the batch isotherm results but different from the batch kinetic results with the same initial DOC concentration. This may be because in the batch study, no DOC was consumed by bacteria because of the presence of sodium azide and thus the intraparticle diffusion was significantly affected by the higher DOC. In the column study, however, a large portion of DOC was removed at the top of the filters, and thus the intraparticle diffusion was less retarded and the adsorption was closer to equilibrium. These results suggest that the relative breakthrough of different compounds in biochar filters can be roughly deduced from their batch adsorption isotherms. Nevertheless, the rapid initial breakthrough of all compounds at the 25% sample port and some of the compounds further down the column indicate that compound removal in the filter is still kinetically limited.

3.3.3 CEC Removal with UV/H_2O_2

The UV/H_2O_2 system showed minimal differences in removing hydrophilic CECs across the two tested H_2O_2 dosages, as illustrated in Figure 5. Approximately 0.04 mM of H_2O_2 degraded when the stock solution was mixed with synthetic stormwater, likely due to interactions with transient metals and dissolved organic matter contributed from the catch basin sediment and straw (McKee, 1969; Petigara et al., 2002). In the UV reactor, around 0.01 mM of H_2O_2 was degraded, and the reactor's performance stabilized after the first five minutes (~1 HRT). All studied CECs, except dicamba, were removed by more than 50%. Despite similar hydroxyl

radical reaction rates for all CECs, the removal rates varied significantly, decreasing in the order: imidacloprid > fipronil > diuron > mecoprop > atrazine > benzotriazole > dicamba. This ranking aligns with the UV photolysis reaction rates listed in Table S10. For instance, the reaction rate of imidacloprid is about 25 times higher than that of dicamba. This result indicates that UV photolysis was the dominant removal process, likely because the DOC in the synthetic stormwater acted as a strong hydroxyl radical scavenger. Duan and Sedlak concluded that when the aqueous DOC concentration exceeds 5 mg C/L, the steady-state concentration of hydroxyl radicals becomes negligible, leading to a significant drop in hydroxyl radical reaction efficacy (Duan and Sedlak, 2021). These findings suggest that direct UV photolysis is more effective for stormwater treatment than radical reactions. In the subsequent column study, a 0.15 mM H_2O_2 dosage was used to prevent excessive H_2O_2 decomposition during the long-term experiment.

When UV/H_2O_2 was applied with the biochar-amended filters, the removal efficiency of six out of seven compounds significantly improved, reflecting the combined effects of AOP and adsorption (Figure 6). The observed H_2O_2 concentration in the column experiment is presented in Figure S9. About half of the H_2O_2 degraded in the mixing chamber (after UV reactor and before biochar filters), and the other half degraded in the top half of the biochar filters. The influent concentrations of all studied CECs, except dicamba, were substantially reduced in the biochar filters due to the involvement of UV/H_2O_2, resulting in lower contaminant mass loading on the biochar filter throughout the experiment. The effluent concentrations of different compounds were ranked as follows: dicamba > mecoprop > atrazine > fipronil > benzotriazole ≈ diuron > imidacloprid. Imidacloprid was barely detected during the experiment, with over 90% degraded in the UV reactor. Both benzotriazole and diuron were found only at the 25% sample port, despite around 80% of diuron being removed in the UV reactor compared to only 50% of

benzotriazole, likely due to benzotriazole's higher affinity for biochar. Fipronil, atrazine, and mecoprop were all detected in the column effluent at the end of the experiment, but their final concentrations were about half of the concentrations in the system without UV/H_2O_2. Dicamba, the most recalcitrant compound in the study, was neither significantly degraded by UV/H_2O_2 nor strongly adsorbed by the biochar filter. The final concentrations of dicamba were around half of the influent concentrations in both systems. However, observed concentrations of dicamba in urban runoff are much lower than regulated limits (see Section 3.4.3 for further discussion). Therefore, even though dicamba is not effectively removed by the proposed systems, it is unlikely to be the limiting factor for the field lifespan of biochar. Nonetheless, these results suggest that compounds with similar properties to dicamba (e.g., anionic), whose concentrations in urban runoff exceed regulatory limits, such as per- and polyfluoroalkyl substances (PFAS), may limit the field lifespan of the systems and required additional attention during system operation and maintenance.

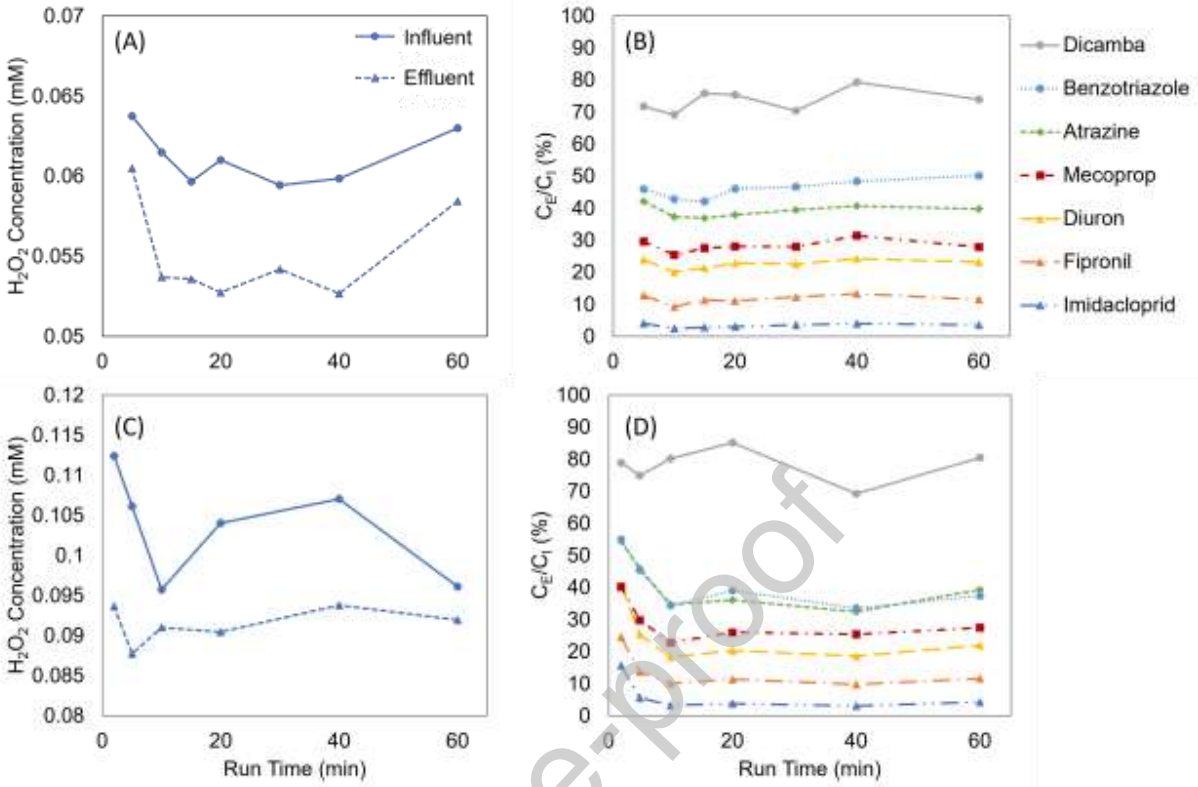


Figure 5. Removal of CECs by UV/H_2O_2 when the influent concentrations of H_2O_2 were set at 0.1 mM (A and B) and 0.15 mM (C and D). C_E represents UV reactor effluent concentration while C_I represents UV reactor influent concentration.

3.4 Modeling Contaminant Transport

3.4.1 Advection and Dispersion

The experimental and modeling results of the tracer tests for the two treatment systems are presented in Figure S11. No early breakthrough was observed, indicating that the filters were properly packed without any short-circuiting. The HRT of the filters in the first system (without UV/H_2O_2) was approximately 21 minutes and in the second system (with UV/H_2O_2) was around 14 minutes. The simulated bromide breakthrough curves closely matched the observed data, with the dispersivities of the two systems determined to be 1.87 ± 0.23 cm and 4.5 ± 0.68 cm, respectively. The Peclet numbers for the two systems were 32 and 13, indicating that the mixing

extent in the filters falls between a completely mixed flow reactor (Pe = 0) and a plug flow reactor (Pe ≈ 100). This is because the heterogeneity of the filter media introduced some mixing mechanisms, while the relatively long filter length compared to the media size made the reactor generally plug-flow like. The Peclet number of the biochar filters with smaller biochar grains (d_{50} = 0.8 mm) was approximately 163, about 10 times higher than the Peclet number in this study (Pritchard et al., 2023). This suggests that biochar filters with smaller grains typically remove contaminants more effectively than those with larger grains, not only due to faster intraparticle diffusion and adsorption kinetics (lower intraparticle tortuosity, see Section 3.4.2 for further discussion), but also because they more closely resemble plug flow reactors, resulting in more uniform residence time across all fluid elements.

3.4.2 Model Calibration and Verification

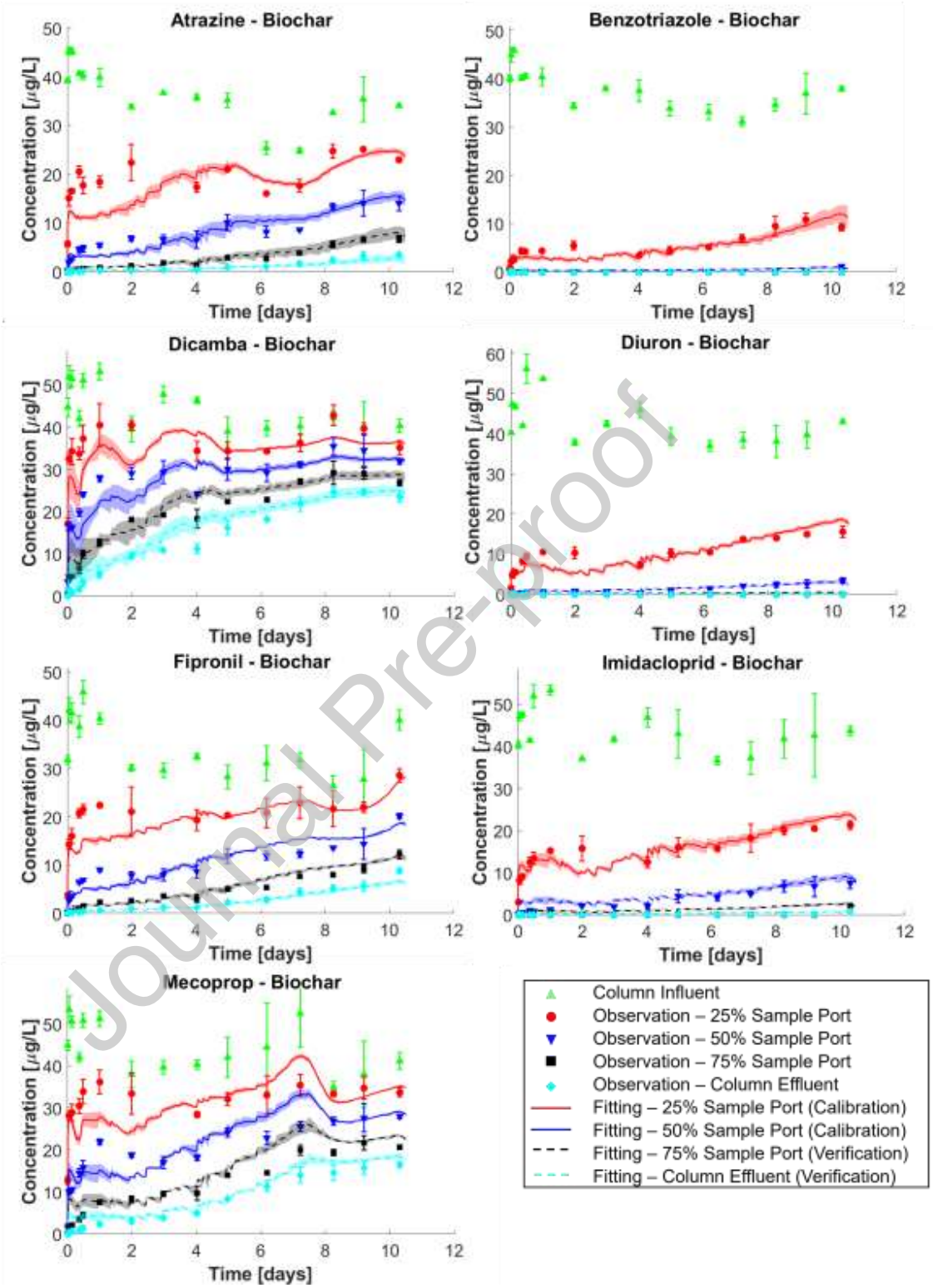
The lines in Figure 6 represent the simulation results (calibration and verification) of the contaminant transport model. The model-generated breakthrough curves were in good agreement with the experimental data in all cases, which is particularly noteworthy given the substantial differences in filter influent CEC concentrations in the two treatment systems.

Table S13 lists the column-fitted sorption and tortuosity parameters, while Table S14 summarizes the batch-fitted tortuosity. The column-fitted isotherms are plotted in Figure S14 alongside the batch isotherms. Compared to the batch studies, all CECs exhibited higher intraparticle tortuosity and greater adsorption affinity to biochar in the column studies. This difference is attributed to the shorter contact time (21 minutes in the column versus 42 days in batch) and lower steady-state DOC concentrations (~4 mg C/L in the column versus ~8 mg C/L in batch) in the column studies.

In the column study, dicamba and mecoprop had the highest breakthrough concentrations at the end of the experiment. This was due to their anionic property under the experimental conditions (pH ≈ 7), which led to repulsion by the negatively charged biochar surface, as reflected by their high intraparticle tortuosity (indicating hindered intraparticle diffusion) and low adsorption affinity. The column-fit equilibrium isotherm of fipronil was like that of mecoprop; however, fipronil's intraparticle tortuosity was only about a quarter of mecoprop's, resulting in a much lower breakthrough concentration. Atrazine had a slightly higher intraparticle tortuosity but a considerably higher adsorption affinity than fipronil, leading to a modestly lower effluent concentration for atrazine. When aqueous CEC concentrations were in the range of 10–30 μg/L, the equilibrium CEC concentrations on the biochar surface for benzotriazole, diuron, and imidacloprid were very close (Figure S14) and much higher than those of the other compounds. Consequently, these three CECs were well retained by the biochar filters. Compared to biochar filters with smaller grains, the studied CECs exhibited greater intraparticle tortuosity in filters with larger grains, indicating higher intraparticle diffusion hindrance within larger biochar particles (Pritchard et al., 2024).

In summary, the fitting results of the contaminant transport model verify its effectiveness in: (1) investigating the diffusion kinetics and adsorption affinity of different compounds in biochar filters; and (2) predicting the performance of filters containing similar filter media under varying inflow conditions.

(A)



(B)

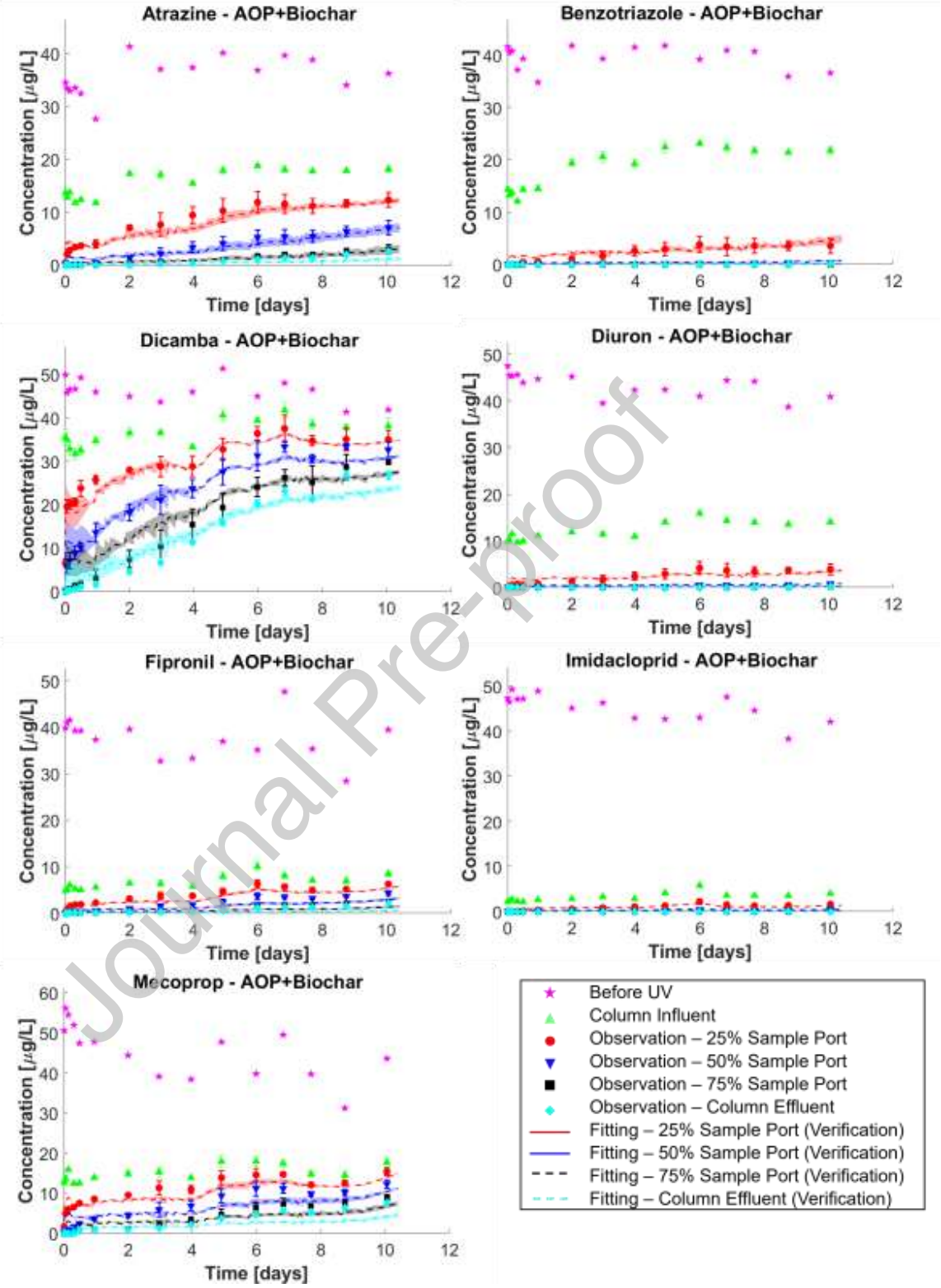


Figure 6. Observed (points) and modeled (lines) CEC breakthrough curves in stormwater treatment systems without UV/H_2O_2 (A) and with UV/H_2O_2 (B). The model was calibrated using data from the 25% and 50% sample ports in the first system (A) and verified against data from the 75% sample port and effluent in the first system, as well as all data from the second system (B). Error bars indicate one standard deviation above and below the mean observed concentrations (n=3). Shaded areas indicate the standard deviation of the predicted breakthrough concentrations.

3.4.3 Field Lifespan Prediction

For the field lifespan prediction, it was assumed that no H_2O_2 would be added to the primary chamber, as UV photolysis was identified as the primary CEC removal mechanism, and generating and storing H_2O_2 on site can be challenging. The highest observed CEC concentrations from this study's field work and previous research were used as influent levels (Table S15). Table 1 presents the estimated field lifespan of the biochar filters with and without UV lamps. It is important to note that the breakthrough of benzotriazole, dicamba, and mecoprop was defined by achieving at least 50% removal, rather than meeting environmental quality standards, because their observed concentrations in urban runoff are below regulatory limits. Therefore, the values listed in Table 1 for these three compounds are intended as a reference for the treatment efficacy of the proposed systems for these compounds or others with similar properties, rather than indicating the actual field lifespan constrained by the compounds.

Without UV lamps, the effluent concentrations of most contaminants will remain below regulatory limits for several years, even decades. Imidacloprid was identified as the limiting contaminant, as its initial breakthrough concentration exceeded the regulatory threshold with 5 wt% (50 v%) biochar due to its removal being highly kinetic-limited. Increasing the biochar

content to 10 wt% (77 v%) resolved this issue, extending the filter's lifespan to approximately four years. Based on the biochar cost of $1,340 per cubic meter, the estimated annual material cost would be approximately $750 per dry well. When UV treatment was added, the influent concentrations of all contaminants in the filter were reduced below regulatory limits, suggesting that the filter's lifespan is no longer constrained by the removal of the studied CECs. Instead, other factors such as clogging or the presence of other contaminants in urban runoff that are recalcitrant to UV photolysis and anionic at pH 7 may become restrictive. Typically, dry wells in the field are maintained once or twice a year to remove accumulated debris and sediment from the primary chamber. For the hydrophilic CECs investigated in this study, if the biochar filter is replaced during the annual maintenance, these contaminants would pose little risk to groundwater, effectively safeguarding groundwater quality through the proposed treatment systems.

Table 1. Potential field lifespan of the proposed stormwater treatment systems. The biochar filters contain 5 wt% biochar and 95 wt% sand unless otherwise stated. When UV is incorporated in the system, the CEC removal efficiency in the primary chamber are listed assuming different mixing regimes in the primary chamber. Influent concentrations are the greater of values from this field work or compiled by Spahr et al. (2020) as listed in Table S15.

Compound	Without UV [lifespan (years)]	With UV[c] Removal Rate in the Primary Chamber		
		Pe = 1	Pe = 10	Pe = 100
Atrazine	23.8 ± 5.0	76.1%	87.7%	92.8%
Benzotriazole	26.2 ± 4.4	51.8%	61.6%	68.2%
Dicamba	0.7 ± 0.2	2.39%	4.00%	7.54%

Diuron	188.4 ± 39.5	88.7%	97.1%	99.1%
Fipronil[a]	7.4 ± 2.3	> 88.7%	> 97.1%	> 99.1%
Imidacloprid[b]	3.9 ± 0.7	98.9%	100%	100%
Mecoprop	2.3 ± 0.5	77.1%	88.7%	93.3%

[a] The direct photolysis rate for fipronil is unavailable; however, Figure 5 shows that fipronil reacts faster than diuron in the UV reactor. The values listed are based on diuron's photolysis rate.

[b] The value for imidacloprid was calculated assuming the filter contains 10 wt% biochar.

[c] Assume $W_{254} = 9.7 \times 10^{-6} \frac{Ei}{cm^2 s}$, as estimated in (Duan and Sedlak, 2021), and HRT = 40 mins. As a result, UV dose is about 10^4 mJ/cm^2. Effluent concentrations of all compounds in the primary chamber are lower than the regulated limits. The lifespan of the filters will not be limited by the compounds.

3.5 Conclusions

- This study is the first to assess the effectiveness of dry wells in removing hydrophilic CECs. Field monitoring revealed that hydrophilic CECs present in urban runoff were not effectively removed by existing dry wells with vegetated swale pretreatment.
- This study pioneers the combination of UV/H_2O_2 and large-grain biochar filters for the removal of hydrophilic CECs in dry wells. By leveraging three complementary contaminant removal mechanisms—UV photolysis, hydroxyl radical oxidation, and biochar adsorption—the proposed system is designed to address a broad spectrum of contaminants commonly present in urban runoff. For the limited number of compounds resistant to all removal mechanisms, we recommend that local agencies monitor their concentrations in urban runoff and evaluate the necessity of restricting their use in consumer products.
- UV/H_2O_2 can efficiently remove most hydrophilic CECs within a contact time of just a few minutes, with direct photolysis with UV serving as the primary removal mechanism,

likely because the DOC in the synthetic stormwater acted as a strong hydroxyl radical scavenger.

- The removal of hydrophilic CECs by biochar filters is predominantly kinetic-limited, with anionic contaminants less effectively retained compared to other hydrophilic CECs.
- This study demonstrates the novel application of an established contaminant transport model in large-grain biochar filters to predict the field lifespan of the proposed treatment system.
- The lifespan is approximately four years with 10 wt% biochar in the filter, indicating that the system can be easily maintained during routine maintenance of dry wells.
- This work enhances our understanding of dry well performance and offers recommendations for improved dry well design, which facilitates stormwater recharge without jeopardizing the groundwater quality. This study makes a valuable contribution to water resource management and the beneficial use of stormwater. The developed treatment systems can increase public acceptance of stormwater capture and support the broader implementation of future stormwater infiltration infrastructure.

Supporting Information.

The supporting information contains more details on the experimental and modeling methods and the results of the study, as is referenced throughout the text.

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Author Contributions

All authors contributed to the manuscript. YL prepared the draft of the paper, conducted the laboratory experiments, and completed the mathematical modeling. JCP helped with the column study and assisted with manuscript preparation. RGL supervised the project, contributed to experimental design, and assisted with manuscript preparation. CW and YA collected stormwater samples in the field. YD provided suggestions on the UV/H_2O_2 process, and YW assisted with the modeling work.

Notes

The authors declare no competing financial interest.

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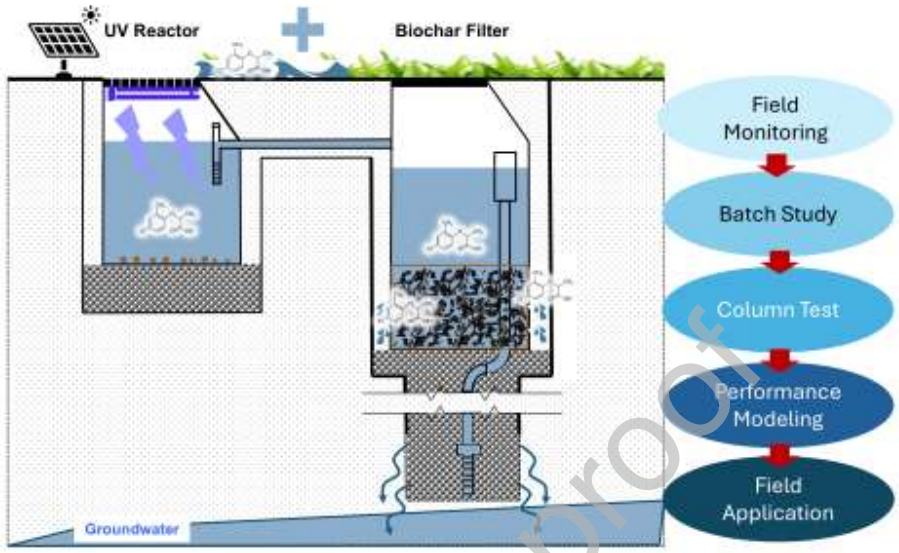
Graphical abstract



Declaration of interests

☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Richard G. Luthy reports financial support was provided by the Los Angeles Department of Water and Power. Richard G. Luthy reports a relationship with the Los Angeles Department of Water and Power that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.