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# **CRITICAL REVIEW**

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# review of treatment performance

Organic micropollutant removal in stormwater: a

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Stormwater runoff is increasingly recognized as an alternative water resource, but organic micropollutant (OMP) contamination poses challenges to its safe harvesting. This study systematically reviews stormwater treatment systems to assess their effectiveness in OMP removal and their potential to mitigate associated risks. Among nature-based solutions (NBS), biofilters demonstrate high removal efficiency (>80%) for most tested OMPs. A significant positive correlation was found between hydrophobicity ( $\log K_{ow}$ ) and removal efficiency (p < 0.05; Pearson and Spearman correlation), suggesting adsorption as the dominant mechanism for hydrophobic compounds, while biodegradation plays a key role in removing many hydrophilic OMPs. Key design features, such as vegetation, submerged zones, and filter media amendments (e.g., biochar, compost), further enhance treatment performance. Constructed wetlands generally achieve removal rates above 60% mainly for hydrophobic OMPs, though challenges remain for emerging refractory pollutants such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). Porous pavements are effective for polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs), particularly with adsorptive materials and geotextile layers, but limited studies restrict broader implementation. Ponds and swales exhibit variable performance, effectively treating PAHs and pesticides but showing lower efficiency for pharmaceuticals and plasticizers. Advanced oxidation technologies demonstrate strong potential, achieving >80% removal for tested PAHs, pesticides and corrosion inhibitors within minutes to hours, making them suitable for post-treatment applications. Despite progress, data gaps hinder robust assessments of design and operational parameters. Future research should focus on optimizing naturebased solutions (NBS) through smart sensors, real-time control strategies, and hybrid approaches integrating advanced oxidation technologies to enhance OMPs removal in stormwater harvesting systems.

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#### Water impact

Stormwater reuse faces challenges due to organic micropollutant (OMP) contamination. This review evaluates treatment system performance, highlighting biofilters and constructed wetlands as effective nature-based solutions and advanced oxidation as a promising post-treatment. By identifying key removal mechanisms and optimization strategies, this work informs future designs integrating real-time monitoring and hybrid technologies to enhance OMP removal in stormwater harvesting.

## 1 Introduction

Stormwater is becoming more valued as a potential alternative water source, which brings both opportunities and challenges for sustainable water management. 1 Its reuse potential is largely influenced by the volume and variety of pollutants it carries, not just biological contaminants and pathogens, but many emerging contaminants, such as microplastics, tire wear particles, and organic micropollutants (OMPs).2,3 Notably, a broad spectrum of chemicals used in domestic and industrial settings, are widely found in urban stormwater outlets (SWO), as well as in combined sewer overflows (CSOs), e.g., polycyclic aromatic hydrocarbons (PAHs), pesticides,

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pharmaceuticals, personal care products (PPCPs), corrosion inhibitors, flame retardants, and other anthropogenic chemicals.3,4 While the OMPs in stormwater are more closely linked to diffuse urban sources—such as road runoff, atmospheric deposition, building materials, and landscape maintenance,5 they may also contain ones that are traditionally found in domestic wastewater. For example, Mutzner, et al. (2022)4 highlighted both the similarities and differences in OMPs detected in stormwater drainage outlets (SWOs) and combined sewer overflows (CSOs). Specifically, PAHs were found to pose high risks in both SWOs and CSOs, whereas PFOS exhibited high risk only in CSOs (risk quotient >1). In contrast, certain phenolic compounds (e.g., 2-tert-octylphenol and pentachlorophenol) were identified as high-risk in SWOs. This shows that proper treatment of stormwater is needed before safely discharging it into the environment, or prior to human reuse.

In response, nature-based systems (NBS) have been developed to address stormwater pollution challenges. Common NBS approaches include vegetated biofiltration systems, constructed wetlands, porous pavements, and swales. While traditionally focused on removing suspended solids, nutrients, and heavy metals, recent research has expanded to investigate their performance in removing emerging contaminants like OMPs.<sup>7-9</sup> Zhang, et al. (2016)<sup>10</sup> investigated the removal of three herbicides in stormwater



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biofilters in situ columns, recording varied effectiveness: atrazine (-7-41%), simazine (-11-30%), and prometryn (22-58%). Similarly, Arslan and El-Din (2021)<sup>11</sup> summarized variable PFAS removal rates in the studies of constructed wetlands, ranging from <6% to >99%, differentiated by their design configurations. Previous studies show high performance variability, and thus, NBS design optimisation or post-NBS treatment are needed for a reliable treatment outcome.

Extensive efforts have been made in optimising NBS design and operation for enhanced treatment, but primarily targeting nutrient removal. For example, vegetation addition in glasshouse biofilters was found to significantly enhance total nitrogen (TN) removal.<sup>12</sup> Adding a submerged zone (SZ) in biofilters was shown to improve both TN and the total phosphorus (TP) removal due to the prolonged retention time and anaerobic condition in SZ. In constructed wetlands, Thalla, et al. (2019)<sup>13</sup> reported that vertical flow wetlands outperformed horizontal flow designs in enhancing ammonia removal. Li, et al.  $(2017)^{14}$  found that the choice of pavement material, specifically shale brick, markedly improved nutrient removal. However, relatively fewer studies were done to understand the design and operational impacts on the removal of OMPs, which undergo very different removal processes compared with nutrient removal, e.g., volatilization, plant uptake, sorption, and microbial degradation.<sup>15</sup> For instance, studies have investigated media amendments in biofiltration systems, including organic carbon, biochar, and geomedia amendments. 16,17 Notably, granular activated carbon (GAC) amendments achieved over 70% OMPs removal (with varying

properties, e.g., triazine herbicides, methylbenzotriazole, oryzalin, TCEP, TCPP etc.), and biochar maintained more than 99% removal for all tested OMPs over a five-month compared operation, to 50% removal only for methylbenzotriazole, oryzalin and TCPP from nonamendment biofilters. 18 Plant species also influenced OMPs removal in biofilter design, e.g., Zhang, et al. (2025)<sup>19</sup> found Canna indica as the best performer for sulfamethoxazole and DEET removal in a one-year study. Moreover, operation impacts towards biofilter performance in OMPs removal have been studied by Zhang, et al. (2024).<sup>20</sup> Soil moisture control operation, which tried to maintain moisture status within the columns, was found to significantly improve the biofilters performance for all tested OMPs removal (e.g., triclosan, diuron, atrazine, paracetamol and caffeine etc.; with average 76.1% removal rate over 41.0% non-controlled columns). These findings highlighted the distinct impacts of design and operational variations on treatment systems. Therefore, a thorough evaluation of system design and operational parameters is essential to understand and improve their impact on treatment performance for OMP removal.

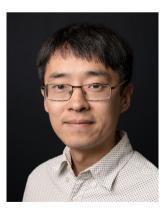
The treatment of OMPs is influenced by their physiochemical properties as well, including hydrophobicity, surface charge (i.e., net molecular charge at environmental pH), half-life, and molecular weight.21 For instance, Zhao, et al. (2024)<sup>22</sup> integrated hydrophobic organic chains into low-cost hydrophilic flocculant matrices, achieving 1.4 to 9.5 times higher removal of all detected dissolved PAHs, primarily due to enhanced binding through hydrophobic interactions, compared to conventional stormwater control measures. Sulfamethoxazole is poorly removed by



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membrane filtration due to its neutral form, whereas paracetamol becomes increasingly negatively charged at higher pH levels, enhancing its removal by membrane processes.<sup>23</sup> Walaszek, et al. (2018)<sup>24</sup> observed that PAHs tend to associate with particles in water and soil matrices in wetland environments. This finding indicated that PAHs, particularly those with higher hydrophobicity, were more likely to be eliminated through filtration, absorption, and sedimentation, processes effective for particulate matter removal. Conversely, LeviRam, et al. (2022)8 discovered that biodegradation plays a significant role in biofiltration systems for atrazine removal. biodegradation is closely linked to the half-life of OMPs, particularly in soil environments. These studies highlighted how the physico-chemical properties of OMPs can determine their degradation pathways in stormwater treatment systems. Thus, the studies of OMPs' physiochemical characteristics in the NBS removal process can provide a comprehensive understanding to facilitate the exploration of removal mechanisms, especially given the significantly different composition of stormwater compared to other water contexts.

In recent years, increasing attention has been given to the presence of OMPs in stormwater and their implications for water quality and reuse. 25-27 Several studies have identified persistent, mobile, and toxic (PMT) substances among stormwater OMPs, highlighting their potential to persist in the environment and impact aquatic ecosystems.<sup>28</sup> A recent review found that out of 629 trace organic chemicals (TrOCs) detected in stormwater, 82 posed high ecological risks, and three were identified as potential health concern.3 These findings reveal the importance of effective treatment strategies mitigate **OMPs** contamination.

To address these concerns, we conducted a systematic review aimed at: (1) gaining a comprehensive understanding of OMPs removal in various types NBS as well as advanced technologies that showed the promising potential as the post-treatment approach in stormwater harvesting process; (2) quantitatively investigating the impact of key design and operational factors, as well as the physical and chemical properties of OMPs on treatment performance; and (3) identifying existing knowledge gaps, assessing the ability of NBS for stormwater OMPs treatment, and outlining future

research directions. Through this review, we aim to provide detailed recommendations to optimize stormwater harvesting practices for higher efficiency and safety.

### 2 Methods

#### 2.1 Systematic literature review

A systematic literature review was undertaken to search relevant articles in Scopus and Web of Science, employing predeveloped search terms (refer to Table S1 in SI). We specifically looked at the treatment data for the removal of OMPs from stormwater, including both laboratory and field tests. Subsequently, a three-tiered exclusion process (see exclusion criteria in Fig. 1) was employed to eliminate irrelevant publications. The whole process followed Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guideline. To ensure the accuracy of the review process and minimize potential biases that could result in data omissions, two researchers independently conducted the shortlisting and data extraction procedures, followed by cross-checking of the results. Furthermore, stormwater quality monitoring papers that included treatment data were incorporated to augment the dataset. These additional sources were identified during full-text review and added according to PRISMA 2020 guidelines as a supplementary pathway for study inclusion.<sup>29</sup> The final list of data sources amounts to 91, with the complete list of publications provided in the SI (Table S2).

#### 2.2 Data collection

Overview of reviewed treatment systems. Five commonly utilized nature-based systems (NBS) were selected: (1) biofiltration, or bioretention systems and rain gardens, which incorporate engineered soil and vegetation to filter pollutants from stormwater;30 (2) constructed wetlands, which simulate natural ecosystems, utilizing aquatic plants and microbes to treat runoff;31 (3) porous pavements, such as permeable asphalt or concrete, can facilitate the infiltration of stormwater through the surface, reducing runoff volume and pollutant load,32 (4) stormwater ponds, designed to detain water, allowing sediments to settle and providing space for additional treatment through aquatic vegetation and biological processes;<sup>33</sup> (5) swales, which are shallow vegetated channels typically applied alongside roads or in green spaces,

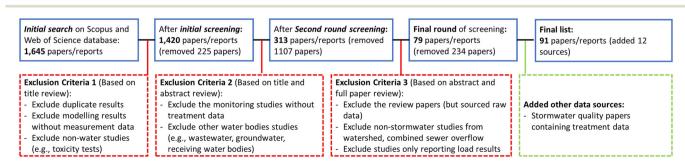


Fig. 1 Schematic procedure of data source shortlist for urban stormwater treatment systems

lead runoff, therefore promoting infiltration, sediment capture, and biological treatment during the process.<sup>34</sup> The schematic figures with design components and main treatment mechanisms for them have been summarized in Table S3. Additionally, we also reviewed and collected treatment data of advanced technologies involving chemical oxidation processes, including ozonation, electrochemical oxidation, photocatalytic oxidation and peroxydisulfate oxidation. 35-38 These technologies rely on the generation of powerful oxidants (e.g., hydroxyl radicals, superoxides, singlet oxygen, etc.) that can rapidly react with many OMPs in stormwater. Briefly, biofilters, constructed wetlands, and swales were found as the top three NBS in terms of research attention for stormwater OMPs removal with 46, 16 and 10 papers reported, respectively. Advanced technologies as the emerging techniques were investigated in 10 papers, focusing on 19 pollutants. Porous pavement and stormwater pond have only been studied in 4 and 5 papers, respectively.

Characterization of collected OMPs. All OMPs included in this study were compiled from the reviewed literature without prior selection, meaning all compounds with available concentration or removal data were included. Based on previous studies,3 the collected OMPs were classified into nine categories: pesticides, pharmaceuticals and personal care products (PPCPs), polycyclic aromatic hydrocarbons (PAHs), per- and polyfluoroalkyl substances (PFAS), flame retardants, plasticizers, polychlorinated biphenyls (PCBs), corrosion inhibitors (CIs), and other industrial chemicals/intermediates/ solvents (OICs). Organic CIs (e.g., benzothiazole benzotriazole) are widely used in broad industrial and household applications, including rubber manufacturing, deicing and anti-icing agents and fungicides.3,39 Table S4 provides detailed information for each OMP, including category, INCHIKEY, CAS number, chemical formula, use classification,  $\log K_{\text{ow}}$ , and estimated half-life in water. A descriptive statistical summary of the dataset is presented in Table S5, with Table S5a summarizing outflow concentrations and Table S5b summarizing removal rates for the 181 OMPs collected across multiple treatment systems.

Performance data and relevant information collection. The inflow, outflow and removal rate data were collected together with other relevant information, including catchment characteristics, climate, sampling, system design and system operation parameters. A summary of the collected parameters is provided in Table S6. Load-based data were found to be limited and often reported in inconsistent units, making them unsuitable for direct comparison with concentration-based data used in the statistical analyses. Moreover, load-based assessments typically require complete mass balance and flow data, which were frequently unavailable or incomplete in the reviewed literature. As a result, our quantitative analysis focused on concentrationbased removal performance, while load reduction findings are discussed qualitatively where relevant. Specifically, we defined "removal" as the reduction in outflow concentration relative to inflow concentration. In this paper, "removal" refers exclusively to concentration-based differences, whereas "load reduction" denotes mass-based removal.

# 2.3 Impact of system design and operational parameters on treatment performance

The system design and operation parameters, which could include either (i) categorical parameters (e.g., plant presence, wetland type), or (ii) numerical parameters (e.g., media depth, infiltration rate) were collected and analyzed for their impact on the treatment performance. Specifically, Kruskal-Wallis test was employed for the categorical parameters, while Pearson (for linear relationships) and Spearman (for nonlinear relationships) correlation analyses were used for numerical parameters. To maintain consistency across studies and reduce potential bias from studies reporting extensive raw datasets, we used summary statistics (e.g., percentile concentrations, minimum, maximum, or means) as reported in the original studies. When only raw data were we calculated these statistics ourselves. provided. Additionally, only the parameters with a minimum of three data points were included in the statistical analysis to ensure basic validity. While larger sample sizes are preferred for statistical robustness, this threshold was selected to balance analytical rigor with the limited availability of comparable data across studies, and is consistent with guidance for exploratory analyses when data constraints exist. 40 Table S7 summarizes the design and operational parameters that underwent the statistical analysis.

# 3 Results and discussion

#### 3.1 Biofiltration systems

**3.1.1 Treatment performance overview.** Biofiltration systems demonstrated effective treatment performance for the 21 tested OMPs, evidenced by the obvious reductions in their concentrations (Fig. 2). These OMPs, classified by Zhang, *et al.* (2024)<sup>3</sup> into five categories—PAHs, pesticides, flame retardants, plasticizers, and CIs – highlighting the diverse range of contaminants biofiltration systems can address.

PAHs were most extensively tested for their removal through biofiltration systems, due to their high detection frequency in road runoff, as a major contaminant in stormwater.41 PAHs are associated with particulate matter, and have the potential to be removed through filtration and adsorption by the filter media.42 Thus, an efficient and consistent removal of many PAHs by a median rate of >95%, benzo(a)pyrene (BaP), chrysene, pyrene, phenanthrene, were observed. Conversely, other PAHs exhibited varied removal rates. An example is fluoranthene, which showed a poor removal efficiency of 7.1% in a study conducted by Boving and Neary (2007)<sup>43</sup> using wood as the sole filter media. In contrast, much better removal (up to >99%) was achieved in a study done by Jay, et al.  $(2019)^{44}$ testing a range of bioretention soil mixtures which included different combinations of materials, such as biosolids,

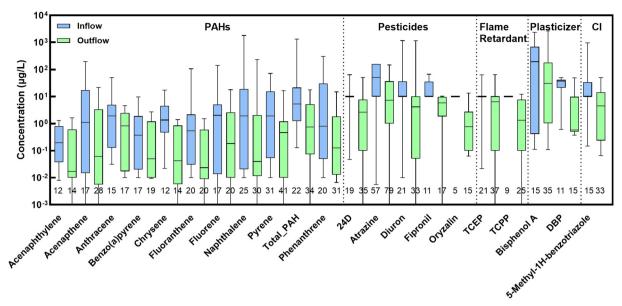


Fig. 2 The inflow and outflow concentration of 21 OMPs for biofiltration systems (CI - corrosion inhibitor; number stands for data points for each plot). The OMPs that have over five reported points are included

composts, water treatment residuals, oyster shells, soil and sawdust etc.

The tested pesticides, such as 2,4-D, diuron, atrazine, fipronil etc., showed positive removal results, with significant differences between inflow and outflow concentrations (p <0.05; Fig. 2). Oryzalin, a relatively hydrophobic compound ( $\log K_{\rm ow} \sim 3.6$ ), exhibited consistent and efficient removal in concentration across studies, likely due to its strong affinity for the organic-rich media such as biochar-enhanced vegetated biofilters that promote sorption-driven processes. 18 In contrast, 2,4-D is more hydrophilic ( $log D_{ow} = -0.83$ ; octanol-water distribution coefficient)<sup>45</sup> and exists predominantly in its anionic form at environmental pH, reducing its sorption to unamended wood chips and potentially leading to desorption and leaching, as reflected by the negative removal rate of -73%. However, when composite geomedia were used, as in Ray, et al. (2019), 46 which likely provided more favourable binding conditions (e.g., increased surface area, charge interactions), removal improved dramatically to 98%.

The remaining categories, including flame retardants, plasticizers, and CIs, showed high inflow concentrations and considerable variability in removal rates (Fig. 2). These categories have received less attention with fewer data points and their studies were often in the exploratory stage of lab experiments, typically involving unvegetated column studies that yielded lower removal performance.<sup>47</sup> For instance, Sabogal-Paz, et al. (2020)<sup>48</sup> reported poor bisphenol A (BPA) removal in household sand (HSSFs), filters where high influent concentrations (~2360 µg L<sup>-1</sup>) and weak biological layer development led to variable or even negative removal outcomes (Fig. 2). In contrast, recent studies have demonstrated that reactive mineral media, such as manganese oxide-coated sands, can oxidatively degrade BPA in situ. Charbonnet, et al. (2018),49 Charbonnet, et al. (2021)<sup>50</sup> showed that these media retain high reactivity through chemical regeneration and mineral phase stabilization. DEHP and DBP have been tested in Flanagan, et al. (2018)'s51 study as well with removal of 7.1% and 35.3%, respectively.

On the other hand, emerging OMPs of major concern, such as PFAS and 6PPD-quinone, have started receiving limited attention in biofiltration literature primarily due to their recent emergence rather than system incompatibility. For PFAS, three studies have reported variable removal performance, ranging from -1.5% to 99.8% for PFOA, 7.3% to >99% for PFOS46 and 72% to 80% for total PFAS removal.<sup>52</sup> 6PPD-quinone (detailed information can be found in Table S4), a transformation product of a tire antioxidant and a known acute toxicant to coho salmon, has been detected in stormwater at a mean concentration of 600 ng L<sup>-1</sup>.3 More recent peer-reviewed studies have now demonstrated that bioretention systems can effectively reduce 6PPD-quinone loads. Rodgers, et al. (2023)<sup>53</sup> reported  $\sim$ 95% mass reduction in a full-scale, mature bioretention cell under typical storm conditions, supported by both field measurements and process-based modelling. Further, Rodgers, et al. (2024)<sup>54</sup> used design simulations to show how system modifications could enhance the capture of both hydrophobic and hydrophilic trace organics, including 6PPDquinone. Additionally, McIntyre, et al. (2023)<sup>55</sup> provided indirect evidence that bioretention filtration can reduce the toxicity of urban runoff to early life stage coho salmon, likely including contributions from 6PPD-quinone removal. These findings collectively highlight the potential of well-designed bioretention systems to address challenging and newly identified stormwater contaminants.

In summary, despite some variability, biofiltration systems have demonstrated clear reductions in many OMPs. However, removal performance is compound-specific, and emerging contaminants such as PFAS (*e.g.*, PFOS and PFOA) are notably resistant to both chemical and biological degradation in the environment. This limitation may constrain the application of biofiltration systems for water reuse. As a result, additional treatment steps are often required, and the optimization efforts have focused on enhancing removal through amendments such as biochar<sup>56</sup> or activated carbon.<sup>57</sup> Further research is needed to develop and refine biofiltration configurations to achieve long-term, effective treatment of a broader range of OMPs, including recently identified emerging contaminants detected in stormwater.

#### 3.1.2 Impact of biofilter design and operation

3.1.2.1 Biofiltration media. Among the eight OMPs (i.e., 2,4-D, atrazine, diuron, naphthalene, pyrene, TCEP, TCPP, and PAHs) showing significant differences in removal across media types (p < 0.05), pyrene and atrazine were selected for detailed illustration in Fig. 3 due to their sufficient data availability (i.e., >3 data points) across media types and their contrasting physico-chemical properties. This allows for both robust statistical comparison and mechanistic insight into how media characteristics influence the removal of different behaviours. compounds with Among unamended media types, sandy media achieved the highest pyrene removal efficiency (median 95%, with relatively low variability). These results were based on a limited dataset (four data points) and may be influenced by specific design features in the study conducted by Zhang, et al. (2014),<sup>58</sup> such as the inclusion of a submerged zone that increased hydraulic retention time. Given pyrene's high hydrophobicity  $(\log K_{\text{ow}} = 4.88)$  and strong particle association, particle filtration by the sand may also have contributed to the high removal observed. Loamy sand and soil media followed, with median removal rates of 85% and 82%, respectively. Amendments further improved median removal: compost addition to sandy media and zeolite addition to loamy sand both enhanced pyrene removal, likely due to increased adsorption capacity. However, these amendments also introduced greater variability in performance compared to their unamended counterparts. For example, the biofilter amended with biosolid yard compost achieved >99% pyrene removal, whereas food-yard compost media demonstrated a lower removal of 65.9%.44 In contrast, when examining atrazine removal, different amendments to sandy media revealed significant performance enhancements, particularly with the incorporation of granular active carbon (GAC) and biochar (Fig. 3). GAC helped biofilters achieve >99% atrazine removal in the study conducted by LeviRam, et al. (2022).8 However, compost amendments resulted in large variability in removal efficiency, with rates as low as 4.8% observed in Ulrich, et al. (2017)16,18 using sand filters with organic compost amendments. This may be attributed to the mobility in subsurface and moderate hydrophobicity ( $\log K_{ow}$  as 2.61-2.7) of atrazine which reduced the effectiveness of the adsorption. In contrast, for compounds such as 2,4-D, diuron, TCEP, and TCPP, biochar amendment to sandy media substantially improved removal efficiency. This enhancement is attributed to the high sorption capacity of biochar, increasing the media's affinity for a broader range of OMPs. Additionally, biofilters incorporating iron and manganese oxides have demonstrated enhanced bisphenol A (BPA) removal via oxidative transformation processes, achieving a median removal of 82.1%.59 While these metal oxides act through chemical reactions, amendments such as GAC, biochar, and compost primarily improve sorption capacity of the media. Despite the differing mechanisms, their

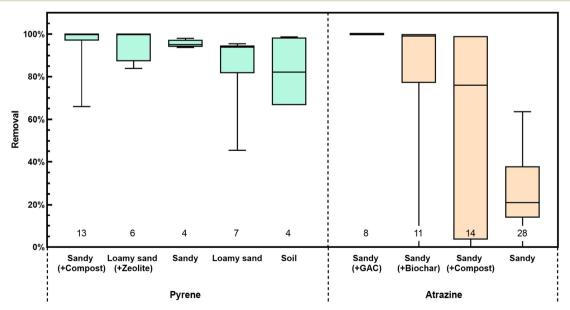


Fig. 3 The impact of filter media used in biofiltration systems towards the treatment performance for pyrene and atrazine. All presented chemicals showed significant differences in removal rates based on concentration levels between media amendment groups (p < 0.05).

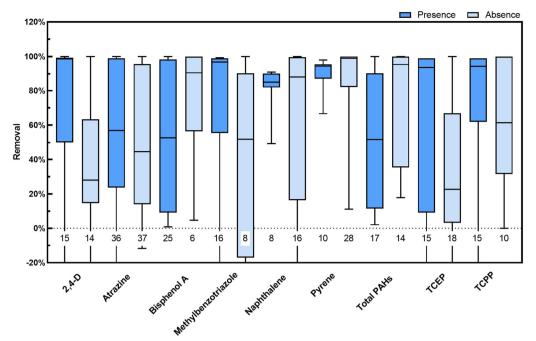


Fig. 4 Removal rate for plant presence (dark blue) and absence (light blue) for OMPs (numbers stand for data points - only those with >5 points presented). All presented chemicals showed significant differences in removal rates between the 'presence' and 'absence' groups (p < 0.05).

performance outcomes can be comparably effective depending on the OMP of interest. However, a recent field study found that biochar-amended biofilters showed limited improvement in removing some mobile and hydrophilic OMPs, such as PFAS and BPA, likely due to factors like large particle size, low contact time, and pore blockage.60 Therefore, it is advisable to consider the strategic use of such amendments, sometimes in combination, to improve overall treatment efficacy. However, practical considerations such as the potential for nutrient leaching from compost and biochar must also be carefully managed in real-world applications.<sup>61</sup>

3.1.2.2 Plant presence. The plant presence in the biofiltration system was found to effectively enhance the removal of nine OMPs out of 33 OMPs, in particular for two pesticides (atrazine and 2,4-D), one corrosion inhibitor (methylbenzotriazole), and two flame retardants (TCEP and TCPP) (p < 0.05; Fig. 4 – only OMP with sufficient data was presented). For example, 2,4-D achieved a median removal efficiency of 99% in vegetated systems, markedly exceeding that observed in non-vegetated biofilters (only 28% median removal). Plant uptake has made a remarkable contribution to OMPs removal, for example Pritchard, et al. (2018)<sup>62</sup> has found that Carex praegracilis effectively facilitated the removal of benzotriazole, achieving a removal rate of 97.1%, with traces detected in both its leaves and roots. Paz, et al. (2016)<sup>63</sup> revealed that wheat can aid in the remediation of pharmaceutical compounds (i.e., carbamazepine) through plant uptake and even facilitate its metabolism into EP-CBZ. Two plants, Typha and Phragmites, were found with the most efficient removal for ibuprofen and iohexol with firstorder removal rate constants of 0.38 and 0.06 day<sup>-1</sup>, respectively.<sup>64</sup> Further, plant species selection was reported with significant impact towards the chemical removal process in biofiltration systems, like the flowers Canna observed with the enhancement sulfamethoxazole and DEET removal compared to other tested.19 grasses, shrubs and trees Interestingly, accumulation patterns of caffeine and DEET suggest root tissues generally exhibit higher concentrations than shoots (e.g., 57 ng  $g^{-1}$  vs. 14.3 ng  $g^{-1}$ ), although this varies with compound properties. For example, caffeine - a hydrophilic compound ( $\log K_{\rm ow} \sim -0.07$ ), showed relatively higher accumulation in shoots compared to DEET. In contrast, DEET, which is more hydrophobic ( $\log K_{\rm ow} \sim 2.2$ ), tends to accumulate more in the roots. These differences are likely due to variations in compound mobility and translocation mechanisms within the plant. Thus, translocation behaviour should be considered in plant selection strategies for targeted contaminant removal.

Notably, vegetation contributes to stormwater treatment not only through direct uptake but also by enhancing sorption and degradation through indirect mechanisms.<sup>65</sup> These include root-zone oxygenation that supports aerobic microbial communities, exudate production that alters microbial consortia, and hydraulic influences that increase retention time and contact with reactive media. These multiple plant-mediated processes provide both chemical hydrological benefits, making vegetation multifunctional component of biofiltration systems.

Total PAHs exhibited more variable removal performance in vegetated biofilters compared to unvegetated systems. This variability may be attributed to the use of media amendments in unvegetated systems to enhance treatment performance, whereas studies on vegetated

predominantly employed traditional media configurations. While plant uptake contributes to OMPs removal, the adsorption capacity of advanced media can surpass plant-mediated effects, especially in short term studies. For example, compost amendments in unvegetated systems achieved an average PAHs removal of over 99%. 66 However, the study using peat in vegetated biofilters reported median PAHs removal ranging from 8.05% to 57.5%, 67 while vegetated biofilters incorporating topsoil still achieved up to 99% removal. These findings indicated that the variability in total PAHs removal in vegetated systems cannot be attributed solely to a lack of plant influence; under comparable conditions, plants may enhance OMP removal performance, especially considering the long lifespan of such systems.

3.1.2.3 Submerged zone. The submerged zone (SZ) is a design modification in biofiltration systems that creates a water-saturated area by elevating the outlet, and is known to enhance denitrification process. <sup>12</sup> Two studies also showed the improved removal of OMPs by incorporating SZ in the operation. <sup>58,69</sup> This is achieved by extending the residence time of stormwater, allowing greater contact between the filter media and pollutants, thus enhancing processes such as adsorption and biodegradation. <sup>58,70</sup>

Our statistical analysis (Kruskal-Wallis test, p < 0.05) demonstrated that the SZ significantly improved the removal of four OMPs, *i.e.*, 2,4-D, TCEP, TCPP, and methylbenzotriazole with average 26.3% increase. This improvement is partly attributed to the anoxic or low-oxygen environment created in the SZ, which promotes denitrification and alters microbial communities. However, these redox conditions can also affect OMP removal in more complex ways. Several studies have shown that many OMPs, particularly those that are more labile and biodegradable under aerobic conditions (*e.g.*, acetaminophen, caffeine), may exhibit lower degradation under anoxic conditions. Thus,

while the SZ may benefit removal of certain compounds through extended contact time and anaerobic pathways, it may not universally improve OMP removal, particularly for compounds that rely on oxidative degradation pathways. Nevertheless, a recent study by Zhang, et al. (2024)<sup>20</sup> proposed innovative real-time control biofilters, and found dynamic operation (releasing SZ water) can lead to better removal of many OMPs, especially the ones that have relatively short half-lives and prefer aerobic degradation (e.g., bisphenol-A, diuron, DEET, paracetamol and caffeine). This is likely due to the enhanced oxygen diffusion into SZ with the dynamic operation. However, for atrazine, lower median removal was observed in SZ biofilters in Fig. 5. This outcome was not directly related to the SZ design but rather to the challenging test conditions. For example, Ulrich, et al. (2017)<sup>18</sup> evaluated atrazine removal under continuous highload dosing, which caused leaching and resulted in negative removal rates (-35%). Conversely, for bisphenol A, lower and more variable removal rates were found in SZ biofilters. Studies reporting high bisphenol A removal in non-SZ systems typically employed metal-amended media, such as iron-enhanced sand filters<sup>47</sup> and manganese oxide modified geo-media,<sup>59</sup> specifically designed to improve treatment. In contrast, amendments to SZ biofilters were less extensively studied, with only one investigation by Lu and Chen (2018),69 who explored various biochar amendments and hydraulic loading rates, leading to variable outcomes. This imbalance in media amendment research between SZ and non-SZ biofilters likely contributes to the lower removal efficiencies for atrazine and bisphenol A in SZ systems, highlighting the need for more comprehensive research on SZ impacts across different pollutants.

3.1.2.4 Infiltration rate. The infiltration rate (IR) is a crucial operational parameter in biofilter systems, previously identified as the impacting factor in nutrient treatment processes.<sup>71</sup> Similarly, machine learning analysis by Fang,

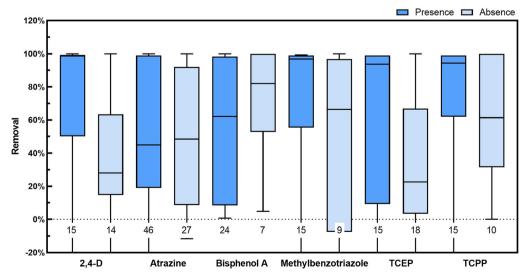


Fig. 5 The impact of submerged zone presence (dark blue) and absence (light blue) in biofiltration towards the removal rate (numbers stand for data points). All presented chemicals showed significant differences in removal rates between the 'presence' and 'absence' groups (p < 0.05).

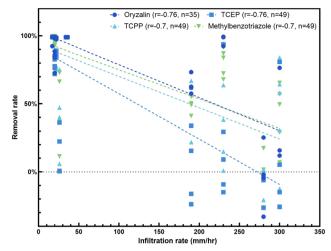


Fig. 6 The impact of infiltration rate towards biofiltration systems performance for four organic chemicals (oryzalin, TCEP, TCPP, methylbenzotriazole)

et al. (2021)<sup>72</sup> highlighted the significance of IR in heavy metal removal in stormwater biofilters. This review extends these findings, demonstrating a significant impact of IR on the removal efficiency of four specific organic chemicals: oryzalin, TCEP, TCPP, and methylbenzotriazole (Pearson correlation, p < 0.05; Fig. 6). It was observed that lower infiltration rates are intended to enhance removal of these chemicals. A recent paper tested the real-time control of IR in biofilter to improve the OMPs removal by 18.4% via controlling IR as 49.6 mm h<sup>-1</sup> compared to uncontrolled columns with 430.7 mm h<sup>-1</sup>.20 However, it is important to consider the potential downside as excessively low infiltration rates might result in increased untreated overflow, posing potential environmental risks to the surrounding regions. To address this trade-off, the use of high-surface-area sorptive amendments such as biochar or GAC provides a promising solution to enhance removal

efficiency through adsorption without substantially impeding infiltration capacity. This dual benefit reveals the importance of media selection in achieving both hydraulic and treatment goals in biofilter design.

3.1.3 Correlation between properties of OMPs and treatment performance. We explored the relationship between the hydrophobicity (based on  $\log K_{ow}$  – octanol/water partition coefficient) and the persistence of organic chemicals (based on half-lives) and their removal behaviour in biofiltration systems. As shown in Fig. 7, a significant positive correlation (Pearson and Spearman correlation; p <0.05) was identified between  $\log K_{ow}$  values and removal indicating that chemicals with efficiency, higher hydrophobicity are more effectively removed in biofiltration systems, generally consistent with previous research. 19,20,73 On the other hand, biodegradation half-lives in water did not present a significant impact on the overall removal efficiency of OMPs (p > 0.05), as OMPs with high half-lives still demonstrated high removal rate (Fig. 7). However, this may be biased by the high removal rates observed for OMPs with long half-lives (e.g., BaP, chrysene, and pyrene - all over 90% removal but with half-lives exceeding 200 days). A closer examination to hydrophilic compounds OMPs (i.e., have low  $\log K_{\rm ow}$  values) revealed a negative correlation between halflives and removal efficiency. For example, as the half-lives of 5-methyl-1H-benzotriazole, atrazine and TCEP increased, their removal efficiency decreased to 72.95%, 48.39% and 36.34%, respectively. This observation suggested that for hydrophilic OMPs, half-lives became a more critical factor influencing removal performance. Therefore, highly hydrophobic OMPs were predominantly removed through adsorption, while hydrophilic OMPs relied more on biodegradation processes. This distinction reflects a broader kinetics versus equilibrium limitation: hydrophobic, recalcitrant compounds are more easily retained by filtration and sorption processes but are often resistant to degradation, whereas hydrophilic compounds may escape capture yet be

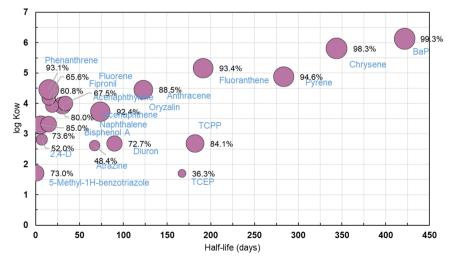


Fig. 7 Relationship between biodegradation half-life (x axis),  $\log K_{ow}$  (y axis), and median removal (bubble size) for different OMPs for biofilter treatment process. Data include all available removal results, representing various treatment mechanisms (e.g., sorption, biodegradation).

more amenable to microbial transformation. Given the persistence of some OMPs-defined here as resistance to biotic or abiotic degradation—long-term accumulation in filter media is a concern, particularly for compounds that are both persistent and sorptive (e.g., PAHs with over 300 days half-lives). In contrast, persistent but highly mobile and nonsorbing OMPs (e.g., short-chain PFAS) may pose risks through leaching rather than accumulation. Enhancing biodegradation processes in biofilter system design is essential to mitigate risks associated with the accumulation of refractory contaminants. A promising approach has been demonstrated in two recent studies by Tanmoy and LeFevre (2024a),74 Tanmoy and LeFevre (2024b),75 who developed biologically active, sorptive composite beads ("BioSorp beads") that encapsulate both black carbon and white-rot fungi. These engineered geomedia rapidly capture trace organics via sorption while supporting microbial metabolism to degrade the contaminants over time, thereby renewing sorption capacity in situ.

#### 3.2 Constructed wetlands

3.2.1 Treatment performance overview. Our review that found only seven chemicals - comprising two PAHs, three pesticides, and two PFAS - had more than five data points for either inflow or outflow concentrations in constructed wetland studies (Fig. 8). These compounds were selected for inclusion in Fig. 8 to ensure meaningful visual comparison, while other chemicals with limited data are discussed separately below. Notably, a reduction in median outflow concentrations relative to inflow concentrations was observed for total PAHs, pyrene, and diuron. Although simazine's median outflow concentration did not decrease compared to its inflow median concentrations, a reduction in both the 25th and 75th percentile concentrations of outflow was noted, suggesting an apparent decrease in simazine levels. On the other hand, atrazine displayed higher outflow than inflow concentrations. A possible reason was that the outflow concentration was biased to high level by the extreme values recorded at one site in Melbourne (0.04 µg L<sup>-1</sup>) compared to its normal level (0.001 µg L<sup>-1</sup>).<sup>76</sup> A marginal reduction in PFOA and PFOS concentrations was also observed, with median removal rates of 5% and 13% for PFOA and PFOS, respectively. This outcome was likely attributed to the limited biodegradability of PFOA and PFOS in natural systems, with sorption being the predominant removal process, as suggested by Arslan and El-Din (2021).11 Furthermore, wetlands, particularly those with horizontal flow designs, do not exhibit significant adsorption capacity, as evidenced by the low removal efficiency of simazine and diuron in a horizontal subsurface flow wetland system reported by Matamoros, et al. (2007).77 Therefore, enhancing the adsorption capability of wetland systems is crucial for improving the treatment of organic chemicals in stormwater.

#### 3.2.2 Impact of system design

3.2.2.1 Wetland design. The design of constructed wetlands plays an important role in determining their effectiveness in the OMPs treatment. One critical design aspect is choosing between surface flow (SF) and subsurface flow (SSF) wetlands. SF wetlands are characterized by shallow water bodies with emergent vegetation, facilitate the pollutant removal primarily through photodegradation and microbial activity at the water-plant interface. 78 These systems mimic natural wetlands, creating an environment where sunlight and microbial interactions actively break down pollutants. On the other hand, subsurface flow wetlands, where water flows beneath the surface through a medium such as gravel, focus more on filtration and adsorption processes.<sup>79</sup> SSF wetlands can be further categorized into vertical SSF and horizontal SSF designs. While the available data were insufficient for comprehensive statistical analysis, the existing evidence indicated that vertical SSF wetlands generally outperformed horizontal SSF wetlands - all exhibited higher OMPs removal efficiencies compared to SF wetlands. For example, Cottin and Merlin (2008)80 found that vertical SSF wetland delivering median 92.7% total PAHs

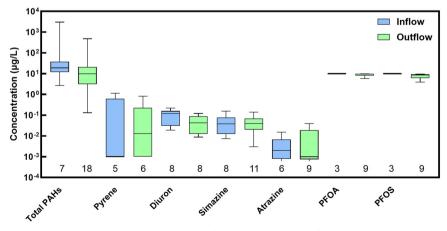


Fig. 8 The inflow and outflow concentration of 7 organic chemicals (at least one of inflow/outflow results with >5 data points) for constructed wetlands.

removal under all the testing conditions. Schmitt, et al. (2015)81 found with over 70% removal for phenanthrene, fluoranthene and pyrene in a residential constructed wetland. In contrast, fewer studies have investigated horizontal SSF wetlands, reporting 59% and 70% removal of total PAHs<sup>82</sup> and variable pesticide removal efficiencies ranging from 46% to 98%.83 SF wetlands, which have been more extensively tested, demonstrated lower performance, with 7.5% median removal of total PAHs<sup>84</sup> and median removal efficiencies of 50.8%, 52.4%, and 62.5% for diuron, simazine, and atrazine, respectively.85

Beyond the basic categorization into flow patterns, other design elements of constructed wetlands also significantly influence treatment efficiency. For instance, the selection and arrangement of plants within the wetland is not merely a matter of ecological aesthetics but critically affects the removal mechanisms. Brisson and Chazarenc (2009)86 reviewed the impact of plant species on the removal efficiency of nutrients, BOD, and COD, reporting significant differences among species. A similar influence is likely for OMP treatment; however, further studies are required to substantiate this hypothesis. Plants in wetlands contribute to the removal of OMPs through processes such as uptake, biodegradation, and by providing surfaces for microbial colonization, which further enhances degradation. <sup>15</sup> For instance, studies have demonstrated that the interaction between plants and endophytic bacteria can facilitate OMP remediation,87 as observed with Conyza canadensis in conjunction with Stenotrophomonas sp., which supported phenanthrene degradation. Additionally, the configuration of the wetland, including its size, depth, and the flow path of water, directly impacts the residence time of water and the extent of pollutant exposure to degradation processes.88 A longer water residence time typically allows for more extensive biodegradation and adsorption, leading to increased pollutant removals. For instance, Sharif, et al. (2013)<sup>89</sup> observed that increasing the hydraulic retention time by more than two-fold enhanced the trace organics removal by 20-60%.

#### 3.3 Porous pavement

3.3.1 Treatment performance overview. Only four studies reported the removal of OMPs by porous pavement (PP). The tested 10 PAHs and four total petroleum hydrocarbons (TPH) predominantly originated from traffic activities 90-92 while the only plasticizer DEHP was found in runoff at industrial area for treatment.<sup>93</sup> In particular, benzo(b)fluoranthene, fluoranthene and pyrene from PAHs and motor oil from TPH were highlighted for their exceptional treatment performance in PP, achieving an average removal rate exceeding 80%. 91 Most of the tested OMPs showed noteworthy results with more than 50% average removal rates, including chrysene, phenanthrene, benzo(g,h,i)perylene from PAHs and diesel H from TPH together with DEHP from plasticizer.91,93 However, the situation for benzo(a)pyrene, a notable concern in stormwater management, was less consistent, with variable removal rates ranging from 20% to 50%. Its mean outflow concentration, recorded between 0.049-0.051 µg L<sup>-1</sup>, notably surpassed the drinking water guidelines of Canada, Australia, and the United States, which were set at 0.01  $\mu$ g L<sup>-1</sup>, 0.01  $\mu$ g L<sup>-1</sup>, and 0.2  $\mu$ g  $L^{-1}$ , respectively, thus posing a significant concern.

Conversely, the removal rates for two other PAHs, 2-methyl-2-propanol-d10 and dibenz(a,h)anthracene, were quite low (<10%). Remarkably, dibenz(a,h)anthracene exhibited net leaching (i.e., negative removal efficiency) in Jayakaran, et al. (2019)'s study possibly due to the high inflow concentration (63.5 µg L<sup>-1</sup>, which is considerably higher than  $0.0761 \mu g L^{-1}$  for pyrene) resulting in the saturation of PP adsorption capacity. Given these findings, it becomes evident that PAHs demonstrating moderate to poor removal performance treated by PP, especially benzo(a)pyrene, necessitate further treatment strategies. On the other hand, the study for TPH is very limited, requiring more effort for PP studies considering their increasing concern in traffic and industrial runoff.

#### 3.3.2 Impact of system design

3.3.2.1 Pavement material. PPs, designed to allow water to percolate through the surface and into underlying layers, rely heavily on the material's physical and chemical properties for pollutant filtration and degradation. 91 Common materials used include porous concrete, permeable interlocking concrete pavers, and porous asphalt, each with unique characteristics affecting pollutants removal.<sup>14</sup> For instance, porous concrete has been found to increase the sorption rate by 34.5% for naphthalene in the column studies, with its strong adsorption and retardation capacity.<sup>94</sup> On the other hand, porous asphalt, due to its bituminous nature, may offer better adsorption capabilities for hydrophobic pollutants (e.g., 88.4% removal for fluoranthene).91

3.3.2.2 Geotextile. Geotextiles, permeable fabrics used in conjunction with soil and other materials, are integral to the filtration and separation processes in PPs.95 The selection of geotextile type in porous pavement systems plays a crucial role in determining the efficacy of OMP removal. Non-woven geotextiles, for instance, with their random fibre orientation and high porosity, are excellent for trapping particulate matter and adsorbing pollutants, including OMPs bound to sediments. This makes them suitable for use in areas with high levels of particulate-bound contaminants (e.g., PAHs). Conversely, woven geotextiles, known for their tighter weave and greater strength, might be less efficient in pollutant adsorption but are more durable in high-traffic areas. 96 The choice of geotextile thus directly impacts the removal efficiency of OMPs, especially those adhering to suspended solids.

Beyond simple filtration, the interaction between the geotextile and microbial communities is another critical aspect affecting OMP removal. For instance, geotextiles were found to incorporate inorganic nutrients to enhance the growth of oil-degrading microorganisms in Newman, et al. (2001)'s<sup>97</sup> study, showing a 99.6% removal rate for oil. On the other hand, the presence of herbicides would inhibit the

microbial activities leading to the reduction for PP's OMP removal. Mbanaso, *et al.* (2013)<sup>98</sup> found the negative impact of glyphosate-containing herbicides on geotextile in retaining hydrocarbons in the PP treatment process. Therefore, the careful selection and integration of geotextiles, targeting OMPs in the stormwater (usually traffic-related chemicals), are essential for optimizing the performance of porous pavement systems in urban water management. However, although the average condition would not result in clogging due to the geotextile application, the flooding condition needs to be considered after 5–10 years operation.<sup>99</sup>

While porous pavement systems and geotextiles are often recognized for their pollutant removal potential, it is important to also consider the risk of contaminant leaching from the materials themselves. For instance, some bitumenbased materials used in porous asphalt may leach PAHs and heavy metals under acidic conditions, particularly in the early life of the pavement. Similarly, geotextiles may release substances (like octyl benzenesulfonate, suberic acid etc.) that could show toxicity to bacteria and algae. Leaching risks may also increase over time due to temperature or chemical degradation of the materials. These potential drawbacks highlight the need for careful material selection and long-term monitoring to ensure that treatment materials do not become secondary sources of pollution.

#### 3.4 Stormwater ponds

Studies on stormwater ponds have only reported treatment data for 16 PAHs and two PPCPs (caffeine and carbamazepine) (Table S5b). Among the PAHs, fluoranthene, pyrene, and total PAHs, the mean removal rates were notably high, exceeding 80%, as reported by Birch, *et al.* (2012), <sup>103</sup> Istenič, *et al.* (2011), <sup>104</sup> illustrating a significant reduction

attributed to the treatment process. In contrast, the removal rates for PPCPs varied. For instance, caffeine showed removal rate of 45–78%, indicating a moderately effective removal process. However, carbamazepine presented a less efficient removal, with rates below 30%, as highlighted in the study by Ivanovsky, *et al.* (2018). This variation in removal rates between different categories of organic chemicals suggested the variability in the treatment effectiveness of pond systems and highlighted the need for further investigation.

#### 3.5 Swales

20 swale systems were evaluated for their efficacy in removing organic chemicals. However, the data available for each specific OMP was limited. Fig. 9 shows nine OMPs with more than five data points out of 47 OMPs, providing a clearer picture of their removal capabilities. 29 OMPs had only one data point, with the median value derived from a single study.<sup>51</sup> Most of PAHs demonstrated effective removal, with mean rates exceeding 50% (e.g., total PAHs, naphthalene etc.). An exception to this trend was noted for benzo(a)pyrene and phenanthrene, with lower removal rates of 9.1% and 47.6%, respectively, as reported by Leroy, et al. (2016). 106 Similarly, most pesticides exhibited mean removal rates above 50% (e.g., atrazine, pyrethroids, glyphosate etc.), with the exception of 2-hydroxy-terbutryn (49.8%), diuron desmethyl (25.4%), and fipronil (leaching). The negative removal rates for fipronil, specifically identified in Anderson, et al. (2016)'s 107 bioswale study, were attributed to the release of bound fipronil from plants during the treatment process. When it comes to plasticizers, around half were effectively removed by swales, with removal rates greater than 50%, including bisphenol A, octyl phenol, and nonylphenol. Conversely, others like DNP (2,4-dinitrophenol), DBP (dibutyl

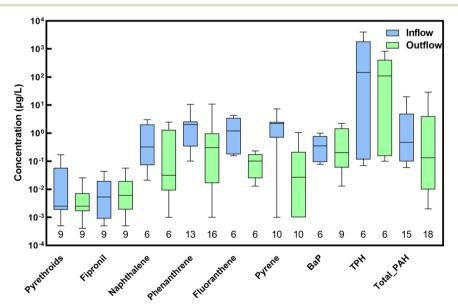


Fig. 9 The inflow and outflow concentration of organic chemicals (at least one of inflow/outflow results with >5 data points) for stormwater ponds.

phthalate), DiBP (di-isobutyl phthalate), nonylphenol monocarboxylate, DMP (dimethyl phthalate), and octyl phenol monoethoxylate, exhibited poorer removal rates (less than 30%), as detailed in Flanagan, et al. (2018).<sup>51</sup>

#### 3.6 Advanced technologies

A range of advanced technologies (e.g., ozonation, photoelectrochemical oxidation, UV/H2O2 and peroxydisulfate oxidation, etc.) have been explored for their efficiency in removing OMPs in stormwater (Table S8). Unlike NBS, which primarily employs adsorption, infiltration, biodegradation, these advanced technologies often depend on high oxidation capacity to transform the chemicals. The use of advanced oxidation processes, such as ozonation and UV radiation combined with H2O2, has led to significant removal rates for PAHs, often exceeding 80%. 108 However, the removal rates for pesticides varied, influenced by the diversity of chemicals and operational conditions. For instance, ozonation yielded only a 24% removal rate for diuron, 35 whereas electrochemical oxidation with 5 V achieved over 90% removal.<sup>36</sup> Representative corrosion inhibitors like benzothiazole also showed over 80% removal through chemical oxidation using peroxymonosulfate (PMS) activated by CuFe2O4, which generates sulfate radicals capable of degrading these compounds, even those generally considered persistent in the environment. 109 A recent study also demonstrated the effectiveness of combining UV/H2O2 pretreatment with large-grain biochar filtration in dry wells for hydrophilic OMPs. The integrated system achieved >90% removal for several insecticides and pharmaceuticals through a combination of direct photolysis and adsorption, while maintaining field applicability and lifespan under high-flow conditions. 110 In addition, Zhuang, et al. (2025)38 reported that biochar can also activate persulfate to produce singlet oxygen, achieving efficient transformation of specific stormwater contaminants such as benzotriazoles, benzothiazoles, and diuron. This combined sorptionoxidation process was robust against high DOC (dissolved organic carbon) and chloride levels, underscoring its promise as a complementary oxidation-based treatment strategy for refractory and mobile OMPs. Notably, these advanced technologies typically can achieve high removal efficiency (often >80%) within shorter treatment durations (ranging from minutes to a few hours) compared to NBS, which generally require extended retention times (days to weeks). However, these tests were still within the laboratory scale, and thus despite their great potential as post-NBS treatment methods, their feasibility in large-scale implementations still needs further exploration.

#### 3.7 Implications for stormwater treatment systems

The removal of OMPs in NBS relies on physical (adsorption, filtration, and sedimentation), chemical (precipitation and redox reactions), and biological (microbial transformation and plant uptake) processes that naturally occur within these systems.41 Recent studies also demonstrated the potential of fungal transformation—particularly by mycorrhizal fungi and white rot fungi-as a critical, though underexplored, biological pathway. For instance, mycorrhizal inoculation has been shown to improve plant biomass and enhance nutrient and pollutant removal in biofilters, 111 while white rot fungi like Trametes versicolor are capable of degrading recalcitrant OMPs such as carbamazepine and tire wear compounds via extracellular enzymes.112 These findings suggest that both natural colonization and targeted bioaugmentation with fungal species may offer promising solutions to improve stormwater treatment performance. Nevertheless, variability performance remains high due to differences in system design, plant selection, media composition and operations. Therefore, to improve the treatment performance of NBS, future designs should incorporate strategies that promote both abiotic and biotic removal mechanisms, e.g., through the inclusion of submerged zones, vertical flow configurations, or the use of porous media and biologically active amendments.

While the short-term removal performance of NBS for OMPs is promising, their long-term operation remains a concern. Much of the removal relies on adsorption, a reversible process subject to saturation of sorption sites. Once adsorption sites reach equilibrium, leaching may occur if degradation pathways are insufficient. 113 On the other hand, chemical and microbial degradation lead to irreversible transformation of OMPs. However, these processes are generally slower and require longer contact time, with biodegradation half-lives varying widely across different chemicals and environmental conditions. 114 Studies have simulated extended loading scenarios using prolonged dosing or high influent volumes, reporting pollutant breakthrough and declining performance over time. For example, breakthrough of simazine and atrazine was observed in biofilters with submerged zones after prolonged OMP inflows, resulting in less than 20% load reduction.<sup>58</sup> These findings highlight the importance of maintenance strategies, such as media replacement, regeneration, or the use of advanced materials. For instance, the operational lifespan of biochar for OMP sorption was found to range from five months to seven years, depending on its properties and the target compounds. 115 This further highlights the importance of enhancing the degradation of various OMPs in stormwater biofiltration systems. For example, Zhang, et al. (2024)<sup>20</sup> recently demonstrated that applying real-time control strategies can significantly improve the removal of a wide range of OMPs through enhanced biodegradation, while also limiting their accumulation in the filter media, and potentially extend the lifespan of biofilter media. It is also important to recognize that transformation processes do not always lead to complete mineralization; some transformation products, such as nonylphenol as the major biodegradation product of nonylphenol ethoxylates, are more toxic than the parent compounds. 116 Therefore, assessing the formation, persistence, and toxicity of transformation products should be an integral part of evaluating long-term NBS performance.

Stormwater biofiltration systems are the most extensively studied for their performance in removing OMPs, followed by constructed wetlands. However, much less data are available for other NBS like porous pavement, ponds, and swales. Compared to conventional pollutants (like nutrients and metals), the scarcity of data limits detailed analyses of these systems, particularly in terms of design and operational impacts. Even for the most studied system, biofilters, the focus of OMPs removal is on traditionally concerning chemicals, like PAHs and pesticides. To establish NBS as reliable barriers for stormwater treatment and harvesting, comprehensive studies, including both laboratory and field tests, are essential. These studies should focus on a broader range of OMPs to confirm the ubiquitous applicability of the findings. For example, recent attention has turned to PFAS, particularly emerging replacement compounds. While most studies have emphasized the environmental persistence of regulated PFAS such as PFOA and PFOS, both of which have largely been phased out,117 there is a growing need to assess the behaviour and treatment efficacy of their substitutes, including GenX, 6:2 fluorotelomer sulfonate (6:2 FTS), and perfluorobutane sulfonate (PFBS). 118 These replacement PFAS are typically shorter-chained, more mobile, and more challenging to be removed by using conventional stormwater treatment technologies.

Furthermore, innovative solutions could further enhance treatment performance by employing the concept of the Internet of Things (IoT). For example, real-time control (RTC), an idea recently developed and tested for its performance in enhancing the removal of nutrients, <sup>119</sup> *E. coli*<sup>120</sup> in biofiltration systems, and microorganisms in constructed wetlands, <sup>121</sup> has shown promises. Specific RTC strategies for enhancing OMPs removal have also been developed by Zhang, *et al.* (2024)<sup>20</sup> and have proven to be very effective in the removal of diverse OMPs. For instance, the best performing strategy – dynamic soil moisture control – presented the highest average removal rate (76.1%) of 10 tested OMPs and showed robustness to various rainfall event.

Further to system optimization, a thorough understanding of fundamental removal mechanisms is critical. This knowledge enables the development of robust models, which in turn support improved system design and maintenance strategies to enhance and sustain the effective treatment of OMPs. For instance, Randelovic, *et al.* (2016)<sup>122</sup> developed stormwater biofilter treatment model (MPiRe) to simulate OMPs removal process. This model was calibrated and validated with field datasets showing promising results for PAHs, phenols, phthalates *etc.* It provides the solid foundation to deliver effective treatment for OMPs in the following operation steps.

Moreover, a treatment chain approach could be proposed to achieve better treatment outcomes, integrating NBS as a preliminary treatment step, followed by advanced treatment methods to address persistent OMPs.<sup>3,36</sup> For instance, PFAS, which are not readily biodegradable, may

require strong oxidation processes (*e.g.*, photocatalytic oxidation, electrochemical oxidation *etc.*) as the post-treatment strategies. The only obstacle is that these advanced technologies are still in the laboratory development phase. More studies are expected to scale them up for stormwater treatment.

## 4 Conclusion

This study presents a systematic review of stormwater treatment systems, specifically focusing on the OMPs removal. Biofilters have been found to be the most popular and effective technology, with over 80% removal for most tested OMPs. A significant correlation was observed between hydrophobicity of OMPs and their removal rates (p < 0.05), indicating that adsorption plays a dominant role in biofiltration systems. In contrast, for hydrophilic OMPs, a negative correlation between half-lives and removal rates was observed, suggesting that, among the compounds analyzed, those that were more mobile and less recalcitrant were more effectively removed-likely due to greater susceptibility to biodegradation. However, it is important to note that mobility alone does not ensure biodegradability, as some mobile OMPs may still be highly persistent (e.g., PFOA and PFOS etc.). Additionally, vegetation and submerged zone have been identified as key design components that support the removal of OMPs. Enhancements such as amending filter media (e.g., with biochar, compost etc.) and reducing the infiltration rates have also been shown to improve OMPs removal efficiency primarily through increased sorption capacity and longer contact time. Constructed wetlands have demonstrated generally effective removal rate (>60%) but faced challenges in treating emerging pollutants such as PFOA and PFOS. Vertical subsurface flow design was found to help with the treatment process. Porous pavements showed overall effectiveness in removing PAHs and TPH, with exceptions noted for certain PAHs such as benzo(a)pyrene. Pavement material with strong adsorption capability and the incorporation of geotextile layers advanced the treatment outcome. Ponds and swales demonstrated mixed results, effectively removing PAHs and pesticides but showing less efficiency with PPCPs and plasticizers. Advanced oxidation technologies stood out for their excellent removal rates achieved within short timeframes which makes it suitable for the further treatment of the residual OMPs in the effluent of NBS.

Existing data gaps in studies on OMPs removal by NBS present challenges for the statistical assessment of design parameters and operational strategies in relation to treatment performance. Addressing these gaps requires greater focus on stormwater OMPs treatment. Additionally, innovative solutions, such as smart sensors and RTC strategies, could enhance system optimization when integrated with mechanistic models. Future research should also explore the potential of hybrid treatment systems that combine NBS with advanced technologies to improve the removal of refractory OMPs in stormwater harvesting processes.

#### **Author contributions**

Zhaozhi Zheng: conceptualization, methodology, investigation, formal analysis, writing - original draft, writing - review & editing; Baigian Shi: writing - review & editing, methodology, formal analysis; David McCarthy: writing review & editing, supervision, conceptualization, funding acquisition; Ana Deletic: writing - review & editing, supervision, conceptualization, funding acquisition; Pierre Le-Clech: writing - review & editing, supervision, conceptualization, funding acquisition; Stuart Khan: writing - review & editing, supervision, conceptualization, funding acquisition; Tim D. Fletcher: writing - review & editing, supervision, conceptualization, funding acquisition; Marty Hancock: writing - review & editing, project administration, funding acquisition; Kefeng Zhang: conceptualization, methodology, investigation, writing - review & editing, supervision, project administration, funding acquisition.

#### Conflicts of interest

There are no conflicts to declare.

# Data availability

Supplementary information: SI associated with this article can be found in the online version. See DOI: https://doi.org/ 10.1039/D5EW00306G.

The data of this review was collected from previously published studies. Referenced data are available in the cited literature.

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