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Enhancing urban wastewater treatment through nature-based solutions: The role of biofilm–plant development in subsurface retention of multiple solutes

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ABSTRACT

Effluents from wastewater treatment plants (WWTPs) deliver a complex cocktail of nutrients and contaminants of emerging concern (CECs) to freshwater systems. These impacts are especially pronounced in water-scarce regions like the Mediterranean, where pollutants can persist due to a lack of dilution. Nature-based solutions (NBS) aim to reduce pollutant concentrations by exposing water to biofilms and plant roots along subsurface flow paths. We conducted an outdoor flume experiment at the Urban River Lab (NE Spain) using treated WWTP effluent in replicated 12-m flumes with fine-grained sediments during the growing season (May–July). Nutrient and CEC retention was assessed under four settings: i) unplanted sediments, ii) sediments planted with *Iris pseudacorus*, iii) with *Cornus sanguinea*, and iv) with *Alnus glutinosa*. Nitrate was consistently retained, likely through denitrification under hypoxic conditions with ample dissolved organic carbon. In contrast, ammonium and soluble reactive phosphorus retention declined over time, with net release by the end of the experiment, likely due to mineralization and clogging. Among the studied CECs, eight were retained (e.g., PEG n5, MEHP, dimethylbenzotriazole), likely via microbial degradation or sorption, whereas five (e.g., diuron, sulfamethoxazole, DEET) were released, possibly due to recalcitrance or formation as degradation byproducts. Water travel time increased over the season but was not positively related to net nutrient retention. Vegetation effects were limited, indicating a dominant role of microbial activity. Our findings highlight the potential of bioengineered systems to retain a broad range of solutes, while also revealing that NBS are not universally effective for all compounds.

1. Introduction

In densely populated watersheds around the world, streams and rivers receive untreated or treated wastewater from municipalities. In cases where wastewater treatment plants (WWTPs) are implemented and meet regulatory standards, their discharges can still impair water quality and alter ecology of receiving streams. The problem is even more acute in regions experiencing water scarcity such as the Mediterranean region (Martí et al., 2010), where climatic characteristics (storms and droughts) and intensive water extraction for human use can reduce or cease streamflow altogether. Abnormally low flow diminishes the dilution capacity of receiving waters and exacerbates pollutant accumulation (Arnon et al., 2015; Marti et al., 2004).

WWTP effluents contain a complex cocktail of solutes (Kaushal et al., 2020), including essential nutrients such as nitrogen (N) and phosphorus (P), and organic matter (OM), which can contribute to nutrient

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saturation and eutrophication (Gucker et al., 2006; Ruggiero et al., 2006). Additionally, effluents contain contaminants of emerging concern (CECs), such as pharmaceuticals and personal care products, which present unknown risks to aquatic ecosystems, potentially affecting biodiversity and ecosystem functions (Miège et al., 2009; Parida et al., 2021). The cumulative impact of these solutes entering streams can result in a cascade of adverse ecological effects, such as shifts in community structure, altered biogeochemical cycles, and degraded ecosystem services (Aristi et al., 2016).

In response to these challenges, the Water Framework Directive (WFD (*Communities*, 2000)/60/EC) has established ambitious goals for achieving good ecological status in water bodies across Europe, emphasizing the need for sustainable and adaptive solutions to urban water management. Although effective at removing common pollutants (especially dissolved organic matter; DOM), convectional wastewater management infrastructure is energy-intensive, and legal effluent limits under the Urban Wastewater Treatment Directive (Directive EU 2024/3019) remain insufficient for streams with low or near-zero dilution capacity. Nature-based solutions (NBS) have emerged as a promising approach to complement conventional wastewater treatment by leveraging natural processes to enhance water quality, reduce solute toxicity (Sanz et al., 2024), restore ecosystem functions, and provide co-benefits for human well-being (Eggermont et al., 2015; Seddon et al., 2020). The design and function of bioengineered systems, as the basis for NBS, is inspired from natural in-stream purification processes occurring in these ecosystems. In particular, hyporheic zones are long-recognized as the 'river's liver' due to the biogeochemical transformations that occur along subsurface flow paths through these sediments (Fisher and Welter, 2005; Boulton et al., 2010; Krause et al., 2011). Also, phytoremediation has long been a strategy for leveraging plant and microbial nutrient uptake to ameliorate water quality in rain gardens, managed aquifer recharge, and other systems (Dillon et al., 2010; Zhang et al., 2024). Thus, "common wisdom" is that if we can better hydrologically connect rivers with their hyporheic zones and vegetated floodplains, we will see improvements in river water quality downstream from WWTP outfalls. However, it is unclear which contaminants in treated wastewater effluents will be most amenable to attenuation by NBS and whether the type of vegetation used in the NBS is relevant for this attenuation. In this context, flume experiments, with controlled and replicated conditions, are an ideal approach to target these questions and isolate the relative influence of NBS characteristics such as water residence times in the subsurface and plant communities.

Plants and biofilms play a key role on water quality outcomes in NBS infrastructure because they affect both hydrodynamics and rates of solute retention and transformation along subsurface flow paths (Nikolakopoulou et al., 2018). Moreover, plants and biofilms are tightly interconnected, as plants can stimulate the metabolic activity of biofilms within the rhizosphere, the root-associated zone characterized by intense microbial interactions and biogeochemical transformations (Chen et al., 2016; Rehman et al., 2017). By modifying sediment permeability, plant roots and biofilms can significantly alter subsurface water travel times (Caruso et al., 2017) and thus the interaction between organisms and available solute. In parallel, they contribute to nutrient retention along subsurface water paths via direct assimilation into plant and microbial biomass. Additionally, biofilms in the rhizosphere contribute to a diverse array of redox-mediated dissimilatory N transformation processes. Nitrification (i.e., the aerobic oxidation of ammonium to nitrate) and denitrification (i.e., the reduction of nitrate to nitrogen gas under suboxic conditions) are particularly prominent transformation processes of dissolved inorganic nitrogen (DIN) (Tang et al., 2020). Other relevant processes, such us anaerobic ammonia oxidation (Annamox), dissimilatory nitrate reduction to ammonium (DNRA) and ammonia volatilization can also contribute to DIN removal (Vymazal, 2007; Zhai et al., 2016). P removal is typically less efficient than N removal because it lacks dissimilatory microbial processes and primarily depends on chemical processes such as adsorption and precipitation rather than on biotic assimilation (García et al., 2010; Shu et al., 2025). Bioengineered systems have also been shown to remove CECs through physical, chemical, and biological processes (Overton et al., 2023). To improve solute (bioessential elements and CECs) retention, NBS should promote mechanisms such as adsorption by plants and sediments, biofilm biodegradation, plant and microbial uptake, photodegradation, and chemical transformations such as oxidation-reduction reactions. While NBS appear as a promising mitigation strategy, further research is needed to have a holistic perspective on the capacity and limitations of NBS to ameliorate water quality of WWTP effluents because they include a broad array of bio-essential and anthropogenic-driven solutes, and some of these solutes can act as contaminants and may persist in the water (Gorito et al., 2017).

This study aimed to investigate how different aquatic plant settings, developed as NBS, influence removal of solutes from a WWTP effluent flowing along subsurface flowpaths. Specifically, we evaluated the capacity of NBS systems with sediments and their biofilms alone, as well as in combination with three phreatophic riparian plant species—*Iris pseudacorus* (herbaceous), *Cornus sanguinea* (shrub), and *Alnus glutinosa* (tree)—to remove bioessential elements (N and P) and dissolved organic matter (DOM) from WWTP effluent water on three dates over the summer growing season. We also examined the capacity of the different settings to remove CECs on a single date during the growing season. By elucidating the contributions of biofilms and riparian vegetation to retention of solute pollutants, this work contributes to informing the development of science-based guidelines for developing and implementing NBS in wastewater management to reduce the influence of point source effluents in receiving streams. Given the diverse structural and functional traits of the selected plant species for this study, along with their tolerance to flow cessation, we hypothesized that each specie would distinctly contribute to nutrient and CEC retention along the subsurface water flow. Woody species, in particular, could support greater long-term nutrient retention through extensive root systems and microbial associations. Additionally, we anticipated that as biofilm and plants developed, they could influence subsurface water travel time, which could in turn influence solute retention along the experimental flumes.

2. Material and methods

2.1. Experimental Setup

This study was conducted at the Urban River Lab (URL; www.urbanriverlab.com). URL is an open-air experimental research facility consisting of 12 artificial flumes (each one 12 m long, 0.6 m wide, and 0.4 m deep), which are continuously supplied with treated effluent water from the WWTP of Montornès del Vallès (NW Barcelona). The flumes were filled with approximately 3 m^3 of heterogeneous sediment that was mostly granitic in origin and had a particle size ranging from 0.063 to 40 mm. WWTP effluent was delivered at a constant flow rate of 3 L min^{-1} to boxes at the inlet of the porous media in each flume. Subsurface flow was primarily one-dimensional through the 12-m sediment box, and the water table was generally located within ~5 cm of the top of the sediment. To simulate the effects of hydrological intermittency, a common feature in Mediterranean streams, on biofilm and vegetation growth, the sediments were periodically drained for several days between sampling events. Continuous subsurface flow was reestablished for at least one week before each sampling date. The experimental setup included three unvegetated flumes (sediment only) and nine vegetated flumes, which were planted with three riparian species representing distinct structural growth forms: *Iris pseudacorus* L. (herbaceous), *Cornus sanguinea* (shrub), and *Alnus glutinosa* (tree). Each species was planted in triplicate (three flumes per species) on 12–13 February. Plants were directly transplanted into the sediment as nursery-grown individuals with intact root balls at a density of 7.7 plants m^{-2}. Mean plant height (± standard error) at planting was 0.21 ± 0.04

m, 0.43 ± 0.05 m and 1.10 ± 0.32 m for *Iris pseudacorus*, *Cornus sanguinea*, and *Alnus glutinosa, respectively*. Mean daily air temperature and relative humidity during the plantation, averaged over the two planting days, were 10.1 °C and 83%, respectively. Meteorological data were provided by the Servei Meteorològic de Catalunya (www.meteo.cat) from a meteorological station located 2.9 km from the experimental facility.

2.2. Field sampling

Within this experimental setting, we conducted monthly water samplings from May to July 2024 at the flume inlet and outlet to capture temporal variation in the net release or removal of bioessential elements found in treated wastewater, including ammonium (NH_4^+), nitrate (NO_3^-), soluble reactive phosphorus (SRP), and dissolved organic carbon (DOC). On each sampling date, we also measured the following physicochemical characteristics at the inlet and outlet of each flume: electrical conductivity (EC; mS cm^{-1}), water temperature (°C), dissolved oxygen (DO) concentration and saturation (mg/L and %, respectively), and pH using a multiparametric sensor (WTW 3320). In May only, we additionally collected a set of inlet and outlet water samples for CECs.

Our sampling scheme utilized a Lagrangian approach, where samples from the inlet and outlet were staggered by the estimated water travel time along the flume (i.e., nominal travel time, or NTT; h). We determined NTT for the 12 flumes before each of the 3 sampling dates using slug additions of salt (NaCl) as a hydrological tracer. NaCl was added at the inlet of each flume and conductivity was continuously recorded at the outlet with a conductivity meter (WTW 3310). NTT was approximated as the elapsed time since NaCl was added in the inlet and the conductivity peaked at the flume outlet. For nutrients, we accounted for potential variation in the concentration of the incoming water by collecting a set of three inlet samples at each flume, which were spaced 1 h apart and, 1 NTT later, we collected a set of three outlet samples spaced 1 h apart. Water samples were collected from the flume inlet and outlet by syringe, filtered through GF/F glass fiber filters, placed in 15 mL vials, and preserved frozen (−18 °C). For CECs, we reduced the number of samples due to the substantial cost and labor of CEC analysis. Specifically, we collected a series of three samples at the inlet of one flume (each separated by 1 h) and one sample at the inlet of three additional flumes to account for potential spatial and temporal variability in CECs concentration at the inlet of the flumes. Because all flumes are fed from the same treated wastewater supply, we assumed that if these 6 inlet samples were similar, the inlet concentration for all flumes could be considered well-constrained over the timescale of sampling for CECs. In addition to these inlet samples, at the second sampling round of nutrients, we collected one water sample for CECs from the outlet of all 12 flumes at one NTT after inlet sampling. We also collected two field blanks to ensure no measurable contaminants were introduced by the sampling procedure. To sample for CECs, water was collected from the flume inlet and outlet by syringe, transferred directly into 250-mL amber glass bottles, and placed immediately in a refrigerator (4 °C) for subsequent filtration and analysis in the laboratory.

2.3. Laboratory analyses

The concentration of NH_4^+ and SRP was analyzed using a standard colorimetric method with a Shimadzu spectrophotometer, following the procedure established for each nutrient. The NO_3^- concentration was analyzed at the Department of Evolutionary Biology, Ecology and Environmental Sciences of the University of Barcelona using the standard colorimetric method with an autoanalyzer. Water samples for DOC analyses were spiked with 4 drops of 10% hydrochloric acid to bring pH < 2.5 and DOC concentration was analyzed in the Labqa service of the CEAB-CSIC using a Shimadzu total organic carbon (TOC) analyser. Samples for CECs were filtered within 24 h of collection using 0.7 µm glass microfiber filters. Then, 50 uL of a mixture of clothianidin-d3 at 1 mg/L was added to the 150 mL water sample, which was pH regulated to 6.5 with ammonia and formic acid and loaded onto a home-made multilayer cartridge (Gago-Ferrero et al., 2015) previously conditioned with 5 mL Ethyl acetate, 5 mL Methanol, and 5 mL ultrapure water. The cartridge was then dried under vacuum for 3 min and further eluted with Ethyl acetate: Methanol mixture: Ammonia solution 32% (47:47:6, *v/v/v*), dried under vacuum for 3 min and reextracted with Ethyl acetate: Methanol mixture and Formic acid 90% (49:49:2, v/v/v/). Then, the sample was dried under N_2 current, reconstituted with 0.5 mL MeOH:H_2O (50:50, v/v), and injected into the LC-HRMS instrument.

The instrumental system to analyze CECs consisted of an ultra-high-performance liquid chromatography (UHPLC) system with an Heated ESI source coupled to an Orbitrap Exploris 120 (Thermo Fischer Scientific, Dreieich, Germany). The chromatographic separation was done with a Waters Cortecs C18 column (C18, 2.7 µm, 2.1 × 100 mm) preceded by a guard column (CORTECTS C18, 1.7 µm 2.1 × 5 mm, Waters, Milford, USA) both maintained at 40 °C during analysis. More details about the instrumental conditions can be consulted elsewhere (Gutiérrez-Martín et al., 2023). A total of 28 chemicals from our in-house database were screened in these samples using TraceFinder software by searching their accurate *m/z*, known RT, at least one fragment ion coeluting with parent, as well as isotopic pattern fitting. The selection of chemicals included artificial sweeteners, illicit drugs (and metabolites), industrial chemicals, plastic additives (and metabolites), perfluorinated chemicals, emulsifiers, pesticides, pharmaceuticals, preservatives, food-related chemicals, tire additives and PCPs, and was intended to provide a holistic overview of the system of many chemicals.

2.4. Data analysis and statistical tests

We calculated the retention capacity of each flume setting for each specific solute (*R*, in percentage of the relative longitudinal change) as:

$$R\ (\%) = \frac{(Conc_{IN} - Conc_{OUT})}{Conc_{IN}}\ x\ 100$$

where $Conc_{IN}$ and $Conc_{OUT}$ are the solute concentrations at the inlet and outlet of the flume, respectively. Positive *R* values denote a net decrease in solute concentration along the flume or net solute retention (uptake > release): the flume acted as a "sink" for a given solute along the flow path. Conversely, negative *R* values indicate a net increase in solute concentration along the flume and thus net production (uptake < release): the flume acted as a "source" for a given solute along the flow path.

To estimate *R* for the different nutrients where we had more samples, we applied a bootstrap-based approach to rigorously compare nutrient retention behavior among different vegetation settings for a given time, and among sampling dates for the same vegetation setting. Specifically, we compared inlet and outlet nutrient concentrations using Monte Carlo resampling (1000 iterations with replacement). To account for potential variation in inlet concentrations among flumes, we generated a distribution of each nutrient concentration by resampling all inlet measurements across flumes and over time within each sampling date. This produced a representative, homogeneous distribution of nutrient concentrations at the inlet for each sampling date. Similarly, we generated outlet concentration distributions for each flume by resampling (1000 times with replacement) all corresponding outlet measurements per flume, nutrient, and sampling. We then obtained median percent nutrient retention (*R*) and associated 95% confidence intervals by grouping the estimated *R* distributions by nutrient and flume experimental setting. This bootstrap method decreases the reliance on individual pairs of inlet–outlet measurements, which can have subtle variations due, for example to subtle differences in concentration at the inlet over time or across flumes. In this analysis, we assumed significant effects on nutrient retention if the 95% Confidence Intervals for *R* did not overlap 0. We used l**inear regressions to assess the relationship**

between water nominal travel time (NTT) and nutrient *R* in the flumes. The bootstrap-based approach and linear regressions were both performed with R 2023.12.0 (R Foundation for Statistical Computing, Vienna, Austria, http://www.Rproject.org/). We estimated *R* only for CEC compounds that exhibited statistically significant differences between $Conc_{IN}$ ($n = 6$) and $Conc_{OUT}$ ($n = 12$) based on a Student's *t*-test, performed in Matlab. In this instance, *R* for each CEC was calculated using $Conc_{IN}$ as the average of the six inlet samples for all 12 flumes, and $Conc_{OUT}$ as the value measured at each flume.

For May sampling (when both nutrients and CECs were analyzed), we explored chemical compositional differences between treated wastewater at the inlet and outlet of the flumes using inferential statistical analysis. Specifically, we calculated Pearson correlation coefficients to screen for linear correlation between pairs of variables and performed a principal component analysis (PCA) in Matlab. The goal of PCA was to reduce the dimensionality of the data and find combinations of variables that best explain total variance among water samples with different chemical characteristics between the inlet and outlet of the different flumes. We examined a total of 30 water quality variables that included measured physicochemical variables (see above) and the concentrations of all 4 nutrients and 22 detected CECs. All variables were first scaled to have a mean of 0 and a standard deviation of 1.

3. Results and discussion

3.1. Retention of all solutes in May

During the early growing-season campaign, treated wastewater that entered the flumes was suboxic (DO concentration < 1.5 mg/L) and circumneutral in pH (Table 1). Mean water conductivity and temperature were 2.1 mS/cm and 22 °C, respectively. DIN concentration was ~6 mgN/L, with NO_3^- accounting for the highest proportion of it (Table 2). Concentrations of DOC (11.5 mg/L) and SRP (~0.4 mgP/L) were relatively high compared to concentrations in water from surrounding natural rivers (Table 2). Of the 28 CECs screened, 22 were detected (Table 2). They include pesticides, personal care products, preservatives, industrial chemicals, tire additives, among other solutes.

In this sampling, all nutrients showed overall positive retention (i.e., $R > 0$) along the flumes, indicating that flumes acted as a net sink for these solutes. NO_3^- underwent the greatest *R* (90%), followed by SRP (50%). DOC was retained to a lesser extent (16%), while NH_4^+ showed the lowest *R* (4%). Observed high NO_3^- retention could be favored by hypoxic conditions (DO <1.2 mg/L) and relatively high DOC concentration (>10 mg/L). These conditions enhance anaerobic heterotrophic activity, enabling NO_3^- reduction to N_2 gas (i.e., denitrification) as a respiratory pathway (Inwood et al., 2007; Lu et al., 2009). In addition, assimilatory uptake of NO_3^- into plant and microbial biomass may have also contributed to net NO_3^- removal along the flumes (Lin et al., 2002; Vymazal, 2011). Remarkable SRP retention could be associated with both assimilatory uptake by plant and microbial assemblages and abiotic uptake, such as adsorption to sediment and fine particulate organic matter (Vymazal, 2007). The observed low *R* for NH_4^+ may be attributed to several factors. NH_4^+ is generally considered the most bioreactive form of DIN, which is primarily retained through assimilation and nitrification (Ribot et al., 2017a; Ribot et al., 2017b). However, the very low DO concentrations in the flumes likely limited nitrification, as this process is mediated by aerobic microorganisms (Prosser, 1990). Organic matter mineralization may have contributed to NH_4^+ production in the pore water, partially masking net NH_4^+ retention (Jahangir et al., 2017). A previous study conducted in the same flumes reported high mineralization rates, supporting this interpretation (Ribot et al., 2017a; Ribot et al., 2017b). Moreover, dissimilatory nitrate reduction to ammonium (DNRA) could also contribute to NH_4^+ production while further contributing to the high NO_3^- retention observed (Burgin and Hamilton, 2007).

The retention behavior of CECs along the flumes varied notably depending on the chemical properties of each compound. Among the 22 CECs detected, eight showed statistically significant net decrease in concentration, or positive *R*, between the inlet and outlet (Student's *t*-test, $p < 0.05$). These compounds, listed in ascending order of *R* from 14 to 94%, include PEG n8, theophylline, benzophenone-3, caffeine, bisphenol S (BPS), dimethylbenzotriazole, mono-2-ethylhexyl phthalate (MEHP), and PEG n5 (Table 2). Conversely, five compounds exhibited a statistically significant net increase in concentration between the inlet and outlet (Student's t-test, $p < 0.05$). Specifically, *R* ranged from −10 to −35% for 4-methylbenzotriazole, benzotriazole, diuron, sulfamethoxazole, and DEET (Table 2). No significant changes in concentration between the inlet and outlet of the flumes was observed for the rest of the compounds (PEG n10, acesulfame, acetaminophen, metformin, 2-hydroxybenzothiazole, *N*,*N*′-diphenylguanidine, benzophenone, PFOA, and PFOS) (Table 2).

Dimethylbenzotriazole and BPS, which were both effectively retained, possess relatively high logKow values (~2), suggesting an affinity for the solid phase. The octanol–water partition coefficient (logKow) reflects a compound's tendency to associate with organic matter; higher values indicate stronger sorption to solids and greater retention potential (Nendza et al., 2025). Their pKa values—above the system pH—indicate they predominantly exist in their neutral forms, favoring sorption and subsequent biodegradation (Franco et al., 2009). Similarly, we interpret that benzophenone-3, despite being partially ionized at the system pH, is sufficiently hydrophobic to undergo partial retention via adsorption. In contrast, caffeine and theophylline, while largely neutral at the operating pH, are highly polar, limiting their adsorption and slowing their biodegradation, resulting in the lower observed net retention. Among the PEGs, PEG n5 exhibited the greatest retention, likely due to its smaller molecular size, which may facilitate microbial degradation in biofilms. In agreement with these results, lower molecular weight PEGs are known to be more biodegradable (Kawai, 2005).

Table 1
Monthly inlet (IN) and outlet (OUT) values of water physiochemistry. Conductivity, temperature, dissolved oxygen (expressed both in mg L^{-1} and as percentage saturation), and pH are presented as mean ± standard error (SE). Nutrient concentrations (NH_4^+, NO_3^-, DIN, soluble reactive phosphorus [SRP], and dissolved organic carbon [DOC]) are presented as medians with 95% confidence intervals (mg/L). Values represent integrated values from all 12 flumes.

	May		June		July	
	IN	OUT	IN	OUT	IN	OUT
Conductivity (mS cm^{-1})	2.06 ± 0.02	2.02 ± 0.00	2.18 ± 0.01	2.18 ± 0.00	2.44 ± 0.00	2.54 ± 0.06
Temperature (°C)	21.58 ± 0.05	21.97 ± 0.2	25.34 ± 0.06	24.87 ± 0.19	28.21 ± 0.14	27.58 ± 0.07
Dissolved oxygen (mg/L)	1.22 ± 0.18	1.05 ± 0.26	1.06 ± 0.11	0.52 ± 0.08	0.52 ± 0.11	0.19 ± 0.02
Dissolved oxygen (%)	13.59 ± 2.02	12.71 ± 2.74	12.53 ± 1.32	6.05 ± 0.96	6.83 ± 1.39	2.43 ± 0.25
pH	7.33 ± 0.00	7.39 ± 0.01	7.39 ± 0	7.44 ± 0.01	7.40 ± 0.01	7.34 ± 0
NH_4^+ (mg/L)	1.20 (1.18–1.22)	1.15 (0.88–1.32)	1.44 (1.40–1.48)	1.48 (1.21–1.69)	1.79 (1.77–1.82)	1.95 (1.86–2.04)
NO_3^- (mg/L)	4.53 (4.05–5.01)	0.46 (0.01–2.39)	5.08 (4.72–5.39)	0.28 (0.10–2.77)	1.74 (1.59–1.91)	0.41 (0.10–0.80)
DIN (mg/L)	5.91 (5.41–6.39)	1.67 (1.09–3.57)	6.52 (6.17–6.83)	1.74 (1.51–3.98)	3.43 (3.37–3.69)	2.32 (2.06–2.71)
SRP (mg/L)	0.40 (0.35–0.46)	0.18 (0.13–0.33)	0.21 (0.19–0.23)	0.22 (0.20–0.30)	0.57 (0.55–0.60)	0.62 (0.49–0.78)
DOC (mg/L)	11.5 (11.2–11.8)	9.66 (9.37–14.2)	13.9 (13.4–14.3)	13.3 (11.5–14.2)	13.71 (13.6–13.9)	13.3 (11.5–14.4)

Table 2
Inlet and outlet solute concentrations (Conc IN and Conc OUT, respectively), reported as median and 95% confidence interval for nutrients (in mg/L), and mean ± standard error for contaminants of emerging concern (in ng/L), % retention (calculated from concentrations reported in the units indicated above and expressed accordingly), along with chemical descriptions sorted by family, measured during the May sampling. For three compounds, select samples were below the limit of detection (LOD), and the concentration was taken as the LOD for calculations (1 ppt for PFOS and 10 ppt for PEG n5 and Mono-2-ethylhexyl phthalate). nd = not detected, ns = no substantial retention based on Student's *t*-test. Positive % retention denotes net retention (i.e., uptake>release); while negative % retention denotes net production (i.e., uptake<release).

Compound	Conc IN	Conc OUT	% Retention	Family
Ammonium (mg/L)	1.20 (1.18–1.22)	1.15 (0.88–1.32)	4 (−11–28)	Nutrient
Nitrate (mg/L)	4.53 (4.05–5.01)	0.46 (0.01–2.39)	90 (45–100)	Nutrient
Dissolved inorganic nitrogen (mg/L)	5.91 (5.41–6.39)	1.67 (1.09–3.57)	72 (38–82)	Nutrient
Soluble reactive phosphorous (mg/L)	0.40 (0.35–0.46)	0.18 (0.13–0.33)	50 (15–69)	Nutrient
Dissolved organic carbon (mg/L)	11.5 (11.2–11.8)	9.66 (9.37–14.2)	16 (−24–20)	Nutrient
Acesulfame (ng/L)	2 ± 0	2 ± 0	ns	Artificial Sweetener
Benzoylecgonine (ng/L)	nd	nd	nd	Drug of abuse
Cocaine (ng/L)	nd	nd	nd	Drug of abuse
4-methylbenzotriazole (ng/L)	1692 ± 25	1869 ± 34	-10 ± 2	Industrial Chemical
Benzotriazole (ng/L)	5318 ± 153	6034 ± 107	−13 ± 2	Industrial Chemical
Dimethylbenzotriazole (ng/L)	56 ± 5	16 ± 2	71 ± 3	Industrial Chemical
BPA (ng/L)	nd	nd	nd	Industrial Chemical
BPS (ng/L)	18 ± 1	7 ± 1	62 ± 5	Industrial Chemical
PEG n10 (ng/L)	43 ± 6	32 ± 4	ns	Personal care products
PEG n5 (ng/L)	330 ± 57	19 ± 7	94 ± 2	Personal care products
PEG n8 (ng/L)	301 ± 12	260 ± 10	14 ± 3	Personal care products
DEET (ng/L)	1221 ± 182	1647 ± 96	−35 ± 8	Pesticides
Diuron (ng/L)	101 ± 12	128 ± 5	−27 ± 5	Pesticides
PFOS (ng/L)	4 ± 2	10 ± 3	ns	PFAS
PFOA (ng/L)	7 ± 0	6 ± 0	ns	PFAS
Metformine (ng/L)	180 ± 8	199 ± 6	ns	Pharmaceutical
Sulfamethoxazole (ng/L)	323 ± 22	430 ± 7	−33 ± 2	Pharmaceutical
Acetaminophen / Paracetamol (ng/L)	8 ± 0	9 ± 0	ns	Pharmaceutical
Mono(2-ethyl-5-hydroxyhexyl) Phthalate (ng/L)	nd	nd	nd	Plasticizer
Mono-2-ethylhexyl phthalate (ng/L)	44 ± 4	10 ± 0	77 ± 0	Plasticizer
Butylparaben (ng/L)	nd	nd	nd	Preservatives
Propylparaben (ng/L)	nd	nd	nd	Preservatives
Caffeine (ng/L)	4643 ± 96	3019 ± 86	35 ± 2	Stimulant
Theophylline (ng/L)	1476 ± 44	1120 ± 34	24 ± 2	Stimulant
2-Hydroxybenzothiazole (ng/L)	326 ± 41	481 ± 57	ns	Tire additive
N,N′-Diphenyguanidine (ng/L)	542 ± 12	521 ± 11	ns	Tire additive
Benzophenone (ng/L)	33 ± 3	35 ± 6	ns	UV filter
Benzophenone-3 (ng/L)	32 ± 2	22 ± 1	30 ± 3	UV filter

PEG n8 showed moderate retention, whereas PEG n10 was not statistically retained (Table 2). Concentration of ionized, polar compounds, such as acesulfame, metformin, and 2-hydroxybenzothiazole, all characterized by low logKow, remained largely similar along the flumes, likely due to poor adsorption and limited microbial degradation. Compounds such as MEHP, PFOS, and PFOA, although predominantly anionic at pH 7, contain long hydrophobic chains. MEHP was substantially retained, likely due to its susceptibility to microbial degradation, while concentrations of PFOS and PFOA—recognized as persistent "forever chemicals"—remained unchanged along the flumes.

Regarding to the CECs that significantly increased in concentration along the flumes (i.e., $R < 0$), the benzotriazoles may have formed from degradation of dimethylbenzotriazole or other similar compounds, while the increases in the others could stem from the deconjugation of phase-II metabolites. Studies have shown that metabolites of sulfamethoxazole can reverse back to the parent compound, particularly under conditions favorable for denitrification (Ma et al., 2021; Rodríguez-Escales and Sanchez-Vila, 2016), and form from glucuronide deconjugation (Brown et al., 2020). This is supported by HRMS data showing a 31% decrease in *N*-acetylsulfamethoxazole, alongside a 33% increase in sulfamethoxazole (Fig. S1), indicating in-situ deacetylation. Attempts to identify similar metabolites for DEET and diuron (e.g., glucuronides) in our samples did not yield confirmatory results, although such transformation pathways remain plausible. For compounds like acetaminophen, concurrent degradation and regeneration may mask changes in concentration. Meanwhile, *N*,*N*′-diphenylguanidine and benzophenone—both previously reported as highly recalcitrant in wastewater systems—showed no significant variation, supported by the specific removal processes for these persistent CECs (Aoudi et al., 2024).

For the PCA analysis all solutes, the first two principal components explained over half (53.5%) of the variability among the 4 inlet and 12 outlet samples (Fig. 1). The first component of the PCA clearly distinguished between the inlet and outlet samples. Water that entered the flumes generally had higher concentration of nutrients and of some specific CEC compounds (e.g., caffeine, dimethylbenzotriazole, MEHP) than water at the flume outlets, indicating that the flumes were effective at transforming the water chemistry of the WWTP effluent. The second component of the PCA distinguished water chemistry among flumes; however, observed variation was not associated to the type of experimental setting (with and without vegetation or among different plant species) (Fig. 1). Thus, during May sampling, presence of vegetation along the flumes was not a key factor driving retention and transformation of both bioessential elements and anthropogenic organic compounds (i.e., CECs).

Results from this sampling demonstrate the potential of bio-engineered systems to retain a large number of nutrients and organic compounds from anthropic origin at early-growing season conditions. Several studies have highlighted the need to develop effective methods to retain and transform CECs from wastewaters, given their potential risks to ecosystems and human health (Bukhari et al., 2025; Das et al., 2025; Di Marcantonio et al., 2023). NBS is an affordable technology that shows promise and can be complemented by more costly technologies such as membrane bioreactors, advanced oxidation, adsorption, and nanomaterial-based photocatalysis, though further research is needed to improve their efficiency, cost-effectiveness, and sustainability. Importantly, this study shows that NBS are not universally effective for all CECs and provides a basis to investigate the mechanisms driving their

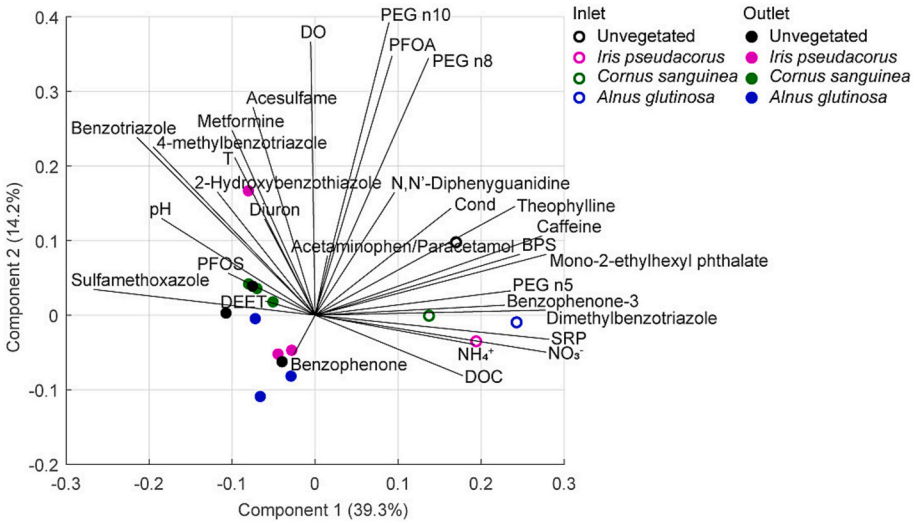


Fig. 1. PCA analysis of 16 water samples, collected in May, based on 30 variables, including physicochemical characteristics, nutrients, and CEC concentrations. Open circles indicate inlet samples, while closed circles indicate outlet samples. Colors correspond to different vegetation settings.

retention and how to optimize NBS design to enhance retention.

3.2. Temporal variation in nutrient retention over the growing season

We observed marked differences in inlet water chemistry throughout the growing season (Table 1). Conductivity increased consistently, reaching its peak in July. In this month, conductivity also increased slightly at the outlet relative to the inlet, suggesting a possible accumulation of dissolved salts along the flumes, likely driven by evapotranspiration, as plants developed (Headley et al., 2012). Average water temperature steadily increased over the study period, rising from approximately 22 °C to 28 °C (Table 1). Dissolved oxygen concentration remained hypoxic at the inlet and slightly declined over the growing season and along the flumes. The decline along the flumes was likely driven by respiration in the presence of DOC (Table 1), which outpaced any potential oxygen exchange through the plant root system. pH

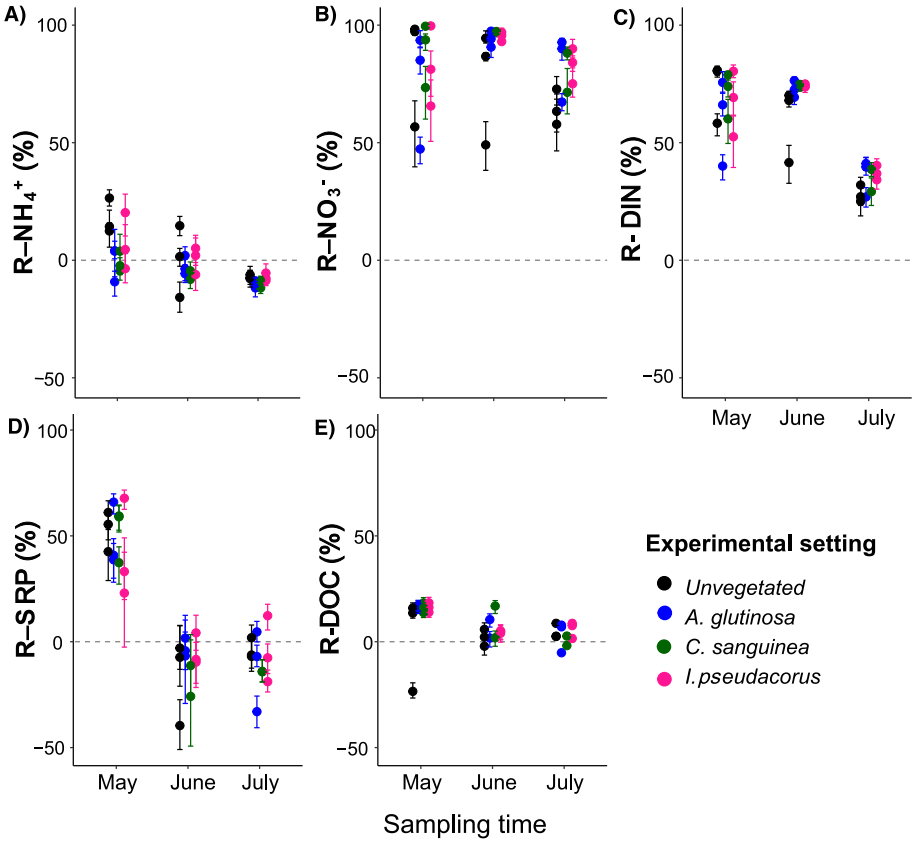


Fig. 2. Temporal variation in percentage retention (R) of nutrients NH_4^+, A; NO_3^-, B; DIN, C; SRP, D; and DOC, E) along the flumes for the four experimental settings during the study period, estimated using bootstrap analysis. Values are reported as medians with 95% confidence intervals. Positive values indicate nutrient uptake > release, while negative values indicate nutrient uptake < release.

remained relatively stable over time and along the flumes. Inlet nutrient concentrations varied over time (Table 1). NH_4^+ increased steadily during the experiment (from 1.2 to 1.8 mg/L), whereas NO_3^- declined sharply from May to July, with concentrations decreasing by ~40%. Consequently, DIN (i.e., $NH_4^+ + NO_3^-$) showed a marked decrease over the study period. SRP showed a more irregular temporal pattern, while DOC concentration increased from May to June and then remained almost constant until the end of the study. Temporal variability in nutrient concentrations is common in WWTP discharges (e.g., (Castelar et al., 2022)) and is mainly associated with changes in the characteristics of wastewater entering the WWTP, internal treatment processes, and the specific biogeochemical controls on individual nutrients, all of which may also be influenced by temperature.

We observed a temporal variation in the nutrient retention capacity, which was more pronounced than the variation observed among the various vegetated settings (Fig. 2). In contrast to our expectations, no significant differences in solute retention were observed among the flumes where the three riparian species (i.e., *Iris pseudacorus*, *Cornus sanguinea*, and *Alnus glutinosa*) grew, despite their contrasting life traits and drought tolerance (Fig. 2). Notably, *C. sanguinea* exhibited visible stress symptoms and partial desiccation, likely reducing its contribution to solute retention under drought conditions. At the end of the experiment, only 62% of individuals survived, with a mean plant height of 0.45 ± 0.09 m. In contrast, *I. pseudacorus* and *A. glutinosa* appeared more resistant, although their growth was less vigorous than in previous studies conducted in the same flumes under permanent flow conditions (Nikolakopoulou et al., 2020). Mean plant height at the end of the experiment was 0.41 ± 0.19 m for *Iris pseudacorus* and 1.13 ± 0.31 m for *Alnus glutinosa*, with individual survival rates of 90% and 87%, respectively. **Therefore,** the lack of differentiation among species may reflect their overall limited development, constrained by intermittent drought and by persistent hypoxic conditions under wet conditions that reduced root oxygenation (Pan et al., 2021). Under these stressed conditions, environmental drivers such as temperature and DO likely overrode potential species-specific influences. It is also possible that differences in plant functional traits require longer timescales or greater biomass accumulation to translate into measurable biogeochemical effects. Overall, the absence of differences in nutrient retention between vegetated and unvegetated flumes indicates that, under the observed low redox conditions and duration of our experiment (i.e., early-growing season plant development), the sediment and its biofilms had a more profound impact on nutrients than vegetation. These results do not exclude stronger vegetation effects under alternative environmental conditions. For example, under more aerobic conditions (due, for example, to changes in effluent chemistry, sediment porosity and permeability, or greater plant biomass; and thus, rhizosphere oxygenation), we would expect greater root respiration, and aerobic nutrient cycling, leading to more plant-driven nutrient retention. Over longer experimental periods, the resulting changes in belowground biogeochemical and physical conditions may allow functional trait differences and stronger root–microbe interactions to develop, thereby amplifying vegetation-mediated effects on nutrient retention.

In general, *R* values for all nutrients and across all vegetated settings were higher in May, and tended to decrease in subsequent samplings (Fig. 2). For instance, median R for NH_4^+ was positive, but low, in May (4%), null in June (0.5%) and negative in July (−8%) with no noticeable differences among vegetated settings (Fig. 2A). Thus, the flumes shifted from being a sink to being a source of NH_4^+ over the study period. This pattern may be explained by increased mineralization rates as water temperature increased and sediment became clogged with particulate organic matter and biofilm growth (both of which were observed anecdotally). All flumes consistently showed a high capacity to retain NO_3^- throughout the study period, with R ranging from 65 to 97% regardless of the setting type (Fig. 2B). This sustained capacity to retain NO_3^- could be explained by the persistent hypoxia conditions and the high DOC concentration, which could favor anaerobic heterotrophic metabolism and denitrification (Inwood et al., 2007). Interestingly, although NH_4^+ showed a decrease in *R* over time, the overall capacity of the flumes to retain DIN (i.e., the sum of NH_4^+ and NO_3^-), remained positive over the study period (Fig. 2C). This indicates that the flumes consistently acted as net sinks of DIN. Median *R* of SRP was positive in May, ranging from 36% to 57% across settings, but dropped sharply to negative values in June and July (−2% to −16% and − 4% to −14%, respectively), indicating that SRP release tended to prevail over retention at the end of the study period (Fig. 2D). An increase in organic matter mineralization, which also releases SRP, may help explain this shift in SRP retention to some extent. Finally, *R* values of DOC were positive during the study, indicating DOC uptake was greater than release along the flumes (Fig. 2E). Retention capacity was greater in May (*R* ranging from 14% to 17%) and tended to decline toward the end of the study period (*R* ranging from 3% to 8%), again consistent with accelerating organic matter mineralization toward the end of the season.

Data from NaCl additions indicated that average nominal travel time (NTT) gradually increased from May to July, with no noticeable differences between vegetated and unvegetated settings (Fig. 3), consistent with the idea that the flumes gradually accumulated particulate organic matter and biofilm over the season. In several tracer additions, the outlet conductivity signal did not reach a well-defined maximum, a pattern that became more evident toward the end of the experiment as travel time distributions generally grew longer and broader. These changes add some uncertainty to the estimation of travel times, but the tendency toward longer NTT over the growing season is overall robust (Fig. 3). As particulate matter accumulates and biofilms grow, the effective sediment porosity and permeability can decrease (Hommel et al., 2018), leading to the observed longer travel times. Unfortunately, we did not collect sediment samples to directly measure sediment physical properties (e.g., porosity and permeability) or biofilm biomass directly before and after the experiments, thus we can only speculate from the behavior of the conservative salt tracer. The observed increase in travel times over the growing season cannot be explained by temperature, since warmer water has lower viscosity and, consequently, greater hydraulic conductivity (Podolsky, 1994). Based on the observed seasonal temperature rise, a ~ 14% decrease in NTT would be expected. Yet, our data show the opposite, suggesting that clogging processes, like biofilm growth, more than compensated for any temperature effect. In contrast to initial expectations, increases in NTT did not coincide with greater *R* for any of the studied nutrients (Fig. 4). In fact, we found a significant

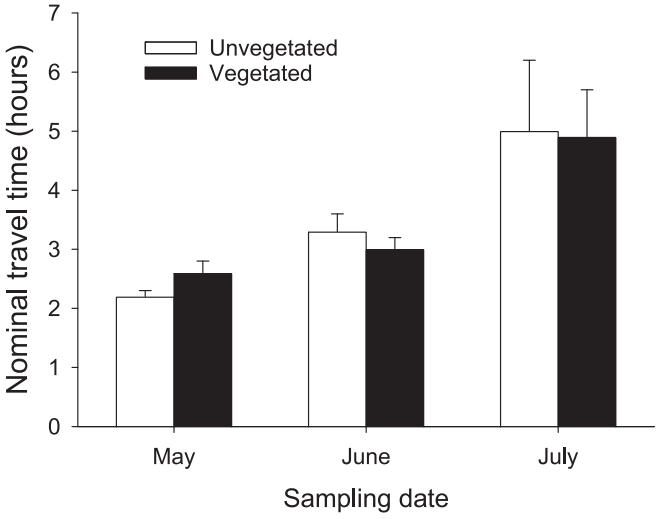


Fig. 3. Water nominal travel time (in hours) measured during the three sampling times using NaCl as a conservative hydrologic tracer. Bars represent monthly averages for two flume settings: unvegetated ($n = 3$) and vegetated ($n = 9$). Error bars indicate ± standard error of the mean (SE) across flumes within each type and sampling date.

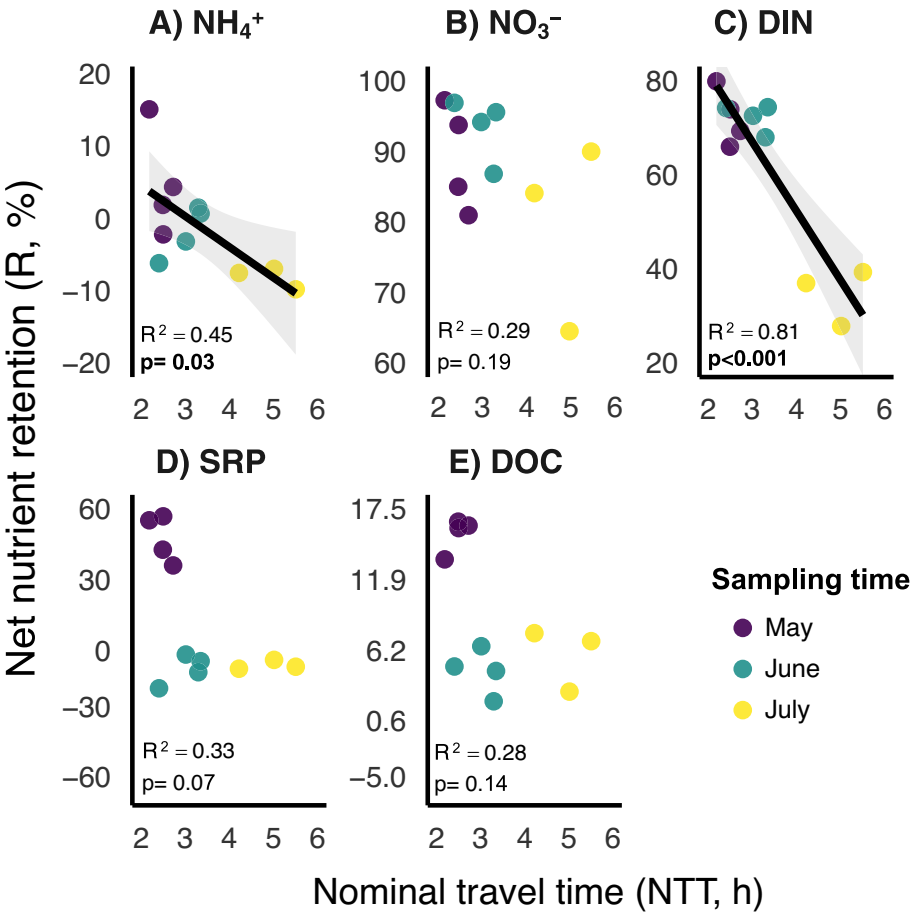


Fig. 4. Relationships between nominal travel time (NTT) and the percentage retention (R) of NH_4^+ (A), NO_3^- (B), DIN (C), SRP (D), and DOC (E). Positive retention values indicate that nutrient uptake > release, while negative values indicate that nutrient uptake < release. **Bold *p*-values** denote statistically significant results ($p < 0.05$). The gray shading represents the 95% confidence intervals of the fitted linear regressions when significant (p-value <0.05).. **Fig. S1:** Extracted ion chromatogram for sulfamethoxazole and its metabolite *N*-acetylsulfamethoxazole at the expected retention time. Chromatograms are examples of a compound that increases along the flume (sulfamethoxazole reduction of 33% is observed) and a compound that decreases along the flume *N*-acetylsulfamethoxazole increase of 31% is observed).

negative relationship (linear regression, $p < 0.05$) between NTT and both NH_4^+ and DIN, driven by net release of NH_4^+ and SRP by the end of the growing season (note that we assessed net retention, or the balance between uptake and release). We interpret that seasonal changes in both physical conditions (e.g., temperature) and biological processes (e.g., biomass growth and decay) promoted more organic matter decomposition under anoxic conditions, which exceeded gross uptake by the end of the experiments. Consistently, a previous study in the same flumes reported high mineralization rates (Ribot et al., 2017a; Ribot et al., 2017b). An important implication is that the overall performance of NBS for nutrient removal may decline over time if rates of organic matter decomposition increase and residence times become extended due to clogging, a problem analogous to the clogging of managed aquifer recharge systems (Rodríguez-Escales et al., 2018).

It is worth noting that nutrient retention in this study differed from earlier work conducted in the same flumes under different sediment types, plant species and flow regime. In that experiment, high DIN retention was also observed, but it was primarily driven by nitrification and biological assimilation of NH_4^+, which only occurred in vegetated flumes (Ribot et al., 2017a; Ribot et al., 2017b). On the other hand, DOC consistently exhibited low but positive retention in both studies. In this present study, flume sediments were finer and more heterogeneous than in past experiments. Additionally, the inlet configuration differed: earlier setups used an open inlet chamber, whereas the current design delivered water via a shaded piezometer, reducing O_2 levels below hypoxia. Therefore, it seems that the combination of finer-grained sediments and mechanisms to reduce oxygen at the inlet likely promoted more reducing conditions within the sediment, favoring anaerobic microbial processes and dissimilatory nitrogen pathways such as denitrification and DNRA. These findings highlight how changes in abiotic conditions alone can significantly influence nutrient removal in bio-engineered systems, and should therefore be considered in the design of NBS.

4. Conclusions

This study shows that NBS strategies designed to promote hyporheic or subsurface flows may be highly effective at transforming a combination of solutes, including nutrients and CECs, in streams that receive treated wastewater. During the growing season, flume sediments were extraordinarily effective in retaining NO_3^- in particular, regardless of the different settings (vegetated or unvegetated), primarily due anoxic conditions, which promoted denitrification. Furthermore, at the early growing stage, a suite of 8 CECs were also retained to varying degrees along the flumes, with the personal care product PEG n5 showing the greatest removal. Our study also suggests that the retention performance of the flume system for different solutes can vary significantly throughout the plant growing season. Temporal changes in physico-chemical conditions, together with plant and biofilm biomass dynamics, likely drove the shift from net uptake of NH_4^+ and SRP early in the experiment to net release toward the end. Although we expected longer water travel time to enhance solute–biofilm interactions and thus

retention, retention of some nutrients instead declined. This finding may be explained by decomposition rates exceeding gross uptake rates, ultimately leading to a net release. Importantly, the temporal variation in solute retention capacity did not strongly depend on vegetation type or presence, at least under the conditions examined in this experiment, suggesting that biofilms in the rhizosphere play a key role in biogeochemical transformations. These findings highlight the importance of environmental conditions in NBS used as quaternary treatment, since they can determine the fate of nutrients and CECs in treated water before reaching receiving stream ecosystems. While this study focused on nutrient and CEC dynamics, pathogen removal (e.g. *Escherichia coli*) represents an additional key function of NBS that warrants explicit assessment in future work. Particularly, when systems are intended as quaternary treatment prior to discharge into receiving stream ecosystems. In addition, longer-term, multispecies treatments and a detailed characterization of sediment microbial communities, as key drivers of biogeochemical processes, would help to better understand system performance under realistic operational conditions and seasonal variability, thereby supporting the development of ecologically sound strategies to mitigate WWTP inputs to receiving streams. Ultimately, such efforts will be essential to move nature-based solutions from experimental settings toward robust, implementable tools for managing WWTP effluents under increasing water scarcity.

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CRediT authorship contribution statement

Miquel Ribot: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Audrey H. Sawyer:** Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Sara Castelar:** Writing – review & editing, Investigation, Data curation. **Adrià Casacuberta:** Writing – review & editing, Investigation, Data curation. **Daniel Nadal-Sala:** Writing – review & editing, Visualization, Software, Formal analysis. **Gabino Carballo:** Writing – review & editing, Investigation, Data curation. **Olivia Ballester-Miró:** Writing – review & editing, Investigation, Data curation. **Francesc Sabater:** Resources, Methodology, Investigation, Funding acquisition, Conceptualization. **Santiago Sabaté:** Resources, Project administration, Funding acquisition. **Ruben Gil-Solsona:** Writing – review & editing, Resources, Funding acquisition. **Pablo Gago-Ferrero:** Writing – review & editing, Resources, Funding acquisition. **Albert Sorolla:** Resources, Project administration. **Eugènia Martí:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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.

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Data availability

data is shared at zenodo
Raw_data_EcolEng (Original data) (Zenodo)

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