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ORIGINAL ARTICLE

Nutrient Dynamics at the Sediment-Water Interface: Influence of Wastewater Effluents

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Abstract

Uptake and regeneration fluxes and concentrations of nutrients, i.e., nitrate (NO_3^-), ammonium (NH_4^+), phosphate (PO_4^{3-}) and dissolved organic carbon (DOC), were evaluated upstream and downstream of a wastewater treatment plant (WWTP) in the River Wandle, UK, from July to October 2019. Using chamber techniques, water-specific nutrient concentrations were measured at two exposures (3 and 10 min) to calculate fluxes. The WWTP effluent contributed to elevated concentrations and modified flux rates, resulting in significant differences at the study sites. Compared with summer, the concentrations of NO_3^- and DOC increased while NH_4^+ and PO_4^{3-} decreased in autumn. Nutrient fluxes varied both temporally and spatially in uptake (i.e., storage in sediments) or regeneration (i.e., release into river water). Under the actions of physical and biological processes, the fluxes of NO_3^- and NH_4^+ showed opposite flux directions. Dissolved oxygen (DO) and bioabsorption mainly affected PO_4^{3-} and DOC fluxes, respectively. Specifically, across all sites, NO_3^- was −0.01 to +0.02 mg/(m^2 s), NH_4^+ was −29 to +2 μg/(m^2 s), PO_4^{3-} was −2.0 to +0.5 μg/(m^2 s), and DOC was −0.01 to +0.05 mg/(m^2 s). Further, we did find that these variations were related to nutrient concentrations in the overlying water. Our results provide further evidence to show that reductions in river nutrients are paramount for improving river ecological conditions. Additionally, we suggest that more research is needed to evaluate chamber-based experimental approaches to make them more comparable to in-situ flux methods.

Highlights

- Sewage effluent resulted in elevated nutrient concentrations and modified fluxes.
- Flux was affected by initial nutrient concentrations, DO and microbial activity.
- Inexpensive approaches to study nutrient dynamics are needed for river restoration.

Keywords Nutrient dynamics · Experimental chambers · Wastewater · Water chemistry · Urban rivers · River Wandle

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1 Introduction

The "Urban Stream Syndrome" (USS) provides a framework for evaluating responses of watersheds to urbanization (Meyer et al. 2005; Walsh et al. 2005; Booth et al. 2016). USS refers to the degradation of rivers in terms of physical, chemical and biological properties, which can greatly reduce the ecological functions and services of these rivers (Chadwick et al. 2006; Ranta et al. 2021). Pollution associated with urbanization is one focus of USS research (Wenger et al. 2009; Smucker and Detenbeck 2014); improved assessment of pollutant stressors discharged into rivers is needed to provide strategies for improving conditions of these degraded ecosystems (Dalu et al. 2019; Hu et al. 2020). There are a wide range of pollutant stressors to urban rivers (Lele et al. 2018) but nitrogen (N) and phosphorus (P) are among the major threats in most countries of the world (Booth et al. 2016). N and P are essential nutrients for aquatic plants and animals to grow and reproduce, but excessive amounts lead to eutrophication (Capps et al. 2016). Dissolved organic carbon (DOC) provides energy for organisms (Mineau et al. 2016); additionally, it is a component of respiratory substrates, thus affecting the uptake of N and P by aquatic organisms (Kirchner et al. 2004; Appling and Heffernan 2014). Therefore, understanding nutrient and DOC dynamics are vital aspects of water quality in urban systems (Rodríguez-Castillo et al. 2019).

Urban areas are the focus of nutrient pollution due to both point and non-point pathways to urban rivers (Wakida and Lerner 2005). For example, urban impervious areas are known to contribute to elevated nutrients in urban rivers (Bedore et al. 2008; Dodds 2006; Li et al. 2020). The loss of vegetation and soils that effectively entrap particulate nutrients can lead to higher loads than if the vegetation and soil were in place. Additionally, the prevention of soil infiltration of soluble nitrogen and phosphorus effectively mobilizes these nutrients to rivers through stormwater runoff (Pfeifer and Bennett 2011). Of course, point sources, such as wastewater treatment plant (WWTP) effluents, significantly increase N, P and DOC concentrations in the receiving water bodies (Preisner 2020). Regardless of the pathways, urban rivers receive pollution which results in nutrient enrichment which impairs environmental quality and affects ecological conditions (Rabalais 2002; Pereda et al. 2020).

Nutrient flux at the water-sediment interface is ecologically important because microbial activity in river sediments is frequently several times greater than in the overlying water column (Wu et al. 2013; Lavelle et al. 2019). Additionally, hydraulic retention and surface area in sediments are much greater (Fellows et al. 2006). Evaluating this ecological function is thus vital for understanding the dynamics of nutrient in streams.

Nitrogen in sediments can be measured in terms of total nitrogen (TN), and NH_4^+ and NO_3^- are the greatest components of TN (Chen and Tang 2005). For NO_3^- and NH_4^+, fluxes are primarily controlled by concentration changes and nitrogen form transformation within the N-cycle (Chen et al. 2012). These processes includes denitrification, nitrification, dissimilatory nitrate reduction to ammonium (DNRA), mineralization, and biological nitrogen fixation, which are mainly performed by microorganisms such as nitrifying bacteria, denitrifying bacteria, and mineralized bacteria associated with the decomposition of organic matter (Fear 2003; Mulholland et al. 2008; Meghdadi 2018). Thus, the fluxes of NO_3^- and NH_4^+ are mainly determined by the microbial activity involved in the N-cycle process (Simon et al. 2010; Lavelle et al. 2019). However, these N-cycle associated transformations are also affected by a range of hydraulic and environmental parameters (see Galloway et al. 2008; Xia et al. 2018).

Mechanisms of PO_4^{3-}-flux at sediment-water interface also involve both biotic and abiotic factors. Phosphate accumulated on urban impervious surfaces enters rivers via surface runoff (Hobbie et al. 2017). Phosphate is used by aquatic plants and microorganisms as nutrients pass along the food chain (Song et al. 2017). However, phosphate is strongly adsorbed by sediments which is a central factor controlling PO_4^{3-}-flux at the sediment-water interface. For example, insoluble compounds formed by iron minerals under oxidizing conditions can adsorb phosphate in large amounts (Amirbahman et al. 2003; Luo et al. 2004). Additionally, the surface area of aluminum minerals can provide a large number of adsorption sites for phosphate (Dapeng et al. 2011). When dissolved oxygen (DO) conditions or water pH changes, insoluble compounds will be converted to soluble, and phosphate can be regenerated into the overlying water. Therefore, phosphate in sediments can be a major source of endogenous phosphorus in aquatic systems, in many cases accounting for a large proportion of total phosphorus (TP). For example, phosphate in sediments of shallow lakes can account for 60–80% of TP in the whole ecosystem (Penn et al. 1995). Studies have pointed out that long-term river pollution leads to a decrease in the uptake capacity of sediments due to saturation of adsorption sites, which therefore increases the risk of regeneration (Lin et al. 2009; Pereda et al. 2020). This observation is similar to the findings of Earl et al. (2006), who studied the effect of WWTP effluents with high phosphate concentrations and fluxes in receiving rivers. Further, Martí et al. (2010) reported that when biofilms were P saturated, phosphate was released from sediments, due to the reduced demand for phosphate as a nutrient, resulting in a decreased overall PO_4^{3-}-uptake capacity of sediments.

Dissolved organic carbon (DOC) flux is not only dependent on the concentration in sediment and overlying water but also related to pH. Aquatic organisms promote biogenic carbonates synthesis through an alkaline environment as energy supply for biological activities, and its carbon source is DOC, hence the sediment in alkaline water is prone to absorb DOC (Braissant et al. 2007; Santomauro et al. 2012). Furthermore, some studies have found that the organic anions in DOC are competitively adsorbed with phosphate on the adsorption sites of sediment minerals, thus affecting the flux of phosphate (Pant and Reddy 2001; Kuznetsov and Andreeva 2006). Understanding the dynamics of DOC in urban streams and its effects on nutrient flux is an area which need further examination.

Under the actions of microorganisms and/or minerals, nutrients carry on cycling and transformation (e.g., from NH_4^+ to NO_3^-) in sediments. In addition, some pollutants which are difficult to degrade will directly be adsorbed by sediments, making sediments become a sink of these nutrients (Lavelle et al. 2019; Preisner 2020). When the physicochemical properties of river water change (e.g., seasonal changes in water temperature and DO), or the microbial activities involved in the nutrient dynamics change seasonally, sediments will release nutrients to the overlying water (Smith et al. 2011). Therefore, quantifying the uptake and regeneration of nutrients at the sediment-water interface is essential for understanding overall dynamics of nutrients.

Urban rivers often receive WWTP effluents (Belmeziti et al. 2015) and there are many studies on nutrient concentrations in effluent-affected rivers (e.g., Andersen et al. 2004; Carey and Migliaccio 2009; Gu and Tooker 2016). There are, however, relatively few studies which focus on nutrient fluxes (i.e., uptake and regeneration) at the sediment-water interface. In this study, the River Wandle, an urbanized tributary of the Thames, UK, provides an opportunity to examine nutrient concentrations and fluxes underwater conditions affected by the effluent. We aimed to answer the following questions: (1) How do nutrient dynamics (e.g., concentrations and fluxes of NO_3^-, NH_4^+, PO_4^{3-} and DOC) in water and sediments vary between sites with and without WWTP discharges? (2) Are there discernable relationships among NO_3^-, NH_4^+, PO_4^{3-} and DOC concentrations and fluxes at these locations? (3) What are the likley drivers which regulate nutrient concentrations and fluxes?

2 Materials and Methods

2.1 Study Area

The River Wandle is a tributary of the River Thames with a channel length of 14 km. The Wandle catchment is located in southwest London with a catchment area of 11 km^2 represented by 47% urban land cover (Smith and Chadwick 2014; Lavelle et al. 2019). The temperature in the river ranges from ~7–22 °C throughout the year, and the lowest and highest temperatures occur in January and July, respectively. The mean precipitation is 22–45 mm/month, and the minimum and maximum precipitation occur in April and June, respectively (Pike et al. 2014). Located in the catchment is the Beddington WWTP which serves 360,000 people and its outfall discharges into the Wandle (River Wandle Catchment Plan 2014). The effluent standards mainly include ammonium (NH_3-N) at 2.5 mg/L, soluble reactive phosphorus (SPR) at 2.6 mg/L, biological oxygen demand (BOD) at 10 mg/L and solids suspended (SS) at 15 mg/L (River Wandle Catchment Plan 2014). To evaluate the impact of the WWTP effluent on nutrient concentration and flux, an upstream sampling site not affected by the effluent and two downstream sampling sites affected by the effluent were selected on the River Wandle (Fig. 1). The upstream site with abundant aquatic plants is 0.2 km above the effluent outfall site (henceforth referred to as U0.2), where the average water depth is 0.25 m and the average channel width is 8 m; the downstream sites are both associated with residential land and urban green parks. The site 1.0 km downstream of the effluent outfall is referred to as D1.0 and has an average water depth of 0.35 m and an average width of 6 m; The site 3.0 km downstream of the effluent outfall is referred to as D3.0 and has an average water depth of 0.45 m and an average width of 3 m. The average flow at U0.2 is ~1.7m^3/s, and the effluent inflow increases the average flow at D1.0 and D3.0 to ~2.7 m^3/s (River Wandle Catchment Plan 2014). The water temperature is also increased by the effluent; annual mean water temperatures of 11.4 °C, 14.0 °C and 13.4 °C at U0.2, D1.0, D3.0 were recorded, respectively (River Wandle Catchment Plan 2014). Sediments at all sites were of a mix of gravel, cobble, silt and clay.

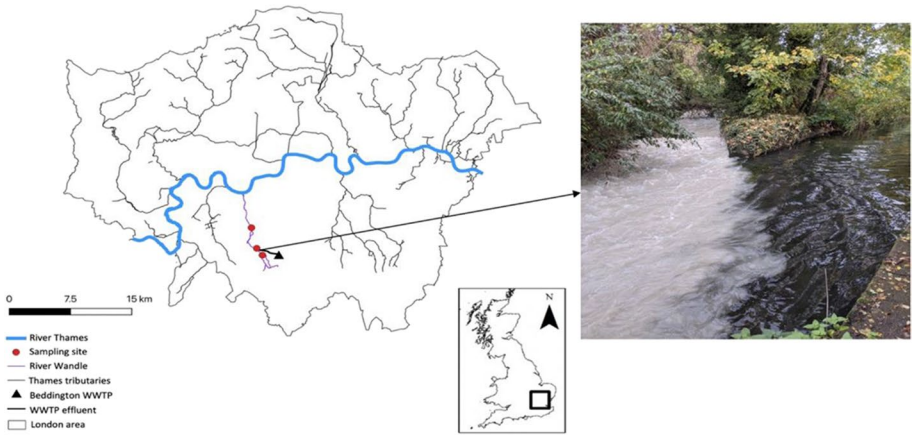

Fig. 1 Sampling sites on the River Wandle, a tributary of the Thames, UK. The sites are U0.2 (upstream of the WWTP), D1.0 (directly downstream of the WWTP) and D3.0 (3 km downstream of the WWTP), respectively. WWTP = wastewater treatment plant

2.2 Sample Collection

River and sediment samples were collected at each sampling site in 8 days with stable discharge avoiding storm events from July to October 2019. Water samples were taken from different depths at each site, and a composite 500 mL sample was collected for laboratory testing. Since NH_4^+ is unstable, at each site, another bottle with 400 mL of working reagent (mixing of sodium sulfite solution, borate buffer solution and ophthalicaldehyde (OPA) solution) was prepared and 100 mL of river water was added and mixed (see: Holmes et al. 1999). Water pH, water temperature and DO concentration were measured on-site using a multiparameter probe (Hanna HI98194 multiparameter meter). For each site, ten patches ~10 cm^2 of the riverbed were randomly selected and 200 mL of sediments (top 2 cm) were collected with a stainless-steel scoop. Water and sediment samples were stored cool separately during transport to the laboratory.

2.3 Concentration Measurement of NO_3^-, NH_4^+, PO_4^{3-}, DOC

NO_3^- and PO_4^{3-} concentrations were measured by ion chromatography (IC; Dionex Aquion). A series of concentration gradient standards were prepared to periodically calibrate the instrument (5 mL of each standard with sodium nitrate or potassium phosphate). The sample concentrations measured were within the concentration gradient range of prepared standards. The DOC concentration was measured as total organic carbon (TOC) analyzer (SHIMADZU TOC-L). Fluorescence photometry was used to measure NH_4^+ concentration (Holmes et al. 1999; Miró et al. 2003). NH_4^+ methods used are described in detail in Holmes et al. (1999). Before measurements, water samples were filtered through a 0.45 μm cellulose membrane in the laboratory.

2.4 Flux Measurement of NO_3^-, NH_4^+, PO_4^{3-}, DOC

Flux experiments were run during baseflow discharge in July and October 2019. In the laboratory, to simulate the interface between water and sediment, the bottom of the 100 mL chamber (we used opaque chambers for NH_4^+ experiments to reduce photodegradation of the working reagent – Holmes et al. 1999) was evenly covered with 20 mL of wet surface sediment, and 70 mL of overlying river water (water containing working reagent for ammonium samples) was then quickly poured onto the sediment. The amount of water and sediment was scaled up by the nitrate flux experiment by Lavelle et al. (2019) in the River Wandle. During the short period after the water was mixed with the sediment, the uptake and regeneration of nutrients were mainly affected by physical disturbance caused by water movement and settlement of sediment particles. About t = 2.5 min after mixing, the particle settlement was visualized, and the water was still. During the following period, nutrient fluxes were mainly affected by the microbial action in the sediment under the condition of static water and sediment (Lavelle et al. 2019). In this study, the overlying water was extracted at t = 0 min before mixing, and t = 3 min and t = 10 min after mixing to measure the concentrations of NO_3^-, NH_4^+, PO_4^{3-}, and DOC to represent the process of physical disturbance and biological action (see Lavelle et al. 2019). Considering that the water extraction at t = 3 min would cause physical disturbance to the system, another experimental set was set up to extract water samples only at t = 10 min. Both sets had 5 replicates. A DO logger (PME MiniDot oxygen logger) was used to continuously measure the DO concentration in the overlying water during two exposures (0 ~ 3 min, 3 ~ 10 min). All flux experiments were carried out at the same room temperature.

2.5 Sediment Analysis

We collected an additional 150 mL of sediment samples at each sampling site, and loss on ignition (Heiri et al. 2001) was used to quantify sediment organic matter content (OM%). Crucibles were placed in a 120 °C drying oven for 48 h, then their net weights were weighed (m_1). The sediments from each sampling site were divided into 3 equal replicates, spread evenly in a tin foil tray, and dried with crucibles for 48 h. After drying and cooling to room temperature, stones and other impurities were filtered out using a 10 mm pore size sieve, then the sediment was sieved into coarse sediment and fine sediment using a 2 mm pore size sieve. The coarse and fine sediments were respectively placed in dried crucibles, and the total weight of each was measured. The net weight of the crucible was subtracted from the total weight to obtain the dry weight of the sediment (m_2). The crucibles containing the sediment were placed in an oven at 550 °C and burned for 2 h, then placed in a desiccator and cooled to room temperature at which point the weight of each (m_3) was measured.

The measurement of sediment grain size was carried out across all sites using Malvern Mastersizer 2000 granulometer. The other half of the fine sediment in the OM% measurement was used for the average grain size analysis. This procedure was repeated three times for each site. Samples were classified as either sand (0.063–2 mm), silt (0.004–0.063 mm), or clay (<0.004 mm) (Lee et al. 2010).

2.6 Data Analysis

For the measurement of NH_4^+ concentration, the matrix effect was derived from the following formula:

$$ME = \frac{\left(F_{std\ spike} - F_{std\ zero}\right) - \left(F_{sample\ spike} - F_{sample\ obs}\right)}{\left(F_{std\ spike} - F_{std\ zero}\right)} \times 100\% \tag{1}$$

where $F_{stdzero}$ is the fluorescence of the blank; $F_{stdspike}$ and $F_{sample\ spike}$ are the fluorescence of the blank and the sample after adding 1 mL of 1 μg/L ammonium stock solution; $F_{sample\ obs}$ is the measured sample fluorescence.

The NH_4^+ fluorescence was obtained after subtracting the background fluorescence:

$$F_{NH_4^+} = F_{sample\ obs} - F_{BF} \tag{2}$$

The final NH_4^+ fluorescence was derived from the following formula:

$$F_{sample} = F_{NH_4^+} + F_{NH_4^+}\left(\frac{ME}{100}\right) \tag{3}$$

NO_3^-, NH_4^+, PO_4^{3-} and DOC fluxes were derived from the following formula:

$$f = \frac{\left(C_2 - C_1\right)V}{A\left(t_2 - t_1\right)} \tag{4}$$

where C_1 and C_2 refer to the nutrient concentration at times t_1 and t_2, respectively; V is the volume of the overlying water (L); A is the surface area of the sediment surface (m^2); t_2–t_1 is the time (s) between the subsequent (t_2) and previous (t_1) water extraction. NO_3^- and DOC fluxes are expressed as mg/(m^2 s); NH_4^+ and PO_4^{3-} fluxes are expressed as μg/(m^2

s). A positive flux indicates the movement of nutrients from the sediment to the overlying water and a negative flux indicates the movement of nutrients from the overlying water to the sediment.

The sediment organic content was derived from the following formula:

$$OM\% = \frac{m_1 - m_3}{m_2} \times 100\% \tag{5}$$

where m_1 is crucible net weight; m_2 is sediment dry weight; m_3 is crucible weight after burning in the oven.

2.7 Data Analysis

We sought to evaluate differences both among our three study sites and between the two-time exposures in the experiments. To accomplish this, we used two-way analysis of variance for each measured water chemistry variable and parameter-specific flux estimates. Due to our relatively small sample sizes, we used non-parametric tests (i.e., Kruskal Wallis). Additionally, to explore overall relationships among water chemistry and flux values, we examined correlations (i.e., Spearman) across these parameters. All statistics were performed in SPSS 18.0 or R language 3.5.2.

3 Results

3.1 River Wandle Water Quality

Nitrate and Ammonium: There were significant differences in NO_3^- and NH_4^+ concentrations among sampling sites ($F=29.446$, $p<0.001$; $F=106.97$, $p<0.001$, respectively), both concentrations were highest at D1.0 and lowest at U0.2 (Fig. 2). NO_3^- ranged from ~4 to 17 mg/L and NH_4^+ ranged from ~0.07 to 1.95 mg/L (Fig. 2a). No significant correlation was observed between the concentrations of NO_3^- and DO ($r^2=-0.344$, $p>0.05$), while NH_4^+ concentration was positively correlated with water temperature ($r^2=0.738$, $p<0.001$; Table 1). Compared with July and August, in September and October, the NO_3^- concentration moderately increased at U0.2 and D3.0 ($p=0.073$, $p=0.885$, respectively), and with a significant increase at D1.0 ($p=0.037$). Similarly, the NH_4^+ concentration moderately decreased at U0.2 and D3.0 ($p=0.070$, $p=0.738$, respectively), and with a significant decrease at D1.0 ($p=0.034$) (Fig. 2b).

Phosphate⁻: The PO_4^{3-} concentration was highest at D1.0 and lowest at U0.2, ranging from ~0.3 to 1.2 mg/L (Fig. 2a). There was a significant difference in the PO_4^{3-} concentration between U0.2 and D1.0 ($p=0.001$), and U0.2 and D3.0 ($p=0.001$), while no significant difference was observed between D1.0 and D3.0 ($p=0.597$). The PO_4^{3-} concentration was negatively correlated with DO, and it decreased at D1.0 and D3.0 in September and October ($p=0.016$, $p=0.126$, respectively), but increased by 5% at U0.2 ($p=0.845$) (Fig. 2b).

Dissolved organic carbon: The DOC concentration was highest at D1.0 and lowest at U0.2, ranging from ~1.6 to 5.5 mg/L (Fig. 2a), and it was significantly different among sampling sites ($F=93.999$, $p<0.001$). In September and October, DOC increased by 3.5% ($p=0.295$), 2.8% ($p=0.794$), and 5.6% ($p=0.359$) at U0.2, D1.0, D3.0, respectively

Fig. 2 **a** Concentrations of nutrients (NO_3^-, NH_4^+, PO_4^{3-}, DOC) and DO and water temperature at the three sampling sites. Each box contains eight corresponding datapoints from eight sampling events from July to October. The concentrations of these four nutrients were the highest at D1.0 and the lowest at U0.2. The concentrations of NO_3^-, NH_4^+ and DOC were significantly different among all sampling sites, while PO_4^{3-} concentrations were only significantly different between U0.2 and D1.0 or between U0.2 and D3.0. Fig. 2**b** Concentrations of nutrients (NO_3^-, NH_4^+, PO_4^{3-}, DOC) and DO and water temperature at the three sampling sites from July to October. The circle represents U0.2, the triangle represents D3.0, and the square represents D1.0. Compared with July and August, in September and October, NO_3^- and NH_4^+ concentrations increased and decreased significantly at D1.0; PO_4^{3-} concentrations decreased significantly at D1.0; There were no significant variations in DOC concentrations among all sites ▶

(Fig. 2b). Across all sites, positive correlations were observed between DOC and other nutrient concentrations (Table 1).

3.2 Sediment Analysis

Sediments used for the flux experiments varied both among and between sites. Generally, fine sediments (particle size <2 mm) contained more organic matter than coarse sediments (particle size >2 mm). Sediments of all sampling sites were mainly composed of silt, with the highest proportion of fine sediment at U0.2 and the highest proportion of coarse sediment at D1.0 (Table 2).

3.3 DO, NO_3^-, NH_4^+, PO_4^{3-} and DOC Fluxes at the Sediment-Water Interface

Nitrate and ammonium: Across all sites, NO_3^- fluxes in both exposure periods ranged from −0.01 to +0.02 mg/(m^2 s) and NH_4^+ ranged from −29 to +2 μg/(m^2 s) (Fig. 3a, 4b). There was no significant difference in NO_3^- ($p = 0.577$) and NH_4^+ ($p = 0.636$) fluxes between July and October. NO_3^- and NH_4^+ fluxes showed the opposite direction at one sampling site, except in the case of U0.2 in October, where both regeneration and uptake occurred. Both nitrate and ammonium fluxes were slower during the 3–10 min experiment when compared to the 0–3 min experiment.

Phosphate: PO_4^{3-} fluxes in both exposure periods ranged from −2.0 to +0.5 μg/(m^2 s) and varied significantly between the two seasons ($p = 0.008$; Fig. 3c). PO_4^{3-} was absorbed by the sediment among all sites in summer sampling events, while it was regenerated in autumn. PO_4^{3-} fluxes decreased with exposure period, the decrease in regeneration fluxes (0.077, 0.072, 0.077 μg/(m^2 s) for U0.2, D1.0, D3.0, respectively) was lower than the decrease in uptake fluxes (0.419, 0.413, 0.18 μg/(m^2 s) for U0.2, D1.0, D3.0, respectively).

Dissolved organic carbon: DOC showed uptake fluxes in both seasons at D3.0 and was regenerated in both exposure periods in autumn sampling events at other sites. DOC fluxes ranged from −0.01 to +0.05 mg/(m^2 s) and no significant difference was observed between the two seasons ($p = 0.902$; Fig. 3d).

DO flux: There was a positive correlation between the DO consumption flux and the regeneration fluxes of NH_4^+ and PO_4^{3-}, while no correlation was observed between the DO consumption flux and NO_3^- or DOC regeneration flux (Table 3). Only the initial PO_4^{3-} concentration was negatively correlated with PO_4^{3-} regeneration flux (Table 3). This indicates that in the overlying water, DO conditions and initial nutrient concentrations cannot completely independently affect nutrient fluxes.

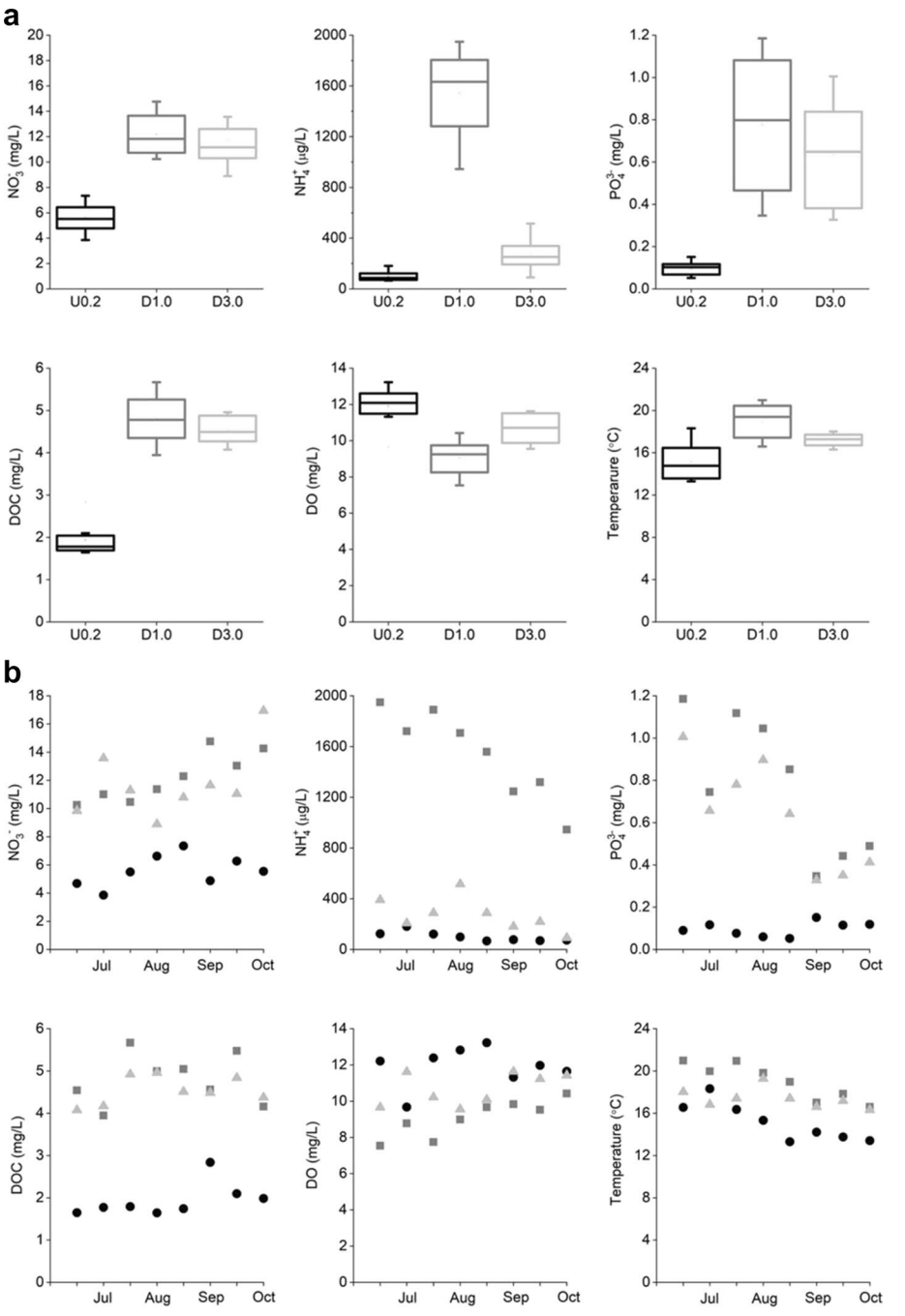
a
NO_3^- (mg/L)
NH_4^+ (μg/L)
PO_4^{3-} (mg/L)
DOC (mg/L)
DO (mg/L)
Temperarure (°C)
U0.2
D1.0
D3.0
b
NO_3^- (mg/L)
NH_4^+ (μg/L)
PO_4^{3-} (mg/L)
DOC (mg/L)
DO (mg/L)
Temperature (°C)
Jul
Aug
Sep
Oct

Table 1 Correlation matrix of River Wandle water quality parameters over the entire experimental period

	NO_3^-	NH_4^+	PO_4^{3-}	DOC	DO
NH_4	$r^2 = 0.421$*				
PO_4^3	$r^2 = 0.481$*	$r^2 = 0.711$***			
DOC	$r^2 = 0.782$***	$r^2 = 0.641$***	$r^2 = 0.780$***		
DO	$r^2 = -0.344$	$r^2 = -0.807$***	$r^2 = -0.832$***	$r^2 = -0.694$***	
temp	$r^2 = 0.353$	$r^2 = 0.738$***	$r^2 = 0.829$***	$r^2 = 0.668$***	$r^2 = -0.880$***

Note: The overall sample size was 24. "r^2" is the Spearman correlation coefficient. "*" indicates a significant correlation of $p < 0.05$; "**" indicates a significant correlation of $p < 0.01$; "***" indicates a significant correlation of $p < 0.001$

4 Discussion

Research to quantify the nutrient dynamics in urban river ecosystems helps to improve river restoration practices and provide needed evidence to support conservation policies geared towards returning rivers to improved ecological conditions. In our study we explored the dynamics of NO_3^-, NH_4^+, PO_4^{3-}, and DOC at the sediment-water interface in an urban river ecosystem (River Wandle) affected by a WWTP outfall. Our results indicated that the discharged WWTP effluent to the sampling site D1.0 contributed the highest nutrient concentrations and the lowest DO concentration (Fig. 2). Compared with the other sites, the sediment at D1.0 was the largest source of NO_3^- and DOC and the largest sink of NH_4^+ in July and October (Fig. 4). Specifically, flux at the sediment-water interface was affected by initial nutrient concentrations, DO conditions in the overlying water and likely patch-scale microbial activity in the sediment affecting nutrient dynamics.

The rate and direction of nutrient flux (i.e., uptake and regeneration) were likely determined by the nutrient concentration in water and sediment, and the concentration changes between the two media are influenced by a combination of physical processes (e.g., water advection) and biogeochemical processes. Generally, the role of sediments as NO_3^- producers/consumers is accompanied by the role as NH_4^+ consumers/producers (Fig. 3), which is related to nitrification, dissimilatory nitrate reduction to ammonium (DNRA) process in the N-cycle, respectively, which are affected by their concentrations, seasonal water temperature and DO (Helton et al. 2011; Reisinger et al. 2016). For PO_4^{3-} flux, insoluble or

Table 2 Sediment condition summary. Category refers to the proportion of fine and coarse sediments in the sample (in brackets); OM% = percentage of organic matter, numbers in followed brackets are standard deviation; Composition refers to the proportion of particle size in the fine sediment. Each sediment sample was measured in three replicates

Site	Category	Mean OM%	Composition	
U0.2	Fine sediment (43.6%)	15.398 (0.39)	Sand 0.0%	Clay 5.2%
	Coarse sediment (56.4%)	4.234 (0.20)	Silt 94.8%	
D1.0	Fine sediment (26.8%)	29.710 (1.08)	Sand 0.0%	Clay 2.2%
	Coarse sediment (73.2%)	8.320 (0.04)	Silt 97.8%	
D3.0	Fine sediment (37.7%)	13.625 (0.69)	Sand 0.0%	Clay 1.8%
	Coarse sediment (62.3%)	3.252 (0.17)	Silt 98.2%	

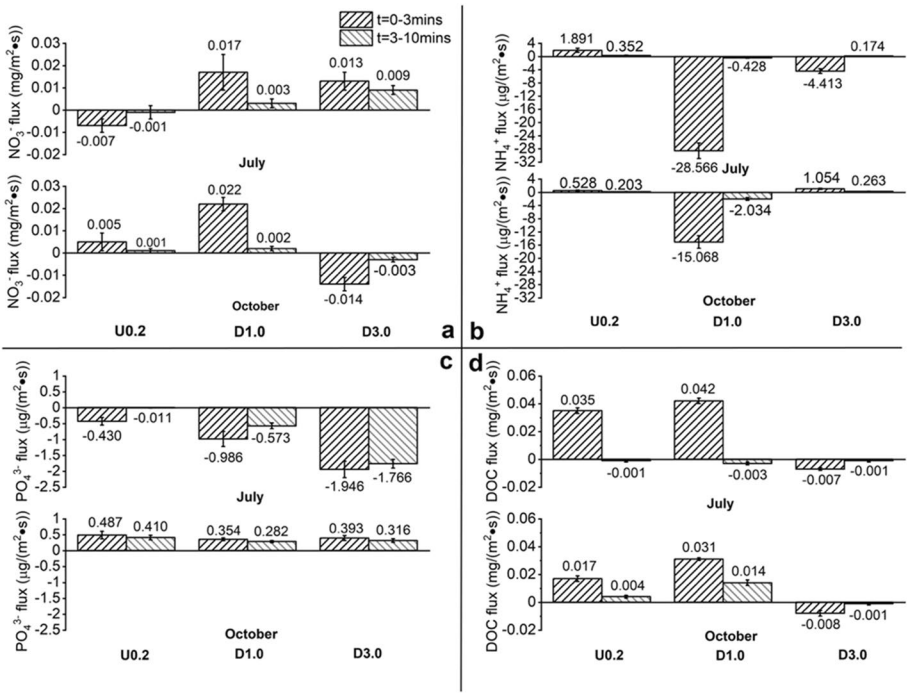

Fig. 3 NO_3^- (a), NH_4^+ (b), PO_4^{3-} (c) and DOC (d) fluxes for both periods during July and October sampling events. NO_3^- and DOC fluxes are in mg/(m^2 s); NH_4^+ and PO_4^{3-} fluxes are in μg/(m^2 s). Downwards flux represents uptake/removal of nutrients from the overlying water to the sediment and upwards flux represents regeneration/release of nutrients from the sediment to the water. The number above bars is the mean of nutrient flux among replicates, and error lines are marked on the bars. In each experiment season, we set up five replicates, each containing 20 mL of sediment and 70 mL of overlying river water. Only phosphate fluxes showed significant seasonal differences

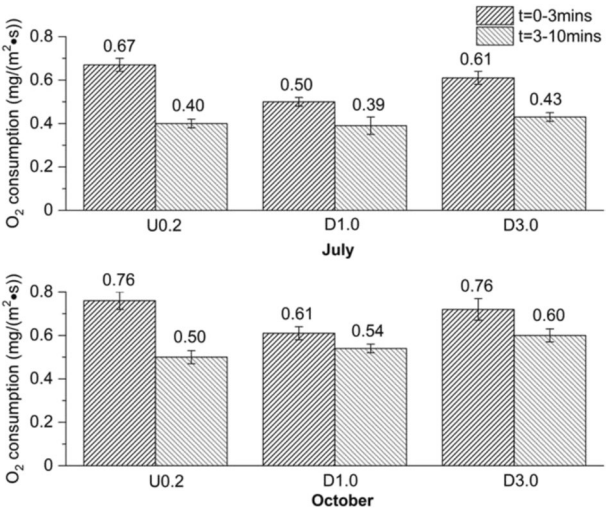

Fig. 4 DO consumption for both periods during July and October sampling events. The number above bars is the mean of the DO consumption flux, and error lines are marked on the bars. The data came from the miniDot logger, which was able to continuously measure DO in the two exposures. We used the difference in DO concentration between the beginning and the end time to estimate DO consumption

Table 3 Correlation matrix between nutrient flux and DO consumption flux in the overlying water and initial nutrient concentration (t = 0 min)

	NO_3^- flux	NH_4^+ flux	PO_4^{3-} flux	DOC flux
DO consumption	r = 0.192 N/A	r = 0.556 *	r = 0.601 *	r = 0.069 N/A
Initial NO_3^- concentration	r = 0.410 N/A			
Initial NH_4^+ concentration		r = 0.286 N/A		
Initial PO_4^- concentration			r = −0.850 **	
Initial DOC concentration				r = 0.075 N/A

The sample size is 12. "r" is Spearman correlation coefficient (positive values represent regeneration flux; negative values represent uptake flux). "*" indicates a significant difference of $p < 0.05$; "**" indicates a significant difference of $p < 0.01$; "N/A" indicates no significant difference

soluble matter in sediment particles affected by DO can interact with minerals and change adsorption sites and adsorption capacity of sediments likely responsible for our observed differences (Bedore et al. 2008; Wu et al. 2018); Additionally, PO_4^{3-} flux relates to the zero equilibrium phosphorus concentration (EPC0). When the PO_4^{3-} concentration in the water column deviates from EPC0, the migration of PO_4^{3-} will increase (McDowell 2015). DOC dynamics, related to its roles as a biological energy source, can be affected by ecosystem metabolism and the content of organic matter in sediments (Kaushal et al. 2014; Zhang and Chadwick, in review).

4.1 Mechanisms Driving NO_3^- and NH_4^+ Concentrations and Fluxes

After water and sediment samples were mixed, the mutual disturbance of the two media caused NH_4^+ to migrate along the concentration gradient. Specifically, in the summer experiments (i.e., July), we observed that D1.0 with the highest NH_4^+ concentration in the overlying water was accompanied by the highest NH_4^+ uptake rate during the 0–3 min and 3–10 min exposures, followed by D3.0, while U0.2 with the lowest NH_4^+ concentration released NH_4^+ with a regeneration rate similar to that reported by Lavelle et al. (2019) (Fig. 3b). In terms of biological processes, the movement of water transferred NO_3^- into the sediment and likely made it bioavailable with microbes associated within sediment surfaces. The DO consumption during both exposures favored the occurrence of the DNRA reaction, so that NO_3^- was transformed into NH_4^+ and returned to the overlying water with the water flow or along the concentration gradient (Altmann et al. 2003). This is consistent with the opposite flux direction of NO_3^- and NH_4^+ observed across all sites (Fig. 3a). Additionally, we found that the NH_4^+ flux rate decreased with decreased NH_4^+ concentration in the overlying water, which occurred not only at each site but also in the later exposure (3–10 min). This was because NH_4^+ generated by microbial transformation gradually decreased with decreased NO_3^- entering the sediment. Under the action of physical and biological processes, the decreased NH_4^+ concentration difference between water and sediment resulted in a decreased flux rate.

Among our study sites concentrations of NO_3^- and NH_4^+ were significantly different among river reaches ($F = 106.97$, $p < 0.001$) with D1.0 having the highest nutrient concentrations. The effluent with elevated water temperatures and the highest content of organic matter (Table 2) promoted the mineralization of organic nitrogen by microbes likely supporting the highest NH_4^+ concentration reaching >1 mg/L and the acceleration

of NH_4^+ uptake (Souza et al. 2011). Further, we observed significant positive correlations between water temperature and NH_4^+ concentration ($r^2 = 0.738$, $p < 0.001$), NO_3^- and DO ($r^2 = 0.818$, $p < 0.001$). The correlation of NH_4^+ was consistent with the findings of Cole et al. (2002) who found that elevated temperatures promoted biological activity, and thus, enhanced mineralization, and the correlation NO_3^- was attributed to nitrification (Fear 2003; Yang et al. 2012).

NO_3^- and NH_4^+ concentrations decreased at D3.0 compared with D1.0. As nutrients were transported from the midriver reach, and the conversion to N_2 gas (i.e., nitrifier denitrification) or other forms of nitrogen (e.g., associated with biological storage) was likely achieved (Fear 2003; Mulholland et al. 2008; Meghdadi 2018). D3.0 concentrations of NO_3^- were higher than the upstream reach, which was consistent with the findings of Perryman et al. (2011) who pointed out that NO_3^- increased downstream with increasing river discharge due to short water residence time. However, at D3.0, NH_4^+ re-entered the overlying water in the 3–10 min exposure, which was likely because the overlying water could not provide sufficient NH_4^+ as NH_4^+ continued to enter the sediment, and the nitrification was inhibited, resulting in decreased NO_3^- regeneration flux and conversion of NH_4^+ from uptake to regeneration flux. These spatial variations across our study sites can be attributed to changes in overall nutrient spiralling dynamics and variations in nutrient supply associated with the WWTP effluents (Grimm et al. 2005; Haggard et al. 2005; Ensign and Doyle 2006).

In autumn experiments (i.e., October), the concentration of NH_4^+ and river water temperature decreased, while an increase in the NO_3^- concentration was observed. The increased seasonal precipitation in southeast England and the River Wandle catchment is likely an important factor for the increased NO_3^- concentration because surface runoff as a non-point source of pollution carried NO_3^- from urban impervious surfaces into the river (Ko et al. 2010). Although increased precipitation and runoff can also dilute NO_3^- concentrations, pollution associated with surface runoff can be significantly stronger than dilution (Monfared et al. 2017) and this needs further attention for the River Wandle. Regardless, we found decreased NH_4^+ fluxes accompanied by reduced NH_4^+ concentrations in October. However, for NO_3^- flux, increased concentrations resulted in an uptake flux of NO_3^- at D3.0, which was the opposite of the case in July.

4.2 Mechanisms Driving PO_4^{3-} Concentrations and Fluxes

The River Wandle catchment management plan (Pike et al. 2014) identified exogenous sources of PO_4^{3-} in the river from WWTP effluents, detergents and oil accumulated on urban impervious surfaces and animal waste. In our study, the highest PO_4^{3-} concentration at D1.0 was owing to the effects of the WWTP effluents; however, the contribution from PO_4^{3-} released from the sediment was less, which was reflected in the lowest PO_4^{3-} regeneration rate at this site in October (Fig. 3c). This was because the high content of organic matter at D1.0 can form biofilms on the sediment surface and reduce the interaction between PO_4^{3-} and sediment (e.g., adsorption site), thereby reducing the regeneration/uptake of PO_4^{3-} from/to the sediment as we observed in both seasons (Pant and Reddy 2001; Kuznetsov and Andreeva 2006).

We observed that PO_4^{3-} concentrations were negatively correlated with DO ($r^2 = -0.832$, $p < 0.001$) and positively correlated with water temperature ($r^2 = 0.829$, $p < 0.001$). DO conditions affect electron receptors in sediments (e.g., Fe^{3+}), thereby affecting the formation of soluble and insoluble substances more than the adsorption of PO_4^{3-} (House and Denison 2000). For example, under reducing conditions, the form of $Fe(OH)_2$

reduces the adsorption sites for PO_4^{3-}; Under oxidizing conditions, the conversion of Fe^{2+} to Fe^{3+} is very slow. Once a large amount of insoluble matter is formed, the PO_4^{3-} uptake by sediments is weakened, resulting in increased PO_4^{3-} concentrations in the overlying water (Zhao et al. 2015; Martí et al. 2021). For the effect of water temperature, Jin et al. (2008) and Wang et al. (2009) found that increased water temperature can promote the generation of phosphatase by aquatic organisms and lead to the production of more soluble phosphorus (e.g., PO_4^{3-}). In our study, we suspect the effect of lower water temperature, slowed metabolism and increased DO in autumn led to a decrease in PO_4^{3-} concentrations.

Sediments at U0.2 contained the highest proportion of fine particles (Table 2), which were easy to resuspend due to the slow sedimentation speed, causing PO_4^{3-} to re-enter the overlying water (Luo et al. 2004). This could explain that U0.2 had the lowest PO_4^{3-} uptake flux in July and the highest regeneration flux in October.

There was a significant positive correlation between PO_4^{3-} and water pH ($r^2 = 0.636$, $p = 0.001$). The river reaches at all sites were alkaline (pH = 7.7 ~ 8.9), causing OH^- and PO_4^{3-} to compete for adsorption sites on the sediment surface and exchange with PO_4^{3-}, consequently increasing the PO_4^{3-} concentration in the water, which is regarded as the mechanism by rivers to regulate PO_4^{3-} levels (Jin et al. 2008).

4.3 Mechanisms Driving DOC Concentrations and Fluxes

In July, the samples at U0.2 and D1.0 with high DOC content released DOC into the overlying water during 0–3 min exposure (Fig. 3d). However, during 3–10 min exposure, sediments among all sites absorbed DOC, which was likely due to the fact that microorganisms increase the saturation index of biogenic carbonate minerals through their metabolic activities, and DOC is a carbon source (Braissant et al. 2007; Santomauro et al. 2012). The fine sediments across all sites were mainly composed of silt, and clay accounted for a small fraction (Table 2). Such sediment textures have a high surface area available for microbial adhesion and colonization, resulting in high microbial biomass and diversity (Sessitsch et al. 2001; Fear 2003). Therefore, the sampling sites may have similar microbial biomass and diversity, resulting in no difference in the DOC uptake flux among all sites in July. Such biological effects were weakened in October, causing regeneration fluxes of DOC at U0.2 and D1.0 during 3–10 min exposure.

In October, the DOC concentration increased across all sites, which was due to the fact that DOC accumulating in riparian areas and urban impervious surfaces likely entered the river with increased stormwater runoff (Correll et al. 2001); Additionally, leaves falling into the river is another main carbon source (Kalbitz et al. 2000). The content of organic matter in sediments varies little with seasons (Hook and Yeakley 2005). For U0.2 and D1.0 samples, the increased DOC concentration in the overlying water caused decreased regeneration fluxes during 0–3 min exposure compared with the same exposure of July. However, in these two seasons, DOC uptake fluxes were measured at D3.0 and the flux rates were almost unchanged, which likely attributed to the increased downstream flow with a dilution effect on the increased DOC concentration in autumn (Worrall et al. 2003).

4.4 Flux Predicted by Nutrient Concentrations and Water Temperature

In our flux experiment, we did not look for interactions across nutrient dynamics. However, using values from our flux measurements and comparing these against ambient river water

quality could provide some additional insight into our observed flux patterns. To investigate this further, we used simple forward selection stepwise multiple regression to evaluate if all of our measured flux rates could be predicted from ambient river water quality. This is a heuristic, exploratory approach because we did not measure changes in all water quality parameters which would relate directly to an individual, chamber-specific flux measurement. Overall, we found significant models for all of our flux measurements (Table 4). For NO_3^- flux, only NH_4^+ concentration explained overall differences. This suggests that nitrification likely plays a strong role in our study which is similar to results from other WWTP affected rivers (Jiao et al. 2009; Merbt et al. 2015). For PO_4^{3-} flux, only PO_4^{3-} concentration explained overall differences, but this was a negative relationship which suggests that increased concentrations in river water may saturate uptake. This fits with the general pattern of mass balance processes driving phosphorus uptake and regeneration dynamics in aquatic systems (Reddy et al. 1999). For NH_4^+ flux, two parameters were selected in the model: NH_4^+ concentration and water temperature. These results could point towards microbial activity associated with assimilative nitrogen uptake as the driving process (Bernal et al. 2017; Webster et al. 2003). However, the negative beta coefficient associated with NH_4^+ concentration suggests that regeneration increases and uptake slows with increased river nutrients, perhaps signalling N saturation or ammonification (Grimm et al. 2005; Jiao et al. 2009). Finally, DOC flux was explained by NH_4^+ and DOC concentrations. In this model, the negative beta coefficient associated with DOC concentration again suggests that increased DOC leads to regeneration rather than uptake of DOC, which was demonstrated in the shift of DOC flux from uptake in July to regeneration in October in the 0–3 min exposure at U0.2 and D1.0. However, the positive beta coefficient associated with NH_4^+ concentration may support DOC as a carbon source for assimilative nitrogen uptake (Webster et al. 2003; Bernal et al. 2017). Evaluating each of these models provides some indication of the relative

Table 4 Stepwise regression (forward selection) between nutrient fluxes and nutrient concentrations and water temperature. Data involved in the regression analysis contains both exposure periods. The final model summary statistics are reported for each flux (below label). Individual parameter fit summary statistics for selected models are given in grid cells (β is the standardized regression coefficient; r^2 is the proportion of variance for a dependent variable that's explained by an independent variable; p is the significance value for each parameter reported). The blacked-out grid cells indicate that these parameters were not selected by the final model

	NO_3^- concentration	NH_4^+ concentration	PO_4^{3-} concentration	DOC concentration	Water temperature
NO_3^- flux		*β= 0.624*			
$F_{1,10}=6.369$		$r^2=0.389$			
$p=0.030$		$p=0.030$			
NH_4^+ flux		*β= − 1.083*			*β= 0.226*
$F_{2,9}=71.02$		$r^2=0.906$			$r^2=0.034$
$p<0.001$		$p<0.001$			$p=0.050$
PO_4^{3-} flux			*β= − 0.572*		
$F_{1,10}=4.859$			$r^2=0.327$		
$p=0.052$			$p=0.052$		
DOC flux		*β= 0.817*		*β= − 0.548*	
$F_{2,9}=11.12$		$r^2=0.436$		$r^2=0.278$	
$p=0.004$		$p=0.002$		$p=0.017$	

importance of biological and physical processes which drive the dynamics of nutrients at the sediment-water interface in urban rivers affected by WWTP effluents.

4.5 Research Limitations

Our results provide further evidence to show that reductions in river water nutrients are paramount for improving river ecological conditions. However, there are some limitations to the flux chambers used in our research, which need to be further investigated. After water and sediments were mixed, we regarded biological processes as separate effects on nutrient fluxes after sediment settlement was visualized (i.e., after 3 min). While our results and those of a previous study (Lavelle et al. 2019) do support the idea of a separation of physical versus biological activity, microbially mediated uptake/regeneration processes clearly would have been active during the initial stages of our experiments when water movement slowed and sediment particles settled. To address this issues, future experiment should include a negative control where chemicals that can stop bioactivity can be added (e.g., $ZnCl_2$), thus providing a clear indication of physical versus biological processes.

Chamber experiments can distinguish between physical and biological processes, which is difficult to achieve with in-situ measurement. Additionally, chamber methods are much less expensive than tracer experiments and can be done quickly across multiple sites. However, chambers clearly cannot simulate the actual chemical and hydraulic conditions of a river. For example, although we collected water samples at different depths, there was still a lack of water advection and hyporheic flow in the flux chambers, which likely resulted in nutrient concentrations which would differ from conditions in the river.

5 Conclusions

This study explored concentrations and fluxes of NO_3^-, NH_4^+, PO_4^{3-} and DOC at the sediment-water interface in an urban river ecosystem affected by a WWTP. Sewage effluent contributed to observed elevated concentrations and modified flux rates, resulting in significant differences across the study sites. Additionally, we observed nutrient fluxes being driven by a combination of physical and biological processes. We suggest that water movement and sediment suspension in our chamber experiments promoted the migration of nutrients between the two media under physical disturbance (e.g., time 0–3 min). Nutrients were brought into contact with sediments and absorbed and utilized by microorganisms, or biogeochemical reactions occurred due to the biological activity of sediment-surface microbes. This resulted in nutrient transformation, thus affected nutrient and DOC concentrations and flux rates in the chambers. Specifically, NO_3^- and NH_4^+ fluxes relating to the N-cycle (e.g., ammonification and nitrification) were affected by seasonal changes in water temperature and DO and presumed levels of microbial activity. For PO_4^{3-} flux, we suggest that both insoluble or soluble matter in sediment affected by organic matter content and DO conditions interact with minerals and change adsorption sites and adsorption capacity of sediments, but this needs additional study to evaluate the temporospatial nature of these conditions. Additionally, competitive adsorption by anions is also a consideration for PO_4^{3-} flux, linking it more directly to water pH. The texture and particle size distribution of sediments affect the surface microbial biomass and diversity, which utilize DOC as energy and carbon source partially determining the DOC flux; this was suggested in the stepwise regression analysis of microbial uptake of DOC for nitrogen assimilation.

Our study suggests that the increase of NH_4^+ in overlying water will lead to the uptake of NO_3^- by sediments, resulting in the risk of large nitrates releases from sediments when water quality conditions change. The increase of PO_4^{3-} and DOC can directly lead to their regeneration, resulting in the risk of eutrophication and organic pollution. Overall, our research on the nutrient dynamics in urban river ecosystems add to the improved understanding of factors affecting nutrient flux at the sediment-water interface and provide additional evidence to support research geared to improving ecological conditions of rivers affected by WWTP effluents by mitigating nutrient concentrations.

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Availability of Data and Material All data are provided within the paper and in a provided Supplementary Material file.

Authors' Contributions M Zhang and M Chadwick designed the research. M Zhang led the field and lab work and wrote the first draft of the manuscript. All authors contributed editing and completion to the final draft.

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Declarations

Conflicts of Interest/Competing Interests The authors declare that they have no conflict of interest.

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