Wastewater effluents affect ecosystem metabolism: an evaluation of activation energy case study from the River Wandle, UK

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Abstract

River ecosystem metabolism (REM) is a measure of ecological function which integrates gross primary production (GPP) and ecosystem respiration (ER). Urban rivers often receive effluents from wastewater treatment plants (WWTP) which frequently alter nutrient concentrations and modify temperature regimes of receiving water bodies. In this study, we applied the nighttime slope method (NSM) to estimate diurnal REM at sites above and below a wastewater outfall on the River Wandle, a tributary to the River Thames, and structural equation modelling (SEM) revealed that nutrient supply, water temperature and light availability were the main factors driving REM. Overall estimated GPP and ER from our study sites were like those of urban impacted rivers in other countries. Upstream to downstream, GPP values ($0 \sim 21.2 \text{ mgO}_2 \cdot \text{L}^{-1} \cdot \text{d}^{-1}$) were similar, but ER values ($5.5 \sim 10.1 \text{ mgO}_2 \cdot \text{L}^{-1} \cdot \text{d}^{-1}$) were significantly higher at the downstream site receiving WWTP effluents. GPP/ER ratios were > 1 indicating heterotrophic conditions during the study. We found that sites had similar activation energy associated with ER suggesting our work provides a useful reference for estimating temperature corrected metabolic processes for other urban rivers in the region. Structural equation modelling (SEM) revealed that nutrient supply, water temperature and light availability were the main factors driving REM. This research highlights the major environmental factors affecting REM providing needed evidence to inform river restoration and future in-stream management.

Keywords: gross primary production, ecosystem respiration, activation energy, wastewater, River Wandle

Article Highlights

- Sewage effluent resulted in elevated GPP and ER rates.
- Nutrient supply and water temperature jointly promoted GPP and ER rates.
- Inexpensive loggers to estimate river metabolism are needed for river restoration.

Introduction

River ecosystem metabolism (REM) is a measure of ecosystem function which integrates gross primary production (GPP) and ecosystem respiration (ER) (Fellows et al. 2006; Rodríguez-Castillo et al. 2019). On a global scale, a major contributor to atmospheric CO₂ is from the respiration of riverine organic matter (Beaulieu et al. 2013; Raymond et al. 2013; Jauhainen et al. 2014), while GPP is important for supporting aquatic biodiversity in river ecosystems (Strayer and Dudgeon, 2010; Ferreira et al. 2020). A wide range of environmental factors affects both GPP and ER (Mulholland et al. 2008; Gernot et al. 2010; Jankowski et al. 2021; Fig. 1a), notably stressors associated with the urban stream syndrome (Meyer et al. 2005; Walsh et al. 2005). For example, increased nutrients from anthropogenic activities, urban impervious surfaces and wastewater treatment plant (WWTP) effluents entering rivers can significantly increase REM in urban rivers by promoting biological activity (Meyer et al. 2005; Dodds 2007; Beaulieu et al. 2013; Fig. 1b). The difference between GPP and ER indicates the carbon budget in the river ecosystem, it is therefore referred to as net ecosystem production (NEP) (Bernhardt et al. 2018). Some studies also use the ratio of GPP to ER to determine whether a river is autotrophic or heterotrophic (Grace and Imberger, 2006; Tank et al. 2010; Escoffier et al. 2018). Considering complex interactions among hydrology, climate, chemistry, and biology, REM has direct implications for water quality and food webs and is an excellent functional indicator of ecological response for environmental change (Tank et al. 2010; Rodríguez-Castillo et al. 2019; Jankowski et al. 2021) which can be used as a holistic tool for the classification of river ecosystem health (Young et al. 2008, Table 1).

Figure 1. River ecosystem metabolism (REM) can be affected by a wider range of factors at multiple scales. **a:** environmental factors which can influence REM; **1b:** examples of factors potentially affecting REM in urban catchments.

Table 1. Framework for assessing river ecosystem health using metabolism measurements; Impacts refer to the degree of impaired ecosystem functioning (Young et al. 2008). GPP=gross primary production; ER=ecosystem respiration.

Assessment parameter	Criterion	Impacts to impaired functioning
GPP ($\text{gO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$)	GPP<3.5	Severe effect
	GPP=3.5 - 7.0	Mild effect
	GPP>7.0	No effect
ER ($\text{gO}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$)	ER=1.6 - 5.8	Severe effect
	ER=0.8 - 1.6 or 5.8 - 9.5	Mild effect
	ER<0.8 or >9.5	No effect

It is widely accepted that polluted rivers with high nutrient and organic matter loads have higher ER which often results in anoxia and hypoxia, a serious water quality problem (Bernhardt et al. 2018). Additionally, WWTP effluents are frequently warmer than ambient stream temperatures which elevate enzymes activity involved in respiration then increase ER rate in urban rivers (Beaulieu et al. 2013; Jauhiainen et al. 2014). For GPP, photosynthesis is strongly influenced by nutrient supply, light availability, and water temperatures (Roberts et al. 2007; Heffernan and Cohen, 2010; Finlay et al. 2011). For example, Bernhardt et al. (2018) noted that GPP often peaks in high nutrient concentrations, warming temperatures and lengthening days.

The respiration process of aquatic organisms is associated with activation energy, which is related to temperature (Yvon-Durocher et al. 2010; Hill et al. 2018). Within a certain temperature range, higher water temperature can promote the activity of enzymes related to respiration, thus improving ER rates and higher activation energy is required, especially for urban rivers receiving WWTP effluents with warmer water temperature (Beaulieu et al. 2013; Jauhiainen et al. 2014). The sensitivity of activation energy to temperature provides a new insight into river water quality management. For example, elevated riverine ER and associated activation energy in summer indicate higher DO consumption, and DO supplementary measures need to be implemented (Perkins et al. 2012).

In this study, we measured REM of the River Wandle, an urban tributary to the River Thames, affected by WWTP effluent. Using the WWTP effluent as a natural experiment, we evaluated how both variations in nutrients and water temperatures affect REM. Additionally, we employed structural equation modelling (SEM), which has been widely used in ecology, to provide regression models to investigate the causality of environmental factors affecting REM (*sensu* Fan et al. 2016). With this knowledge, we then sought to use our River Wandle case study to inform further river restoration and future in-stream management options.

Materials and methods

Study sites

The River Wandle, a tributary of the River Thames in southwest London, has a catchment area of 11 km² and urban coverage of ~50% (Smith and Chadwick, 2014; Lavelle et al. 2019). The river is 14 km in length with an average discharge of 1.70 m³/s (River Wandle Catchment Plan, 2014). Within the catchment, Beddington WWTP serves 360,000 people and discharges into the Wandle (Schnell et al. 2015). The upstream site is located 0.2 km above WWTP effluent outfall (henceforth U0.2 in the paper); The downstream site located 3 km below the effluent outfall is referred to as D3.0 (Fig 2). U0.2 has abundant riparian vegetation and submerged macrophytes; D3.0 flows through a residential area.

Figure 2. Study sites on the River Wandle, a tributary of the Thames, UK. The blue dot is the outfall location of the WWTP effluent to the river. Red dots are the upstream site (U0.2) and the downstream site (D3.0). The black triangle denotes Beddington WWTP.

Water quality and light data

50mL of water sample was collected and water temperature was measured at each study site (Hanna HI98194 multiparameter meter). Water samples were stored cool separately during transport to the laboratory. In the laboratory, water samples were passed through 0.22 µm membrane filters before nutrient measurements. NO₃⁻ and PO₄³⁻ concentrations were measured by ion chromatography (Dionex Aquion). NH₄⁺ concentration was measured using Turner Designs AquaFluor handheld fluorometer (Holmes et al. 1999). DOC concentration was measured by total organic carbon (TOC) analyzer (SHIMADZU TOC-L). The website <http://environment.data.gov.uk> provides data of photosynthetic active radiation (PAR) for the study reaches, which are used as a measure of light availability.

Measurement of river metabolism

During the study period (19 to 22 September 2019), water levels at U0.2 and D3.0 remained at 0.20-0.25 m, 0.35-0.40 m, respectively (<https://flood-warning-information.service.gov.uk>). The stable flow conditions were suitable for using the open-water, single station method (Grace and Imberger, 2006; Demars et al. 2015). Specifically, the night-time slope modelling (NSM) was applied for GPP, ER and reaeration estimates in this study (Hill et al. 2018), which is based on the principle of no GPP during nighttime to simplify the oxygen mass balance equation (eq. 1, eq. 2) to establish the linear regression between DO change rate and ER. We measured DO and water temperature at both sites simultaneously. Due to the limited number of loggers, these measurements were made using two lab calibrated data loggers (MiniDOT logger and Arduino logger (Chan et al 2020)); collection frequency was once per minute for the MiniDOT logger and 9 times per minute for the Arduino logger.

$$\frac{dC_{DO}}{dt} = k(C_{DOs} - C_{DO}) + GPP - ER \quad (1)$$

$$\frac{dC_{DO}}{dt} = k(C_{DOs} - C_{DO}) - ER \quad (2)$$

where C_{DO} is DO concentration (mg/L); C_{DOs} is DO saturated concentration (mg/L); k is reaeration coefficient (d^{-1}); $k(C_{DOs}-C_{DO})$ is reaeration rate (mg/(L d)).

Oxygen from the atmosphere transported across the air-water interface (reaeration) also causes changes in dissolved oxygen (DO) in rivers (Hill et al. 2018). Reaeration coefficient k measures the speed of the reaeration process (Jin et al. 2012; Omole et al. 2013). Soares et al. (2013) noted that k is proportional to the flow velocity and river channel slope, suggesting that disturbances that speed up water flow can accelerate reaeration (e.g., flooding) (Raymond et al. 2012). In our study, given the uniform nature of the river channel and river velocities across the study reaches the night-time slope modelling approach was appropriate for estimating k (Grace and Imberger, 2006; Hill et al. 2018).

C_{DOs} was derived from eq. 3:

$$C_{DOs} = 1.4276 \exp[-173.4292 + 249.6339(\frac{100}{T}) + 143.3483 \ln(\frac{T}{100}) - 21.8492(\frac{T}{100})] \quad (3)$$

where T is mean water temperature (K).

The night-time period was selected from the time of sunset to the time when the difference between DO saturation concentration and DO concentration (DO deficit) reached the maximum (Hill et al. 2018). The ER obtained by eq. 2 requires temperature correction, which is related to Arrhenius activation energy E_a , (i.e., the energy required for respiration of aquatic organisms, Gillooly et al. 2001). Higher E_a indicates that ER is more sensitive to temperature changes (Hill et al. 2018), which depends on resident biodiversity, especially

heterotrophic organisms that do not change significantly on seasonal scales (Perkins et al. 2012; González-Pinzón et al. 2016). Therefore, the calculated ER is used to obtain GPP values in *eq. 1*.

$$\theta_R = \exp\left(\frac{E_a}{k_B T_0 T}\right) \quad (4)$$

where E_a is Arrhenius activation energy (eV) that was derived from *eq. 5*:

$$\ln(ER) = -E_a\left(\frac{1}{k_B T} - \frac{1}{k_B T_0}\right) + \ln(ER_0) \quad (5)$$

where k_B is Boltzmann constant (8.62×10^{-5} eV/K); T is mean water temperature (K); T_0 is reference water temperature (288.15 K); ER_0 is respiration rate at T_0 .

The temperature corrected ER was derived from *eq. 6*:

$$ER^* = ER \theta_R^{T-20^\circ C} \quad (6)$$

GPP required temperature correction:

$$GPP^* = GPP \theta_P^{T-20^\circ C} \quad (7)$$

where $\theta_P = 1.066$, the correction coefficient.

The temperature-corrected reaeration rate was derived from *eq. 8*:

$$k(C_{DOs} - C_{DO}) \theta_a^{T-20^\circ C} \quad (8)$$

where $\theta_a = 1.024$, the correction coefficient.

GPP, ER and reaeration rate were temperature corrected to obtain the diurnal variation data during the experimental period. Differences in REM between sites were evaluated using Paired T-Tests. Correlations between environmental variables were analyzed using the Pearson correlation coefficients (Table 5a). All data analysis was performed using Excel and SPSS 26.0.

Structural equation modelling (SEM)

By evaluating potential interactions among hydrology, climate, chemistry, and biology (Figs 1a and 1b), we established pathway analysis (Fig. 3) to investigate the influence of the WWTP effluent (i.e., 4 nutrient concentrations in the effluent and elevated water temperatures) on downstream water quality and REM. The arrow points to the affected factor, among them, the nutrient concentrations in the WWTP effluent were derived from Zhang et al. (2021), the PAR data was from <http://environment.data.gov.uk>, other data, except bioactivity, were derived from our measurements and estimates. Bioactivity (e.g., phytoplankton and aquatic animals) is a variable we did not measure and cannot obtain data directly from literatures or websites (referred to as central latent variable, in the oval) but aquatic organisms are the main body of river metabolic processes. Structural equation

modelling (SEM) allows us to include bioactivity in pathways and estimate its correlations with other measured variables (in the box) (Fan et al. 2016). The SEM was performed in SPSS 21.0 AMOS.

Figure 3. Pathway analysis for REM pattern and decomposition process in the reach affected by the WWTP effluent. Variables linked by arrows have causal relationships. The box represents the observed variable; The oval represents the latent variable.

Results

Light and water flow

The data of light availability were measured by PAR for the River Wandle (Table 2a); The water flow data from the South Wimbledon flow monitoring station near to D3.0 (<http://nrfa.ceh.ac.uk/data/station/info/39003>) provides an opportunity to further study the effect of water flow Q on DO dynamics (e.g., reaeration coefficient k , Table 2b).

Table 2a. Data of photosynthetic active radiation (PAR) for the River Wandle (<http://environment.data.gov.uk>). The nighttime PAR (7 pm-5 am) was 0 and was not displayed in the table.

Date	Time	PAR (KJ·m ⁻²)	Time	PAR (KJ·m ⁻²)	Time	PAR (KJ·m ⁻²)	Time	PAR (KJ·m ⁻²)
19/09	1-3 pm	1255.8	3-5 pm	327.6	5-7 pm	112.6		
20/09	5-7 am	49.9	7-9 am	691.2	9-11 am	1711.1	11-1 pm	2222.4
	1-3 pm	2085.1	3-5 pm	1281.7	5-7 pm	294.4		
21/09	5-7 am	47.7	7-9 am	699.2	9-11 am	1705.6	11-1 pm	2205.2
	1-3 pm	2030.6	3-5 pm	1213.2	5-7 pm	255.7		
22/09	5-7 am	15.0	7-9 am	300.2	9-11 am	924.1		

Table 2b. Data of water flow from the South Wimbledon flow monitoring station near to D3.0 (<http://nrfa.ceh.ac.uk/data/station/info/39003>).

Date	Water flow (m ³ /s) (mean (min-max))	Date	Water flow (m ³ /s) (mean (min-max))
19/09	1.192 (0.637-4.000)	20/09	1.161 (0.609-5.360)
21/09	1.224 (0.655-4.570)	22/09	1.581 (0.580-4.170)

DO profiles

During the experimental period, the sunrise and sunset were around 6:00 am and 6:40pm, respectively. At both sites, there were strong diurnal patterns in DO with the maximum DO deficit occurring at around 3:40 am at U0.2

and around 6:30 am at D3.0 (Fig. 4). The mean saturated DO concentrations at U0.2 and D3.0 were 10.29 ± 0.16 mg/L and 9.50 ± 0.13 mg/L, respectively.

Figure 4. Diurnal variation of DO during the study period for the two study sites. U0.2=upstream of WWTP; D3.0=downstream of WWTP.

Reaeration and activation energy estimates

For both sites, the daily temperature-corrected reaeration rate in the nighttime was significantly higher than in the daytime ($p=0.009$, Fig. 5a). The highest reaeration rate was found at D3.0 ($p=0.238$), where the reaeration coefficient k was significantly lower than at U0.2 ($p=0.012$, Table 3, Fig. 6) and presented as a function of discharge with a regression coefficient of 0.897 (Fig. 5b). The diurnal reaeration rate was not correlated with ER ($r^2=0.775$, see below for ER estimates), while the nighttime reaeration rate was positively correlated with ER ($r^2=0.013$). A similar activation energy required for ER was observed between the two sites (U0.2=0.97 eV, D3.0=0.95 eV).

Figure 5. a. Diurnal variation of reaeration rate during the study period for the two study sites. Reaeration was estimated using the night-time slope modelling; **b.** Reaeration coefficient calculated from the NSM method for D3.0 normalized to 20°C with θ_a during the study period. The flow data was derived from the South Wimbledon flow monitoring station near to D3.0 site (<http://nrfa.ceh.ac.uk/data/station/info/39003>).

Figure 6. Equations fitted by nighttime slope method (NSM) at two sites during the experimental period.

Table 3. Reaeration coefficient (k) and ecosystem respiration (ER) from eq. 3; Activation energy (E_a) from eq. 5

Site	Night-time	eq. 3	k (d ⁻¹)	eq. 5
U0.2	19/9-20/9	$y=6.396x-14.347$ ($r^2=0.941$)	6.396	$y=-0.949x+8.539$ ($r^2=0.985$)
	20/9-21/9	$y=8.000x-19.493$ ($r^2=0.962$)	8.000	
	21/9-22/9	$y=6.195x-16.856$ ($r^2=0.923$)	6.195	
D3.0	19/9-20/9	$y=4.073x-13.601$ ($r^2=0.303$)	4.073	$y=-0.971x+2.412$ ($r^2=0.949$)
	20/9-21/9	$y=4.951x-18.216$ ($r^2=0.375$)	4.951	
	21/9-22/9	$y=3.595x-14.487$ ($r^2=0.495$)	3.595	

Note: The intercept of eq. 3 is ER in $\text{mgO}_2\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ and the intercept of eq. 5 is the logarithm of ER at the reference water temperature (288.15K).

GPP, ER and NEP estimates

For both sites, GPP and NEP peaked around 1~3 pm (Fig. 7); GPP ranged from 0~23.4 $\text{mgO}_2\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ and NEP ranged from -13.7~13.2 $\text{mgO}_2\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ (Table 4). No significant difference in GPP was observed between U0.2 and D3.0 ($p=0.196$). GPP was positively correlated with ER, water temperature and regional photosynthetic radiation (Table 5a). ER ranged from 5.4 ~ 16.3 $\text{mgO}_2\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ (Table 4) and was significantly higher at D3.0 (11.9 ± 2.0 $\text{mgO}_2\cdot\text{L}^{-1}\cdot\text{d}^{-1}$) compared with U0.2 (7.1 ± 1.2 $\text{mgO}_2\cdot\text{L}^{-1}\cdot\text{d}^{-1}$, $p=0.020$). ER was positively correlated with water temperature ($r^2=0.889$, $p<0.001$). At both sites, negative NEP indicated carbon depletion in the river. For D3.0, the higher ER supported a significant higher rate of carbon depletion ($p=0.024$). Further, ratios of daily GPP to ER were < 1 (Table 4), indicating that the river was in a heterotrophic state.

Figure 7. Diurnal variations of GPP, ER and NEP during the study period. Daytime hours were 7:00 am - 6:40 pm, nighttime hours were 6:40 pm - 7:00 am. Data measurement for U0.2 and D3.0 started at 1:00 pm and 3:00 pm on September 19 and ended at 12:00 pm and 1:00 pm on September 22, respectively. GPP=gross primary production; ER=ecosystem respiration; NEP=net ecosystem production; U0.2=upstream of WWTP; D3.0=downstream of WWTP.

Table 4. Site-specific river ecosystem metabolism (GPP & ER) and associated energy input and output of the River Wandle. GPP=gross primary production; ER=ecosystem respiration.

Site	GPP ($\text{mgO}_2 \cdot \text{L}^{-1} \cdot \text{d}^{-1}$)	ER ($\text{mgO}_2 \cdot \text{L}^{-1} \cdot \text{d}^{-1}$)	GPP/ER	NEP ($\text{mgO}_2 \cdot \text{L}^{-1} \cdot \text{d}^{-1}$)
U0.2	4.471 (0 ~ 21.20)	7.055 (5.45 ~ 10.11)	0.634 (0 ~ 2.64)	-2.584 (-7.95 ~ 13.18)
D3.0	4.722 (0 ~ 23.36)	11.942 (8.98 ~ 16.34)	0.395 (0 ~ 1.82)	-7.220 (-13.70 ~ 9.75)

Note: GPP and ER are averages followed by (min ~ max) values for the study period.

Table 5a. Correlation matrix among metabolism and nutrients and environmental factors of the River Wandle.

	GPP	ER	Temp	Light	Nitrate
GPP					
ER	$r^2=0.900$ ***				
Temp	$r^2=0.858$ ***	$r^2=0.889$ ***			
Light	$r^2=0.907$ ***	$r^2=0.570$ **	$r^2=0.682$ ***		
Nitrate	$r^2=0.403$ *	$r^2=0.901$ ***	$r^2=0.788$ ***	$r^2=0.383$ N/A	
Phosphate	$r^2=0.806$ ***	$r^2=0.546$ **	$r^2=0.874$ ***	$r^2=0.725$ ***	$r^2=0.381$ N/A

Note: “*” indicates a significant difference of $p<0.05$; “**” indicates a significant difference of $p<0.01$; “***” indicates a significant difference of $p<0.001$; “N/A” indicates no significant difference.

Table 5b. A summary of nutrient concentrations (mg/L) and water temperatures ($^{\circ}\text{C}$)

Site	NO_3^-	NH_4^+	PO_4^{3-}	DOC	Temp
U0.2	6.09	0.09	0.08	2.00	14.80

	(1.11)	(0.02)	(0.05)	(0.56)	(1.33)
D3.0	10.65	0.32	0.66	4.72	17.67
	(1.23)	(0.14)	(0.25)	(0.26)	(1.13)

Note: Values in parathesis denote one standard error.

Nitrate and phosphate concentrations of the Wandle were positively correlated with ER, and a negative correlation between phosphate and GPP was observed (Table 5a), suggesting significant impacts of nutrient supply on aquatic biological activities involved in river metabolism. Further, significant positive correlations between GPP and PAR were recorded at both sites ($r^2=0.921$, $p<0.001$ for U0.2; $r^2=0.829$, $p<0.001$ for D3.0, Fig. 8), suggesting that the GPP determined by the NSM method was reasonable.

Figure 8. Correlation between GPP and PAR during the study period at two study sites.

SEM regression analysis

To investigate the effects of downstream nutrients (at site D3.0) affected by the WWTP effluent and light availability and water temperature on river metabolism, we obtained correlation coefficients from running SEM (Fig. 9; Table A1). The SEM allows to include bioactivity without data into the pathways and estimate the correlations between bioactivity and metabolic processes (i.e., GPP and ER), water quality (i.e., nutrients and water temperature) and light availability through regression calculations.

Figure 9. Standardized SEM results. The numbers on the arrows represent the correlation coefficient; thicker arrows indicate significant correlations.

The four nutrients in the WWTP effluent all contributed significantly to the elevated nutrient concentrations in the WWTP-affected reach (Fig. 8), resulting in differences in the rates of REM-related processes (Table 4). Although no significant effect of DOC on bioactivity was observed, we still noted that other nutrients and water temperature contributed significantly to bioactivity, thus affecting ER, which played a decisive role in reaeration rates, suggesting that the DO consumed by ER will be significantly supplemented by reaeration. For GPP, it was directly controlled by light availability (PAR).

Discussion

Comparison with other studies

We compared our results with other rivers also receiving WWTP effluents or in similar conditions (e.g., elevated temperature and nutrients) in different regions. Overall, reported GPP and ER values for these studies were within the range of our results (our results were multiplied by the water depth to make the units consistent, U0.2 = 0.25 m, D3.0 = 0.40 m, Table 6), supporting the role of WWTP effluents and associated conditions in regulating REM, despite different channel characteristics, nutrient loads, aquatic organism composition, and local climate might contribute to the differences in these results.

Levi and McIntyre (2020) estimated the mean ER in the effluent-impacted reaches was 6.9 times higher than in the reference reaches in six urban rivers in Wisconsin, USA, which was consistent with the significantly elevated ER we observed at D3.0. Fuß et al. (2017) reported that the ranges of GPP and ER in agricultural rivers with highly loaded DOM and nitrates (i.e., like the WWTP effluent) were higher than in the forest rivers and covered the range at D3.0 in our study. Similarly, Rodríguez-Castillo et al. (2019) reported that the GPP and ER thresholds in the effluent-impacted reach of the River Cares, Spain, were within the range at D3.0. Arroita et al. (2018) showed that reduced nutrients significantly reduced GPP and ER after the operation of the WWTP on the

280 River Oria, Spain. However, in many studies on river metabolism, including our study, GPP and ER estimates
281 were based on river reaches and did not indicate which part of the river they came from (e.g., algae, aquatic
282 macrophytes), which requires further research.

Table 6. Comparison between river ecosystem metabolism (REM) for this study and other similar published studies. Reported GPP and ER ranges or mean values for these studies were within the range of our results. This finding supports the role of WWTP effluents and associated conditions in regulating REM.

Authors	River location	River size (km ²)	River characteristics	Methods	GPP (gO ₂ /(m ² •d))	ER (gO ₂ /(m ² •d))
This study	River Wandle, London, UK	11	Reference & effluent	Single-station	1.1 (0 - 5.3) (ref) 2.1 (0 - 10.5) (effluent)	1.8 (1.4 - 2.5) (ref) 5.4 (4.0 - 7.4) (effluent)
Levi and McIntyre (2020)	Urban rivers, Wisconsin, USA	3.0 - 55.4	Reference & effluent	Modelling	1.4 (ref) 17.4 (effluent)	1.6 (ref) 11.0 (effluent)
Fuß et al. (2017)	Rivers in central Europe	15.8 - 316.4	Agricultural & forest	Single-station	0.01- 0.9 (forest) 1.0 - 3.3 (agriculture)	1.9 - 6.0 (forest) 6.2 - 11.7 (agriculture)
Rodríguez-Castillo et al. (2019)	Deva-Cares catchment, Spain	495	Reference & effluent	DO record & modelling	<2.5 (ref) >2.5 (effluent)	<2.5 (ref) 2.5 - 3.5 (effluent)
Aristi et al. (2015)	Segre River, Iberian Peninsula	287	Reference & effluent	Single-station & two-station	0.54 (ref) 0.7 - 2.3 (effluent)	3.1 (ref) 6.6 - 8.8 (effluent)
Escoffier et al. (2018)	Urban part of the Seine River, France	18,748	Effluent	Single-station	0.04 -15.7 (effluent)	0.03 - 17.6 (effluent)
Arroita et al. (2018)	River Oria, Alegia, Spain	333	Before and after a WWTP installation	Single-station	6.8 (before) 3.8 (after)	12.4 (before) 4.22 (after)

DO profiles across study sites

The continuous monitoring of DO concentrations provides information about anoxia and hypoxia, which are vital for evaluating habitat suitability for aquatic organisms (Pollock et al. 2007; Rode et al. 2016; Eloise et al. 2017). The magnitude of diurnal DO swings at D3.0 was higher than at U0.2 resulting from high rates of photosynthesis and organic matter respiration (Fig. 5), which can cause physiological stress in aquatic organisms (Pollock et al. 2007). Regarding spatial distributions of DO, affected by the WWTP effluent, the mean DO concentration at D3.0 was lower, but the DOC concentration was higher (Table 5b), indicating that respiration supported by DOC contributed to DO consumption (Fig. 9). Additionally, high concentrations of DOC were partly attributed to the decomposition of organic matter, which also consumed DO and needs further investigation in these reaches (Ferreira et al. 2020).

The maximum DO deficit at the two study sites appeared before sunrise, around 3:40 am at U0.2 and around 6:30 am at D3.0. On the one hand, the lower nighttime water temperature resulted in high concentrations of saturated DO; On the other hand, the DO concentration was lower in the nighttime, leading to the maximum DO deficit at night (Hill et al. 2018). The SEM model revealed that the higher water temperature and nutrient supply of the WWTP effluent at D3.0 promoted the consumption of DO by ER (Fig. 9), which significantly increased the reaeration rate to supplement DO (Fig. 5a), resulting in the maximum DO deficit at D3.0 occurring later than at U0.2.

Factors driving GPP and ER

WWTP effluent in this study was used as a natural experiment to investigate the effects of nutrient loads and elevated water temperatures on urban river ecosystem metabolism. We found that the WWTP effluent resulted in similar GPP ($p=0.196$), but higher ER ($p=0.020$) in the WWTP-affected reach (Fig. 7). These results are like other research which have evaluated REM in streams affected by similar stressors to our study (e.g., elevated temperatures and nutrients, Table 6). Further, based on the criteria reported in Table 1, our study sites would be classified as severely to mildly impaired. Although GPP and ER were measured at specific locations, they can represent the metabolic patterns of the studied reaches and be used to assess ecological functions, because of the natural movement and mixing of water in a river (Young et al. 2008). Overall, this suggests that both the WWTP effluent and the urbanized catchment have negative impacts on river ecological function and health.

The Beddington WWTP effluents had elevated nutrients, such as nitrates and phosphates, relative to the ambient River Wandle water quality during our study and this has been reported previously (Millier et al. 2010;

South East Rivers Trust, 2010). Available nitrogen and phosphorus often act as limiting nutrients for aquatic vegetation (Woodward et al. 2012; Bristow et al. 2017). The SEM model revealed that NO_3^- , NH_4^+ and PO_4^{3-} were key nutrients affecting aquatic biological activity, and these increases can promote the growth and reproduction of aquatic organisms (e.g., phytoplankton), thus accelerating GPP and ER (Tank and Dodds, 2003; Noormets, 2009). Aristi et al. (2015) referred to the increase in GPP and ER in heterotrophic rivers as the "subsidy" effect of WWTP effluents. As a result of this, a positive correlation between GPP and ER was found ($r^2=0.900$, $p<0.001$), which has also been widely reported by many studies (e.g., Chen et al. 2009; Hall and Beaulieu, 2013; Yan et al. 2018; Hung et al. 2020). However, organic matter associated with WWTP effluents (e.g., higher DOC concentrations at D3.0) can be an important energy input exceeding *in-situ* GPP (Gücker et al. 2006; Aristi et al. 2015); Additionally, GPP is directly controlled by light availability (Griffiths et al. 2013; Ferreira et al. 2020). Therefore, the increase for ER and GPP in reaches with elevated nutrients are not always consistent (Bernhardt et al. 2018), which explains the inconsistency between the increased significance of GPP and ER at D3.0 in our study. Furthermore, changes of light availability led to the diurnal variation of GPP as we observed that the GPP was the highest between 11 am and 1 pm then decreased to 0 in the nighttime (Fig. 7). Reach-scale riparian vegetation is also a key factor affecting GPP because abundant riparian vegetation blocks the light transmission into the river, as the case at U0.2, resulting in lower GPP values at U0.2 in our study (Wondzell et al. 2019; Tan et al. 2021, Table 4).

ER was positively correlated with water temperatures ($r^2=0.889$, $p<0.001$) due to temperature-related enzymes activity involved in respiration (Beaulieu et al. 2013; Jauhainen et al. 2014). The SEM model also showed that biological activity was significantly affected by water temperature, which in turn affected ER. As a result, due to the warm WWTP effluent (Table 5b), ER at D3.0 was significantly higher than at U0.2 ($p=0.020$). However, ER will not increase indefinitely with increasing temperature due to factors like substrate limitation and/or protein degradation (Demars et al. 2011; Manning et al. 2018). As a result, with the continuous DO consumption by ER and decomposition and the potentially limited carbon supply due to the metabolism of carbon compounds, the maximum DO deficit was reached before sunrise and the initiation of photosynthesis (Hill et al. 2018). In some systems, this can produce anoxic or hypoxic periods (Reid et al. 2019), but this was not the case during our study. By studying the decomposition of organic matter in the five tributaries of the Thames River in London, Lavelle (2018) proposed that water temperature can also promote the decomposition process thus accelerating the DO consumption, which likely caused biological activity (e.g., invertebrates and microbes) at

D3.0 with elevated water temperature and nutrients to be stimulated (Woodward et al. 2012), resulting in higher DO consumption, which needs to be further explored in our study river.

River respiration is more sensitive to temperatures and more vulnerable to climate change when higher activation energy (E_a) is required (Perkins et al. 2012), however, similar E_a was observed between both sites (U0.2=0.97 eV, D3.0=0.95 eV) in our study, which could be applied to other rivers in the region for making temperature corrections to metabolic processes (Hill et al. 2018). However, these two results are higher than the average activation energy (0.65 eV) of river respiration proposed by Yvon-Durocher et al. (2010), which is likely due to the narrow reaches and dense distribution of aquatic vegetation (e.g., phytoplankton) in our study compared with most rivers, resulting in higher ER and required activation energy (Gillooly et al. 2001; Hill et al. 2018).

The balance of GPP and ER plays an important role in the carbon cycle which are affected by anthropogenic factors, such as WWTP effluents and DOM inputs (Kaushal et al. 2014). As we found, WWTP effluent significantly increased ER which has implications for CO₂ emissions. According to the respiratory quotient of 0.85 (Grace and Imberger, 2006), U0.2 and D3.0 released 8.228 g/m³ and 13.948 g/m³ of CO₂ respectively on average during the study period. Strategies to reduce nutrient loads in WWTP effluents via improved WWTP operations are paramount to reducing overall ER in affected systems, thereby lowering the associated CO₂ emissions (de la Barrera and Hooda, 2016).

Factors driving reaeration

Significantly increased nighttime reaeration was mainly due to the lack of oxygen supply from photosynthesis; Also, the lower water temperature at night promoted oxygen solubility (Roberts et al. 2007). There was no correlation between diurnal reaeration rates and ER, but a positive correlation was found between nighttime reaeration rates and ER ($r^2=0.013$), indicating that the nighttime reaeration replenished the DO consumed by ER, and GPP contributed to daytime DO replenishment in addition to reaeration. The higher reaeration rate at D3.0 was closely linked to higher ER caused by the effluent (Fig. 9). As a result, positive values of reaeration rate were observed at night, representing the oxygen entering the river from the atmosphere; In the daytime, the reaeration rate was sometimes negative, representing the saturated DO escaped from the river to the atmosphere (*see supplementary materials*). Conversely, U0.2 was estimated by a significantly increased reaeration coefficient k , which we relate mainly to river features and substrate. The U0.2 reach is wide and shallow with natural substrates (e.g., cobbles) when compared to D3.0. These features provide a large frictional contact area for oxygen disturbance to water flow and oxygen-water mixing even under baseflow conditions (Zappa et al. 2007; Alin et

al. 2011). Additionally, abundant submerged vegetation at U0.2 affected hydraulic roughness and increased small-scale turbulence leading to increased reaeration coefficients (Nifong, et al. 2020). As k is primarily physically driven, in our study, k is a power function of discharge Q (Fig. 5b), which is consistent with the results of Hill et al. (2018).

Both GPP and reaeration play a key role in increasing DO content, and many riverine ecological restoration practices are based on increasing GPP or reaeration to avoid anoxia (Levi and McIntyre, 2020). With the River Wandle, the river was re-meandered by constructing berms, riffles and marginal wetlands to encourage aquatic vegetation habitats and enhance GPP (Pretty et al. 2003; Bukaveckas, 2007; Lorenz et al. 2013). For other urban rivers, increasing biotic habitat through natural channel design (Reisinger et al. 2019) or providing benthic habitat through rock deployment in the channel (Levi and McIntyre, 2020) are also ways to enhance GPP. Regarding the improvement of reaeration, enhanced oxygen exchange by flow sinuosity can be achieved by deploying wood, spoil or stones in the channel, such as the Pool River (River Restoration Centre, 2012) and the Hogsmill River (South East Rivers Trust, 2013) in London, UK. Improving GPP and reaeration should therefore be goals of further river restoration practice. However, elevated ER can result in a reduced NEP as in the case of D3.0 in our study, indicating a net loss of energy and an increased risk of anoxia. We suggest that REM estimates could therefore be used as benchmarks for both river restoration success and overall river health.

Conclusions

Our results showed that significant increased ER downstream of the WWTP effluent was associated with both elevated water temperatures and nutrients. Increased ER resulted in elevated oxygen deficit and associated reaeration rate elucidated by our structural equation modelling exercise. During stable river discharge, we found that both sites were heterotrophic and no significant difference in GPP was observed. When compared to other studies, our results support the finding that urban rivers affected by WWTP effluents (or with elevated nutrient loads) have comparable levels of river ecosystem metabolism (REM) with similar ranges of GPP and ER. Future work should focus on evaluating the roles of storm flows and seasonal climate environments in affecting GPP, ER and NEP in urban rivers and to what extent restoration effort can be used to modify REM. For example, improving instream conditions by promoting reaeration and aquatic primary production should be considered and REM measurements could become robust benchmarks for evaluating restoration success and overall river ecosystem health. Finally, we suggest that utilizing WWTP effluents across a wide range of rivers as a natural experiment is a powerful approach for understanding how river ecosystems will be affected by future climate change and eutrophication scenarios.

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413 Authors' contributions: M Zhang and M Chadwick designed the research. M Zhang led the field and lab work and
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650 **Supplementary Tables**

651

Table S1. SEM estimations. SE=standard error; CR=critical ratio.

Variables	SE	CR	p value
$\text{NO}_3^- \leftarrow \text{NO}_3^-$ in the effluent	0.215	3.139	0.002
$\text{NH}_4^+ \leftarrow \text{NH}_4^+$ in the effluent	0.304	6.020	0.001
$\text{PO}_4^{3-} \leftarrow \text{PO}_4^{3-}$ in the effluent	0.033	22.640	0.001
$\text{DOC} \leftarrow \text{DOC}$ in the effluent	0.039	12.848	0.001
Bioactivity $\leftarrow \text{NH}_4^+$	2.005	26.806	0.001
Bioactivity $\leftarrow \text{PO}_4^{3-}$	0.979	-11.283	0.001
Bioactivity $\leftarrow \text{NO}_3^-$	0.078	26.795	0.001
Bioactivity $\leftarrow \text{DOC}$	0.472	0.744	0.450
Bioactivity $\leftarrow \text{Temperature}$	0.017	2.176	0.004
ER $\leftarrow \text{Bioactivity}$	0.002	1.991	0.004
GPP $\leftarrow \text{PAR}$	0.001	4.182	0.001
GPP $\leftarrow \text{Bioactivity}$	0.571	0.487	0.626
Reaeration $\leftarrow \text{GPP}$	0.322	2.206	0.042
Reaeration $\leftarrow \text{ER}$	0.039	2.308	0.003
Reaeration $\leftarrow \text{Decomposition}$	6.575	0.262	0.794
Reaeration $\leftarrow \text{Temperature}$	1.302	0.447	0.665
DOC $\leftarrow \text{Decomposition}$	0.178	5.693	0.001
Decomposition $\leftarrow \text{Bioactivity}$	0.006	9.167	0.001

652 Note: The absolute value of CR greater than 1.96 at 95% confidence level is considered a significant effect.

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654

Table S2. SEM fitting indexes

NPAR	CMIN	DF	p	CMIN/DF
46	189.362	73	0.055	2.594
RMR	GFI	AGFI	PGFI	
0.024	0.957	0.954	0.745	

655 Note: NPAR=Number of parameters; CMIN=Chi-square; DF=Degree of freedom; CMIN/DF<3, the model fit is
656 good; RMR=Root mean square of residual, good model fit with the value <0.05; GFI=Goodness of fit index, the
657 range is 0-1, with the best fit at 1; AGFI=Adjusted goodness of fit index, the range is 0-1, with the good fit at
658 least 0.9; PGFI=Plain goodness of fit index, the range is 0-1, with the good fit at least 0.5.