Influences of Elevated Nutrients and Water Temperature from Wastewater Effluent on River Ecosystem Metabolism

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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. To investigate how variations in nutrients and water temperature affect REM, we applied the night-time slope modelling to estimate diurnal REM at sites above and below a wastewater outfall on the River Wandle, UK. Overall, estimated GPP (0–21.2 mgO₂·L⁻¹·d⁻¹) and ER (5.5–10.1 mgO₂·L⁻¹·d⁻¹) from our study sites were similar to those of urban impacted rivers in other countries. GPP values were similar between sites, but downstream ER values were significantly higher affected by the WWTP effluent. GPP/ER ratios were <1 indicating heterotrophic conditions and the river as a carbon source 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. Furthermore, structural equation modelling revealed that nutrient supply, water temperature and light availability were the main factors driving REM. This research highlights the major environmental factors affecting REM, which helps to understand the response of river metabolism and river regulation of regional carbon cycle to future climate change and provide evidence to inform river restoration and future in-stream management.

Article highlights
● Sewage effluent resulted in elevated metabolic rates.
● Nutrient supply and water temperature jointly promoted metabolic rates.
● Inexpensive loggers to estimate river metabolism are needed for river restoration.

Keywords Gross primary production · Ecosystem respiration · Activation energy · Wastewater · River Wandle

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1 Introduction

River ecosystem metabolism (REM) is a measure of ecosystem function to regulate dissolved oxygen (DO) dynamic balance and regional carbon cycles, 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 CO$_2$ is from the respiration of riverine organic matter (Beaulieu et al. 2013; Raymond et al. 2013; Jauhiainen et al. 2014), while GPP is a process of CO$_2$ fixation and important support for aquatic biodiversity (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).

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 respiratory enzyme activity, then increasing 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 2011). For example, Bernhardt et al. (2018) noted that GPP often peaks in high nutrient concentrations, warming temperatures and lengthening days; Bernot et al. (2010) noted that reduced riparian vegetation due to urban land use allows more intensive light to enter rivers and promotes GPP.

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).

There are two important sources of river DO supply, one is the GPP process, the other is the reaeration process, which refers to the transfer of oxygen in the atmosphere into the water across the air-water interface (Hill et al. 2018). The reaeration rate is related to oxygen deficit and reaeration coefficient $k$, where $k$ measures the efficiency 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).
Urban rivers often receive WWTP effluents (Preisner 2020; Zhang et al. 2021), but there are few studies on the mechanism of REM responding to effluents. Furthermore, considering that elevated nutrients and water temperature in effluents can be used as indicators for REM prediction under environmental changes, we measured REM of the River Wandle, an urban tributary to the River Thames, which is affected by WWTP effluent. Using the WWTP effluent as a natural experiment, we evaluated how both variations in nutrients and water temperatures affect REM. Many studies have used a variety of methods to measure GPP (e.g., $^{14}$C tracer was used by Son et al. (2005) and Wen et al. (2012)), ER (e.g., incubation in light/dark bottles were used by Wang et al. (2014) and Pei et al. (2018)), and respiration (e.g., tracer gas was used by Nifong et al. (2019)), but these methods are complex or expensive. In this study, we applied low-cost DO loggers and night-time slope modelling to simultaneously obtain rich river metabolic information from DO concentration changes (see Sect. 2.3). 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 (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.

2 Materials and Methods

2.1 Study Sites

The River Wandle, a tributary of the River Thames in southwest London, has a catchment area of 11 km$^2$ and urban coverage of $\sim$50% (Smith and Chadwick 2014; Lavelle et al. 2019). The river is 14 km in length with an average discharge of 1.70 m$^3$/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 downstream of 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.

2.2 Water Quality and Light Data

50 mL water samples were collected and water temperature was measured at each study site (Hanna HI98194 multiparameter meter). Water samples were stored in coolbox separately during transport to the laboratory. In the laboratory, water samples were passed through 0.22 μm membrane filters before nutrient measurements. NO$_3^-$ and PO$_4^{3-}$ concentrations were measured by ion chromatography (Dionex Aquion). NH$_4^+$ concentration was measured using Turner Designs AquaFluor handheld fluorometer (Holmes et al. 1999). Dissolved organic carbon (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.
2.3 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). We measured DO and water temperature at both sites simultaneously (Supplementary Material (SM); Table SM1). Specifically, the night-time slope modelling (NSM) was applied for GPP, ER and reaeration estimates in this study (Hill et al. 2018; Tables SM2 to SM4), which is based on the principle of no GPP during night-time to simplify the oxygen mass balance equation (Eqs. 1 and 2) to establish the linear regression between DO change rate and ER:

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

(1)
\[
\frac{dC_{DO}}{dt} = k(C_{DOs} - C_{DO}) - ER
\] (2)

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

In our study, given the uniform nature of the river channel and river velocities along 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):

\[
C_{DOs} = 1.4276 \exp[-173.4292 + 249.6339 \left(\frac{100}{T}\right) + 143.3483 \ln\left(\frac{T}{100}\right) - 21.8492\left(\frac{T}{100}\right)]
\] (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).

ER requires temperature correction, and the coefficient \(\theta_R\) was derived from Eq. (4):

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

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

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

where \(k_B\) is Boltzmann constant (8.62 \times 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):

\[
ER^* = ER \theta_R^{20^\circ C}
\] (6)

GPP required temperature correction:

\[
P^* = \frac{GPP}{\theta_P^{20^\circ C}}
\] (7)
where $\theta_p = 1.066$, the coefficient.

The temperature-corrected reaeration rate was derived from Eq. (8):

$$k(C_{DOs} - C_{DO}) \theta_t^{t-20^\circ C}$$

where $\theta_a = 1.024$, the coefficient.

$t$ in Eqs. (6)-(8) is the water temperature ($^\circ C$).

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. All data analysis was performed using Excel and SPSS 26.0.

### 2.4 Structural Equation Modelling (SEM)

By evaluating potential interactions among hydrology, climate, chemistry and biology (Fig. 1), 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 at 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 the literature 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.
3 Results

3.1 Light and Water Flow

The data of light availability were measured by PAR for the River Wandle (Table 2). The night-time PAR (7 pm-5 am) was 0 and was not displayed in the table.

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 3).

3.2 DO Profiles

During the experimental period, the sunrise and sunset were around 6:00 am and 6:40 pm, 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.

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**Table 2** Data of photosynthetic active radiation (PAR) for the River Wandle (http://environment.data.gov.uk). The night-time 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 | 1:00–3:00 pm    | 1255.8            | 3:00–5:00 pm    | 327.6             | 5:00–7:00 pm    | 112.6             | 11:00 am–1:00 pm | 2222.4           |
| 20/09 | 5:00–7:00 am    | 49.9              | 7:00–9:00 am    | 691.2             | 9:00–11:00 am   | 1711.1            | 11:00 am–1:00 pm | 294.4             |
|       | 1:00–3:00 pm    | 2085.1            | 3:00–5:00 pm    | 1281.7            | 5:00–7:00 pm    | 294.4             | 11:00 am–1:00 pm | 2205.2           |
| 21/09 | 5:00–7:00 am    | 47.7              | 7:00–9:00 am    | 699.2             | 9:00–11:00 am   | 1705.6            | 11:00 am–1:00 pm | 255.7             |
|       | 1:00–3:00 pm    | 2030.6            | 3:00–5:00 pm    | 1213.2            | 5:00–7:00 pm    | 294.4             | 11:00 am–1:00 pm | 2205.2           |
| 22/09 | 5:00–7:00 am    | 15.0              | 7:00–9:00 am    | 300.2             | 9:00–11:00 am   | 924.1             |                 |                   |

**Table 3** 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)                  |
3.3 Reaeration and Activation Energy Estimates

For both sites, the daily temperature-corrected reaeration rate in the night-time 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 4; 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 night-time 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).

3.4 GPP, ER and NEP Estimates

For both sites, GPP and NEP peaked around 1:00–3:00 pm (Fig. 7); GPP ranged from 0 to 23.4 mgO$_2$·L$^{-1}$·d$^{-1}$ and NEP ranged from −13.7 to 13.2 mgO$_2$·L$^{-1}$·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 5). ER ranged from 5.4 to 16.3 mgO$_2$·L$^{-1}$·d$^{-1}$ (Table 4) and was significantly higher at D3.0 (11.9±2.0 mgO$_2$·L$^{-1}$·d$^{-1}$) compared with U0.2 (7.1±1.2 mgO$_2$·L$^{-1}$·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 6), indicating that the river was in a heterotrophic state.

Nitrate and phosphate concentrations of the Wandle were positively correlated with ER, and a negative correlation between phosphate and GPP was observed (Table 5), 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.

### 3.5 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; Tables SM5, SM6). The SEM allows to
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Table 5 Site-specific river ecosystem metabolism (GPP and ER) and associated energy input and output of the River Wandle. GPP = gross primary production; ER = ecosystem respiration.

| Site | GPP (mgO₂·L⁻¹·d⁻¹) | ER (mgO₂·L⁻¹·d⁻¹) | GPP/ER | NEP (mgO₂·L⁻¹·d⁻¹) |
|------|---------------------|--------------------|--------|---------------------|
| U0.2 | 4.471 (0–21.20)     | 7.055 (5.45–10.11) | 0.634  | -2.584              |
| D3.0 | 4.722 (0–23.36)     | 11.942 (8.98–16.34)| 0.395  | -7.220              |

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

Table 6 Correlation matrix among metabolism and nutrients and environmental factors of the River Wandle.

|          | GPP      | ER       | Temp       | Light      | Nitrate   |
|----------|----------|----------|------------|------------|-----------|
| GPP      |          |          |            |            |           |
| ER       | *r²=0.900|          |            |            |           |
| Temp     |          | *r²=0.889|            |            | ***       |
| Light    | *r²=0.907| *r²=0.570| r²=0.682   |            | ***       |
| Nitrate  | *r²=0.403| *r²=0.901| r²=0.788   | r²=0.383 N/A|           |
| Phosphate| *r²=0.806| *r²=0.546| r²=0.874   | r²=0.725 ***| r²=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.

influence of 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.

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 6). 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).
4 Discussion

4.1 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, \( U_{0.2} = 0.25 \text{ m}, D_{3.0} = 0.40 \text{ m}; \) Table 8), 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 dissolved organic matter (DOM) and nitrates (i.e., like the WWTP effluent) were higher than in forest rivers and covered the range at D3.0 in our study. Similarly, Rodriguez-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 River Oria, Spain. However, in many studies on river metabolism, including our study, GPP and ER estimates were based on river reaches and did not indicate which part of the river they came from (e.g., algae, aquatic macrophytes), which requires further research.

### 4.2 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; Elosegi 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 7), 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 night-time water temperature resulted in high concentrations of saturated DO. On the other hand, the DO concentration was lower in the night-time, 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.

| Site | \( \text{NO}_3^- \) (mg/L) | \( \text{NH}_4^+ \) (mg/L) | \( \text{PO}_4^{3-} \) (mg/L) | DOC (mg/L) | Temp (°C) |
|------|-----------------|-----------------|-----------------|-------------|-----------|
| U0.2 | 6.09 (1.11)     | 0.09 (0.02)     | 0.08 (0.05)     | 2.00 (0.56) | 14.80 (1.33) |
| D3.0 | 10.65 (1.23)    | 0.32 (0.14)     | 0.66 (0.25)     | 4.72 (0.26) | 17.67 (1.13) |

Table 7: A summary of nutrient concentrations (mg/L) and water temperatures (°C). Values in parentheses denote standard error.
4.3 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 8). 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

Table 8 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) | 1.8 (1.4–2.5) (ref) |
| | | | | | 2.1 (0–10.5) (effluent) | 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) | 1.6 (ref) |
| | | | | | 17.4 (effluent) | 11.0 (effluent) |
| Fuß et al. (2017) | Rivers in central Europe | 15.8–316.4 | Agricultural & forest | Single-station | 0.01–0.9 (forest) | 1.9–6.0 (forest) |
| | | | | | 1.0–3.3 (agriculture) | 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 (ref) |
| | | | | | >2.5 (effluent) | 2.5–3.5 (effluent) |
| Aristi et al. (2015) | Segre River, Iberian Peninsula | 287 | Reference & effluent | Single-station & two-station | 0.54 (ref) | 3.1 (ref) |
| | | | | | 0.7–2.3 (effluent) | 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) | 12.4 (before) |
| | | | | | 3.8 (after) | 4.22 (after) |
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; Arísti 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 11:00 am and 1:00 pm, then decreased to 0 in the night-time (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 6).

ER was positively correlated with water temperatures ($r^2=0.889$, $p<0.001$) due to temperature-related enzyme activity involved in respiration (Beaulieu et al. 2013; Jauhiainen 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 7), 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 to 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 dissolved organic matter (DOM) inputs (Kaushal et al. 2014). As we found, WWTP effluent significantly increased ER which has implications for CO$_2$ emissions. According to the respiratory quotient of 0.85 (Grace and Imberger 2006), U0.2 and D3.0 on average released 8.228 g/m$^3$ and 13.948 g/m$^3$
of CO₂, respectively, 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).

4.4 Factors Driving Reaeration

Significantly increased night-time 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 night-time reaeration rates and ER ($r^2=0.013$), indicating that the night-time 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. 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. 2019). 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.

5 Conclusions

Our results showed that significant increased ecosystem respiration (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 gross primary production (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 extend 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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Author 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 in editing and completion of the final draft.

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Data Availability All data are provided within the paper and Supplementary Material.

Declarations

Conflicts of interest/Competing interests N/A.

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