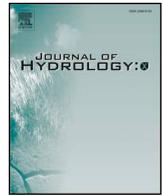




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# Intense summer floods may induce prolonged increases in benthic respiration rates of more than one year leading to low river dissolved oxygen



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## ABSTRACT

The supply of readily-degradable organic matter to river systems can cause stress to dissolved oxygen (DO) in slow-flowing waterbodies. To explore this threat, a multi-disciplinary study of the River Thames (UK) was undertaken over a six-year period (2009–14). Using a combination of observations at various time resolutions (monthly to hourly), physics-based river network water quality modelling (QUESTOR) and an analytical tool to estimate metabolic regime (Delta method), a decrease in 10th percentile DO concentration (10-DO, indicative of summer low levels) was identified during the study period. The assessment tools suggested this decrease in 10-DO was due to an increase in benthic heterotrophic respiration. Hydrological and dissolved organic carbon (DOC) data showed that the shift in 10-DO could be attributed to summer flooding in 2012 and consequent connection of pathways flushing degradable organic matter into the river. Comparing 2009–10 and 2013–14 periods, 10-DO decreased by 7.0% at the basin outlet (Windsor) whilst median DOC concentrations in a survey of upstream waterbodies increased by 5.5–48.1%. In this context, an anomalous opposing trend in 10-DO at one site on the river was also identified and discussed. Currently, a lack of process understanding of spatio-temporal variability in benthic respiration rates is hampering model predictions of river DO. The results presented here show how climatic-driven variation and urbanisation induce persistent medium-term changes in the vulnerability of water quality to multiple stressors across complex catchment systems.

## 1. Introduction

Dissolved oxygen (DO) is a fundamental indicator of river ecological health. Low DO concentrations can harm a wide range of species across various trophic levels: effects in fish and benthic macro-invertebrates are seen at 3–4 mg DO L<sup>-1</sup> (Garvey et al., 2007). Accordingly, maintaining DO levels is a primary concern of the Water Framework Directive (European Commission, 2000). Depletion of oxygen is the consequence of a number of widespread pressures, notably elevated loads of effluents and higher rates of eutrophication (Sánchez et al., 2007; Dodds and Smith, 2016), which lead to increased heterotrophic microbial breakdown of organic matter. Globally most freshwaters are thought to be net heterotrophic systems (Duarte and Prairie, 2005). Accelerated heterotrophic activity has the potential to reduce oxygen concentrations towards undesirable levels across a wide spectrum of rivers worldwide. Alongside the exacerbating effect of the warmer conditions expected to become more prevalent, a future lowering of the oxygen-holding capacity of freshwaters is likely.

Oxygen is depleted by microbial breakdown of organic matter in the water column, the potential for which is quantified by measurements of biochemical oxygen demand (BOD). Importantly, through benthic microbial respiration, the underlying bed sediments also consume oxygen. Benthic respiration is often the dominant component of total respiration in headwater streams (Vilmin et al., 2016). Aside from these processes, and especially during warm and slow flowing conditions in summer when physical and climatic requirements for phytoplankton growth are favourable, autotrophic respiration and photosynthesis are important components defining the metabolic regime of riverine ecosystems. From numerical methodologies, regimes can be established from continuous measurements (Chapra and Ditoro, 1991), although this requires estimation of reaeration flux which is notoriously challenging to calculate reliably (Aristegi et al., 2009; Hall and Ulseth, 2019). Quantifying ecosystem metabolism through high-resolution measurements is however increasingly achievable and is powerful in pinpointing potentially degraded freshwater environments where ecosystem respiration (ER) may substantially exceed gross primary productivity (GPP).

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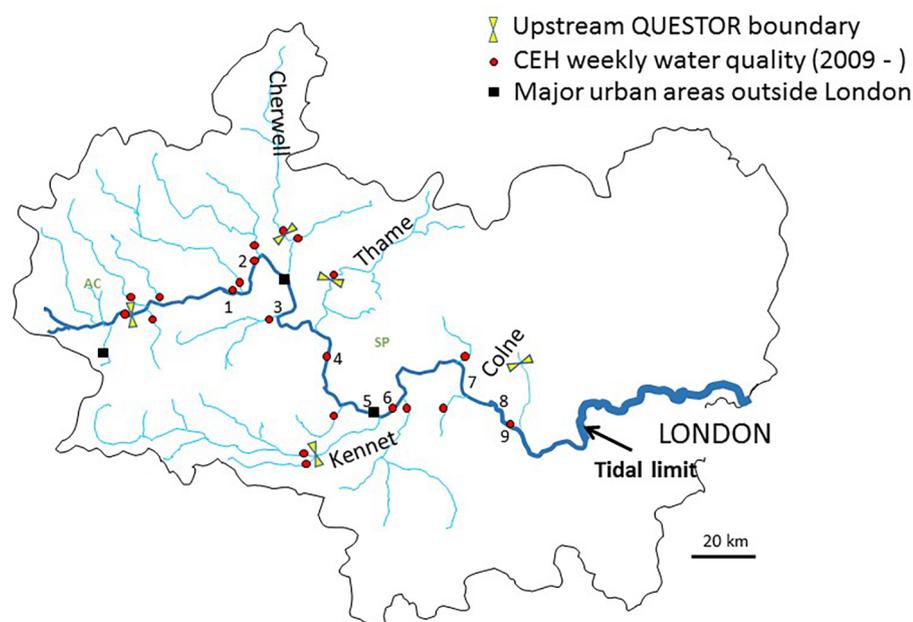
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**Fig. 1.** Map of River Thames indicating locations of monitoring sites. Figure adapted from Hutchins et al. (2016). Water quality observations are available each week (or more frequently) and used to test QUESTOR model at: Newbridge (1), Eynsham (2), Abingdon (3), Wallingford (4), Caversham (5), Sonning (6), Taplow (7), Windsor (8) and Runnymede (9). The QUESTOR upstream boundaries of the river network are on the main Thames (at Hannington), the Cherwell, Thames and Kennet. Continuous water quality monitoring data from EA were available from the Thames (at Hannington, and at Sites 3, 4, 5, 7 and 8) and the Kennet. Data from the weekly CEH Thames Initiative (Bowes et al., 2018) are represented with red dots. Daily River flows are available at Sites 2, 5 and 8 and at all tributary sites where weekly water quality are available. Groundwater levels are recorded at Stonor Park (SP) and Ampney Crucis (AC). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Consequently, river regimes displaying negative net ecosystem production have been identified (Hoellein et al., 2013; Bernhardt et al., 2018) and these may therefore deviate from the balance expected for most aquatic ecosystems, as conceptualised by Odum (1956). Studies have sought to identify drivers both proximal (river environment including typology) and distal (catchment characteristics including land use) that might be related to variation in net ecosystem production (Bernot et al., 2010). Whilst also quantifying components of metabolism, applications of process-based models (of which important examples are summarised by Cox (2003)) are particularly valuable when undertaken as part of a sensitivity analysis, highlighting attention on key variables controlling DO (Bailey and Ahmadi, 2014). By using model sensitivity analysis, Wang et al. (2018) identified the seasonally-important role of heterotrophic respiration in oxygen depletion. Such findings corroborate process-studies, for example, Vilmin et al. (2016) identified that benthic respiration accounted for 31% of the total respiration observed along a stretch of the Seine (France).

Direct measurements of benthic respiration flux are invaluable but suffer from the shortcoming of only providing point measurements of the riverbed where spatial variability is likely to be high. They are however routinely undertaken, employing a spectrum of established techniques to quantify oxygen removal such as in-situ chambers (Jahnke and Christiaansen, 1989; Jones et al., 1995) and aquatic eddy correlation (Berg et al., 2003; Rovelli et al., 2017). Alongside these, indirect estimates gained from metabolic data analysis and mathematical modelling of river channel environments (as described above) are commonplace given the increasing proliferation of river water quality data at basin-scale. Nevertheless, despite the usability of basin-scale data analysis and modelling techniques and the substantial wealth of assessment arising from their application (e.g. even at large national extent: Appling et al. (2018)), current understanding of the controls on benthic respiration rate is poor. A synthesis of our sparse knowledge is summarised below.

Benthic microbial respiration varies seasonally. Recent studies clearly reveal higher fluxes in warmer summer conditions (e.g. Lee et al., 2018; Akomeah and Lindenschmidt, 2017). Rates are controlled by supply of readily-degradable organic matter in the riverbed, yet much uncertainty surrounds what controls provision of this substrate and how it might vary spatially. Stretches of river impounded by weirs are likely to promote sedimentation which will increase the potential for riverbed oxygen removal (Lee et al., 2018). Downstream of large

urban effluent discharges, evidence suggests heterotrophic respiration rates are elevated and bed sediments are of higher organic matter content compared to upstream (Izagirre et al., 2008; Vilmin et al., 2016). Otherwise, evidence of relationships between benthic respiration and river morphological characteristics or catchment descriptors appears fragmentary. For example, in a local survey of headwaters, Collins et al. (2017) found the provenance of degradable organic matter to be primarily from decaying in-channel vegetation rather than wastes from agricultural sources. Further, geological origin may play an indirect role in determining the characteristics of bed sediment, the organic matter therein and its potential for fostering respiration (Comer-Warner et al., 2018). Any extension beyond site-specific conclusions such as these is limited to conjectural assertion.

Uncertainties in understanding the mechanistic controls on benthic respiration hamper predictions of future river DO response to climate and anthropogenic pressure. Little is known of the longer-term drivers of bed sediment DO sinks. In order both to contribute to this knowledge-base and to illustrate implications of this current shortcoming we undertook a study of the River Thames (UK) using deterministic water quality modelling techniques (Hutchins et al., 2016) coupled with data analytical methods (the Delta method: Chapra and Ditoro, 1991). The Thames basin is the subject of long-term monitoring (Bowes et al., 2018) making for a suitable case study especially given increasing population stress and intensification of land use which threatens water resources and quality (Hutchins et al., 2018). The objectives of the present study were to assess over a 6-year period (2009–14): (i) evidence for spatial and temporal change in the rates of benthic respiration in river reaches along the Thames, (ii) the effect of changes in benthic respiration rates on river DO concentrations, (iii) the causes of changes in benthic respiration.

## 2. Methodology

### 2.1. Study area and data sources

The River Thames (Fig. 1) has a catchment area of 7046 km<sup>2</sup> at Windsor (Site 8; NGR SU980772). Land use is predominantly agricultural (arable and grassland accounting for 40.4% and 34.0% of the land area respectively) with 10.5% urbanised. Despite the relatively low urban extent upstream of Windsor, the river and its tributaries supply most of the water supply to the ca. 13 million inhabitants in the

increasingly urbanised basin district which includes London. A considerable proportion of the catchment is underlain by chalk and oolitic limestone aquifers and the river has a baseflow index of 0.72. Mean annual rainfall is 696 mm and mean river flow  $59.2 \text{ m}^3\text{s}^{-1}$  (NRFA, 2019). Nutrients are in excess throughout the Thames and its main tributaries (Thame, Cherwell and Kennet), the lowest mean concentrations of TP and TDN being  $0.171 \text{ mg P L}^{-1}$  at Newbridge (Site 1: Fig. 1; NGR: SP403013) and  $4.2 \text{ mg N L}^{-1}$  at Woolhampton on the Kennet (NGR: SU572667) respectively (Bowes et al., 2018).

A six-year period of record (2009–14) was used in the study, a period of highly volatile rainfall and runoff patterns (NRFA, 2019). Weekly nitrogen, phosphorus, dissolved organic carbon, chlorophyll-a and water temperature data for 6 sites along the River Thames and 15 sites on its major tributaries were provided by the CEH Thames Initiative (TI) research platform (Bowes et al., 2018), available from the CEH Environmental Information Data Centre. Chlorophyll-a and DO concentration and water temperature data were supplied at hourly resolution by the Environment Agency (EA) sensor network (Wade et al., 2012). Additional data to define tributary inputs and to calibrate and test models along the main Thames are available from periodic monitoring programmes undertaken by the EA. These are accessible from a data portal: <http://environment.data.gov.uk/water-quality/view/landing>. Daily river flow data were accessed via NRFA: <http://nrfa.ceh.ac.uk/data/search>. Solar radiation observations were accessed at the British Atmospheric Data Centre (<http://archive.ceda.ac.uk/>). For the period 2009–12 radiation inputs from the Little Rissington station were modified to account for the effects of riparian tree shading as described by Waylett et al. (2013). Gridded hourly shade maps of the river channel at 1 m resolution (Bachiller-Jareno et al., 2019) were available for part of the period of interest (2013–14) and these were also used in conjunction with data from Little Rissington.

## 2.2. Assessment tools

### 2.2.1. QUESTOR: River network water quality model

The QUESTOR model (Hutchins et al., 2016) was applied at daily resolution using a biological model based on a mixed population of phytoplankton. A description of model determinands, processes and equations is provided in Appendix A. A mixed population (Eq. A1) was chosen as it had given better DO performance in the Thames between 2009 and 2011 than other more-specific formulations based on diatoms or green algae (Waylett et al., 2013).

Full details of reaches and their influences are provided (Appendix B). In summary, above the downstream limit (Site 9 on Fig. 1) the model represents 229.4 km of river network (comprising the Cherwell, Thame and Kennet tributaries and the main Thames; of lengths 14.9, 19.6, 13.8 and 181.1 km respectively) split into 74 reaches. The model accounts for 6 abstractions and 40 weirs and is fed by 35 tributaries and 15 major sewage treatment works (STWs). Other STWs (e.g. from the large town of Swindon) are represented indirectly by data from the tributaries into which their effluents flow. The model was tested using monitoring data from 21 sites of which 9 have water quality data at a resolution of weekly or finer (numbered 1–9 on Fig. 1). Of these, hourly EA continuous monitoring data were available at Sites 5, 7 and 8.

The six-year record was split into three periods of two years each. As described by Hutchins et al. (2016) calibration of the model was undertaken at successive sites downstream along the network for two of the periods (Model A: 2009–10 and Model B: 2013–14). Model goodness of fit statistics for all main determinands are shown (Appendix C).

### 2.2.2. Delta model: Analysis of diurnal dissolved oxygen curves to calculate primary production and respiration

Time-series of hourly diurnal DO curves from the EA continuous water-quality sondes at Sites 5, 7 and 8 were used to evaluate stream metabolism (Jarvie et al., 2003, Palmer-Felgate et al., 2009). The Delta method (Chapra and DiToro, 1991; Williams et al., 2000) was used to

calculate daily average gross primary production, daily average ecosystem respiration and the reaeration coefficient, using a piecewise solution of the mass balance DO model (O'Connor and DiToro, 1970) simplified for the situation where the deficit does not vary spatially (Eq. (1)).

$$dD/dt + k_a D = ER_{av} - GPP_{av}(t) \quad (1)$$

where  $D$  is the DO deficit ( $\text{mg O}_2 \text{ L}^{-1}$ ),  $t$  is the time (days),  $k_a$  is the reaeration coefficient,  $ER_{av}$  is the ecosystem respiration ( $\text{mg O}_2 \text{ L}^{-1} \text{ d}^{-1}$ ), and  $GPP_{av}$  is the gross primary production ( $\text{mg O}_2 \text{ L}^{-1} \text{ d}^{-1}$ ); these are standard measures of ecosystem respiration and gross primary production in river systems (Bernhardt et al., 2018). Further details of the Delta model can be found in Williams et al. (2000).

From these calculations further derivations were made. The carbon fixed in primary production was defined stoichiometrically as a fraction (12/32) of the oxygen produced ( $GPP_{av}$ ). Ecosystem respiration comprises autotrophic and heterotrophic components. Autotrophic respiration has been estimated to be 50% of  $GPP_{av}$  (Hall and Beaulieu, 2013; Jarvie et al., 2018). Therefore total heterotrophic respiration  $HR_{av}$ , which represents the sum of heterotrophic respiration in the river bed (benthic respiration) and in the water column, was estimated (Eq. (2)).

$$HR_{av}(t) = ER_{av}(t) - 0.5 * GPP_{av}(t) \quad (2)$$

Moreover, the analysis focused specifically on the  $ER_{av}$  values calculated in the late summer period (July to October), which is after chlorophyll concentrations and  $GPP_{av}$  become low in the Thames and when respiration therefore likely becomes dominated by heterotrophs. The mean daily rate of carbon fixation under primary production ( $GPP_{av}$ ) in the January to October period of each year was also calculated.

## 3. Results

The section is sub-divided as follows:

- Observations of DO concentrations are presented showing their variation along the River Thames and across the 6 years studied.
- Results from the QUESTOR application are presented to illustrate differences in performance of the model in time and space when calibrated for the two different periods. The results are compared to observations and we attribute possible change in the light of differences in parameterisation arising from the two calibrations.
- Results from the Delta method are compared with the observations and QUESTOR modelling to identify additional corroborative evidence for change.
- Presentation of data on river flow and dissolved organic carbon.

### 3.1. Dissolved oxygen observations

The 10th percentile DO concentrations (10-DO) are indicative of midsummer conditions when levels are at their lowest. Values for the period 2009–14 are displayed (Table 1) for locations with hourly continuous monitoring (Sites 5, 7 and 8). Data pooled together for eight additional are also summarised to illustrate evidence of change across the six years. Highest levels of 10-DO were observed in 2011–12. Lowest levels were seen in 2013–14 at Sites 7 and 8, but in 2009–10 at Site 5.

### 3.2. QUESTOR applications

Goodness-of-fit statistics (NSE and PBIAS) are presented for DO at sites along the network together with optimised values for the model parameters (Table 2). For the phytoplankton sub-model, values optimised by Waylett et al. (2013) of 1.35, 0.23 and 0.23 were used in Model A for photosynthesis ( $^1k_0$ ) respiration ( $^2k_0$ ) and death ( $^3k_0$ )

**Table 1**  
10th percentile DO ( $\text{mg L}^{-1}$ ) (with ranges given in brackets to indicate the 95% confidence intervals). At 90th percentile temperature ( $19.5^\circ\text{C}$ ) DO % saturation is approximately 66%, 77%, 88%, 99% and 110% at 6, 7, 8, 9 and 10 mg DO  $\text{L}^{-1}$  respectively.

Reach	2009–10		2011–12		2013–14		Model B	Model A	
	Observed	Model A	Model B	Observed	Model A	Model B			Observed
T 40 (site 5)	8.09 (8.04 – 8.14)	6.96 (5.23 – 8.21)	8.64 (7.19 – 8.94)	9.01	8.87	8.87	8.80 (8.76 – 8.82)	9.66 (9.52 – 9.90)	9.48 (9.23 – 9.64)
T 55 (Site 7)	9.07 (8.98 – 9.16)	9.58 (9.50 – 9.62)	9.19 (9.13 – 9.24)	9.16	9.60	9.29	8.93 (8.90 – 8.97)	9.57 (9.53–9.62)	9.43 (9.38 – 9.46)
T 60 (Site 8)	9.12 (9.08 – 9.15)	9.05 (9.01 – 9.10)	8.38 (8.32 – 8.43)	9.16	9.22	8.44	8.51 (8.49 – 8.53)	9.14 (9.07 – 9.20)	8.53 (8.50 – 8.67)
Pooled data from 8 other Thames sites	8.47 (8.27 – 8.66)						7.06 (6.81 – 7.74)		

respectively. In Model B values of 1.35 for  $^1k_0$ , 0.28 for  $^2k_0$  and 0.28 for  $^3k_0$  were used. The models perform better during their respective periods of calibration: 2009–10 for Model A and 2013–14 for Model B. In both cases corroborative testing was also carried out for each of the other two periods not used for calibration. Results are not shown for the middle period (2011–12), during which robust performance for the full range of output variables had been demonstrated using Model A (Hutchins et al., 2016).

The variation in 10-DO apparent from continuous monitoring data at Sites 5, 7 and 8 during the period 2009–14, described in Section 3.1, was simulated by the two models (Table 1). For the majority of site/time-period combinations, 10-DO concentrations simulated by Model B are lower than Model A. As to be expected, in terms of NSE and PBIAS (Table 2) and simulation of 10-DO levels, with a few exceptions Model A clearly better simulates the early period (2009–10) whereas Model B performs better in 2013–14. Model A overestimates DO in 2013–14 (Table 2: PBIAS > 0) whilst Model B underestimates DO in 2009–10 (Table 2: PBIAS < 0). Results indicate that conditions in 2009–10 are best represented by Model A and those in 2013–14 are best represented by Model B.

Time-series plots of simulated and observed DO from Site 4 illustrate an apparent reduction in concentrations in the latter part of the study period (Fig. 2). Comparison of 10-DO values calculated for 2009–10 with those calculated for 2013–14 (Fig. 3) summarises this change. Simulated data are displayed for seven locations. Sufficient observed data were available at Sites 5, 7 and 8, and these too are plotted. At these three sites the directions of change in 10-DO simulated by the model are in agreement with observations, and in all cases are significant at the 95% level (Table 1). Of the seven sites in total, six show a downward shift, and upstream (at Sites 2 and 4) these exceed 20%. In contrast, Site 5 shows an upward shift. Lastly, data from eight additional sites along the main stem of the Thames which had been sampled at approximately monthly resolution were pooled together. In aggregate these indicated a decrease in 10-DO of  $1.41 \text{ mg L}^{-1}$  (approximately 17%) which is significant at the 95% level (Table 1). Each individual site showed decreases. To summarise Fig. 3, both modelling and observations suggest an increase in 10-DO at Site 5 whereas at all other sites a decrease is indicated consistently. Possible explanation for this localised anomaly is covered in Section 4.2.

In terms of contributory processes, the differences in DO concentration between Models A and B cannot be explained by changes in physical factors controlling reaeration. For example, mean values (and standard deviation) of  $k_{\text{rea}}$  (Appendix A: Eq. A.7) as calculated at Site 8 were  $1.11 \text{ d}^{-1}$  (+/- 0.43) and  $1.34 \text{ d}^{-1}$  (+/- 0.60) for Models A and B respectively. Instead, differences largely lie in terms of heterotrophic respiration which comprises two constituents: benthic (bed sediment) oxygen demand ( $^4k$ ) and BOD decay in the water column ( $^5k$ ). On a stretch-by-stretch basis, calibrated rates of sediment oxygen demand are much higher in Model B than in Model A (Table 2). Representative rates of the two components of heterotrophic respiration across the whole river network can be estimated by weighting the geographic-specific rates in Table 2 by the length of the stretches to which they are applied (Table A1), and then calculating mean values. For Model A the mean network-wide rates of  $^4k$  and  $^5k$  were  $0.02 \text{ d}^{-1}$  and  $0.30 \text{ d}^{-1}$  respectively. In contrast for Model B,  $^4k$  was much higher ( $0.83 \text{ d}^{-1}$ ) whereas  $^5k$  was very slightly lower ( $0.26 \text{ d}^{-1}$ ). To conclude, QUESTOR model applications suggest benthic respiration rates ( $^4k$ ) were much higher in 2013–14 than in 2009–10.

### 3.3. Independent corroborative insights from continuous monitoring data and stream metabolism calculations

Daily average gross primary productivity and ecosystem respiration are plotted for Site 8 (Fig. 4). Median, upper quartile and 90th percentile concentrations are presented for  $ER_{\text{av}}$  and the derived values of  $HR_{\text{av}}$  (Table 3). When comparing the early years (2009–10) with the later years (2013–14) there is strong evidence that respiration was higher in the latter

**Table 2**  
 Goodness of fit statistics for Dissolved Oxygen and model parameters. Paired values, separated by a comma, represent the Nash-Sutcliffe efficiency (NSE) (Nash and Sutcliffe (1970)) and the percentage error in mean (PBIAS). Numbers in brackets next to the names in the “monitoring site” column refer to locations on Fig. 1.

Reach	Monitoring Site	Model A (2009–10 calib)										Model B (2013–14 calib)									
		2009–10	2013–14	5 <sup>k</sup>	4 <sup>k</sup>	10 <sup>k</sup>	6 <sup>k</sup>	8 <sup>k</sup>	9 <sup>k</sup>	2009–10	2013–14	5 <sup>k</sup>	4 <sup>k</sup>	10 <sup>k</sup>	6 <sup>k</sup>	8 <sup>k</sup>	9 <sup>k</sup>				
C 3	North Oxford	0.30, -2.1	0.00, 9.8	0.05	0.2	0.25	4	0.005	0.1	-0.38, -14.3	0.74, -0.6	0.14	0.55	0	1.2	0.02	0				
T 3	Dorchester	0.12		1.4	0.3	0.25	4	0.005	0.1	-0.33, -11.6	0.10, 0.2	0.97	0.49	0	4	0.015	0				
K 3	East Reading	0.72	0.47,	0.7	0	0.2	4	0	0	0.22, -9.4	0.68, -1.0	0.65	0	0	80	0.35	0				
T 10	Newbridge (1)	0.38, 3.6	-0.16, 14.6	0	0	0	0	0.035	0.25	0.09, -8.3	0.55, 1.7	0.19	1	0	1.4	0.035	1				
T 11	Farmoor	0.52, 6.2	-0.40, 14.6	1.5	0	0	0	0.025	0.1	-0.14, -7.8	0.32, 2.3	0	1.1	0	1.5	0.03	1				
T 12	Eynsham (2)			0	0	0	0	0.025	0.1			0.6	0.7	0.2	1.6	0.015	1				
T 15	Godstow	0.04		0	0	0.25	4	0.005	0.1	-1.25, -9.1											
T 17	Central Oxford	0.04		0	0	0.25	4	0.005	0.1	-0.64, -8.0		0.06	0.7	0	1.6	0.08	1				
T 19	South Oxford	0.11, 2.1	0.13, 9.8	0.1	0	0.25	4	0.005	0.1	-0.43, -8.7	0.73, -1.7	0.06	1.1	0.2	0.5	0.08	0				
T 22	Radley College	0.21, -0.4	0.35, 9.4	0.05	0	0.25	4	0.005	0.1	-0.80, -9.5	0.69, -0.6	0.1	1.1	0.2	0.5	0	0				
T 23	Abingdon (3)	0.36		0.15	0	0.25	4	0.005	0.1	-1.63, -26.4											
T 27	Sutton Courtenay			0.4	0	0.25	4	0.005	0.1												
T 30	Days Lock	0.75, -3.3	0.33, 11.7	0.4	0	0.25	4	0.005	0.1	-0.18, -15.0	0.58, 0.7	0.09	1.5	0	2.1	0	0				
T 33	Wallingford (4)	0.72, -1.4	-0.10, 12.6	0.9	0	0.25	4	0.005	0.1	-0.32, -14.3	0.31, 1.0	0.4	1.1	0.15	2	0	0				
T 37	Goring	0.40	-0.40	0.5	0	0.2	4	0	0	-1.4, -24.0	0.77, 0.7	0	1.6	0	0.25	0	0				
T 40	Caversham (5)	0.16, -5.8	0.16, -5.6	0.2	0	0.2	4	0	0	0.30, -7.7	0.23, -6.7	0.47	0	0	0.6	0	0				
T 42	Sonning (6)	0.66, -2.3	0.69, 6.6	0.4	0	0.2	4	0	0	0.07, -10.3	0.85, 0.1	0.65	0.5	0.16	4.6	0	0				
T 53	Cookham	0.22, -2.1	0.48, 5.5	0.3	0	0.3	4	0.012	0.1	-0.04, -12.0	0.64, -0.1	0.46	0.45	0	1.2	0	0.05				
T 55	Taplow (7)	0.57, -4.8	0.52, -4.1	0	0	0.3	4	0.012	0.1	0.54, -6.5	0.56, -4.8	0	0	0	4.5	0	0				
T 59	Windsor Leisure										-0.19, 1.4	0	1.5	0	4.5	0	0				
T 60	Windsor (8)	0.37, -8.3	0.57, -3.3	0	0	0.3	4	0.012	0.1	0.16, -11.7	0.48, -5.9	0	0	0	4.5	0	0				
T 63	Runnymede (9)			0.2	0	0.3	4	0.012	0.1			0	0	0.54	4.5	0	0				

BOD decay = <sup>5</sup>k.  
 Benthic oxygen demand = <sup>4</sup>k.  
 Deamination = <sup>10</sup>k.  
 Nitrification = <sup>6</sup>k.  
 Denitrification = <sup>8</sup>k.  
 P mineralisation = <sup>9</sup>k.

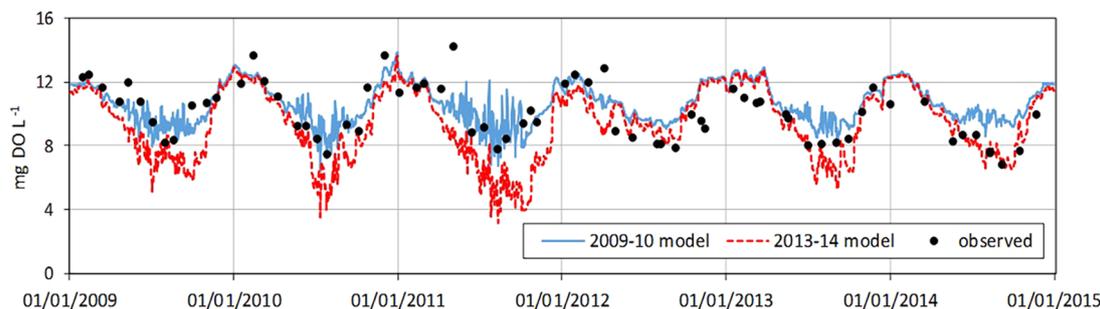


Fig. 2. Dissolved Oxygen concentration ( $\text{mg DO L}^{-1}$ ) as observed at Wallingford (Site 4) and simulated by Models A (calibrated in 2009–10) and B (calibrated in 2013–14).

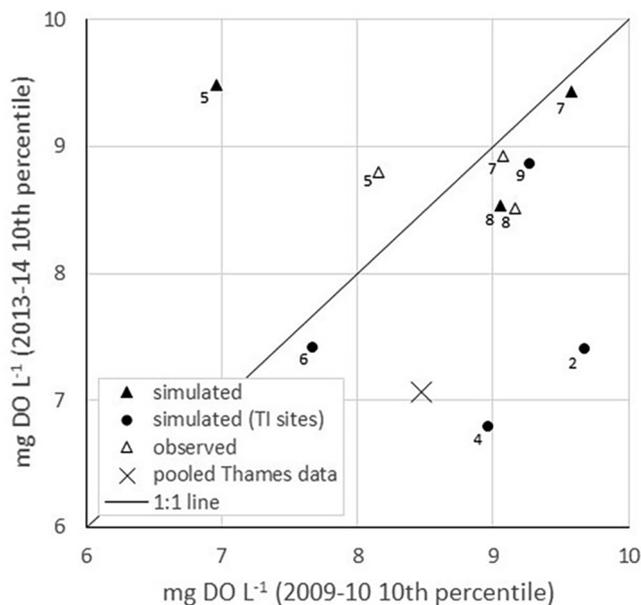


Fig. 3. Scatter plot of 10th percentile DO (10-DO:  $\text{mg L}^{-1}$ ) values comparing 2009–10 with 2013–14. Where symbols are numbered these represent sites shown in Fig. 1. For simulations, in 2009–10 results from Model A were used, whereas for 2013–14 Model B was applied. The pooled Thames data represent aggregation of observations at eight sites along the River Thames.

period. Between the two periods upper quartile values for annual  $HR_{av}$  and July to October  $ER_{av}$  increased from 3.2 to 5.5  $\text{mg O}_2 \text{ L}^{-1} \text{ d}^{-1}$  and from 5.8 to 9.8  $\text{mg O}_2 \text{ L}^{-1} \text{ d}^{-1}$  respectively. In contrast there was little apparent change between 2009–10 and 2013–14 in  $GPP_{av}$  (Table 3). Elsewhere, similar process rates are observed in US rivers (Hoellein et al., 2013) with mean values reported across 215 sites of  $GPP_{av}$  and  $ER_{av}$  of 2.4 and 6.7  $\text{mg O}_2 \text{ L}^{-1} \text{ d}^{-1}$  respectively. Mejia et al. (2019) note that the seasonal response of GPP and ER is dynamic and diverse across a catchment and appears strongly controlled by climatic drivers.

In terms of reaeration, the Thames data suggest little difference between 2009–10 and 2013–14. Of relevance to this, neither were any differences apparent between the water temperatures or river flows typically seen in the summers of those years, as represented by the 90th percentile water temperature and Q95 flow respectively. Physical factors (river water velocity, depth and temperature) are important in controlling the reaeration flux. The Delta method indicated a small increase in reaeration between the two periods. Hall and Ulseth (2019) exercise caution in the interpretation of reaeration rates inferred from approaches employing mass balance estimates in conjunction with diurnal oxygen measurements (such as Delta), recommending recourse to predictive equations of the type used in QUESTOR. The dynamics of the flux, as quantified from observations using the equation included in QUESTOR, is displayed for both periods (Appendix D). Whilst it is

apparent in both cases there is some relationship with river flow it is not strong, and water temperature and DO concentration are also important determinants. There is no evidence of lower reaeration fluxes at elevated flows (above  $59.2 \text{ m}^3 \text{ s}^{-1}$  the long-term mean flow at Site 8) in 2013–14 compared to the earlier period. Mejia et al. (2019) also observe weak relationships between flow and reaeration.

#### 3.4. Observations of flow and dissolved organic carbon

For the Wallingford site (4), time series of observed dissolved organic carbon (DOC) and simulated river flow are presented (Fig. 5). Temporal variability in river flow at Site 4 is broadly typical and representative of all reaches in the Thames. Data for DOC are available at all CEH TI sites, which are further summarised graphically (Fig. 6). Through the six-year study period the annual variation in mean DOC, mean flow and Q95 (low flow) are tabulated (Appendix E). Insufficient data were available to calculate mean annual DOC for 2010 and 2011. These tabulated values summarise (i) the low flow levels prevalent in 2011 and the substantially wetter conditions in succeeding years, (ii) the increase in DOC in 2012 which persisted into following years.

## 4. Discussion

Interpretation of the results is discussed in two sections:

- Analysis of hydrological variation through the study period is undertaken. The potential persistent significance of summer storm events is considered. Additional evidence for the consequences of these events in controlling DO is assessed using DOC data. A mechanism for driving change in benthic respiration is postulated.
- In terms of controls on DO and the influence of benthic respiration dynamics, explanation for localised anomalous behaviour along the River Thames is offered.

#### 4.1. Explanations for a possible step change in dissolved oxygen

Whilst there appears little evidence for differences between 2009–10 and 2013–14 in terms of  $GPP_{av}$ , summer water temperature and summer river flows, the exceptional seasonal variability in river flow exhibited within this timespan provides possible insights. Flows at Site 8 approached the lowest on record during the summer and autumn of 2011. Subsequently, the May–October runoff in 2012 exceeded previous maxima and notably high flows were maintained through most of the following two winters (NRFA, 2019). As illustrated by time series data (Fig. 2) it is apparent that during summer 2012 the 2009–10 model (Model A) no longer provided the better DO simulation, which was now more realistically represented by a 2013–14 calibration (Model B).

Foul sewer systems and urban runoff are the predominant sources of oxygen-consuming river BOD loads, together with livestock waste (Williams et al., 2012; Vigiak et al., 2019). In wastewater treatment these loads are reduced, as are the loads of bioavailable total organic

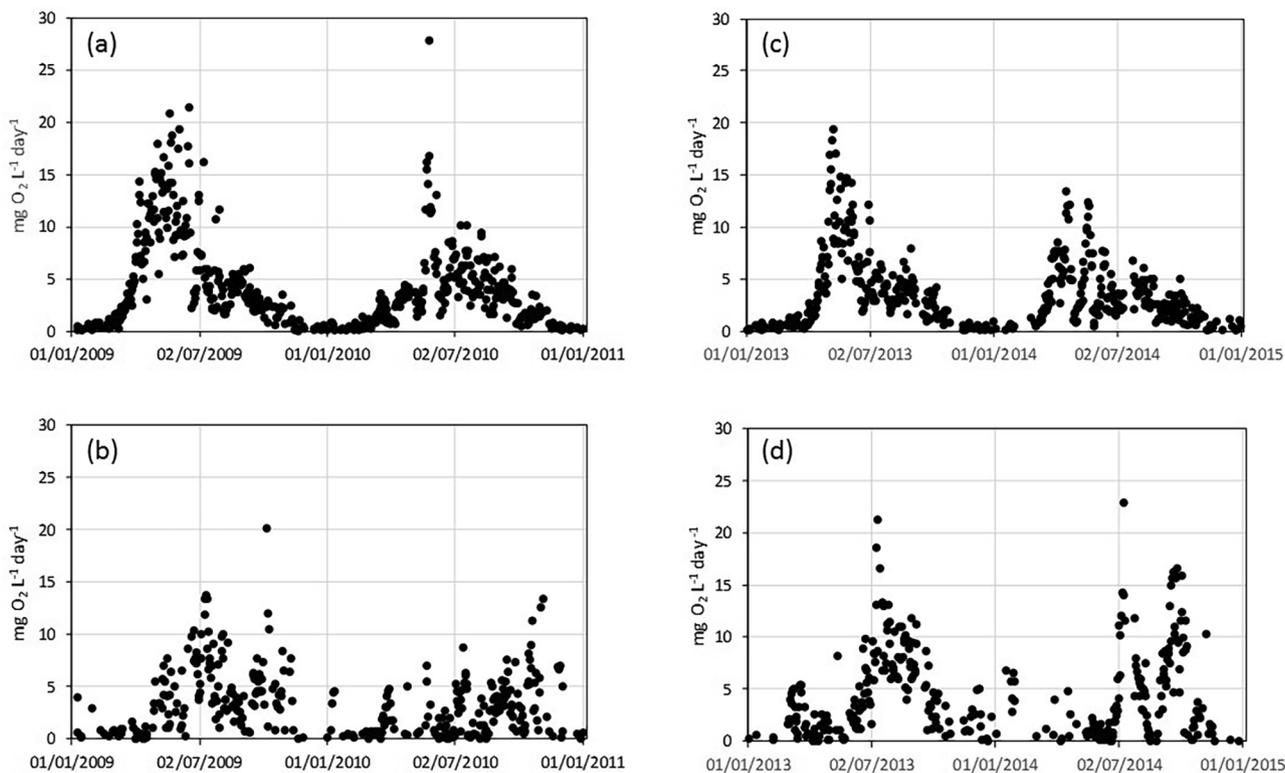


Fig. 4. Delta model time series plots for Windsor (Site 8). For 2009–10: (a) photosynthesis ( $GPP_{av}$ ) and (b) ecosystem respiration ( $ER_{av}$ ). For 2013–14: (c) photosynthesis ( $GPP_{av}$ ) and (d) ecosystem respiration ( $ER_{av}$ ).

Table 3

Summary statistics for Site 8. Respiration is calculated in units of  $mg\ O_2\ L^{-1}\ d^{-1}$ . Reaeration is presented as a rate ( $d^{-1}$ ). Primary productivity, respiration and reaeration statistics are calculated using the delta method. Temperature and river flow statistics are taken from continuous monitoring.

	2009	2010	2013	2014
Upper quartile $HR_{av}$	4.3	2.5	5.3	7.8
90th percentile $HR_{av}$	6.7	4.6	6.3	10.0
Median $ER_{av}$ (July to October)	4.6	3.2	7.4	6.3
Upper quartile $ER_{av}$ (July to October)	7.3	5.1	9.6	10.1
Mean $ER_{av}$ (July to October)	5.7	3.8	6.9	6.8
Median reaeration (July to October)	7.1	7.4	7.4	7.5
Upper quartile reaeration (July to October)	7.7	11.2	7.7	11.5
Mean reaeration (July to October)	7.0	7.6	7.3	8.1
Mean $GPP_{av}$ (January to October) ( $mg\ C\ L^{-1}\ d^{-1}$ )	2.2	1.4	1.7	1.4
90th percentile water temperature ( $^{\circ}C$ )	19.2	19.7	19.6	19.4
Q95 (low flow) $m^3\ s^{-1}$	15.2	16.8	16.7	20.0

carbon; and these parameters are significantly correlated (Servais et al., 1999). However, to help understand the spatio-temporal variation of fluxes of potentially degradable organic matter across the Thames, DOC

data (Bowes et al., 2018) provide more comprehensive coverage. Measurements of DOC represent a wide variety of organic carbon moieties, often containing a substantial refractory portion. Moreover, as sources of DOC in an urbanised basin such as the Thames are multiple and diverse, building a conceptual model of supply, transport and fate is not straightforward and beyond the scope of the present study. General and valuable insights can nevertheless be gained.

Although the unseasonably high flows of 2012 did not persist beyond the summer, from Fig. 5 it can be seen that DOC concentrations, which had been low beforehand ( $< 10\ mg\ L^{-1}$ ) increased considerably and appear to have remained high for the rest of the study period which also encompassed a period of severe winter flooding (Schaller et al., 2016). Exceptional and sustained high flows characterised January and February 2014, when the average flows in the Thames were the highest seen for those months in a record beginning in 1883. In comparing a pair of 2-year periods (2009–10 and 2013–14), an increase in median DOC is apparent at all CEH TI sites (Fig. 6).

The strong evidence arising from QUESTOR and Delta model applications for an increase in heterotrophic and in particular benthic respiration has been outlined in Sections 3.2 and 3.3 above. Based on

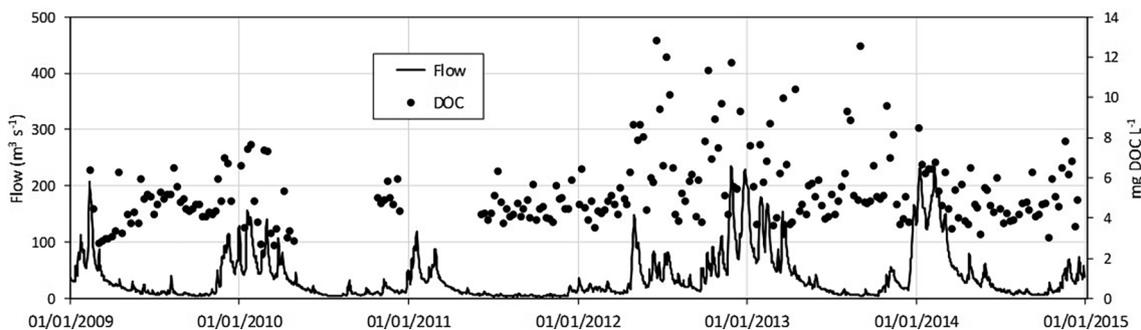
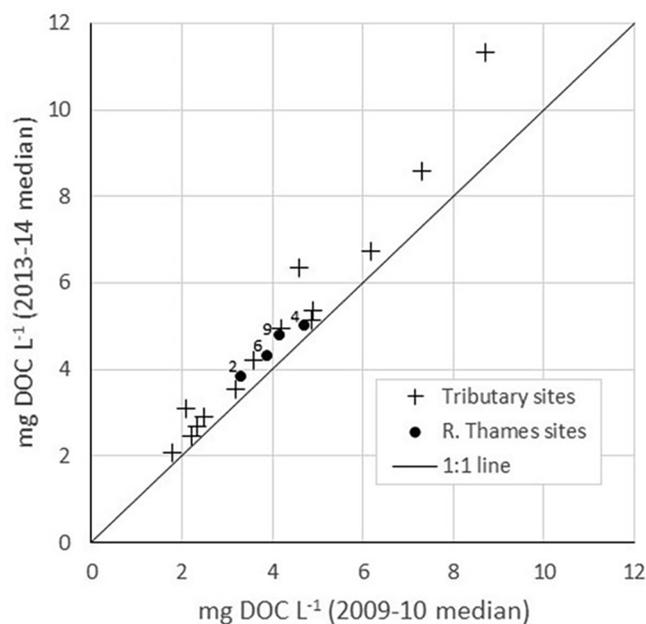


Fig. 5. River flow ( $m^3\ s^{-1}$ ) and DOC ( $mg\ L^{-1}$ ) at Wallingford (Site 4).



**Fig. 6.** Scatter plot of observed median Dissolved Organic Carbon concentration ( $\text{mg C L}^{-1}$ ) comparing 2009–10 with 2013–14. Data are from the weekly CEH Thames Initiative (Bowes et al., 2018). Where symbols are numbered these represent sites on the main Thames shown in Fig. 1.

flow and DOC observations, we contend that this was driven by influx of readily-degradable organic sedimentary matter flushed into the system at some time between 2010 and 2013. In 2012, summer flooding likely washed in organic matter from sewer overflows and organic-rich material from the valley floodplain, connectivity being established between floodplain and channel through overbank flooding. Impacts of storm events on DO and organic matter dynamics in urbanised systems have been identified elsewhere. For example, (i) net ecosystem production suffered short/medium-term declines after flooding in urban streams in USA (Qasem et al., 2019); (ii) influence of sewer overflows on river bed sediments has been identified in Germany (David et al., 2013). Enhanced connection of urban infrastructure with the river channel following the 2012 floods seems plausible. A gradual microbial breakdown of the organic matter in the months following the flooding, as indicated by elevated heterotrophic respiration and accompanied by elevated DOC, offers likely mechanistic explanation. The TI sites showing the largest increase in median DOC concentration (Fig. 6) are those in tributaries draining the most urbanised catchments: by 2.74 and 1.74  $\text{mg L}^{-1}$  in the Cut and Loddon respectively. Considering DOC in the River Thames, Noacco et al. (2019) attribute long term increase to land use change and urban growth; and, in accordance with the present study, explain short-term variability in terms of climate conditions.

Low DO conditions in the Thames were also observed following summer flooding in 2007. Borehole records (BGS, 2019) suggest antecedent groundwater levels in the chalk (e.g. SU78/45A Stonor Park in lower Thames basin) were lower in 2007 compared to 2012 and were conversely slightly higher in the oolitic limestone (e.g. SP00/62 Ampney Crucis in upper Thames basin) (Appendix F). As 2007 preceded the start of the TI programme, data and modelling are insufficient for rigorous comparative analysis of the two storms. Nevertheless corroborative hydrological records such as these potentially provide helpful localised indication of where connectivity with floodplains and urban point sources is most likely to be made following storms, and consequently where river DO conditions may become vulnerable. For example, differences between 2007 and 2012 are apparent in this respect. At Site 4 which drains the upper Thames basin, 5.26  $\text{mg DO L}^{-1}$  was observed on 26th July 2007, much lower than values seen further

downstream at Site 6 (minimum of 8.07  $\text{mg L}^{-1}$ ). In contrast, low values in summer 2012 followed a more even spatial distribution in the middle reaches (between Sites 2 and 7) with values only dropping below 7  $\text{mg DO L}^{-1}$  downstream at Site 8. Detailed water quality data from 2007 are available online (<http://environment.data.gov.uk/water-quality/view/landing>).

#### 4.2. Variations along the river system

In 2009–10 lower 10-DO were observed at Site 5 than elsewhere. At 11 other sites both upstream and downstream along the network 10-DO concentrations ranged between 8.40 and 9.16  $\text{mg L}^{-1}$  in 2009–10, whereas at Site 5 10-DO was 8.16  $\text{mg L}^{-1}$ . In 2013–14, 10-DO values below 8  $\text{mg L}^{-1}$  were generally only observed upstream of Site 5 which itself had 10-DO of 8.80  $\text{mg L}^{-1}$ .

Simulations using Model A for 2009–10 reaffirmed this stretch to be of low 10-DO in concert with high peak BOD levels. Furthermore, output from the Delta model at Site 5 also suggests the stretch was subject to high rates of DO removal through respiration in 2009–10. Upper quartile values for annual  $HR_{av}$  and July to October  $ER_{av}$  were 7.9 and 11.3  $\text{mg-O}_2 \text{ L}^{-1} \text{ d}^{-1}$  respectively. These values are much higher than in 2013–14, a time when they were also lower than further downstream at Site 8. A tendency for development of low DO in future in these middle reaches has also been predicted by Cox and Whitehead (2009). The stretch is long, with a low flow residence time of about 5 days, and has an absence of any significant nutrient inputs until wastewater effluent from Reading joins via the Kennet between Sites 5 and 6. Upstream of Site 5, if phytoplankton growth is at elevated levels it can temporarily use up available soluble phosphorus, which may curtail further algal growth. Observations of Soluble Reactive Phosphorus (SRP) at Site 4 by Bowes et al. (2012) suggest that partial P limitation probably happened in 2009, and this was consistent with simulations. Exhaustion of SRP was not observed or modelled elsewhere in the mid-summer of 2009.

This spatial anomaly near Site 5 was less apparent in Model A simulation for later periods. Likewise, for all sub-periods Model B suggests considerable variation in 10-DO along the whole length of river, driven primarily by variation in benthic respiration rate (Table 2). Alongside high levels (above 8.5  $\text{mg L}^{-1}$ ) at sites further downstream the highest 10-DO under Model B is simulated at Site 5 (9.48  $\text{mg L}^{-1}$ ). These spatial patterns are in broad accordance with observations. In Model B, phytoplankton blooms become relatively less well-developed than in Model A, and thereby less susceptible to ecologically-damaging crashes. This is attributable to differing calibrations, which for the 2013–14 period (Model B calibration) suggested higher respiration rates than earlier. Consequently there are relative levels of 10-DO between Model A and Model B at Site 5 in 2009–10 which are at odds with the relative 10-DO levels between these two models at all other sites and time periods (Table 1). In all these other cases Model B 10-DO concentrations are consistently lower than Model A.

The stretch between Pangbourne and Caversham (Site 5) appears especially vulnerable to low DO arising from phytoplankton crashes and the decay of water column BOD arising from dead and decomposing algal cells. Despite the diluting influence of the River Kennet, the consequences are apparent downstream until the Loddon joins near Site 6. At other times and elsewhere, simulation of low DO appears to primarily be a consequence of elevated benthic respiration and lower oxygen holding capacity in warm summer waters.

#### 5. Conclusions

A study of dissolved oxygen dynamics in the River Thames was undertaken using a combination of modelling approaches alongside direct interpretation of observations. Throughout the network, a change in oxygen conditions over the six-year period of study is apparent from various independent lines of evidence. At numerous sites an apparent

change in 10-DO is apparent from QUESTOR modelling which corroborates observations (Fig. 3). The detail underpinning this evidence is summarised for Site 8 where between 2009–10 and 2013–14:

- (i) 10-DO, indicative of the summer low values, decreased from 9.12 to 8.51 mg L<sup>-1</sup>
- (ii) QUESTOR modelling similarly represented this decrease (from 9.05 to 8.53 mg L<sup>-1</sup>) and attributed it to an increase in benthic respiration rate
- (iii) As derived from the observed DO data using the Delta model, an upper quartile value of heterotrophic respiration representative of summer values increased from 3.2 to 5.5 mg O<sub>2</sub> L<sup>-1</sup> d<sup>-1</sup>
- (iv) An increase in heterotrophic respiration rate is simulated by QUESTOR throughout the Thames network. Upstream of Site 8 the average change in the rate as estimated through calibration is from 0.32 in 2009–10 (Model A) to 1.10 in 2013–14 (Model B)
- (v) The increase in heterotrophic respiration in the network corresponds with increases in median DOC concentration of 5.5–48.1% across 18 sites.

The results suggest that DO concentrations in lowland rivers such as the Thames may be vulnerable to suppression due to a combination of (i) authigenic processes (e.g. as seen near Site 5 in 2009–10) where enhanced rates of photosynthesis are followed by microbial breakdown of the algal biomass, and (ii) allochthonous processes whereby benthic respiration follows delivery of organic matter into the river channel as a result of intense wet summer conditions (e.g. as seen in 2013–14 extensively in the Thames following summer floods of 2012). More generally, the impacts identified demonstrate the threat posed by convergence of climate change and urbanisation to bring about environmentally-damaging flooding events whose impacts extend beyond localised and short-term consequences. The research also highlights the importance of information provided by concerted long-term continuous monitoring of hydrology and water quality in rivers. Furthermore it pinpoints a need to better understand in what way other factors, in particular those of a geogenic and biochemical nature, may be moderating rates of benthic respiration in river systems.

#### CRedit authorship contribution statement

**M.G. Hutchins:** Conceptualization, Methodology, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Data curation, Formal analysis, Validation. **G. Harding:** Conceptualization, Investigation, Formal analysis, Visualization, Writing - original draft. **H.P. Jarvie:** Formal analysis, Conceptualization, Writing - review & editing. **T.J. Marsh:** Writing - review & editing. **M.J. Bowes:** Resources. **M. Loewenthal:** Resources.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.hydroa.2020.100056>.

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