Water Research 247 (2023) 120815

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

MAKING WAVES: Effluent to estuary: Does sunshine or shade reduce downstream footprints of cities?

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ARTICLE INFO

Keywords:
Photolysis
Dissolved organic matter
Riparian canopies
Greenhouse gas
Wastewater
River

ABSTRACT

Riparian tree canopies are key components of river systems, and influence the provision of many essential ecosystem services. Their management provides the potential for substantial control of the downstream persistence of pollutants. The recent advent of new advances in mass spectrometry to detect a large suite of emerging contaminants, high-frequency observations of water quality and gas exchange (e.g., aquatic eddy covariance), and improved spatial resolution in remote sensing (e.g., hyperspectral measurements and high-resolution imagery), presents new opportunities to understand and more comprehensively quantify the role of riparian canopies as Nature-based Solutions. The paper outlines how we may now couple these advances in observational technologies with developments in water quality modelling to integrate simulation of eutrophication impacts with organic matter dynamics and fate of synthetic toxic compounds. In particular regarding solar radiation drivers, this enables us to scale-up new knowledge of canopy-mediated photodegradation processes at a basin level, and integrate it with ongoing improvements in understanding of thermal control, eutrophication, and ecosystem metabolism.

1. Riparian canopies: an opportunity to combat future ecosystem threats

Under population growth and a warmer future with more extreme events, waterbodies will become exposed to increased inputs of degradable organic matter (Regnier et al., 2022) and emerging synthetic contaminants (Polazzo et al., 2021). Urban effluent signatures and their biogeochemical effects are most pronounced in deep slow-flowing lowland rivers where they often dominate volumetrically in summer (Luthy et al., 2015); acting as hotspot drivers of diverse modes of environmental impairment downstream (e.g., increased chemical toxicity, altered structural and functional ecological status, enhanced greenhouse gas (GHG) efflux). However, river channels provide essential ecosystem services including water purification and habitat provision, notably enhanced by riparian canopies and vegetation (Feld et al., 2018). Simply measuring pollutant concentrations to determine impact is not enough. In aquatic environments, organic compounds undergo microbial and photolytic degradation and transformation into secondary metabolites. Full understanding of controls of and interplay between degradation processes of natural and synthetic river organic matter is needed for more effective river restoration and mitigation of future threats.

Climate controls effective rainfall, which is a key determinant of water residence time in river networks. Residence time substantially controls the persistence of riverine pollutants and their secondary effects (Bowes et al., 2012). As well as providing habitat, riparian trees are pivotally located within basins; moderating light inputs, cooling surface waters, and thereby putting a brake on residence time-driven processes. Moderation of light inputs is especially marked in narrow headwater reaches. By managing riparian canopies we can shape how and where catchment-scale pollutant dispersion and downstream ecological impact occurs in sensitive summer low flow conditions. Drought risk in all its

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https://doi.org/10.1016/j.watres.2023.120815
Received 15 April 2023; Received in revised form 9 September 2023; Accepted 29 October 2023
Available online 1 November 2023

forms, including reduced river flows in summer, is rising (Vicente-Serrano et al., 2022). However, understanding of canopy structure at a river network scale is currently insufficient to advance knowledge of key riverine processes, hampering the effectiveness of mitigation. Establishing canopy shade can substantially modify water quality, but it is unclear how to balance benefits and trade-offs of competing issues in polluted rivers (Fig. 1a). To address this shortcoming and identify optimal riparian shade across catchments subject to differing anthropogenic stressors, process-based modelling frameworks can unify the relevant fields at the forefront of advancing systemic understanding of river environments.

In the present paper, we first outline the state of understanding in relevant areas of environmental science. Then we offer recommendations from a technical perspective for research going forward. The longer-term intention is that research outcomes will better support policies accounting for the multiple environmental benefits of riparian canopies.

2. Current state of knowledge

Widespread evidence is emerging that net ecosystem respiration (NER), a key metric of freshwater ecosystem health, is controlled by seasonality, temperature, and light (Bernhardt et al., 2022). Hence, riparian canopies can substantially inhibit not only unwanted accelerated eutrophication, but also desirable breakdown of toxic organic compounds. Substantial decrease in the potential for photodegration arises. They may also promote a shift to net heterotrophic systems which may make occurrence of low dissolved oxygen more likely. Lower temperatures in shaded rivers will also reduce rates of GHG emission, but effects of riparian canopies on other interacting factors determining GHG fluxes are uncertain. These outcomes further interdepend mechanistically, including (a) long-term increases in river antibiotic loads driving greater benthic methane emissions (Bollinger et al., 2021); (b) substantial photo-oxidation of bulk dissolved organic matter (DOM) (Wang et al., 2021). The latter pivotally impinges on NER, on indirect photolytic pathways of toxic organic compounds, and on dissolved gas concentrations.

Conceptual interlinkages between key areas of evolving environmental research activity are illustrated (Fig. 1b). These also form a schematic summary for how modelling may develop in parallel. Two fields of increasing environmental concern and their measurement are highlighted (in red on Fig. 1b), namely GHG emission and toxic chemical exposure. A third field relates to technical advances in spectral observations above and below the water surface. These three actively evolving fields of research are well positioned to provide data to improve understanding of riparian canopy effects, and are summarised below.

2.1. Organic matter and GHGs

Globally, river environments are hotspots of GHG emissions (Catalan et al., 2016). Molecular composition is the primary determinant of river carbon degradation rate (Kothawala et al., 2020); with labile compounds consumed first, causing recalcitrant forms to dominate downstream as residence time increases (Mosher et al., 2015). Local deviations from this downstream progression are often substantial and attributable to ecosystem properties (e.g., nutrient availability, shade and detritus from riparian trees, river temperature regime, and channel morphology) (Catalan et al., 2016; Soares et al., 2019; Cotner et al., 2022), which all also affect hydrological influences on biological dynamics across trophic levels (Zhou et al., 2020). The increasing availability of high-resolution continuous sensor measurements (Rode et al., 2016) underpins integrated linkages between river quality (Jarvie et al., 2018) and biogeochemical processes (von Schiller et al., 2017). Computational modelling of process rates (Segatto et al., 2020; Pathak et al., 2022) provides powerful functional-level metrics of response to change. However, due to observational challenges, uncertainties surrounding heterotrophic respiration (component of NER) have hitherto hindered simulation of eutrophication response to multiple environmental stressors. This can be overcome *via* underwater aquatic eddy covariance (AEC), a relatively new technique providing high-resolution spatially-integrated continuous measurement of benthic metabolism (Fig. 2a) (Berg et al., 2003, 2022). Given its narrow footprint (the area on the riverbed that gives the flux signal: Berg et al. 2007), it can be applied in both small and large rivers. Light, hydrology and seasonality substantially control NER downstream of wastewater effluents (Ledford et al., 2021); and although the specific contribution of heterotrophic respiration currently remains unknown, it can potentially be resolved through combination of AEC measurements, organic matter characterisation and process-based NER modelling.

2.2. Photolysis and synthetic organic compounds

Discharge of anthropogenic chemicals is an increasingly important environmental pressure, one for which current regulatory approaches are inadequate and fate in rivers is generally poorly understood (Posthuma et al., 2020). Chemicals are subject to a wide range of attenuation processes in surface waters, of which biotic and abiotic fate processes

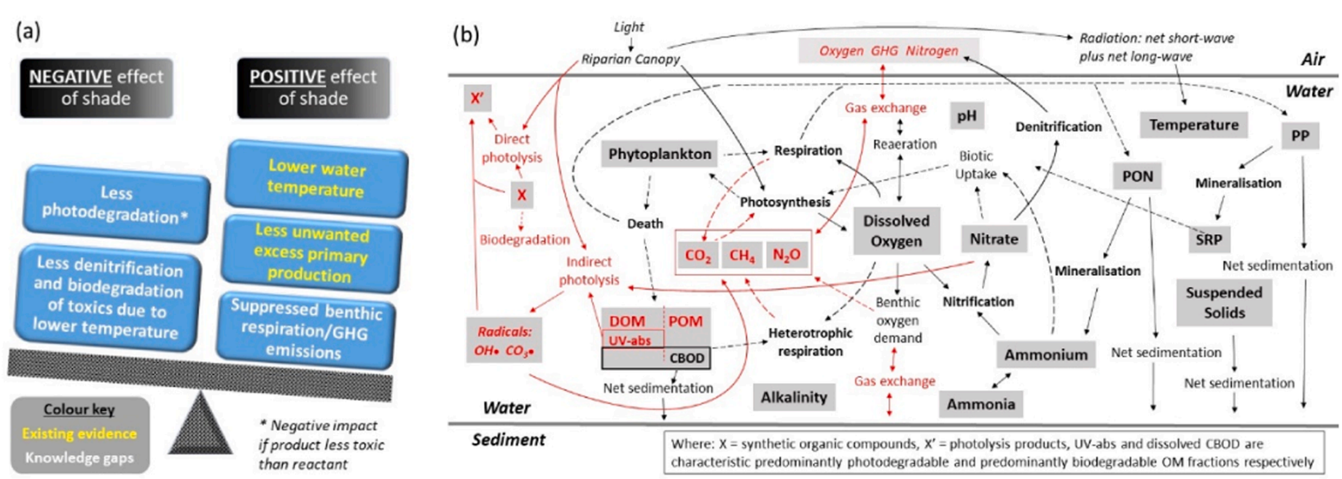

Fig. 1. (a) Trade-offs of riparian shade (b) conceptual biogeochemical process interlinkages in a river system illustrating new components (in red) and their relation with riparian canopies; built around an existing example used for process-based hourly eutrophication and ecosystem metabolism modelling (Pathak et al., 2022) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

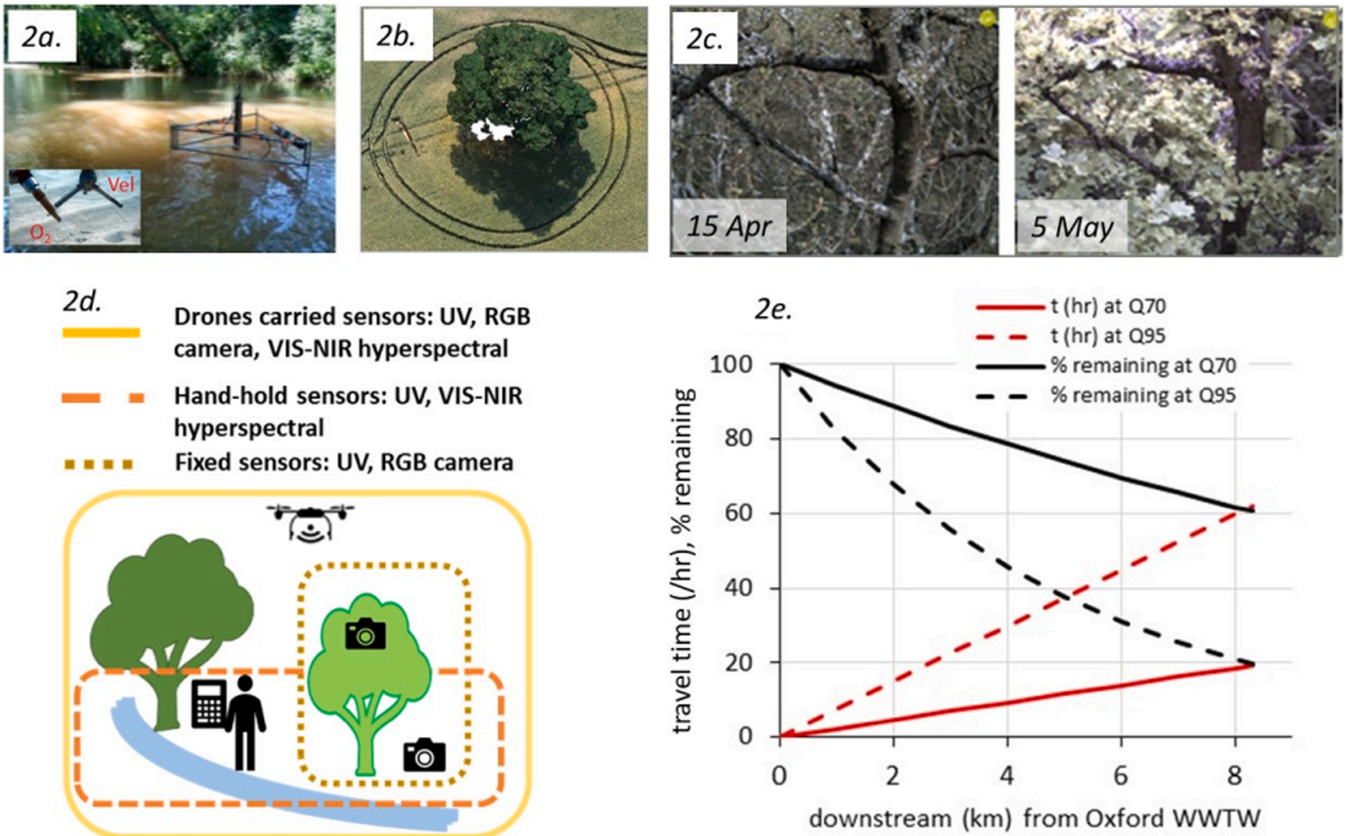

Fig. 2. (a) Aquatic eddy covariance, (b) Structure from Motion point-cloud captured by drone-based instruments, (c) photographs from RGB cameras sited in canopies, (d) assemblage of earth observation instrumentation for characterising riparian canopy shade, (e) estimated travel time (t) and change in sulfapyridine concentration under fixed light and low flow (Q70 or Q95) conditions along an 8.3 km stretch of the River Thames (UK) downstream of Oxford wastewater treatment plant (assuming first order photolytic rate kinetics of 0.026 (+/- 0.009) h^{-1} ($n = 7$, $p < 0.05$), Hanamoto et al. 2018).

such as partitioning (sorption and desorption), hydrolysis and bio-degradation have been well studied. In contrast, photolysis of, for example, active pharmaceutical and personal product ingredients is more uncertain but nevertheless important in determining overall fate in aquatic systems (Cheng et al., 2021). The process occurs either through direct absorption of light, or indirectly *via* reactions with photochemically-produced intermediates generated from photolysis of DOM (e.g., hydroxyl and carbonate radicals) (Carena et al., 2020). Nitrate can also enhance indirect photolysis (Lam et al., 2003). Photolysis is not always desirable however, as products may be more toxic and persistent than parent compounds (Dong and Hu, 2016). Whilst environmental fate models widely reflect detailed studies of sorption/desorption, degradation processes are usually aggregated within a total in-stream removal rate or ignored completely. Although methods to combine information on local solar irradiation and waterbody characteristics to adapt photolysis rates determined in the laboratory have been available for many years (Zepp and Cline, 1977), these have not been readily incorporated in river network process-based models due to difficulties in estimating spatio-temporal variation of light intensity at the water surface. There is an increasing need to characterise each process separately and enable models to better depict overall exposure of the biota to harmful chemical effects throughout a river network.

2.3. Earth Observation (EO)

Before recent advances in access to and processing of EO data, quantifying benefits of riparian canopies has been difficult, with little direct knowledge arising about canopy morphology and how it regulates river processes. Canopy attenuation of light penetrating to waterbodies has been linked to water quality modelling at basin-scale (Bachiller-Jareno et al., 2019), but accuracy at a local level is limited. As opposed to routinely-used low-resolution DEM products, high-resolution Structure from Motion (SfM) is now available (Fig. 2b) to more accurately quantify the substantial cooling effects of riparian canopies on rivers. The shortwave radiative flux at the water-air interface, a key component of the stream energy balance, can be reduced by establishing tall riparian vegetation (Dugdale et al., 2018, 2020). Opportunities are also emerging to use combinations of UV radiation sensor measurements above and below canopies alongside co-orientated UV radiometers (using a hyper-spectral-radiometer for ground reference data) and RGB cameras (Fig. 2c) to relate canopy penetration and canopy structure metrics through the growing season. In addition, in conjunction with submersible absorbance and fluorescence probe measurements, hyperspectral sensors capturing upward and downward fluxes can improve estimates of water column photolysis, and contribute to identification of chromophoric DOM (CDOM).

3. Recommendations

To pinpoint where tree planting will maximise multiple environmental benefits requires steps forward in river water quality modelling. Whilst typically synthesising current understanding of energy balance, eutrophication and NER, we need to ensure that hourly-resolution process-based modelling adequately integrates an extended set of features. In this respect, techniques for measuring canopy structure, degradation of synthetic organic compounds, and gas transfer at sediment-water and water-air interfaces can be brought together to integrate knowledge of dissolved GHGs, DOM properties and selected anthropogenic chemicals.

Testing the following hypotheses will lead to a step change in holistic riverine understanding:

- Riparian canopy coverage significantly controls the extent to which anthropogenic disturbances due to wastewater effluent and eutrophication alter the composition of DOM along river continua.
- Chronic increase in benthic respiration and GHG efflux occur downstream of wastewater effluents.
- Photo-oxidation of DOM is the dominant contributor to GHG efflux.
- Riparian canopies provide the primary environmental control on microbial and photodegradation processes that decompose synthetic organic compounds and bulk DOM in river networks.

By integrating both a set of field techniques and also modelling of toxic substances and organic pollution, none of which have been previously united for holistic process understanding, we suggest these hypotheses can be tested using:

- Continuous flow mesocosm experiments to identify effects of light and temperature on photo- and bio-degradation pathways of bulk organic matter and selected anthropogenic pollutants, and to establish aquatic ecotoxicological endpoints.
- Regular and campaign-based monitoring of hydrochemistry, phytoplankton, high-resolution gas transfer, and novel earth observation at a reach-scale; to better characterise light penetration through riparian canopies and improve understanding of pollutant process interaction in rivers downstream of wastewater effluents.
- Integration of long-term hydrochemical monitoring with additional surveys of gas analysis in shaded and open stretches; to understand catchment-scale persistence of pollutants.
- Extension of river quality modelling through development of new structural elements, calibration and testing (for example, as illustrated schematically in Fig. 1b).

Various activities and recently-developed techniques can support these endeavours:

- For earth observation, combinations of drone-based, hand-held and fixed instruments support hyperspectral measurement and high-resolution imagery (Fig. 2d).
- Aquatic eddy covariance and floating chamber headspace analysis enables determination of high-resolution gas transfer fluxes.
- As well as providing valuable diagnosis of DOM photo-oxidation, recent advances in analytical chemistry (e.g. LC-Q-Orbitrap mass spectrometry) enable non-target screening of freshwaters for a wide spectrum of synthetic compounds and their metabolites, which are emitted into rivers through wastewater treatment plant effluents. Consequently it is possible to identify a suite of compounds which are abundant in rivers, span a range of reported photodegradation half-lives (Martínez-Zapata et al., 2013) and have differing relative importance of photolytic and biodegradation fate pathways.
- Suitable river stretches in lowland urbanising basins exist where specific fate pathways of pharmaceuticals have been identified from mass-balance studies (Hanamoto et al., 2018) (Fig. 2e).
- Degradation rates of bulk organic matter and synthetic compounds can be calculated from a combination of *in-situ* multi-parameter sonde measurements, hyperspectral imagery and micro-spectrometry, in concert with laboratory analysis. Given these capabilities, and alongside recent advances in remote sensing to measure solar penetration through canopies, the approach of Zepp and Cline (1977) can now be incorporated into models of river systems.
- Approaches for using UV absorbance diagnostics to conceptualise change in DOM functional group composition and dynamics along river continua are available (Anderson et al., 2019); which, when embedded in river network process-based models, facilitate a powerful scaling-up across basins from effluent to estuary.

4. Conclusions

Uniting higher-resolution EO data collection with monitoring and controlled experiments will enable step-change in understanding of river ecosystem metabolism, gas exchange, and photo-degradation pathways for synthetic and natural organic compounds. Development of a reliable globally-applicable basin-scale modelling framework is of paramount importance to underpin this holistic emerging understanding of river environments, and to predict future response to change. Aside from advancing understanding of the role of riparian canopies as Nature-based Solutions, such a system would have other substantial benefits. It would enable the incorporation of findings into (a) wider considerations of how to best mitigate river GHG efflux in context of other emission pathways across terrestrial and marine systems, (b) improved national regulatory toxic exposure assessment.

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.

Data availability

No data was used for the research described in the article.

Acknowledgments

The authors are grateful to numerous Environment Agency staff who provided constructive suggestions for shaping recommendations from a regulatory perspective. We thank Andrew Johnson (UKCEH) for providing comments on the text.

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