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Longitudinal Variability in the Oxygen Demand of Channel Bed Matrix Sediment in a UK Agricultural Catchment: Implications for Managing the Sediment Problem

S. Pulley | C. Reigate | A. L. Collins

Net Zero and Resilient Farming, Rothamsted Research, Okehampton, UK

Correspondence: S. Pulley (simon.pulley@rothamsted.ac.uk)

Received: 11 October 2024 | **Revised:** 3 March 2025 | **Accepted:** 19 March 2025

Funding: This work was supported by UKRI-BBSRC (UK Research and Innovation-Biotechnology and Biological Sciences Research Council) and the data integration and production of this article was funded by the Institute Strategic Programme Resilient Farming Futures via grant award BB/X010961/1—specifically work package 2—BBS/E/RH/230004B.

Keywords: fine sediment management | in-channel river management | matrix sediment | sediment oxygen demand | streambed processes

ABSTRACT

The presence of excess fine-grained matrix sediment in channel beds can exert an oxygen demand in this critical habitat for fish spawning and invertebrates. Therefore, reducing the oxygen demand of channel bed sediment through targeted intervention may deliver better cost–benefit from catchment management. To assess the potential for targeted interventions to deliver benefits, sediment oxygen demand (SOD) was measured in pools, riffles, bars, and runs at nine sites along the River Taw in the southwest of the UK. This river flows from upland semi-natural grassland, to lowland agriculture with sewage treatment work discharges. SOD was measured for 5 days on the $<25\,\mu$m fraction of the bed matrix sediment using a laboratory-based dissolved oxygen probe. Samples of potential sediment sources were also analysed, and a colour-based method was used to determine the provenance of the channel bed sediment. SOD did not vary significantly longitudinally or by riverine feature and was higher in the river bed matrix sediment than its sources. Using settling to isolate the ultra-fine fraction of the sediment showed the highest SOD was concentrated here. The entrapment of autochthonous algal material in this fraction is the probable source of this high SOD. Since reducing within-stream productivity is likely to be challenging, a combined approach targeting sediment source protection to water erosion and in-channel measures to increase matrix sediment exfiltration is warranted. This would reduce the reduction in pore spaces in the bed matrix by fine sediment ingress, thereby limiting the entrapment of the ultra-fine material controlling SOD.

1 | Introduction

A decline in the ecological status of fresh waterbodies has been observed worldwide, with modern agricultural practices, river modification, and industrial and residential expansion being linked to increased sediment and nutrient losses to water and their subsequent detrimental ecological impacts (Quinton et al. 2010; Borrelli et al. 2017; McDowell et al. 2016). Consequently, significant investment is being made towards mitigating pollutant losses to water through a range of policy instruments including, for example, regulation and agri-environment initiatives (McDowell et al. 2016; Environment Agency 2019).

Globally, the often-limited attempts to detect improvements within-stream after the implementation of mitigation measures have rarely shown compelling positive benefits, resulting in high uncertainties surrounding the expected or technically feasible

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outcomes of any planned programmes of measures (Stalnacke et al. 2003; Kay et al. 2009; Meals et al. 2010; Pastuszak et al. 2012; Lloyd et al. 2014; McGonigle et al. 2014). Typically, the efficacy of mitigation measures is quantified as a reduction in source-specific contributions to riverine loads (tonnes transported) which are important for reducing water treatment costs or impacts on lakes and estuaries (Newell Price et al. 2011). However, from the standpoint of improving waterbody ecological status, a reduction of concentrations ($mg\,l^{-1}$) during ecologically sensitive periods with high biological productivity may have greater potential for delivering positive outcomes and require different mitigation measures (Jarvie et al. 2006; Mellander et al. 2024). Here, a range of potential pollutant sources might need to be targeted, including, for example, proximal sources to river channels like riparian critical source areas, distributed sources such as farmyards and tracks, and point sources of nutrient losses, such as sewage treatment plants, which may release pollution to watercourses during all flow conditions (Lloyd et al. 2019; Jordan et al. 2007). However, high nutrient and sediment concentrations are not present in the water column of all rivers, especially in headwater streams. Jarvie et al. (2018), using monthly samples retrieved from 249 river monitoring sites, reported that 23% of UK headwater streams were P-impaired, compared with 51% of UK rivers of all sizes. Yet, sediment and nutrients may be a source of degraded habitat quality when concentrations in overlying waters are low due to their accumulation in channel bed gravels, which are critical habitats for fish spawning and invertebrates (Kemp et al. 2011; Jones et al. 2012). For example, Buendia et al. (2013) and Descloux et al. (2014) showed changes in invertebrate assemblages in channel beds suffering excess sedimentation. A review by Chapman (1988) found that salmonid embryo survival in redds was usually negatively correlated with the percentage of fine sediment present. Fine sediment has been shown to infiltrate deeply into fish spawning gravels during winter high flow events (Soulsby et al. 2001). Whilst sequestered on and within the channel bed framework, deposited fine-grained matrix sediment may also adsorb dissolved phosphorus during low flows, further increasing its potential for ecological harm (McDowell et al. 2020).

In addition to blocking physical space in channel bed framework gravels, excess fine-grained matrix sediment prevents oxygen diffusion, which is required for fish egg and invertebrate respiration (Greig et al. 2005). Fine sediment also increases oxygen consumption through microbial respiration, reducing oxygen availability to aquatic biota (Cheng et al. 2024). Dissolved oxygen in intra-gravel water has been shown to be positively correlated with fish embryo survival (Chapman 1988). The oxygen demand of deposited sediment may also be high enough to impose a significant demand on the dissolved oxygen (DO) content of the overlying water (Butts 1974). A recent study by Jones et al. (2023) compared hydro-chemical data obtained alongside high-frequency invertebrate monitoring over 3 years to replicated biological data and found that all the stressor-specific invertebrate indices tested were most strongly correlated with low DO concentrations. As a result, a high SOD is associated with changes in the structure and functioning of riverine ecology, especially in benthic habitats (Levin et al. 2009).

The number of investigations into SOD in gravel bed rivers has been limited to date (Theurer and Theurer 1986; Greig 2004; Sear et al. 2017) and has shown significant variability in the results, which may be due to the type and quantity of organic matter present (Lundkvist et al. 2007; Thomann and Mueller 1987) or particle size effects (House 2003). The assessment of the oxygen demand of channel bed sediments is often carried out in situ (Coenen et al. 2019) with the data generated reflecting the amount of sediment present, local hydrological conditions, and the flows of sediments and water through the channel bed matrix (Boudreau and Guinasso 1982; DiToro 2001). SOD is strongly controlled by sediment-associated organic matter content, which can decay and oxidize, therefore competing with aquatic ecology for the DO present (Chevalier et al. 1984; Greig et al. 2005). Sediment from different sources has been shown to exhibit varying oxygen demand and impacts on biota. For example, highly organic sewage effluent and damaged road verge sediments were found to be significantly more deleterious to the mortality and fitness of alevin than sediment derived from eroding channel banks or agricultural topsoils (Sear et al. 2016).

A targeted reduction in the oxygen demand of channel bed sediment deposits therefore represents a key potential mechanism for improving the ecological status of waterbodies where bed deposition represents an important component of the fine-grained sediment budget. However, to date, limited studies have compared the oxygen demand of sediments in detail through a single river system with the aim of establishing the practicality of achieving this goal. This study therefore aimed to gain an indication of how the oxygen demand of fine-grained matrix sediment ($mg\ O_2\ g^{-1}$) varies spatially within the River Taw, a headwater river catchment, and if this can be linked to sediment properties, sediment sources, catchment land use, or riverine features.

The objectives of this study were:

1. To measure the longitudinal variability of channel bed fine matrix sediment oxygen demand during a transition from semi-natural peatland to intensive agriculture.
2. To compare the oxygen demand of channel bed fine matrix sediment with its sources.
3. To identify the major factors controlling channel bed fine matrix sediment oxygen demand.

2 | Methods

2.1 | Study Site

The study was conducted in the catchment of the Upper River Taw (41.3 km^2) located in the Southwest of the UK (Figure 1). This catchment was selected for study due to the high contrasts in land use between the upper and lower catchment and therefore high potential longitudinal variability in SOD. The river originates in the upland (> 200–300 m a.s.l.) semi-natural grassland of Dartmoor, overlying peat and podzol soils, which are used for rough grazing. It flows into a lowland (< 200 m a.s.l.) agricultural landscape that supports dairy, beef, and sheep production. Lowland soils are a combination of poorly draining clay-rich gley soils and more freely draining brown earths. Cereals and fodder maize are also produced,

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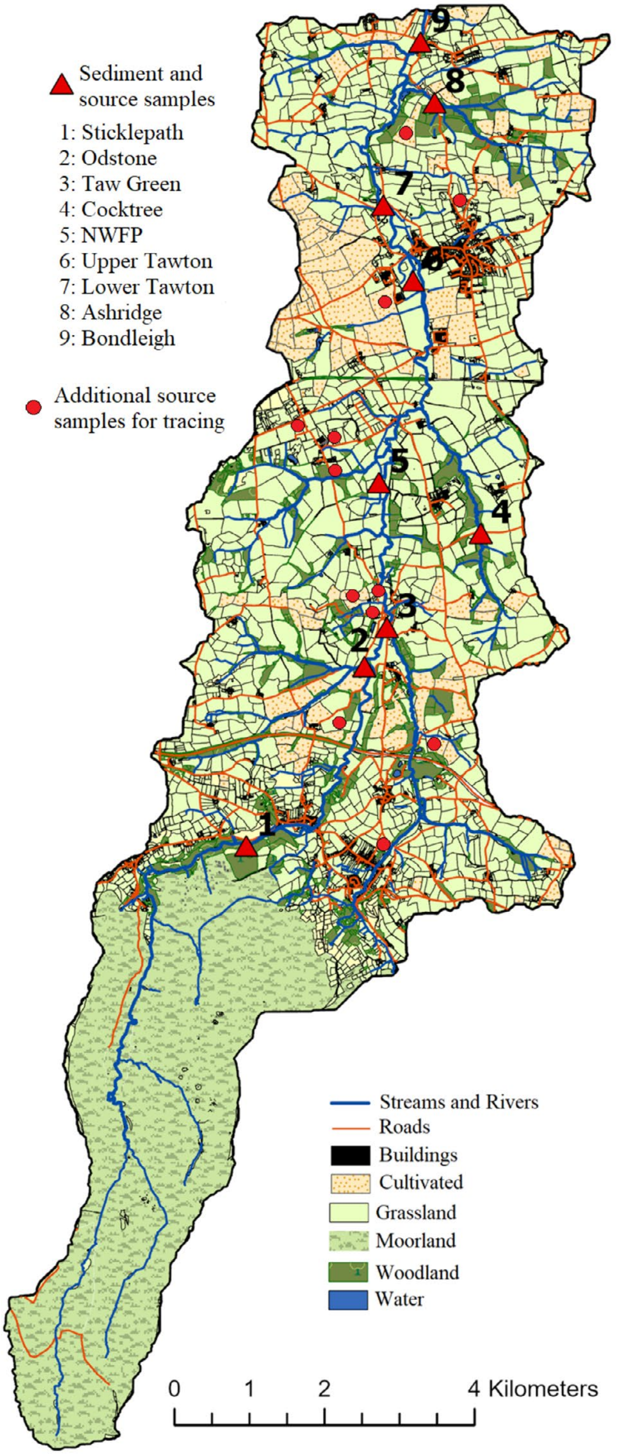

FIGURE 1 | Land use in the upper River Taw catchment and the channel bed sediment sampling locations, field boundaries from Ordinance Survey Mastermap and land cover from CROME 2020 (Rural Payments Agency 2023). [Color figure can be viewed at wileyonlinelibrary.com]

particularly on the sandier, free-draining soils. The catchment has a high mean annual rainfall of 1040 mm (measured at North Wyke) which, when combined with the poorly draining soils, leads to a primarily 'flashy' surface water driven hydrology, although flow is maintained during dry periods by throughflow and groundwater. The village of North Tawton is in the lower catchment and contains a sewage treatment works, from which discharge is released into the river downstream of the village.

2.2 | Sampling Strategy

Nine sampling sites were identified based upon roughly even spacing along the river network and ease of accessibility. Two sites were sampled each week between the 31st May and the 26th June 2024, as incubator capacity limited sample throughput (Table S1; objective 1). This period is the end of the Salmonid, Escoidae, and Petromyzontidate fish spawning seasons (ending late May) and during Cyprindae, Cottidae, and Percidae spawning (Kemp et al. 2011). At each site, a sample of fine-grained sediment stored within the channel bed framework gravels was obtained from riffles, pools, runs, and gravel bars. A hand-operated dredge was used to collect gravels and matrix sediment from the river bed in approximately 5 locations within 2 m of the sampling point assigned to the approximate centre of each of the four in-stream features. The gravels and associated matrix sediment were transferred into a 15 L plastic bucket until it was full, sampling to a maximum depth of approximately 20 cm, which is a depth where fish eggs are likely to develop (DeVries 1997). Gravel depth was significantly shallower in riffles, runs, and pools than in gravel bars. The gravels within the bucket were removed by hand, and the water containing sands, silts, and clays was allowed to settle until clear. Excess water was then decanted and the sediment transferred to 1 L nalgene bottles. In addition, samples of channel bank at each sampling site were retrieved from the bottom two-thirds of the bank profile, and a sample of the nearby topsoil was taken from the top 2 cm of the soil profile using a metal trowel. These topsoil sources comprised cultivated fields, woodland, grassland, and damaged road verges/fords. Seventeen additional samples of topsoils were retrieved from across the catchment for sediment source tracing only. For laboratory SOD measurements, native river water was required, which was collected in a 50 L plastic container. The water was collected by submerging the bottle in an area of high flow whilst taking care not to disturb any sequestered channel bed sediments. After filling, the bottle was left to settle for 10 min, and the top 25% of the water was poured off to minimise the amount of low-density organic matter present. The water was then left to settle for an hour before the top two-thirds were decanted off into a plastic bucket through a 25 μm sieve for use, discarding the bottom third where most of the low amounts of suspended material had settled.

2.3 | Laboratory Analysis

There currently is no widely accepted standardized measurement method for SOD (Miskewitz et al. 2010). Collins et al. (2017) incubated 200 mL of sediment slurry in 1 L flasks whilst continuously measuring the oxygen concentration in the bottles. Whilst this method was effective, it requires individual oxygen meters for each sample, which was beyond the budget of this study given the need to replicate measurements. Instead, an alternative method based upon the measurement of the BOD of water was used (Cross and Summerfelt 1987; Delzer and McKenzie 2003). Five-day SOD was measured as

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longer periods would not allow for a complete longitudinal survey of the study river before seasonal changes might impact sediment deposition, retention, and composition as well as the composition of river water biota. SOD was measured using the following steps:

1. Matrix sediment and source sampling and collection of native river water
2. Fractionation of samples to < 25 μm, settling and removal of excess water to form a slurry
3. Filling of BOD bottles with homogenised river water and addition of 1, 2, and 3 spatulas of the sediment slurry creating three replicates per sample.
4. Initial measurement of the water and fine matrix sediment DO concentrations using a benchtop meter.
5. Incubation in an orbital shaker at 20°C for 5 days.
6. Re-measurement of water and fine matrix sediment dissolved oxygen concentration.
7. Isolation, drying, and weighing of the sediment contained in each bottle.
8. Calculation of oxygen consumption per unit mass of fine matrix sediment

Within 3 h of sample collection, the sediment and source material samples were passed through a 25 μm stainless steel sieve and the < 25 μm fraction isolated for analysis. This fraction was selected to minimise the potential for sediment particle size to impact its oxygen demand. The sieved sediment was allowed to settle for at least 1 h until excess water could be decanted off, leaving a slurry. Clean 270 mL glass BOD bottles were submerged into the bucket of prepared river water to fill them whilst stirring continuously to ensure that the water was homogenous. Three replicates of the prepared slurry from each sediment and source material sample were added to the filled bottles using a plastic spatula whilst continuously stirring to ensure it remained homogenous. The replicates consisted of one, two, and three spatula scoops of the slurry to allow for repetition and to maximise the probability that the results of at least one sample fell into the acceptable range of values for accurate measurement after incubation (> 2 mg O_2 l^{-1}). The mean mass of sediment added to the bottles was 0.24 g. Three samples of river water containing no sediment were also analysed so that the river water oxygen demand could be separated from that of the fine-grained sediment.

After filling the bottles, their dissolved oxygen concentration was measured using an Orion Star A213 Dissolved Oxygen Benchtop Meter whilst continuously stirring using a magnetic stir bar. To confirm that the river water used for incubation was homogenous, one of the three replicates of every sediment and source material sample was also measured. The samples were incubated for 5 days in the dark at 20°C whilst being agitated at 130 rpm in an orbital shaker (New Brunswick Scientific Innova 44 incubator shaker series) and subsequently re-measured for DO concentration. After measurement, the weight of the bottle with added water was recorded and the sediment in the bottles was allowed to settle. The clear overlying water was decanted off and disposed of, and the bottle was weighed to calculate the volume of water it contained. The bottom ~20% of the water and sediment were decanted into foil trays and oven dried at 50°C. The mass of sediment contained in the trays was then recorded.

SOD was calculated by multiplying the DO concentration (mg O_2 l^{-1}) of the river water before and after incubation by the volume of water contained in each bottle and subtracting the two values to calculate the mass of oxygen consumed (mg). This was then divided by the mass of sediment incubated to calculate total five-day sample oxygen demand (SOD_5; mg O_2 l^{-1}). The mean oxygen demand of three river water samples measured without the addition of sediment was then subtracted. Any measurements where the oxygen concentration fell below 2 mg O_2 l^{-1} after incubation were discarded as sediment oxygen consumption is only independent above this threshold (Edwards and Rolley 1965; Chevalier and Murphy 1985).

The sources of the channel bed fine matrix sediment samples (objective 2) were determined by comparing their colour to that of potential sources within the study catchment (Pulley and Collins 2021). A total of 34 source samples were collected from road verges and fords (3), cultivated topsoils (7), grassland topsoils (11), woodland topsoils (4) and channel banks (9). Topsoil sources were sampled to a depth of 2 cm, and channel bank samples were collected from the bottom two-thirds of the bank profile using a stainless steel knife. The remaining sediment after subsampling for SOD measurement was used in this analysis. All source and sediment samples were fractionated to < 25 μm by wet sieving through a stainless steel sieve. Hydrogen peroxide sample treatment was used to remove organic matter from the samples. 80 mL of 30% hydrogen peroxide was added to ~0.2 g of sediment and heated at 80°C for 4 h (Pulley and Collins 2022). This sample treatment reduces the potential uncertainties associated with changes in sediment colour during its erosion, transport, and within-stream storage. A ~ 0.2 g subsample of each source and sediment sample was transferred to a 50 mL centrifuge tube, and 8 mL of 30% hydrogen peroxide was added. The samples were left to stand overnight to reduce effervescence before being heated at 70°C for 4 h and then 90°C until dry. The treated sediment samples were packed into transparent polythene bags, and images of them were captured using a Ricoh MP colour scanner. The red, green, and blue values in the RGB colour space were captured on a scale of 0–255 in Gimp 2 open-source image editing software.

To identify the major factors (excluding source) controlling SOD variability in SOD based upon its settling velocity, which will be controlled by its organic matter content and particle size, was examined (objective 3). Here, sieved matrix sediment collected from a gravel bar at the NWFP sampling site was placed into a 50 mL burette with the prepared river water and shaken for 30 s. The sample was then allowed to settle, and the bottom 5 mL was transferred to a filled BOD bottle at 1-min intervals for a total of 10 min.

A second trial was conducted wherein dried sediment from a combination of riverine and agricultural sediment sources was sterilised by oven drying at 105°C for 24 h. This sediment was

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added to the BOD bottles with the prepared river water and SOD was measured using the methods outlined above. This trial aimed to determine how much of the SOD was caused by microorganisms in the fine-grained matrix sediment, which may have originated from terrestrial agricultural sources, when compared to those present in the river water oxidising the sediment-associated organic carbon.

2.4 | Data Analysis

To measure the longitudinal variability of channel bed fine matrix sediment oxygen demand (objective 1) the mean and standard deviation SOD_5 of the replicates from each sampling site and riverine feature were plotted longitudinally from upstream in the peat area to the downstream area of intensive farming. It was observed if there was an increase in SOD_5 associated with this downstream transition in land use. Additionally, a Kruskal–Wallis test was used to determine if there was a significant difference between the SOD_5 of the four riverine features (runs, riffles, bars, and pools) across the entire dataset.

To compare the oxygen demand of channel bed fine matrix sediment with its sources (objective 2) the colour-based tracing method was used. The hydrogen peroxide treated red and blue values of the sediment and source samples were included in a scatter plot, which was used to qualitatively interpret sediment sources (Pulley and Collins 2021). The mean and standard deviation SOD_5 of the channel bed sediment SOD_5 and that of the major sediment source groups (road verges and fords, cultivated topsoils, grassland topsoils, woodland topsoils, and channel banks) were compared, and a Kruskal-Wallis test was used to determine if significant differences are present between the sediment and its sources.

To identify the major factors controlling fine matrix bed sediment oxygen demand (objective 3) SOD_5 was plotted against its settling time in the burette to identify if a lower setting velocity (finer particle size) was associated with an increased oxygen demand. Additionally, the mean and standard deviation of SOD_5 of the source and sediment samples were compared before and after heating at 105°C to identify if the sterilisation of sediment-associated microorganisms, which may originate from terrestrial agricultural sources, caused its reduction. Should a reduction in SOD_5 not be observed, it suggests that the metabolism of sediment-associated organic carbon by aquatic organisms is the most important contributor to overall SOD_5.

3 | Results

3.1 | To Measure the Longitudinal Variability of Channel Bed Matrix Sediment Oxygen Demand

When compared to the river water, the channel bed sediment had a much higher 5-day oxygen demand per unit mass (river water mean 2.64 mg O_2 l^{-1}; channel bed sediment mean 6.24 mg O_2 g^{-1}). There was significant variability between the extremes in SOD_5 of the channel bed sediment samples, with a pool at Sticklepath having a mean of 27.34 mg O_2 g^{-1} compared to the lowest value of 1.95 mg O_2 g^{-1} in a run section at Upper Tawton (Figure 2). However, outside of these extremes, variability was lower, with the 25th, 50th and 75th percentiles for all channel bed sediment samples being calculated at 3.83, 5.21, and 6.65 mg O_2 g^{-1} respectively. Moderate variability was found between the three repeats for many of the individual samples, with a mean coefficient of variation of 0.44 mg O_2 g^{-1}. There was no indication of increased SOD_5 in a downstream direction where the catchment becomes more intensively farmed and a greater number of arable fields are present. There was also not a significantly higher SOD_5 in the Lower Tawton sampling site, which is just downstream of the sewage treatment works outlet. There was no statistically significant difference (Kruskal–Wallis Test, $p > 0.05$; Figure 3) between the oxygen demand of the channel bed sediment retrieved from the different within-channel features. Variability in the pools was much higher, however, than in the other in-channel features sampled, suggesting that in some pools, such

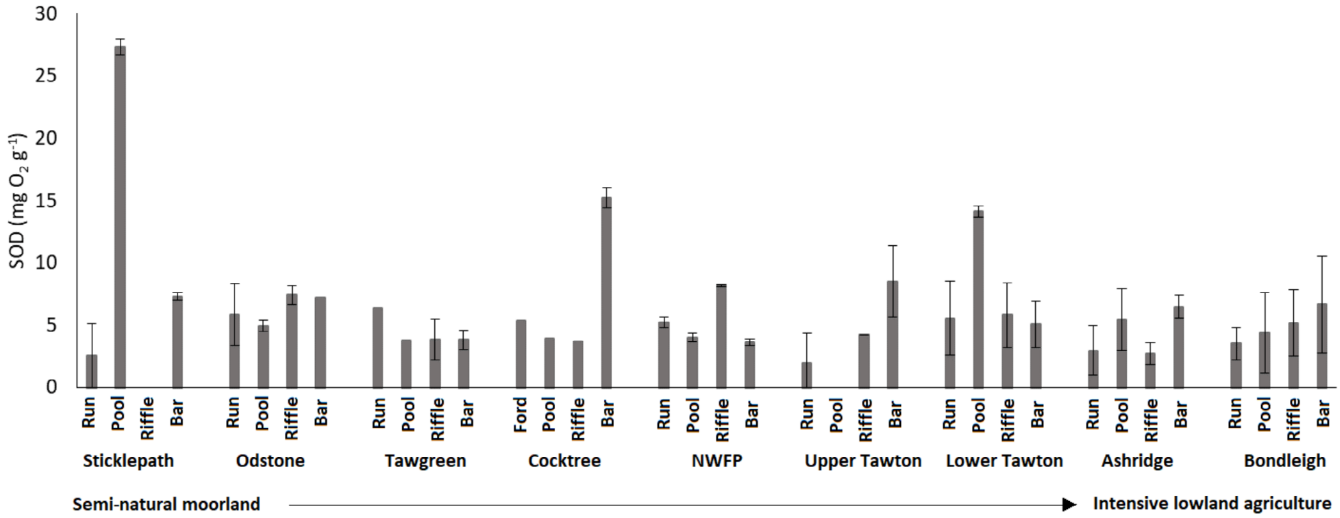

FIGURE 2 | Mean and standard deviation five-day source material and sediment oxygen demand for the successfully measured replicates (maximum 3) from each feature at each site. [Color figure can be viewed at wileyonlinelibrary.com]

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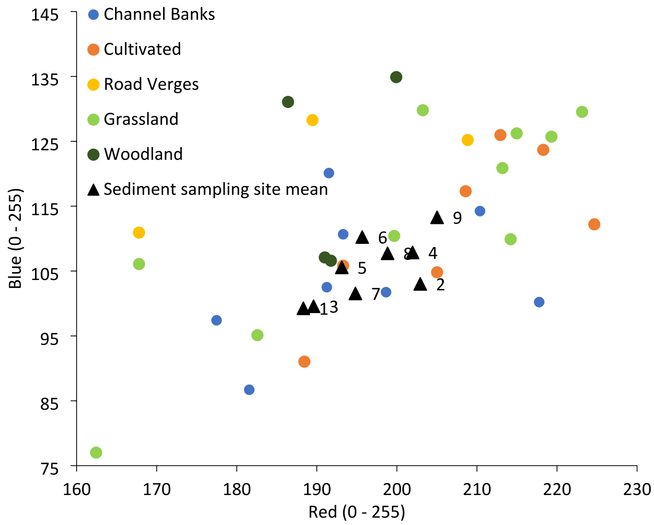

FIGURE 3 | Hydrogen peroxide treated channel bed sediment and source material red and blue values for illustrating sediment source. [Color figure can be viewed at wileyonlinelibrary.com]

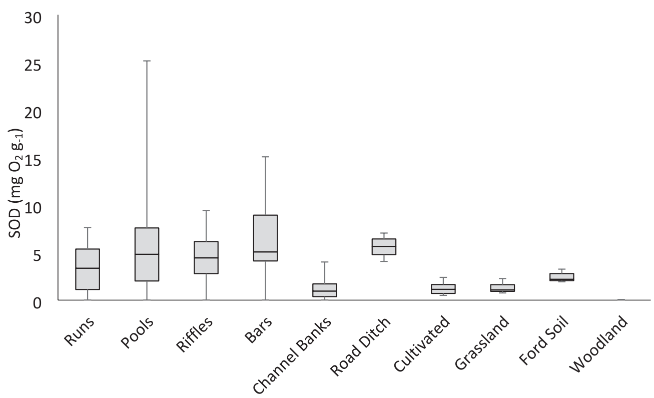

FIGURE 4 | 5th, 25th, 50th, 75th, and 95th percentile SOD_5 in the different riverine features and source material sample categories.

as that sampled at Sticklepath, sediment with a high SOD_5 is present.

3.2 | To Compare the Oxygen Demand of Channel Bed Fine Matrix Sediment With Its Sources

Comparing the colour of the channel bed sediment to its potential sources after organic matter removal using hydrogen peroxide suggested that the sediment originates from channel banks and topsoils which had a generally lower red and blue value than the other sources (Figure 3). The SOD_5 of the source material samples (mean 1.35 mg O_2 g^{-1} for channel banks and 2.59 mg O_2 g^{-1} for cultivated and grassland topsoils) was significantly lower than that of the channel bed sediment (Figure 4). An exception was material collected from a ditch at Taw Green where road runoff accumulated which exhibited a similar SOD_5 of 5.59 mg O_2 g.$^{-1}$ Therefore, most of the oxygen demand of the channel bed matrix sediment likely originates from within-stream sources or enrichment processes rather than being controlled by the properties of its original source materials.

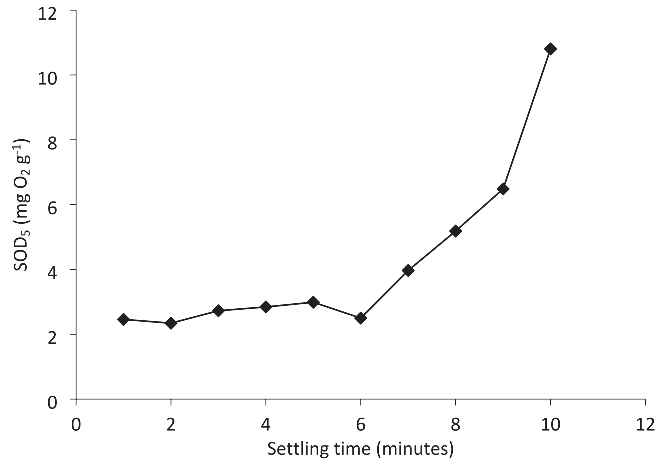

FIGURE 5 | SOD_5 with settling time in a burette.

TABLE 1 | Mean oxygen demand of the untreated channel bed sediment and source material samples compared to samples sterilized by heating at 105°C.

	Untreated	Sterilised using heat
Bed sediment	6.38	9.09
Channel banks	1.35	3.00
Cultivated	1.28	4.48
Grassland	1.33	8.11
Woodland	0.05	7.74

3.3 | To Identify the Major Factors Controlling Channel Bed Fine Matrix Sediment Oxygen Demand

As variability in SOD_5 was not found to be related to either upstream land use or sediment source settling velocity, which reflects particle size and density, it was examined as a potential causal factor. After settling in the burette, the SOD_5 of the heaviest sediment fractions, which settled in 6 min or less, varied little from a mean of 2.64 mg O_2 g^{-1} (Figure 5). This is close to double the mean of the sediment source material samples, but significantly lower than the mean SOD_5 of the channel bed sediment of 6.38 mg O_2 g^{-1}. At between 7 and 10 min of settling, SOD consistently increased. By the time the final two samples were extracted (after 9 and 10 min of settling), all visible sediment aggregates had been extracted, and only the ultra-fine material with a clayey colloidal appearance left in suspension remained. This material had the highest oxygen demand of 10.8 mg O_2 g,$^{-1}$ which was higher than that found in all but three of the channel bed sediment samples.

To examine if the metabolism of sediment-associated organic matter by aquatic microbes, or the action of sediment-associated microbial life, was a greater control on SOD_5, the sediment and source materials were sterilised by heating at 105°C for 24 h. After heating, SOD_5 increased when compared to the samples analysed without heating (Table 1; Figure 6). The increase was highest in the grassland and woodland source material samples and lowest in the channel bed sediment and channel bank samples. Sheep manures and cattle

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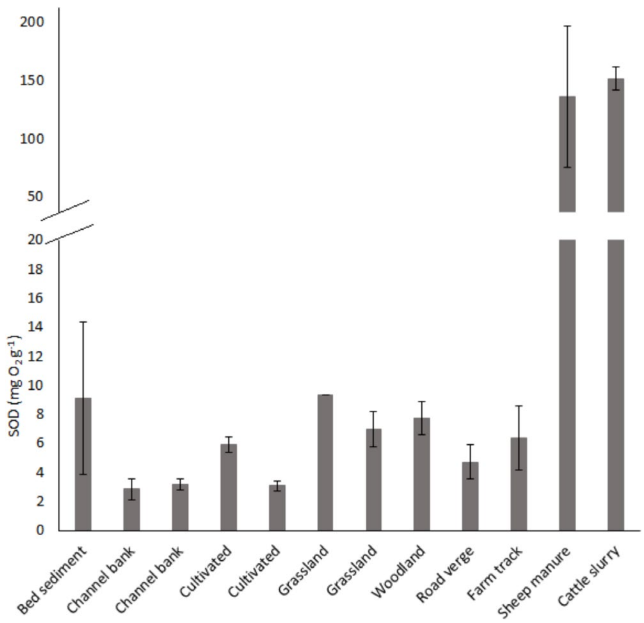

FIGURE 6 | Mean and standard deviation of five-day oxygen demand of sediment and source material samples after drying at 105°C for 24 h and incubation in native river water. [Color figure can be viewed at wileyonlinelibrary.com]

slurry had too high an oxygen demand to be measured when samples were untreated and still had a SOD_5 over 10x higher than the other source material and sediment samples after sterilisation.

4 | Discussion

The oxygen demand of the channel bed fine matrix sediment did not vary according to riverine feature or change in a downstream direction (objective 1). Given that the upper part of the study catchment is predominantly moorland and low grazing intensity semi-natural grassland, and the lower catchment is intensive agriculture with sewage treatment work discharges, this finding again suggests a disconnect between catchment sources and channel bed SOD_5.

The SOD_5 of the sediment sources was significantly lower than that of the channel bed sediment deposits, again showing a disconnect between catchment sources and channel bed SOD_5 (objective 2). Sear et al. (2017) suggested that SOD_5 was associated with a higher organic content and more intensive land use when comparing SOD in different UK rivers. In that specific study, 20-day SOD was more associated with arable farming and a high proportion of silt in the sediment. Therefore, when comparing different rivers, SOD_5 could be expected to vary based on land use characteristics, but within the River Taw studied herein, such variation with changing land use downstream was not found. As a significant downstream transition in land use is present in the River Taw study catchment, it is unlikely that a lack of variability here is contributing to the lack of variation in SOD_5. Further work in different seasons could identify if variability changes more in the late summer season where a greater time has passed since flood events able to cause sediment ingress into the gravel framework. However, this time will not correspond to fish spawning and therefore may be of lesser ecological importance.

The high SOD_5 values measured have significant potential for ecological harm. In a study of 54 aquatic invertebrate species, respiration rates were halved by a DO concentration of 6.44 mg l^{-1}, with reproductive rates halved at 3.66 mg l^{-1}, growth at 1.77 mg l,$^{-1}$ and feeding rates at 0.77 mg l^{-1} (Galic et al. 2019). At a DO concentration of 2.3 mg l^{-1}, Brown Trout egg survival was shown to decrease (Einum et al. 2002). Therefore, the mean SOD_5 of the sediment in the River Taw of 6.24 mg O_2 g^{-1} could rapidly reduce the mean oxygen concentration of the river water (9.5 mg l^{-1}) to a level able to cause adverse ecological impacts, provided that a significant mass of sediment was present, and throughflows of water in benthic gravels were low. The impacts of SOD compared to the oxygen demand of fish eggs are likely to be variable, with a demand of 0.0156 to 0.036 mg O_2 per chum salmon egg in 5 days if scaled up from hourly rates (Wickett 1954). Higher rates of 0.1116 to 0.6252 mg for chum salmon were found by Alderdice et al. (1958) with demand increasing with embryo size. Therefore, the oxygen demand of a single egg is low when compared to the fine matrix sediment, but a high density of eggs may exert a significant collective oxygen demand.

The SOD_5 in the River Taw (mean 6.38 mg O_2 g^{-1}) was relatively high compared to that measured in many UK rivers, with values of 1 mg O_2 g^{-1} found in the Rivers Lod, Lugg, and Blackwater, 2 mg O_2 g^{-1} in the Ithon, 3 mg O_2 g^{-1} in the Test, 4 mg O_2 g^{-1} in the Axe and Aran, 5 mg O_2 g^{-1} in the Frome and Tywi, and 15 mg O_2 g^{-1} in the Camel Valley (Collins et al. 2017). However, fractionating the sediment to $<25\,\mu m$ in the River Taw may have resulted in a higher oxygen demand than was measured on the $<63\,\mu m$ fraction in the other catchments listed above, as SOD can be particle size dependent (Bateman 2012).

After the sterilisation of the channel bed sediment by heating, its oxygen demand increased, suggesting that organic matter content rather than microorganism abundance in the sediment is the major control on its SOD_5 (objective 3). Organic matter is the primary nutrient input for respiration within streams (Jones et al. 1994). As such, differences in fish embryo survival and Alevin fitness characteristics when exposed to fine-grained sediment sampled from different sources have been explained by its organic matter content (Sear et al. 2016). However, rather than the oxygen demand of the channel bed sediment in the River Taw being primarily controlled by its source materials and their organic matter content, the ultra-fine colloidal fraction of the sediment exerts a disproportional effect on its overall oxygen demand. In the settling experiment, the SOD_5 of the most rapidly settling sediment was approximately double that of the dominant channel bank source and similar to that of agricultural topsoils, whilst that of the ultra-fine fraction was approximately eight times higher than that of channel bank material. This fraction may be composed of a significant proportion of algal material and other fine-grained seston which is continuously deposited onto the channel bed (Cushing et al. 1993; Wanner and Pusch 2000). Dissolved and particulate organic carbon can be classified into labile and refractory components, with the former being more available for microbial decay (Inekkot 1988). Phytoplankton can contribute towards both components (Jewell

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and McCarty 1971; Otsuki and Hanya 1972; Otten et al. 1992) and has been identified as an important source of dissolved organic matter in rivers and lakes (Song et al. 2019). Positive relationships have been found between oxygen demand, algae, and chlorophyll-a concentration (Heiskary and Markus 2001; MacPherson et al. 2007), although in some rivers this relationship is not present (Fallon and Brock 1979). In the Klamath River, USA, labile organic matter mostly associated with particulate algal material contributed most to BOD_5 (Sullivan et al. 2010), although in this specific case, the refractory component contributed more towards BOD over longer time periods. Against this background, it is likely that the ultra-fine fraction of the channel bed sediment identified as having a high oxygen demand in the River Taw study catchment contains much of this labile nano-plankton (2–20 μm) derived material.

Evidence suggests that most dissolved organic carbon in non-urbanised watersheds originates from terrestrial, rather than autochthonous, sources (Palmer et al. 2001; Hood et al. 2005; Cartwright 2010; Wilkinson et al. 2013). Additionally, research in the River Taw catchment by Upadhayay et al. (2022) used multiple biotracers to show a change in sediment source from channel banks to agricultural topsoils with extreme winter rainfall, also suggesting sediment-associated organic matter mostly originates from terrestrial sources. Most of such organic matter is, however, more likely to be transported out of the river catchment than to be broken down by biological processes (Webster et al. 1999). The ultra-fine fraction of the sediment may also have a higher autochthonous algal component than when examining a wider particle size range. The hypothesis that algae contribute significantly to SOD_5 is further supported by the lack of change in SOD_5 throughout the length of the River Taw despite significant change in potential catchment sediment sources (e.g., a change in the intensity of land use) suggesting the SOD_5 originates from a within-stream source that is largely independent of the catchment slope-to-channel sediment delivery cascade.

The ultra-fine fraction of sediment has a large mass-specific surface area which is subject to decomposition, increasing its SOD (House 2003), although some studies have shown reduced rates of bacterial respiration with decreasing particle size of organic matter derived from tree leaves (Yoshimura et al. 2008; Yoshimura et al. 2010; Wurzbacher et al. 2016). This may be linked to an increasing proportion of refractory material remaining by the time that the seston is reduced to a fine particle size (Amon and Benner 1996). Therefore, it is unclear how particle size effects might contribute to the increased oxygen demand in the ultra-fine fraction.

Some of the increased SOD_5 of the river channel bed fine matrix sediment, compared with its source materials, may also be a result of the preferential transport of organic matter rather than mineral sediment to the river channel. Whilst mineral sediment is likely to often originate from channel bank sources in UK streams (Pulley and Collins 2024), the organic fraction of sediments may come from alternative sources. For example, working in the River Taw, Upadhayay et al. (2022) found that, using biotracers, there was a substantial shift in contributions, from stream banks dominating (70% ± 5%) in the winter of 2018–19 to arable land dominating (52% ± 7%) in the extreme wet winter of 2019–20. However, a study on the North Wyke Farm Platform in the River Taw catchment by Upadhayay et al. (2021) did not show an enrichment in total carbon concentration when comparing the top 5 cm of the soil in grassland fields to sediment transported out of the field by runoff. Therefore, the effects of the preferential delivery of organic matter are probably unlikely to be of sufficient magnitude to explain the increased SOD_5 of the channel bed sediment, relative to source material samples, in the River Taw study catchment.

If the ultra-fine fraction of the sediment has a major algal or bacterial component which is contributing significantly to channel bed SOD_5, then improving river hydrological status through targeted catchment management may be challenging. Reducing the nutrient content of overlying waters and therefore growth of algae which can enter channel bed gravels may, however, deliver benefits (Carpenter 2008). An alternative approach is reducing the accumulation and storage of this material on the bed.

Channel bed sedimentation is controlled by the suspended sediment concentration of overlying waters, particle density, and the erosion/transport capacity of the stream (Vercruysse et al. 2017; Wilkes et al. 2019). This sediment ingress and egress is also highly dependent on the gravel framework of the riverbed, which determines the amount of fine sediment it can sequester, dependent on the availability of framework pore space and ease of infiltration (Wooster et al. 2008; Gibson et al. 2009). Reducing the overall deposition of silts on the channel bed through reduced loads is one potential route towards achieving this, as a channel bed framework composed of a range of particle sizes is required to provide a matrix in which ultra-fine material can be entrapped. Measures for reducing sediment deposition on channel beds include improving peak river velocities, which may remobilise deposited sediments and increase oxygen infiltration into the bed gravels (Stuart 1953; Olsson and Persson 1988; Sear et al. 2008; Pulley et al. 2016). However, high velocities have been shown to be an important mechanism for the infiltration of matrix sediments into deeper layers of the channel bed framework, so benefits of this approach are uncertain (Casas-Mulet et al. 2017). An additional complication is that very fine particulate organic material has been shown to have very short residence times on the channel bed. For example, Webster et al. (1999) calculated the standing stock of deposited organic matter in a woodland stream was replaced in 19 h. Only 1% of seston deposited in an Idaho stream was able to be recovered after 24 h had passed, by Cushing et al. (1993), and weighted mean residence times of very fine particulate organic matter were 2.2 days in a mountain stream in Idaho, US (Newbold et al. 2005). Therefore, increasing flows to exfiltrate fine-grained sediment from the channel bed is likely to deliver most benefits through increasing oxygen diffusion rather than removing the ultra-fine sediment with a high SOD, which may be quickly replenished. Fine sediment exfiltration will increase pore space in the channel bed framework, thereby limiting opportunities for ultra-fine material to be sequestered at all.

A range of interventions can be used to increase channel transport capacity for sediment to encourage fine matrix sediment exfiltration. These include, for example, the careful management of instream vegetation or the installation of woody material, which can be used to create reaches with higher flow velocity for increasing bed shear stress and bed sediment remobilisation

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(Gurnell et al. 2006; Osei et al. 2015; Parker et al. 2017). The removal of river channel obstructions including weirs can also increase localised water velocities (Lenders et al. 2016). Such management techniques are more self-sustaining than previous remedial approaches such as gravel washing, which provides a very short-term solution to fine matrix sediment ingress and retention at the treatment site.

5 | Conclusions

At a first glance, a reduction in channel bed fine matrix sediment SOD_5 appears as a potentially valuable aim for catchment management to target, which could help in the drive towards improving river ecological status. However, in systems such as the River Taw studied herein, SOD_5 does not significantly vary spatially in response to changing land use and agricultural practices despite a significant longitudinal transition in land use and intensity. Instead, the largest potential cause of increased SOD_5 is the accumulation of the ultra-fine fraction of the sediment, which is likely to originate from the entrapment of autochthonous algal material. Mitigating this source of SOD_5 could theoretically be achieved through reducing the nutrient concentration and productivity of overlying waters; however, a lack of significant difference in SOD_5 between upland semi-natural areas and downstream of agriculture and sewage treatment works in the River Taw suggests this approach has limited potential. Instead, rather than reducing the SOD_5 of the sediment deposited, reducing the overall mass of fine matrix sediment entrapped within the channel bed to increase oxygen diffusion and increase pore space in the bed framework, thereby limiting the retention of ultra-fine sediment, is likely to deliver greater benefits. Given that the efficacy of many interventions for reducing sediment delivery to rivers is reasonably limited and changing climate is resulting in extreme weather patterns capable of compromising that efficacy even further, a combination of source control and in-channel measures is required. In-channel measures focusing on increasing the exfiltration of fine matrix sediment would be priority here. Our findings serve as a timely reminder that mitigation of the sediment problem requires consideration of both the inorganic and organic fractions of fine-grained sediment.

Acknowledgements

Rothamsted Research receives strategic funding from UKRI-BBSRC (UK Research and Innovation-Biotechnology and Biological Sciences Research Council) and the data integration and production of this paper was funded by the institute strategic programme Resilient Farming Futures via grant award BB/X010961/1—specifically work package 2—BBS/E/RH/230004B; Detecting agroecosystem 'resilience' using novel data science methods.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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