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A rapid and inexpensive colour-based sediment tracing method incorporating hydrogen peroxide sample treatment as an alternative to quantitative source fingerprinting for catchment management

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ABSTRACT

Accessible sediment provenance information is highly desirable for guiding targeted interventions for reducing excess diffuse agricultural sediment losses to water. Conventional sediment source fingerprinting methods can provide this information, but at high cost, thereby limiting their widespread application for catchment management. The use of sediment colour measured using an office document scanner represents an easy, fast, and inexpensive alternative method to trace sediment sources. However, the potential for poor source discrimination and its non-conservatism due to enrichment in sediment organic matter content during sediment transport represent possible limitations to its use. As such, the treatment of samples using hydrogen peroxide to remove organic matter can potentially improve source discrimination based upon geology or soil type, and the mapping of differences in colour between source and sediment samples removing the need for a priori source groups, were trialled in a new colour-based tracing framework. The River Avon in southwest England and Holbeck/Wath Beck in northeast England were studied as they have been identified as being of high priority for the targeting of onfarm advice delivered through a long-running agri-environment initiative. In both catchments, colour was effective at identifying that a small proportion of each which would be considered as being low erosion risk was the dominant source of the sampled sediment. This was due to poor connectivity between fields deemed to be at high risk of erosion and stream channels. The hydrogen peroxide sample treatment confirmed that sediment colour was not significantly altered by enrichment in organic matter content. This treament and the mapped comparison between source and suspended sediment colour improved source discrimination allowing for the more spatially-refined identification of critical sediment source areas. It is argued that this new inexpensive procedure can potentially deliver more precise and reliable information to catchment managers than costly quantitative sediment source fingerprinting methods. This method can greatly increase the availability of catchment-specific sediment source data and therefore the robust targeting of management efforts on a national scale.

1. Introduction

A reduction in diffuse sediment losses from agriculture is needed to meet global water quality targets (Collins and Zhang, 2016; Davey et al., 2020). Whilst basic mandatory rules for farming to deliver good agricultural and environmental condition represent a starting point towards reducing these excessive losses, it is recognised that regulation alone is not sufficient to reach the desired environmental outcomes (Poole et al., 2013; Collins and Zhang, 2016). As a consequence, agri-environment initiatives are being increasingly used to achieve enhanced environmental outcomes through delivering advice for win-win solutions and grants to farmers for more costly interventions. Here, for example, between 2007 and 2013, over €22 billion of Common Agricultural Policy (CAP) payments in the EU were delivered through agri-environment initiatives. Similarly, the Conservation Security Program in the USA delivered \$8 billion in grants between 2009 and 2018 to initiate and maintain conservation measures. In the UK, the Catchment Sensitive Farming (CSF) initative has engaged with 19,776 farms covering 34% of England and has recently been expanded to cover the whole of the country with an annual budget increased from 15 m to £30 m. However, to deliver good value for the public purse, on-farm advice and grants must be targeted effectively to the most important sources of sediment

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within a catchment (Jones et al., 2017).

Variability in the dominant sources contributing to the sediment problem in different rivers and streams makes the prediction of which sediment sources to direct advice and mitigation options towards challenging and uncertain (Walling et al., 2008; Pulley and Collins, 2021a). Sediment source fingerprinting is a method by which the percentage contribution of different potential sources, based upon land use, soil type or geology, can be estimated, providing this much-needed information (Klages and Hsieh, 1975; Collins et al. 1997, 2017). The method has proven effective in many catchments and is experiencing increasing global uptake (Collins et al., 2020). However, state-of-the-art approaches are time consuming and expensive, and also have highly complex data analysis requirements including the application of various statistical procedures for source discrimination and mass balance models for source apportionment (Collins et al., 2017). As a result, the global use of this method to improve the delivery of catchment management measures continues to be hampered by the specialist skills and budgets required for studies using the latest detailed and resource demanding procedures (Mukundan et al., 2012).

Sediment colour and spectral fingerprints are increasingly being used for source tracing reducing the need for costly more conventional laboratory analyses (Martinez-Carreras et al., 2010; Barthod et al., 2015; Brosinsky et al., 2014; Evrard et al., 2019; Ramon et al., 2020; Amorim et al., 2021). In parallel, the use of an office document scanner for colour measurement is also experiencing increased uptake in research, removing the need for expensive specialist equipment and therefore greatly increasing the accessibility of the fingerprinting approach (Krein et al., 2003; Pulley and Rowntree, 2016; Pulley et al., 2019; García--Comendador et al., 2020). Here, a recent publication by Pulley and Collins (2021b) trialled the identification of sediment provenance using source and sediment colour presented in simple scatter plots reducing the need for complex statistical and modelling source estimation methods. It was found that the method produced useful sediment provenance data in six of the eight catchments studied in England and could potentially be as effective or more effective at identifying the sediment sources most in need of mitigation than state-of-the-art costly multi-tracer quantiative sediment fingerprinting. Similar scatter plots are also being increasing used with multiple sediment properties to gain an indication of sediment provenance, discrimination between potential sediment sources, and also to determine if tracers are conservative or are being transformed during sediment redistribution and transport (Oldfield and Wu, 2000; Pulley et al., 2015; Habibi et al., 2019; Kroese et al., 2020). There does, however, remain scope to further refine the qualitative use of sediment colour for source tracing as Pulley and Collins (2021b) found that colour failed in two catchments investigated due to poor source discrimination and tracer non-conservatism. One possible methodological improvement concerns sample treatment using hydrogen peroxide to remove organic matter (Pulley and Collins, 2018). This has the potential advantage of reducing the uncertainties associated with the enrichment of sediment-associated organic matter content during its redistribution and transport which can result in erroneous sediment provenance results (Koiter et al., 2018). It may also increase source discrimination based upon geology or soil type once the colour of organic matter, which is typically in high concentrations in land uses such as woodland or grassland, has been removed. An additional methodological development which has yet to be trialled with colour tracers is the direct comparison of mapped source and sediment properties as demonstrated by Pulley et al. (2017). This approach has the potential to qualitatively indicate the areas of a catchment most likely to be contributing sediment to a river channel without being constrained by a priori land use or geology based source groups, and therefore may be able to add precision to the identification of critical sediment source areas and reduce the risk of tracers being unable to discriminate between sediment sources sufficiently well to inform catchment management.

When these potential methodological improvements are considered

alongside the recent finding that the sources of <25 µm sediment did not change significantly with flow condition in most of the eight English catchments studied by Pulley and Collins (2021a) a further possibility is also raised. This concerns the fact that a short (~1–3 month) sampling campaign combined with rapid and inexpensive colour measurement can provide the critical sediment provenance information needed for supporting target catchment management within England and possibly elsewhere worldwide. Accordingly, here we trial this proposed new approach in two catchments in England and assess if it can provide the information necessary for supporting targeted mitigation through CSF as a current strategic agri-environment initative for addressing the water quality problem associated with modern intensive farming.

2. Materials and methods

2.1. Study sites

The catchments of the River Avon upstream of Patney village and Holbeck/Wath Beck were selected for study at the request of CSF as they are considered as high priority for targeted mitigation due to sediment related pressures on water quality. The River Avon study catchment (51°19′23.38″N; 1°53′46.46″W) has an area of 28.5 km² and is located in an area of low gradient land in southwest England surrounded by the uplands of the North Wessex Downs to the north and Sailsbury plain to the south. It is characterised by flat ground in the valley bottom underlain by greensand, alluvium and peat deposits, which is surrounded by chalk hills around the watershed (Fig. 1). The peat deposits are mostly adjacent to stream channels and often form their banks. Soils adjacent to the river channel are loamy and clayey floodplain soils with naturally high groundwater. Over the greensand, soils have a more sandy texture and are loamy and freely draining, whereas over most of the chalk geology, soils are freely draining loamy and lime-rich.

Cultivated fields dominate land use on the chalk hills and in the southern part of the catchment. The flat land adjacent to most ditches and stream channels over most of the peat and greensand geology is primarily utilised as grassland although some cultivated fields are also present (Fig. 1). At the time of sampling in early May 2021, most cultivated fields contained bare soil in preparation for maize germination. Other cereals such as wheat covered a smaller proportion of the catchment area. At the time of sampling, only ${\sim}5$ grassland fields were observed to contain livestock, which were mainly cattle. Field size generally varies according to land use, with large cultivated fields on the chalk hillslopes and small grassland fields in the flatter peat and greensand valley bottom area. Hedgerows dividing fields are typically narrow and consist of only a single row of trees or a wire fence which in many cases are unlikely to pose a significant barrier to sediment movement. The flat valley bottom area is drained extensively with dry ditches adjacent to the margins of many fields. Channel beds are mostly covered by gravels although in some places deposits of clay or peat from slumping banks are present. Thick sediment deposits on the channel bed are uncommon although can be found in vegetation patches or in pools at the stream margins at some locations. A canal and railway present two longitudinal barriers to sediment movement across the catchment. Streams are piped under these features permitting connectivity, although these sediment transport pathways are limited to six such locations. In the lowermost catchment, just upstream of Patney, levees and wide buffer strips are located between cultivated land and the river channel which appear likely to trap the majority of sediment mobilised from these fields. Riparian buffers are typically over 3 m in width in most of the remaining catchment.

The combined catchment of Holbeck and Wath Beck (area 105 km^2 ; $54^{\circ}11'36.43''$ N; $0^{\circ}54'47.82''$ W) is in the northeast of England to the south of the North Yorkshire Moors and contains part of the Upland Howardian Hills. The study catchment is characterised by a flat valley floor in the north which is underlain by clays, mudstone and superficial sand and gravel deposits, which covers approximately 30% of the



Fig. 1. Land use and geology in the River Avon study catchment upstream of Patney. Roads and rivers mapped from an Ordnance Survey 1:250,000 raster; elevation data from an Ordinance Survey Terrain 5 DTM, land use mapped in the field and derived from aerial photographs and the Crop Map of England (CROME; Rural Payments Agency, 2018); geology from the British Geological Survey Geology of Britain viewer (https://mapapps.bgs.ac.uk/geologyofbritain/home.html).



Fig. 2. Geology and land use in the Holbeck/Wath Beck study catchment. Roads and rivers mapped from an Ordnance Survey 1:250,000 raster; elevation data from an Ordnance Survey Terrain 5 DTM, land use mapped in the field and derived from aerial photographs and the Crop Map of England (CROME; Rural Payments Agency, 2018); geology from the British Geological Survey Geology of Britain viewer (https://mapapps.bgs.ac.uk/geologyofbritain/home.html).

catchment area. The valley floor is surrounded by sandstone and limestone hills which are most extensive in the south and cover the remaining 60% of the catchment area (Fig. 2). Wath Beck flows in a south-north direction from its source near the village of Terrington in the sandstone hills to its confluence with Holbeck close to the catchment outlet. The larger Holbeck rises to the southwest of Ampleforth village and flows to the east. It has five tributaries which, like Wath Beck, flow in a south-north direction from their source in the sandstone hills. Soils on the flat valley bottom are loamy with naturally high groundwater in the east and slowly permeable seasonally wet status in the west. At the furthest eastern extent of the valley bottom floor, loamy and clayey floodplain soils with naturally high groundwater are present as the beck crosses the floodplain of the large River Rye, which is ~ 1 km downstream of the sampling site. Soils on the hillslopes over the sandstone and limestone are freely draining acid loamy with a sandy texture.

Most of this study catchment is cultivated for wheat, barley, oats, potatoes, rape and field bean production, with a small number of fields used as grassland, which are mostly in the north and west. Grassland is mostly used for sheep grazing or hay production, and there is an outdoor pig farm located in the southeast of the catchment. Large patches of commercial pine forestry are located over the sandstone hills, with smaller areas of deciduous woodland also present in some areas. Stream banks generally have a gently sloped profile and were almost all well-vegetated during the sampling period in May–June 2021. Buffer strips were present between most cultivated land and river channels, although their width was variable, ranging from 20 m in the sandstone hills to only 5 m in the valley bottom.

2.2. Methods

Two time-integrating suspended sediment traps based upon the design of Phillips et al. (2000) were installed at the Environment Agency flow gauging station on the River Avon at Patney on the January 26, 2021 and emptied on May 4th, 2021 (Fig. 3). A trap was also installed 300 m downstream of the confluence of Holbeck/Wath Beck on May 7th, 2021 and one on May 14th, 2021. Both traps were emptied on June 14th, 2021 (Fig. 3). The traps were installed at the edge of the channel as deep as accessibility allowed, since river levels were high at the time of installation. One of the samplers in the River Avon failed to trap any

sediment and as such only a single sediment sample was available for analysis here. Flow data was obtained from the River Rye at Ness gauging station approximately 3 km upstream of its confluence with Holbeck/Wath Beck. When compared to typical winter high flows, discharge during the study period was low; however, on one day, mean daily flow exceeded the lowest mean daily discharge in the wet January of 2021 (Supplementary Figure 1). Therefore, the sampling period is likely to be reasonably representative of a period of relatively high rainfall and river discharge.

Ninety-six samples of potential sediment sources were retrieved in the River Avon and One hundred and thirty-three in Holbeck/Wath Beck (Fig. 3). The samples were retrieved from all major land uses as well as channel banks with the aim to sample all parts of the study catchments and all major geologies therein. This sampling strategy was deployed to allow for the qualitative interpretation of sediment sources based upon mapped differences between source and sediment colour using the methods of Pulley et al. (2017) rather than for tracing sources only according to land use and geology – a typical sampling strategy selected a priori by many previous source tracing studies reported in the international literature (Fig. 3). Approximately 100 g samples of cultivated, grassland and woodland topsoils were collected from the top 2 cm of the soil profile as a composite of three subsamples collected within a 5 m radius of the sampling point as this is the depth to which erosion processes are expected to operate (Evans et al., 2016). Channel bank samples were collected from the bottom two-thirds of visibly eroding banks to avoid contamination from surface material and assist maximum source discrimination. Where thick sediment deposits were observed on the channel beds of the River Avon, a grab sample was retrieved by hand to a depth of approximately 5 cm. Deep water in Holbeck and Wath Beck meant that it was not possible to collect bed sediment here.

Source and sediment samples were passed through a 25 μ m stainless steel mesh whilst still wet from the field. The samples were placed into a beaker with ~200 ml of water and disaggregated using a metal spatula before being gently rubbed through the sieve by hand. The <25 μ m fraction was selected for analysis to minimise the potential for particle size associated uncertainties (Pulley and Rowntree, 2016; Laceby et al., 2017). It was also found that 14.8 g of the 25.2 g of sediment collected by the time-integrating trap in the River Avon fell into the <25 μ m size range and 64 g of the 119 g collected in Holbeck/Wath Beck. The <25



Fig. 3. Source and suspended sediment sampling locations in the River Avon at Patney and Holbeck/Wath Beck.

 μ m fraction therefore represented over half of each study river's suspended sediment load, and importantly, as is the particle size fraction with the greatest potential for pollutant transport (Horowitz and Elrick, 1987). The fractionated samples were oven dried at 105 °C and disaggregated using a mechanised pestle and mortar. The prepared samples were packed into transparent polythene bags and images were captured of them using a Ricoh MP office document scanner. The values of reflected red and blue light in the RGB colourspace (0–255) were extracted using the Gimp 2 open-source image editing software (Krein et al., 2003; Pulley and Rowntree, 2016; Pulley and Collins, 2018).

The prepared samples were then treated using hydrogen peroxide to remove organic matter (Pulley and Collins, 2018). Approximately 0.2 g of each sample was placed into a 25 ml plastic centrifuge tube and 8 ml of 30% hydrogen peroxide was added. The samples were left to stand overnight before being heated at 80 °C for 4 h. The samples were then heated at 60 °C until dry and manually disaggregated using a pestle and mortar for colour measurement using the method described above.

The sediment colour data was interpreted using scatter plots of red

and blue with each potential sediment source group colour coded following the method described in Pulley and Collins (2021b). Plots were produced based upon catchment land use and geology and presented where colour was able to discriminate between at least two potential source groups. Additionally, maps of the percentage difference between the red value of each individual source sample and the mean value for the sediment samples were produced following the methods of Pulley et al. (2017).

3. Results

3.1. River Avon

Differences between the colour of potential sediment sources in the River Avon catchment are primarily based upon geology (Fig. 4). Soil colour can be observed to fall on a continuum from chalk with the highest reflected light and peat with the lowest. The colour of the soils over alluvium deposits appears to reflect that of its parent material



Fig. 4. Bi-plot of red and blue for the untreated (a) and hydrogen peroxide treated (b) $< 25 \,\mu$ m source and time-integrated suspended sediment samples from the River Avon at Patney study site. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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which is upslope of the sampling location. Land use has little impact on soil colour suggesting that the presence of the dark peat is masking any differences in colour associated with grassland compared to cultivated land. Channel banks have a colour which reflects their underlying geology and as such, there is no discrimination from surface sources.

The time-integrated suspended sediment has a colour most comparable to the source samples retrieved over the peat and greensand geology, but significantly lighter than channel bank material composed of pure peat, suggesting that topsoils in the south and centre of the study catchment dominate sediment losses to the river. The samples of sediment deposited on channel beds varied in colour; three samples were very dark and likely composed of collapsed adjacent peat deposits whilst the remaining samples had a similar colour to the suspended sediment. All of the bed sediment samples had a slightly higher colour blue value in relation to red when compared to most source samples suggesting the enrichment in its organic matter content. This indicates that sediment may be stored on the channel bed for some time, or alternatively, that organic matter is preferentially transported to the river from topsoil sources. This observation was also made for the time-integrated suspended sediment sample suggesting that it may have been stored on the channel beds before being transported during higher flows.

After hydrogen peroxide treatment, the sediment exhibited a similar provenance to when it was untreated suggesting that the enrichment in sediment organic matter content during its erosion and transport is not a significant source of uncertainty (Fig. 4b). Discrimination between chalk topsoils and other sources was reduced after the treatment, although still distinct. It is notable that most source samples fall on a straight line in the bi-plot with a consistent red:blue ratio; however, a group of samples took on a distinct orange colour after treatment with a low blue value in relation to red. When the red:blue ratio was mapped, these samples were mostly collected from cultivated land in the lower catchment; however, they do not form a distinct cluster which can be used to refine a sediment source area (Fig. 5). Nevertheless, the results show that the timeintegrated suspended sediment sample does not take on this red



Fig. 5. Mapped red:blue ratio after hydrogen peroxide treatment. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

colour after treatment and therefore the areas with red soil after treatment are not contributing significant amounts of sediment to the stream indicating non-uniform sediment losses across the valley floor. It was noted that the mapping of the percentage difference between sediment and source colour that this study aimed to test did not accurately identify the source samples taking on the red colour, and as such, the red:blue ratio was used.

3.2. Holbeck/Wath Beck

Source discrimination in the catchment of Holbeck/Wath Beck is entirely based on land use using colour with the untreated samples. Discrimination is provided by the amount of reflected light with woodland soils having a darker colour than cultivated and grassland soils (Fig. 6). Woodland soils also often have a lower red:blue ratio than the other sources providing additional discrimination. The woodland samples fall into two distinct clusters on the plot likely representing darker samples composed mostly of leaf litter and those with a shallower



Fig. 6. Bi-plot of red and blue for the untreated (a) and hydrogen peroxide treated (b) $<25~\mu m$ source and time-integrated suspended sediment samples grouped by land use from the Holbeck/Wath Beck study site. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

litter layer where the underlying soil is exposed. The colour of channel banks overlaps with cultivated topsoils although some samples have a particularly light colour, likely reflecting their low organic matter content. Some bank samples also have a darker colour suggesting that they may be composed of displaced topsoil material or that they reflect a specific underlying geology. Most grassland source samples have a colour falling between the cultivated and woodland samples. However, there is considerable overlap with the colour of cultivated soils meaning that discrimination between these two sources is poor. There was no discrimination between soils over different geologies using colour when the samples were untreated (Supplementary Fig. 1).

The two time-integrated suspended sediment samples have a colour falling along the edge of the range measured for the cultivated source samples and within the range of values measured for grassland samples suggesting that woodland is unlikely to be a major source of sediment entering the watercourses. The colour values on the edge of the range found in most agricultural soil samples suggest that sediment inputs to Wath Beck may be localised to a small area of the study catchment.

When treated with hydrogen peroxide, discrimination between land uses based upon colour remains, despite the destruction of organic matter (Fig. 5b). Cultivated soils throughout most of the study catchment took on a red colour after the treatment, but most woodland and many grassland samples did not and, as a result, have higher proportional reflected blue light. Therefore, discrimination between grassland and cultivated land becomes stronger after the treatment, and the colour of grassland soils becomes dissimilar to the time-integrated suspended sediment samples, making it possible to identify that sediment losses from grassland are likely to be minimal. As with the untreated samples, the colour of the suspended sediment samples falls on the edge of the range of values measured in the source samples suggesting localised inputs from cultivated land dominate sediment contributions. It was not possible to determine how much of the suspended sediment was likely to originate from channel banks using colour on either untreated or treated samples. However, channel banks were observed to be well-vegetated during the sampling period suggesting that erosion rates are likely to be low.

As the examination of the samples classified by land use identified that contributions of suspended sediment from grassland and woodland are likely to be minimal, only cultivated source samples were considered when attempting to refine key sediment source areas based upon geology after hydrogen peroxide treatment. Most cultivated soil samples took on a red-orange colour after the treatment; however, notably the time-integrated suspended sediment samples did not (Fig. 7). Almost all source samples from over the sandstone hills took on this red colour suggesting that sediment primarily originates from the valley bottom area.

When the percentage difference between the red value of the timeintegrated suspended sediment samples and each individual source sample was mapped, a trend of sources in the eastern valley floor having the most similar colour to the sediment samples was observed (Fig. 8). Some soil samples on the valley floor did, however, also take on a red colour after treatment, suggesting that sediment inputs from this critical area are likely to be spatially variable with some fields contributing more sediment than others.

4. Discussion

A critical management question fort the River Avon study site concerned whether the cultivated land over the sloped chalk geology was the dominant source of sediment contributing to the stream due to its higher potential erosion risk relative to other areas of the catchment. Typically, erosion rates on cultivated fields are significantly higher than on grassland and high slopes are associated with increased erosion (Evans et al., 2016; Evans et al., 2016); therefore, on a risk assessment basis, this source could feasibly be expected to dominate catchment sediment losses. Texture-based risk assessments do, however, run the risk of selecting incorrect priority areas for sediment management on account of the potential for a mismatch between erosion risk and importance as a source of sediment actually delivered to river channels (Collins and Walling, 2004). Against this context, the tracing results showed that the high-risk arable source on chalk geology was not contributing significantly to the sampled suspended sediment. This finding can be explained by the observation that the chalk hills are separated from most drainage channels by flat land over the greensand and peat geologies. Sediment eroded from the chalk hills therefore lacks connectivity pathways through which to reach watercourses.

With the most visibly high-risk fields discounted as a source of fine sediment in the local streams, the flat valley bottom land over the greensand and peat geologies was identified as the most important suspended sediment source. As this area is mostly used as grassland, most of which is not being presently grazed, options for mitigating sediment losses here are limited. The finding that sediment inputs from this area are not heterogenous does, however, raise the possibility that some fields erode disproportionally and could be targeted for mitigation.



Fig. 7. Bi-plot of red and blue for the hydrogen peroxide treated ${<}25~\mu m$ cultivated land use source and time-integrated suspended sediment samples grouped by geology from the Holbeck/Wath Beck study site. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 8. The mapped percentage difference between the red value of each individual source sample and the time-integrated suspended sediment samples after hydrogen peroxide treatment; red symbols are more likely to contribute sediment to the beck. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

At the time of sampling, bare soils were present on most cultivated land due to maize production; therefore, if maize production continues to feature in the cropping regimes of local farms, targeted soil cover and management options such as under-sowing with grass and compaction management should be encouraged as part of on-farm advice for water quality. Additionally, delivery pathway interception should also be encouraged. Here, the finding that many of these maize fields are not likely to be contributing sediment to the river means that any in- or edge-of-field interventions would need to be targeted appropriately rather than in a blanket fashion for this specific crop.

Approximately 60% of the Holbeck/Wath Beck study catchment is covered by sandstone hills which have a high erosion risk sandy overlying soil texture and are predominantly cultivated thereby enhancing that erosion risk. Again, however, the source tracing indicated that suspended sediment contributions from this area were low. As with the chalk hills in the River Avon study area, this finding can be explained firstly by a low stream density and absence of artificial draining ditches, meaning that most fields are not adjacent to a watercourse. The stream channels here are also often bordered by low erosion risk woodland or grassland fields meaning that few cultivated fields are adjacent to watercourses despite their covering much of the sandstone hills area. Additionally, woodland covers a large proportion of the sandstone hills area and does not contribute much sediment to the becks due to its low erosion risk. Whilst most hedgerows are narrow, and many field margins only consist of a wire fence, a significant number of well-vegetated field margins are also present representing additional barriers to sediment transport across the landscape. Riparian grassland and woodland buffer strips are also extensively present where cultivated fields are adjacent to river channels. These are often more than 20 m in width and much wider patches of unmanaged grassland are not uncommon. There are also two lakes disrupting longitudinal connectivity meaning that the $\sim 10\%$ of the sandstone hills area upstream of these lakes cannot contribute sediment to the beck. Therefore, despite the large area of the study catchment being covered by the sandstone hills, and the corresponding high texture-based erosion risk, there are few places where sediment-laden runoff from this area is likely to enter watercourses.

When compared to the sandstone hills area, the density of stream channels on the valley floor which the source tracing identified as the most important sediment source, is significantly higher and some artificial ditches are present meaning that more fields are adjacent to watercourses. Additionally, woodland and grassland are much less common here, resulting in a higher proportion of the stream banks being adjacent to cultivated fields. Riparian buffers are present but are often much narrower than in the sandstone hills area with a typical width of only \sim 6 m. The higher contribution of suspended sediment from the eastern side of the valley floor area, when compared to the west, is likely a result of its larger size and greater density of stream channels. Grassland is also more abundant in the western side of the study catchment which represents a lower erosion risk. Advice delivered through CSF should therefore clearly target the eastern valley floor area of the study catchment to improve the cost: benefit of on-farm interventions.

Collectively, the new work herein clearly demonstrates the challenges associated with predicting which sources dominate catchment scale sediment contributions to streams based on texture-based and perceived (e.g., crop type) erosion risk. In both study catchments, connectivity was indicated to be the major control on suspended sediment sources rather than erosion risk. Connectivity is being increasingly recognised as a framework to understand sediment transport through a catchment but is difficult to quantify (Turnbull et al., 2018; Hooke and Souza, 2021). As a result, the longstanding aim of scientific researchers and catchment managers to predict the relative importance of sediment sources accurately through walkover surveys, field observations, mapping, modelling and application of erosion risk typologies, is likely to remain challenging until a greater amount of sediment source data is available. In this context, a more widespread strategic application of the low-cost source tracing method described herein provides an

alternative, pragmatic solution to improving the extent of a reliable and compelling evidence base for decision-making focussed on sediment management.

In both study catchments, hydrogen peroxide sample treatment provided distinct benefits over the analysis of untreated samples alone. Firstly, it confirmed that the enrichment of sediment-associated organic matter was not a major source of uncertainty associated with the use of colour in either catchment. Such enrichment has been identified as a major source of concern associated with the use of most tracer types (Collins et al., 2017; Koiter et al., 2018). In both study sites, it also improved source discrimination and the refinement of critical sediment source areas for targeting through CSF. In the River Avon study catchment, the use of the treatment identified that suspended sediment losses from the valley bottom area were not homogenous. In Holbeck/Wath Beck, it was able to improve discrimination between cultivated land and grassland, as well as allowing for the tracing of sediment sources based upon geology, critically providing a basis for confirming cultivated fields the eastern valley floor as the likely dominant source of sampled sediment. Beyond this work, Tiecher et al. (2019) used different phosphorus fractions to trace sediment sources in southern Brazil indicating that similar sample treatments can be applied successfully with other tracer types in future source fingerprinting research. One potential risk associated with the hydrogen peroxide treatment is that there is the incomplete destruction of organic matter. In this study an excess of hydrogen peroxide was used to minimise this risk and the fine particle size of the fractionated samples removed any larger pieces of organic matter. However, repeated treatments may be required if a coarser particle size fraction is used, or organic matter is resistant to decomposition by the treatment.

The mapping of the differences between source and suspended sediment colour was also critical for the assessment of sediment provenance in both study catchments, although in the River Avon, this method had to be modified to mapping the red:blue ratio of the source samples to provide optimum information. Many published sediment source fingerprinting studies only base source groups *a priori* upon land use or geology. Taking such an approach in the two study catchments herein would have limited the conclusions which could be reached and therefore the usefulness of the results for catchment management. Whilst also tracing using geology-based source groups would have delivered much more information it would not have been sufficient to isolate the eastern valley floor critical source area in Holbeck/Wathbeck or identify non-uniform sediment losses from the valley floor areas in both catchments.

One limitation of the trialled method is that in the River Avon study catchment, all source samples fell on a straight line on both the untreated and hydrogen peroxide treated scatter plots meaning that equifinality related uncertainties were potentially present. As the suspended sediment sample clearly fell within the range of colours found for the non-chalk topsoils, this was unlikely to be a major source of uncertainty. However, with a greater number of sediment source groups, the use of only two correlated tracers could be insufficient to determine sediment sources reliably.

Based upon our results, we argue that the colour-based tracing approach trialled here can potentially deliver more spatially-refined information with less uncertainty than a state-of-the-art quantitative sediment source fingerprinting approach. The specific advantages are that:

- Sediment colour is inexpensive to measure meaning more individual source samples can be analysed for the same cost increasing the representativeness of sampling and potential to refine critical source areas based upon mapped source properties.
- Organic matter is removed from the samples reducing the potential for uncertainty from its enrichment during sediment mobilisation and delivery.

- Colour is controlled by the major components of soils and sediments meaning that small changes to sediment composition due to withinstream chemical conditions or particle size selectivity are likely to have less of an impact when compared to the measurement of low concentrations of trace soil constituents.
- The hydrogen peroxide treatment of samples allows for a single inexpensive tracer type to potentially discriminate based on both land use and on geology further refining the identification of critical source areas for targeted catchment management.
- The interpretation of sediment sources is not constrained by predefined source groups.
- Uncertainties associated with quantitative source apportionment and the use of different un-mixing modelling approaches (i.e., frequentist or Bayesian) are removed.
- Issues of equifinality and limited source discrimination which are often poorly recognised and discussed explicitly in quantitative sediment fingerprinting studies are clearly visible to the researcher and the end user.

5. Conclusions

Sediment colour was effective at providing the critical sediment source information needed for the targeted delivery of advice and capital grants through CSF in both study catchments. Reductions in uncertainty and increased precision in the identification of critical source areas was added by the hydrogen peroxide treatment of samples and the mapping of sediment colour without the *a priori* selection of source groups. Therefore, these developments have the potential to greatly increase the utility of sediment colour as a simple and inexpensive tracer.

The low-cost tracing approach trialled here can arguably refine understanding of critical sediment source areas with less uncertainty than a costly conventional quantitative sediment fingerprinting study. Researchers and catchment managers should therefore assess carefully if the ability to apportion contributions from sediment sources numerically provides sufficient benefits over a simple colour-based approach especially in the context of the higher costs. The method trialled herein could also act as a preliminary stage in a sediment tracing study before the application of additional targeted tracers aimed at answering outstanding sediment provenance questions. This might include, for example, the use of ¹³⁷Cs to discriminate between surface and subsurface sources.

A lack of affordable, accessible and reliable site-specific sediment source data has been recognised as a major limitation to delivering greater cost-benefit from catchment management strategies. The method trialled herein, however, has the potential to provide this information at low cost and at scale, meaning there should be greater scope for delivering significant environmental benefits to address the widespread problem of excess fine sediment delivery to rivers and streams.

Credit author statemant

Pulley S: Conceptualization, Methodology, Investigation, Writing – original draft, Funding acquisition. **Collins AL:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Simon Pulley reports financial support was provided by Environment Agency.

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Appendix A. Supplementary data

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References

- Amorim, F.F., da Silva, Y.J.A.B., Nascimento, R.C., da Silva, Y.J.A.B., Tiecher, T., do Nascimento, C.W.A., Minella, J.P.G., Zhang, Y., Upadhayay, H.R., Pulley, S., Collins, A.L., 2021. Sediment source apportionment using optical property composite signatures in a rural catchment, Brazil. Catena 202, 105208. https://doi. org/10.1016/j.catena.2021.105208.
- Barthod, L.R., Liu, K., Lobb, D.A., Owens, P.N., Martínez-Carreras, N., Koiter, A.J., Petticrew, E.L., McCullough, G.K., Liu, C., Gaspar, L., 2015. Selecting color-based tracers and classifying sediment sources in the assessment of sediment dynamics using sediment source fingerprinting. J. Environ. Qual. 44, 1605–1616. https://doi. org/10.2134/jeq2015.01.0043.
- Brosinsky, A., Foerster, S., Segl, K., Kaufmann, H., 2014. Spectral fingerprinting: sediment source discrimination and contribution modelling of artificial mixtures based on VNIR-SWIR spectral properties. J. Soils Sediments 14, 1949–1964. https:// doi.org/10.1007/s11368-014-0925-1.
- Collins, A.L., Blackwell, M., Boeckx, P., Chivers, C.A., Emelko, M., Evrard, O., Foster, I., Gellis, A., Gholami, H., Granger, S., Harris, P., Horowitz, A.J., Laceby, J.P., Martinez-Carreras, N., Minella, J., Mol, L., Nosrati, K., Pulley, S., Silins, U., da Silva, Y.J., Stone, M., Tiecher, T., Upadhayay, H.R., Zhang, Y., 2020. Sediment source fingerprinting: benchmarking recent outputs, remaining challenges and emerging themes. J. Soils Sediments 20, 4160–4193. https://doi.org/10.1007/s11368-020-02755-4.
- Collins, A.L., Pulley, S., Foster, I.D.L., Gellis, A., Porto, P., Horowitz, A.J., 2017. Sediment source fingerprinting as an aid to catchment management: a review of the current state of knowledge and a methodological decision-tree for end-users. J. Environ. Manag. 194, 86–108. https://doi.org/10.1016/j.jenvman.2016.09.075.
- Collins, A.L., Walling, D.E., Leeks, G.J.L., 1997. Source type ascription for fluvial suspended sediment based on a quantitative composite fingerprinting technique. Catena 29, 1–27. https://doi.org/10.1016/S0341-81629600064-1.
- Collins, A.L., Walling, D.E., 2004. Documenting catchment suspended sediment sources: problems, approaches and prospects. Prog. Phys. Geogr. 28, 159–196. https://doi. org/10.1191/0309133304pp409ra.
- Collins, A.L., Zhang, Y., 2016. Exceedance of modern 'background' fine-grained sediment delivery to rivers due to current agricultural land use and uptake of water pollution mitigation options across England and Wales. Environ. Sci. Pol. 61, 61–73. https:// doi.org/10.1016/j.envsci.2016.03.017.
- Davey, A.J.H., Bailey, L., Bewesm, V., Mubaiwa, A., Hall, J., Burgess, C., Dunbar, M.J., Smith, P.D., Rambohul, J., 2020. Water quality benefits from an advice-led approach to reducing water pollution from agriculture in England. Agric. Ecosyst. Environ. 296, 106925. https://doi.org/10.1016/j.agee.2020.106925.
- Evans, R., Collins, A.L., Foster, I.D.L., Rickson, R.G., Anthony, S.G., Brewer, T., Deeks, L., Newell-Price, J.P., Truckell, I.G., Zhang, Y., 2016. Extent, frequency and rate of water erosion of arable land in Britain – benefits and challenges for modelling. Soil Use Manag. 32 (Suppl. 1), 149–161. https://doi.org/10.1111/sum.12210.
- Evrard, O., Durand, R., Foucher, A., Tiecher, T., Sellier, V., Onda, Y., Lefevre, I., Cerdan, O., Laceby, J.P., 2019. Using spectrocolourimetry to trace sediment source dynamics in coastal catchments draining the main Fukushima radioactive pollution plume (2011-2017). J. Soils Sediments 19, 3290–3301. https://doi.org/10.1007/ s11368-019-02302-w.
- García-Comendador, J., Martínez-Carreras, N., Fortesa, J., Borràs, A., Calsamiglia, A., Estrany, J., 2020. Analysis of post-fire suspended sediment sources by using colour parameters. Geoderma 379, 114638. https://doi.org/10.1016/j. geoderma.2020.114638.
- Habibi, S., Gholami, H., Fathabadi, A., Jansen, J.D., 2019. Fingerprinting sources of reservoir sediment via two modelling approaches. Sci. Total Environ. 663, 78–96. https://doi.org/10.1016/j.scitotenv.2019.01.327.
- Hooke, J., Souza, J., 2021. Challenges of mapping, modelling and quantifying sediment connectivity. Earth Sci. Rev. https://doi.org/10.1016/j.earscirev.2021.103847, 103847.
- Horowitz, A.J., Elrick, K.A., 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Appl. Geochem. 2, 437–451. https://doi.org/10.1016/0883-2927(87)90027-8.

- Jones, J.I., Murphy, J.F., Anthony, S.G., Arnold, A., Blackburn, J.H., Duerdoth, C.P., Hawczak, A., Hughes, G.O., Pretty, J.L., Scarlett, P.M., Gooday, R.D., Zhang, Y.S., Fawcett, L.E., Simpson, D., Turner, A.W.B., Naden, P.S., Skates, J., 2017. Do agrienvironment schemes result in improved water quality? J. Appl. Ecol. 54, 537–546. https://doi.org/10.1111/1365-2664.12780.
- Klages, M.G., Hsieh, Y.P., 1975. Suspended solids carried by the gallatin river of southwestern Montana: II. Using mineralogy for inferring sources. J. Environ. Qual. 4, 68–73. https://doi.org/10.2134/jeq1975.00472425000400010016x.
- Koiter, A.J., Owens, P.N., Petticrew, E.L., Lobb, D.A., 2018. Assessment of particle size and organic matter correction factors in sediment source fingerprinting investigation. 2017. IEEE INFORMATION INFORMA
- investigations: an example of two contrasting watersheds in Canada. Geoderma 325, 195–207. https://doi.org/10.1016/j.geoderma.2018.02.044.
- Krein, A., Petticrew, E., Udelhoven, T., 2003. The use of fine sediment fractal dimensions and colour to determine sediment sources in a small watershed. Catena 53, 165–179. https://doi.org/10.1016/S0341-8162(03)00021-3.
- Kroese, J.S., Batista, P.V.G., Jacobs, S.R., Breuer, L., Quinton, J.N., Rufino, M.C., 2020. Agricultural land is the main source of stream sediments after conversion of an African montane forest. Sci. Rep. 10, 14827. https://doi.org/10.1038/s41598-020-71924-9.
- Laceby, J.P., Evrard, O., Smith, H.G., Blake, W.H., Olley, J.M., Minella, J.P.G., Owens, P. N., 2017. The challenges and opportunities of addressing particle size effects in sediment source fingerprinting: a review. Earth Sci. Rev. 169, 85–103. https://doi.org/10.1016/i.earscirev.2017.04.009.
- Martinez-Carreras, N., Krein, A., Gallart, F., Iffly, J.F., Pfister, L., Hoffmann, L., Owens, P. N., 2010. Assessment of different colour parameters for discriminating potential suspended sediment sources and provenance: a multi-scale study in Luxembourg. Geomorphology 118, 118–129. https://doi.org/10.1016/j.geomorph.2009.12.013.
- Mukundan, R., Walling, D.E., Gellis, A.C., Slattery, M.C., Radcliffe, D.E., 2012. Sediment source fingerprinting: transforming from a research tool to a management tool. J. Am. Water Resour. Assoc. 48, 1241–1257. https://doi.org/10.1111/j.1752-1688.2012.00685.x.
- Oldfield, F., Wu, R., 2000. The magnetic properties of the recent sediments of Brothers Water, N W England. J. Paleolimnol. 23, 165–174. https://doi.org/10.1023/A: 1008049419623.
- Phillips, J.M., Russell, M.A., Walling, D.E., 2000. Time-integrated sampling of fluvial suspended sediment: a simple methodology for small catchments. Hydrol. Process. 14, 2589–2602. https://doi.org/10.1002/1099-10852000101514:14<2589::AID-HYP94>3.0.CO;2-D.
- Poole, A.E., Bradley, D., Salazar, R., Macdonald, D.W., 2013. Optimizing agrienvironment schemes to improve river health and conservation value. Agric. Ecosyst. Environ. 181, 157–168. https://doi.org/10.1016/j.agee.2013.09.015.
- Pulley, S., Collins, A.L., 2018. Tracing fine sediment sources in a temperate agricultural catchment, UK, using the new SIFT (SedIment Fingerprinting Tool) open source

software. Sci. Total Environ. 653, 838-858. https://doi.org/10.1016/j. scitotenv.2018.04.126.

- Pulley, S., Collins, A.L., 2021a. Can agri-environment initiatives control sediment loss in the context of extreme winter rainfall? J. Clean. Prod. 311, 127593. https://doi.org/ 10.1016/j.jclepro.2021.127593.
- Pulley, S., Collins, A.L., 2021b. The potential for colour to provide a robust alternative to high-cost sediment source fingerprinting: assessment using eight catchments in England. Sci. Total Environ. 792, 148416. https://doi.org/10.1016/j. scitoteny.2021.148416.
- Pulley, S., Foster, I.D.L., Rowntree, K., 2015. Conservatism of mineral magnetic signatures in farm dam sediments in the South African Karoo; the potential effects of particle size and post depositional diagenesis. J. Soils Sediments 15 (12), 2387–2397. https://doi.org/10.1007/s11368-015-1265-5.
- Pulley, S., Goubet, A., Moser, I., Browning, S., Collins, A.L., 2019. The sources and dynamics of fine-grained sediment degrading the Freshwater Pearl Mussel (Margaritifera margaritifera) beds of the River Torridge, Devon, UK. Sci. Total Environ. 657, 420–434. https://doi.org/10.1016/j.scitotenv.2018.11.401.
- Pulley, S., Rowntree, K., 2016. The use of an ordinary colour scanner to fingerprint sediment sources in the South African Karoo. J. Environ. Manag. 165, 253–262. https://doi.org/10.1016/j.jenvman.2015.09.037.
- Pulley, S., Van Der Waal, B., Collins, A.L., Foster, I.D.L., Rowntree, K., 2017. Are source groups always appropriate when sediment fingerprinting? The direct comparison of source and sediment samples as a methodological step. River Res. Appl. 33 (10), 1553–1563. https://doi.org/10.1002/rra.3192.
- Ramon, R., Evrard, O., Laceby, J.P., Caner, L., Inda, A.V., de Barros, C.A.P., Minella, J.P. G., Tiecher, T., 2020. Combining spectroscopy and magnetism with geochemical tracers to improve the discrimination of sediment sources in a homogeneous subtropical catchment. Catena 195, 104800. https://doi.org/10.1016/j. catena.2020.104800.
- Rural Payments Agency, 2018. Crop Map of England (CROME) 2018. https://data.gov. uk/dataset/fb19d34f-59e6-48e7-820a-fe5fda3019e5/crop-map-of-england-crome -2018. (Accessed 15 April 2021). accessed.
- Tiecher, T., I Ramon, R., Laceby, J.P., Evrard, O., Minella, J.P.G., 2019. Potential of phosphorus fractions to trace sediment sources in a rural catchment of Southern Brazil: comparison with the conventional approach based on elemental geochemistry. Geoderma 337, 1067–1076. https://doi.org/10.1016/j. geoderma.2018.11.011.
- Turnbull, L., Hütt, M.T., Ioannides, A.A., Kininmonth, S., Poeppl, R., Tockner, K., Bracken, L.J., Keesstra, S., Liu, L., Masselink, R., Parsons, A.J., 2018. Connectivity and complex systems: learning from a multi-disciplinary perspective. Appl. Netw. Sci. 3, 47. https://doi.org/10.1007/s41109-018-0067-2.
- Walling, D.E., Webb, B.W., Shanahan, J., 2008. Investigations into the Use of Critical Sediment Yields for Assessing and Managing Fine Sediment Inputs into Freshwater Ecosystems. Natural England Research Report NERR007. Natural England, Sheffield.