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Seasonal variability of sediment controls of carbon cycling in an agricultural stream

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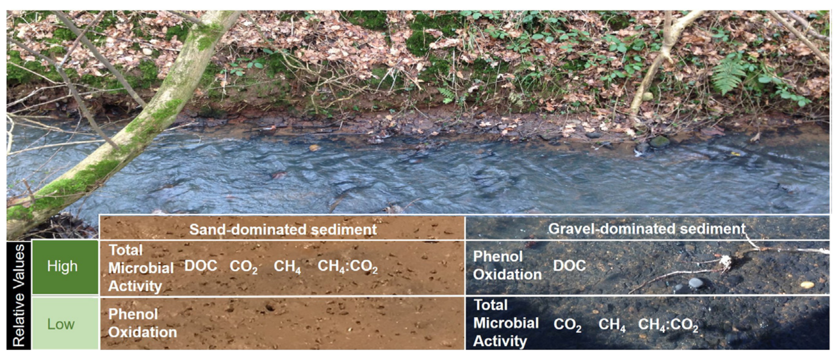
HIGHLIGHTS

- Controls of streambed carbon cycling on CO_2 and CH_4 are insufficiently understood.
- Drivers determined in stream sediment incubations and porewater observations.
- Sand sediments had higher microbial activity, CO_2 and CH_4 than gravel sediment.
- CO_2 and CH_4 were not greatly affected by season.
- Sediment type is a strong control on streambed CO_2 and CH_4.

GRAPHICAL ABSTRACT



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ABSTRACT

Streams and rivers are 'active pipelines' where high rates of carbon (C) turnover can lead to globally important emissions of carbon dioxide (CO_2) and methane (CH_4) from surface waters to the atmosphere. Streambed sediments are particularly important in affecting stream chemistry, with rates of biogeochemical activity, and CO_2 and CH_4 concentrations far exceeding those in surface waters. Despite an increase in research on CO_2 and CH_4 in streambed sediments there is a lack of knowledge and insight on seasonal dynamics. In this study the seasonally variable effect of sediment type (sand-dominated versus gravel-dominated) on porewater C cycling, including CO_2 and CH_4 concentrations, was investigated. We found high concentrations of CO_2 and CH_4 in the streambed of a small agricultural stream. Sand-dominated sediments were characterised by higher microbial activity and CO_2 and CH_4 concentrations than gravel-dominated sediments, with CH_4:CO_2 ratios higher in sand-dominated sediments but rates of recalcitrant C uptake highest in gravel-dominated sediments. CO_2 and CH_4 concentrations were unexpectedly high year-round, with little variation in concentrations among seasons. Our results indicate that small, agricultural streams, which generally receive large amounts of fine sediment and organic matter (OM), may contribute greatly to annual C cycling in freshwater systems. These results should be considered in future stream management plans where the removal of sandy sediments may perform valuable ecosystem services, reducing C turnover, CO_2 and CH_4 concentrations, and mitigating greenhouse gas (GHG) production.

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1. Introduction

Since streams and rivers have been recognised as 'active pipelines', where biogeochemical processes alter solutes transported in their water, there has been an increased interest in their role in the carbon (C) cycle (Battin et al., 2009; Cole et al., 2007; Comer-Warner et al., 2018; Raymond et al., 2013; Trimmer et al., 2012). C turnover in streams is substantial, with a large portion of C released directly to the atmosphere annually as carbon dioxide (CO_2) through gas exchange (Cole et al., 2007; Striegl et al., 2012; Tranvik et al., 2009; Trimmer et al., 2012). The C turnover in streams and rivers is predominantly due to microbial and plant respiration, producing CO_2 as well as methane (CH_4). The production of greenhouse gases (GHGs) in streams results in surface waters which are often supersaturated with respect to the atmosphere (Crawford and Stanley, 2016; Frankignoulle et al., 1998; Kling et al., 1991; Maurice et al., 2017; Park et al., 1969; Raymond et al., 1997, 2013; Sanders et al., 2007), resulting in CO_2 outgassing from streams and rivers (Richey et al., 2002).

Streams and rivers are recognised as globally important with respect to C emissions, contributing 1.8 Pg CO_2-C yr^{-1} (Raymond et al., 2013), and 26.8 Tg CH_4-C yr^{-1} (Stanley et al., 2016) into the atmosphere. The flux of CH_4 is relatively small compared to the CO_2 flux, however, when considered as C equivalents in terms of its global warming potential on mole per mole basis, it may offset over 25% of the terrestrial C sink, and CH_4 fluxes can be regionally significant (Bastviken et al., 2011; Crawford et al., 2014a; Panneer Selvam et al., 2014). Small streams have been found to be of disproportionate importance, and are estimated to contribute ~15% of the annual CO_2 flux from streams and rivers (Raymond et al., 2013).

The majority of research into GHG production in streams and rivers has focussed on surface water fluxes to the atmosphere (Rasera et al., 2008; Hotchkiss et al., 2015; Raymond et al., 2013; Richey et al., 2002). However, stream sediments are 'hotspots' of nutrient spiralling and metabolic activity, with 40 to 90% of total stream metabolism resulting from hyporheic exchange (Battin et al., 2003), producing enhanced rates of C turnover (Krause et al., 2013; Lautz and Fanelli, 2008; McClain et al., 2003; Trimmer et al., 2012).

Increased C turnover in streambed leads to higher GHG concentrations in sediments and surface waters respectively, with concentrations as high as 5 mmol CO_2 l^{-1} and 134 μmol CH_4 l^{-1} observed in streambeds (Hlaváčová et al., 2005; Trimmer et al., 2009). Despite recent research indicating the global importance of C emissions from streams and rivers, as well as observations of elevated concentrations in porewaters relative to surface waters, the importance of streambed contributions to overall C emissions and drivers of enhanced concentrations in sediments remain insufficiently understood (Battin et al., 2009; Cole et al., 2007; Comer-Warner et al., 2018; Striegl et al., 2012; Trimmer et al., 2012; Yvon-Durocher et al., 2011). Developing this understanding is of increasing importance given projected changes in climate and land use, which are expected to increase CO_2 and CH_4 production in the future (Acuña et al., 2008; Kaushal et al., 2010; Orr et al., 2015; Stanley et al., 2016; Venkiteswaran et al., 2014).

As end-products of respiration, CO_2 and CH_4 concentrations in streambeds are controlled by multiple drivers such as microbial metabolic activity, residence time, temperature, substrate (e.g. C and nitrogen) and terminal electron acceptor availability (e.g. Brunke and Gonser, 1997; Fischer et al., 2005; Marzadri et al., 2013;). Residence time and redox conditions are primarily controlled by sediment type, with less conductive sand and finer sediments typically resulting in higher residence times (Baker et al., 2000), and more anoxia (Baker et al., 2000; Boulton et al., 1998), than hydraulically more conductive gravel sediments.

Streambed sediments, furthermore, greatly affect CO_2 and CH_4 production, with fine sediments acting as a source of both CO_2 and CH_4 (Crawford and Stanley, 2016; Jones and Mulholland, 1998; Sanders et al., 2007; Stanley et al., 2016; Trimmer et al., 2009), and coarse, gravel sediments acting as a source of CO_2 and a sink of CH_4 (Trimmer et al., 2010). CH_4 production in particular is heavily influenced by fine, organic matter (OM)-rich sediments (Baulch et al., 2011; Sanders et al., 2007; Sawakuchi et al., 2014; Stanley et al., 2016), which are often present in streams of agricultural catchments (Stanley et al., 2016). In addition to autochthonous OM sources, C cycling in agricultural streams is significantly influenced by the quantity and quality of organic C entering the stream (Graeber et al., 2012; Romeijn et al., 2019; Stanley et al., 2012).

This study investigates streambed C cycling in a lowland stream that is fed by a predominantly agricultural catchment. We aim to identify and analyse the factors controlling the production of streambed CO_2 and CH_4. We specifically determine the seasonally variable impact of predominant sediment type (sand-dominated versus gravel-dominated) on site-scale CO_2 and CH_4 concentrations observed in streambeds under varying temperature and substrate availability.

2. Materials and methods

2.1. Study site

Field experiments of this study were conducted at the Wood Brook at the Birmingham Institute of Forest Research, Staffordshire, UK (https://www.birmingham.ac.uk/research/activity/bifor/index.aspx). The Wood Brook is a small, lowland stream, located in a mixed-use catchment where most of the area was arable land used predominantly for wheat in 2016 and for grass in 2017, with patches of deciduous woodland (Fig. 1a). The experiments focussed on a 700 m section of the Wood Brook, which flows through arable land before entering the study area. The study area itself is located at the border between arable land and mature deciduous woodland, so that at the upstream end of the study area the stream is bordered by fields on one side and woodland on the other, before flowing into the woodland so that further downstream there is some woodland between the stream and the arable land. The regional groundwater aquifer is Permo-Triassic sandstone on top of which are glacial till deposits (up to 10 m depth) overlain by sandy clay sediment between 0.15 and 0.6 m depth (Blaen et al., 2017).

2.2. Laboratory incubation experiments

Field sediments were collected and incubated to investigate substrate, environmental and physical controls on streambed cycling. Fluorescein diacetate (FDA) hydrolysis and extracellular phenol oxidase activity provide information on substrate controls on microbial activity, and C and N uptake. FDA hydrolysis includes the activity of proteases, lipases and esterases in soils and sediments, which represents microbial-mediated organic C turnover and decomposition rates, through the secretion of these extra-cellular enzymes. Sediment type can have a large influence on the quality and quantity of organic C, and thus FDA can be used as a surrogate of total microbial activity and organic C decomposition to understand biogeochemical reactivity (Sinsabaugh and Findlay, 1995; Schnürer and Rosswall, 1982). This is particularly important in hyporheic sediments, where enzyme activity is poorly studied. Extracellular phenol oxidase activity is used to indicate the microbial decomposition of aromatic phenolic compounds for the procurement of C and nutrients, particularly N (Sinsabaugh, 2010). This assay predominantly captures the activity of tyrosinase, monophenol oxidase and laccase enzymes, where phenolic compounds are oxidized using O_2 as a terminal electron acceptor.

Sediments were collected at two locations in June 2015, gravel-dominated sediments were collected from site 3 and sand-dominated sediments representative of those in sites 1 and 2 were collected 15 m upstream in a section of the stream with woody debris (Fig. 1a). An AMS slide hammer (5 cm dia.) and trowel were used to collect five pseudo-replicate sediment samples from between 0 and 10 cm depth at each site. Sediment samples were homogenised and sieved (2 mm) within 36 h of collection and stored cold.

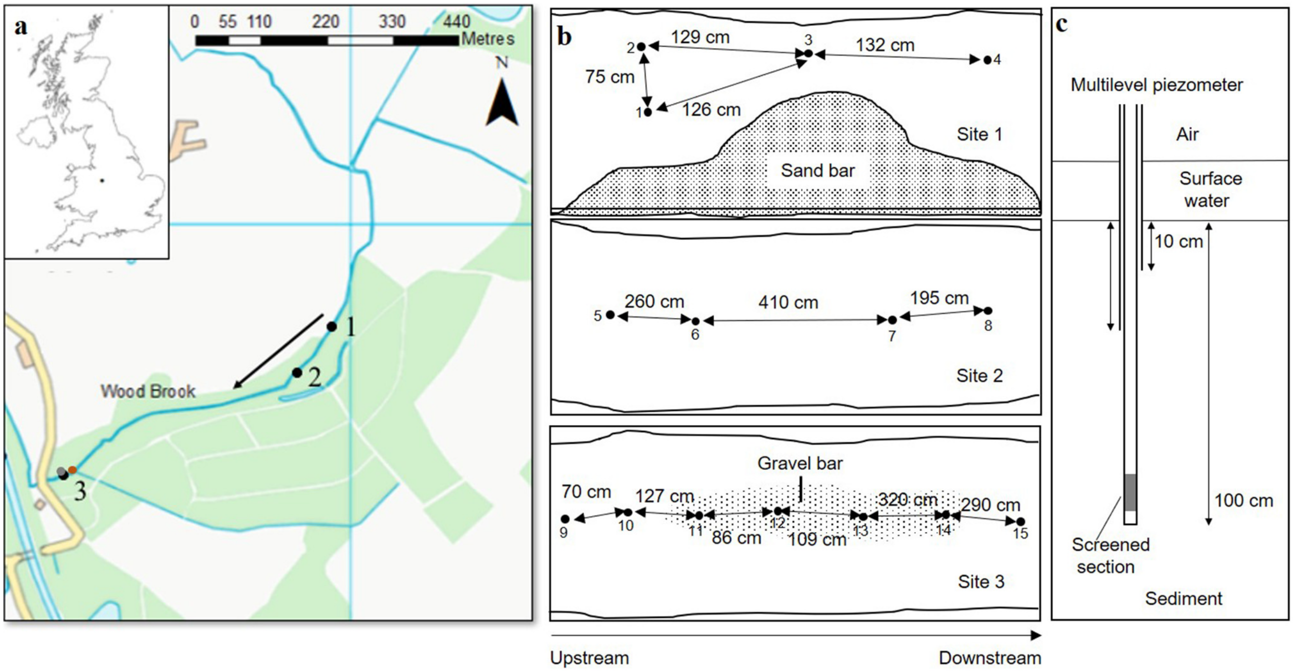

Fig. 1. a. The location of the Wood Brook within the UK at 52°47′58.2″ and N 2°18′16.5″W, and the Wood Brook showing the three study sites (black dots), the site of sampling of sediment representative of gravel-dominated sediments (grey circle) and sand-dominated sediments (orange circle), the direction of stream flow (black arrow), woodland (green area) and fields (white area). The map contains data from the Ordinance Survey, b. A diagram of the position of the piezometers within the three experimental sites with the shaded area in site 1 representing a sand bar at one side of the stream and the shaded area in site 3 representing a gravel bar close to the centre of the stream, and c. A diagram of the multilevel piezometers used to sample porewater at 10 and 20 cm depth.

FDA hydrolysis activity was determined as follows on three replicates from each site, with a further replicate used as a control, based on the methodology of Adam and Duncan (2001) and Prosser et al. (2011). 1 g of homogenised air-dried sediment was weighed into 125 ml Erlenmeyer flasks, and 50 ml of 1 M tris-hydroxymethyl-aminomethane (THAM) buffer and 0.5 ml of FDA substrate were added to each flask. A blank sample of 1 M THAM buffer and FDA substrate with no sediment, and a control sample of sediment with 1 M THAM buffer and 0.5 ml of acetone, but no FDA substrate, were also prepared. The flasks were then mixed, stoppered and incubated at 37 °C for 3 h. An incubation temperature of 37 °C was used to enable the optimum potential hydrolase activity expression for a stable coloured compound to be obtained for subsequent spectroscopic measurement. After that, the flasks were removed from the incubator and 2 ml of acetone was added to each flask to prevent further FDA hydrolysis. FDA substrate was added to the control and mixed thoroughly. Samples were then filtered (Whatman No.2) and the absorbance at 490 nm was measured on a spectrophotometer (Agilent, Varian Cary UV–Vis, Santa Clara, USA).

Phenol oxidase activity was determined as follows on five replicates from each site. 0.5 g of air-dried sediment was weighed into four 15 ml centrifuge tubes (three replicates with one non-substrate control). 3 ml of deionised water was added, and the tubes were gently mixed on a shaker for 10 min, after which, 2 ml of 10 mM dihydroxy-phenylalanine ($_L$-DOPA) was added to each replicate. The tubes were shaken on a platform shaker (100 rpm) for 30 min at 25 °C. After 30 min, the tubes were centrifuged for 15 min, at 4000 rpm at 25 °C, to terminate the reaction. The slurry was then filtered (GF/C filter paper) and the absorbance of the end colorimetric product, dopachrome, was determined at 475 nm on a spectrophotometer (Agilent Varian Cary UV–Vis, Santa Clara, USA). The phenol oxidase activity is reported here in μmol of dopachrome formed per gram of sediment per hour (Toberman et al., 2008).

2.3. In-situ observations

Surface water and sediment porewater samples were collected seasonally from three distinct sites within the main experimental site (Fig. 1a and b), in July 2016, October 2016, January 2017 and March 2017. Sites varied with regards to their sediments, with sites 1 and 2 being predominantly sand-dominated and site 3 gravel-dominated, with respective differences in OM content and particle size (Table S1).

2.3.1. Water and gas sampling and in-situ analyses

Porewater samples were manually extracted at depths of 10 and 20 cm from multi-level piezometers installed into the streambed (Fig. 1c), following a piezometer design of (Krause et al., 2013 and Rivett et al., 2008). A surface water sample was also taken at each site, during each period of piezometer sampling. Once collected, the dissolved oxygen (DO) and temperature (YSI ProODO or EcoSense ODO200) and pH and electrical conductivity (Hanna HI98129) of the samples was immediately measured in-situ. Water samples were then sequentially filtered at 0.45 and 0.22 μm (Thames Resteck Nylon, ultrapure water-rinsed (18.2 MΩ)) into sterile centrifuge tubes (10% HCl-rinsed), and frozen until analysis.

Gas samples for analysis of GHG concentrations were generated in the field using a headspace equilibrium method (McAuliffe, 1971). 14 ml of ultrapure helium was introduced to a 7 ml porewater sample and shaken for 2 min to allow equilibration between gases in the porewater and the headspace. The headspace was then injected into a pre-evacuated exetainer and the gas sample was stored in the dark, at room temperature until analysis.

2.3.2. Laboratory chemical analyses

Dissolved organic carbon (DOC) concentrations were analysed on a total organic carbon (TOC) analyser (Shimadzu TOC-L CPH with ASI-L autosampler, Kyoto, Japan), with an accuracy and precision of 0.16 and ±0.45 mg l^{-1} for a 15 mg l^{-1} standard, respectively. The limit of detection (LOD) was 0.5 mg l^{-1}.

The concentrations of CO_2 and CH_4 within the headspace gas samples were measured using a gas chromatograph (GC) (Agilent 7890A, Santa Clara, USA) fitted with a flame ionisation detector (FID) for CH_4 analysis and a thermal conductivity detector (TCD) for CO_2 analysis. The GC was used in splitless mode with a 250 μl sample loop, a 60 °C oven temperature, a 250 °C FID temperature and a 250 °C TCD temperature. Helium was used as a carrier gas with a flow rate of 25 ml min^{-1}, and the FID was set up with a hydrogen flow of 30 ml min^{-1} and an air flow of 400 ml min^{-1}. A run time of 2 min was used, with CH_4 and CO_2 eluted at 0.6 and 0.97 min, respectively. 15,000 ppm standards of CO_2 gave an accuracy and precision of 275 and ± 326 ppm, and 1000 ppm standards of CH_4 gave an accuracy and precision of 35 and ± 11 ppm. The LOD was 0.5 mg CO_2 l^{-1} and 0.5 μg CH_4 l^{-1} and is provided in mg l^{-1} as this represents the amount of dissolved gas based on the sample sizes analysed. The headspace concentration was converted to porewater concentration using Henry's constant (Hudson, 2004; Wilhelm et al., 1977).

2.3.3. Analysis of statistical inference

A Welch's Two Sample *t*-test or the non-parametric equivalent (Wilcoxon Rank Sum Test) was used to determine significant differences in responses of the sand- and gravel-dominated sediments for the incubation assays.

A linear mixed-effects model was fitted using the residual maximum likelihood in the *nlme* package in R (Pinheiro et al., 2017), to determine the effect of site and season on C cycling. The data for piezometer 1 at 10 cm was omitted from the statistical analysis as the oxygen data indicated that this sample was surface water, and the inclusion of this data point prevented model residuals from meeting the necessary model assumptions. To account for the repetition in sampling with time and within site, the data were nested by both site and season, and where the residuals did not fit the Gaussian assumption the data were shifted so that any values less than or equal to zero were positive and transformed ($\log_{10}$, reciprocal or square root) depending on which transformation resulted in the best residual fit. The Akaike Information Criterion (AIC) was used to judge whether a model with (Eq. (1)) or without (Eq. (2)) the interaction between site and season should be considered, with the model with the lowest AIC used.

$$y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \gamma_i + \gamma_k + \varepsilon_{ijk} \tag{1}$$

where y_{ijk} is the observation for site i, season j and sample k; μ is the mean of y; α_i is the fixed effect for site i; β_j is the fixed effect for season j; $(\alpha\beta)_{ij}$ is the interaction fixed effect for site i and season j; $\gamma_i \sim N(0,\sigma_\gamma^2)$ is the random event for site i; $\gamma_k \sim N(0,\sigma_\gamma^2)$ is the random event for the sample and $\varepsilon_{ijk} \sim N(0,\sigma^2)$ is the residual.

$$y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_i + \gamma_k + \varepsilon_{ijk} \tag{2}$$

where y_{ijk} is the observation for site i, season j and sample k; μ is the mean of y; α_i is the fixed effect for site i; β_j is the fixed effect for season j; $\gamma_i \sim N(0,\sigma_\gamma^2)$ is the random event for site i; $\gamma_k \sim N(0,\sigma_\gamma^2)$ is the random event for the sample and $\varepsilon_{ijk} \sim N(0,\sigma^2)$ is the residual.

3. Results

3.1. Influence of sediment type on microbial activity

Extracellular FDA hydrolysis, a proxy for total microbial activity, was significantly higher (p-value = 0.004, Table S2) in the sand-dominated (1.35 mg fluorescein kg^{-1} soil h^{-1}) than gravel-dominated (0.36 mg fluorescein kg^{-1} soil h^{-1}) sediments (Fig. 2a), whereas extracellular phenol oxidase activity, a proxy for the uptake of recalcitrant phenolic organic compounds, was significantly higher (p-value = 0.032, Table S2) in the gravel-dominated (2.76 μmol dopachrome g^{-1} soil h^{-1}) than in the sand-dominated (1.70 μmol dopachrome g^{-1} soil h^{-1}) sediments (Fig. 2b).

3.2. In-situ C cycling

3.2.1. Temperature

Spatial trends in temperature between the sites varied greatly depending on season (Fig. 3a). Temperature varied throughout the year, with minimum temperatures found in winter and maximum temperatures found in summer. In general, temperatures in the streambed reflected those in the surface water of the respective site (Fig. S1). However, in site 2 in winter, temperatures were higher in the streambed, and in site 3 temperatures were generally lower in the streambed.

3.2.2. Dissolved oxygen

Clear spatial and temporal trends in DO were not observed in the streambed porewaters (Fig. 3b). All piezometer samples revealed DO concentrations below 50% saturation, except at 10 cm in piezometer 1, which had a similar DO concentration to the surface water of site 1 in all seasons (between 77.7 and 88.3%), and at 10 cm in piezometer 9 in spring and winter (Fig. S2). Variation in DO was relatively small in summer, with % saturation slightly higher in site 3 than site 1.

3.2.3. DOC

Porewater DOC concentrations were consistently high across all sites with no significant difference observed (p-value >0.252, Table S3), although concentrations in site 2 were slightly higher than in sites 1 and 3 in autumn (Fig. 4a). Average DOC concentrations in the streambed porewater were season-dependent (9.2 ± 0.2 to 20.9 ± 0.4 mg C l^{-1}), with lowest concentrations found in winter and spring (9.2 ± 0.2 mg C l^{-1}) although these concentrations were still high. The variation in DOC concentrations between seasons was statistically significant (p-value < 0.001, Table S3). DOC concentrations were lower in the surface water than in the porewaters at all sites in summer and autumn, in winter and spring DOC concentrations were not consistently higher or lower in surface waters than porewaters in sites 1 and 2, and were generally higher in the surface water than porewaters in site 3 (Fig. S3).

3.2.4. Gas concentrations

Streambed porewater CO_2 concentrations were generally highest in site 2 and lowest in site 3, which was consistent across all seasons (Fig. 4b), resulting in statistically significant differences between sites (p-value < 0.001, Table S3). There was little variation in CO_2 concentrations between seasons, leading to no significant difference between seasons (p-value >0.746, Table S3). CO_2 concentrations were lower in the surface water than in the porewaters at all sites (Fig. 5).

Streambed porewater CH_4 concentrations were generally highest in sites 1 and 2, and lowest in site 3, which was consistent across all seasons (Fig. 4c), resulting in statistically significant differences between sites (p-value < 0.001, Table S3). Variation in CH_4 concentrations between seasons was low, however, they were significantly different between autumn and spring, and autumn and winter (p-value <0.006, Table S3). CH_4 concentrations were lower in the surface water than in the porewaters at all sites (Fig. 6).

CH_4:CO_2 ratios in streambed porewater were generally highest in site 2, and lowest in site 3, which was consistent across all seasons (Fig. 4d). CH_4:CO_2 ratios varied by season, but this was not consistent between sites and were generally higher in the porewater than the surface water (Fig. S4).

4. Discussion

4.1. Spatial variation

C cycling rates were greater in the sand-dominated sediments at sites 1 and 2 than in the gravel-dominated sediments of site 3 as demonstrated by the relatively high total microbial activity and CO_2 and CH_4 concentrations observed in the sand-dominated sediments. We hypothesise that this is due to higher residence times in the sand-

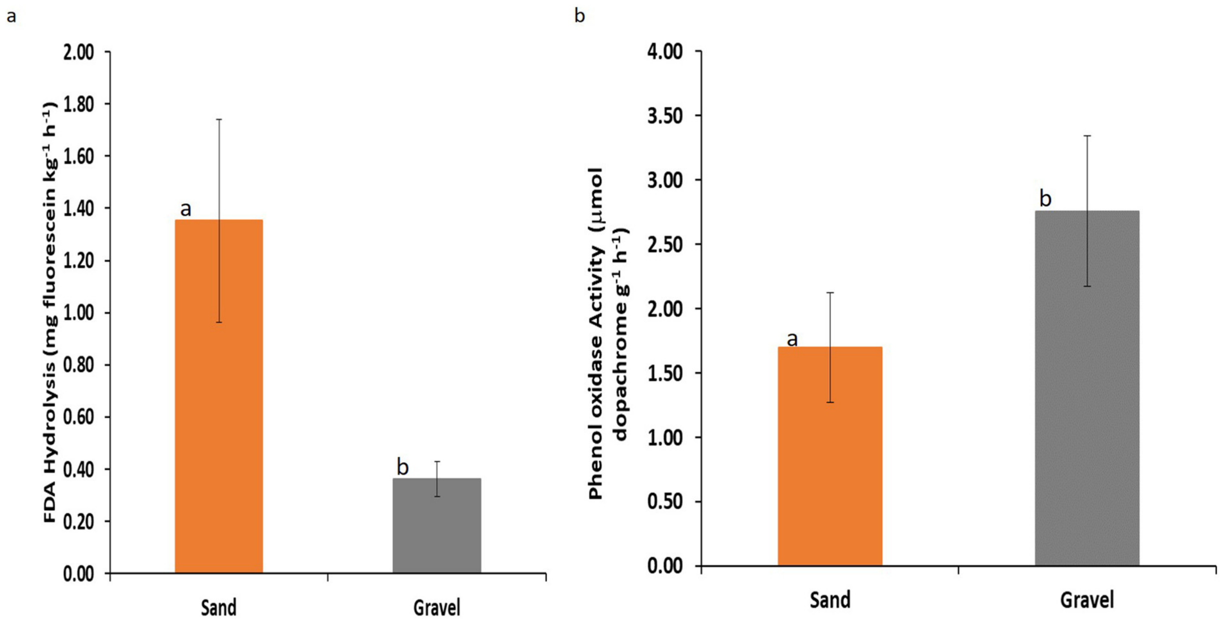

Fig. 2. a. The total microbial activity in sand and gravel sediments, expressed in mg fluorescein kg^{-1} h^{-1} and b. The phenol oxidation activity in sand and gravel sediments, expressed in μmol dopachrome g^{-1} h^{-1}. The error bars represent one standard deviation and letters above the bars indicate a significant difference between samples from the ANOVA results if different to each other.

dominated sediments (Table S1), which are typically associated with smaller particle size (Baker et al., 2000). Fine, OM-rich sediments are usually associated with high CH_4 production (Baulch et al., 2011; Crawford et al., 2014b; Crawford and Stanley, 2016; Sanders et al., 2007; Sawakuchi et al., 2014; Stanley et al., 2016), here we found a significant increase in both CO_2 and CH_4 concentrations with increasing OM content, even when OM content was very low (<3%). Significant differences in CO_2 and CH_4 concentrations measured between different sized sediments here was not seen previously between pools with sandy loam versus sand sediments, suggesting that these differences are not persistent between all sediment size classes (Vidon and Serchan, 2016). The low CH_4:CO_2 ratios measured in the gravel-dominated sediments are likely due to oxidation of CH_4 to CO_2 in these generally well oxygenated sediments with low potential for methanogenesis, and that gravel sediments are usually sources of CO_2 but sinks of CH_4 (Trimmer et al., 2010). High DOC concentrations across all sites, indicate that there was little C limitation here, which may explain the high CO_2 and especially CH_4 concentrations observed here in the sand-dominated sediments, and a lack of C limitation on potential rates of denitrification has been determined at this site (Comer-Warner et al., submitted).

Organic C turnover and decomposition rates, indicated by the FDA hydrolysis assay (Sinsabaugh and Findlay, 1995), were higher and uptake of recalcitrant C lower, in the sand-dominated sediments. This provides further evidence of differences in rates of biogeochemical reactions between sand- and gravel-dominated sediments and suggests the microbial community of the gravel-dominated sediments was better adapted to less bioavailable C. Although the uptake of recalcitrant C was highest in the gravel-dominated sediments, the uptake was still high in the sand-dominated sediments. This suggests that C quality is higher in sand- than gravel-dominated sediments and, alongside higher OM content in sites 1 and 2 (Table S1), may further explain the higher CO_2 and CH_4 concentrations in the sand-dominated sediments as higher CO_2 and CH_4 production are associated with higher OM content and quality (Romeijn et al., 2019).

4.2. Seasonal variation

Porewater DOC concentrations varied seasonally and were highest in summer likely due to an increase in C fixation by autotrophic microbial and plant or benthic communities within the stream during this time (Blaen et al., 2017; Jaffé et al., 2008). These high C concentrations

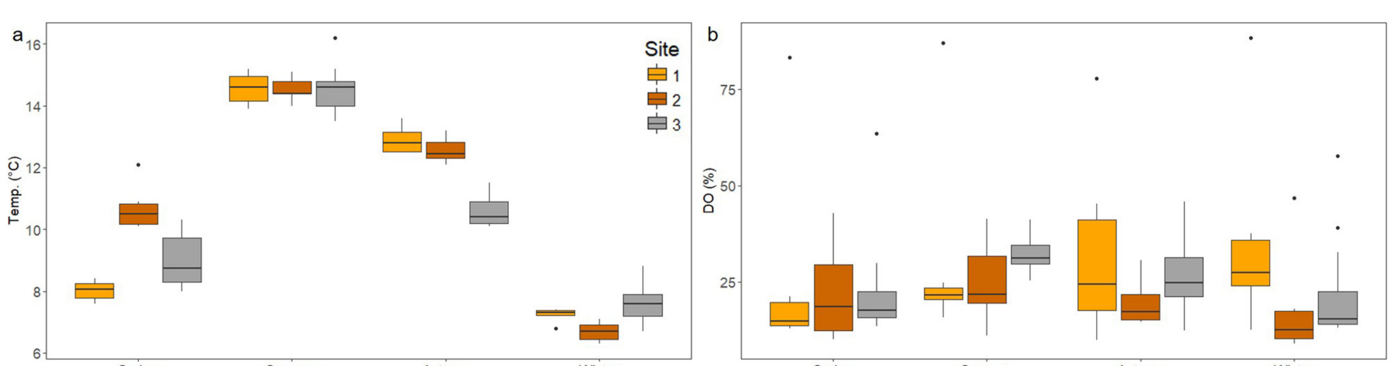

Fig. 3. Boxplots between sites and across seasons of a. Temperature and b. DO. The sediments of sites 1 and 2 are sand-dominated and of site 3 are gravel-dominated. The bold line indicates the median of the data and the lower and upper hinges represent the first and third quartiles, respectively. The lower and upper whiskers represent the smallest and largest values, respectively, but extend no further than 1.5* the inter-quartile range of the lower or upper hinges. Data outside of the whiskers are considered outliers and are plotted as individual points.

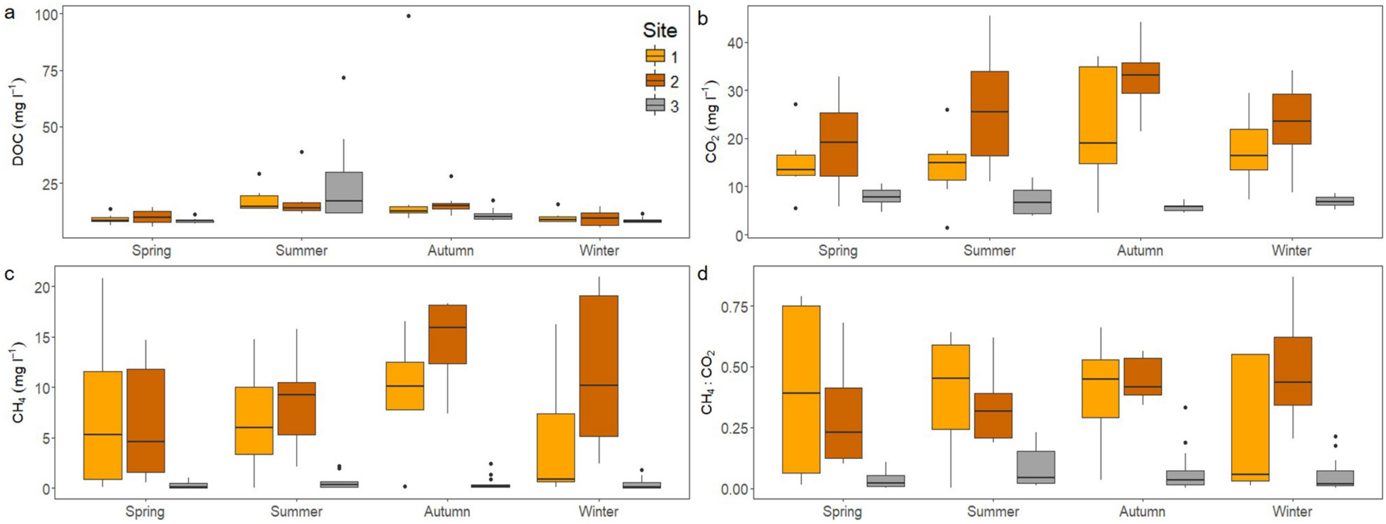

Fig. 4. Boxplots between sites and across seasons of a. DOC concentrations, b. CO_2 concentration, c. CH_4 concentration and d. CH_4:CO_2. The sediments of sites 1 and 2 are sand-dominated and of site 3 are gravel-dominated. The boxplots are defined in the figure heading of Fig. 3.

coupled with the known increase in DOM availability to microbes in agricultural landscapes (Williams et al., 2010; Wilson and Xenopoulos, 2009), may maintain high rates of metabolism year-round. This may have contributed to the low seasonal variation in CO_2 and CH_4 in the sediment porewaters in this study (although the variation was significant for CH_4), with high concentrations of CO_2 and CH_4 observed year-round.

There have been limited studies that measured concentrations of streambed CO_2 and CH_4 in winter. Given the large concentrations found year-round in this study, further work is required to determine the contribution of benthic fluxes to overall stream emissions in all seasons, as well as the drivers controlling these, to enable C emissions from streams and rivers to be better understood and quantified. Here, temperature (alongside DOC concentrations) may have been controlling the low seasonal variation in CO_2 and CH_4 concentrations. Although temperature increased from 5 to 7 °C in winter to 14 to 17 °C in summer, this range is below the threshold of elevated temperature of 26 °C required to produce a substantial increase in sediment CO_2 and CH_4 production in sandstone streams (Comer-Warner et al., 2018), therefore this may explain some of the limited variation.

4.3. Biogeochemical processes

Concentrations of CO_2 and CH_4 are affected by multiple interacting reactions, where CO_2 is produced in aerobic and anaerobic respiration (including methanogenesis) and methane oxidation, and CH_4 is

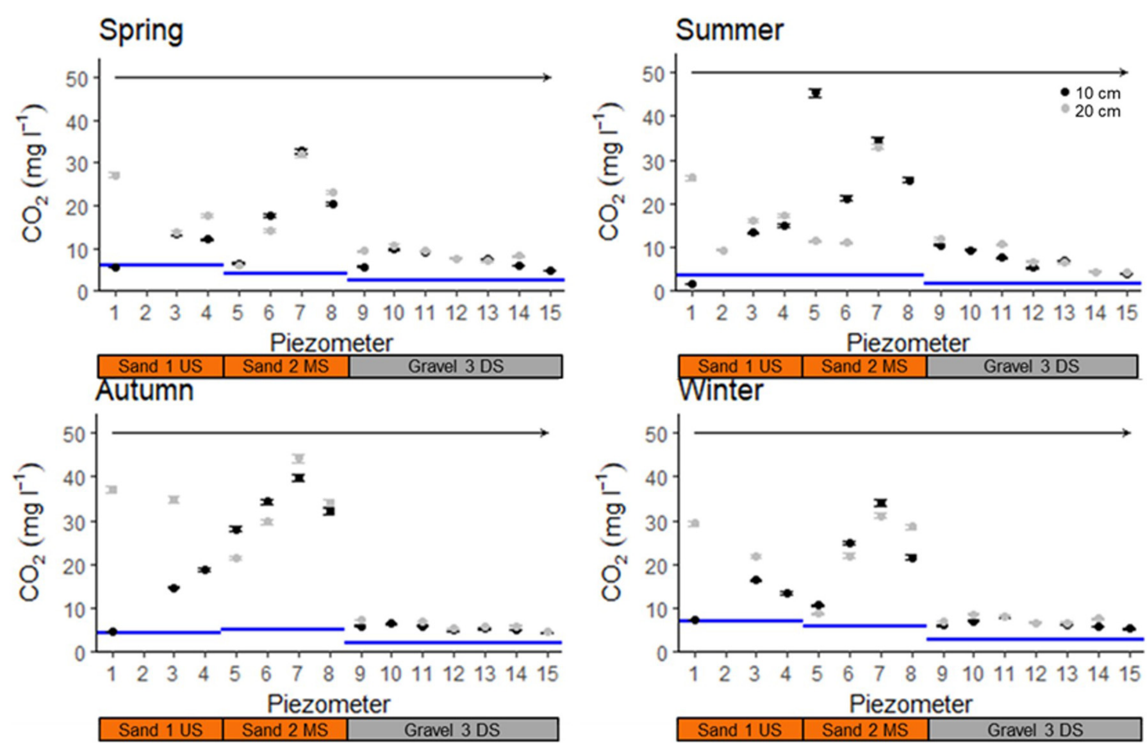

Fig. 5. Porewater CO_2 concentrations at 10 (black) and 20 (grey) cm depth, with surface water concentrations for each site shown with a blue line. The black arrow represents direction of surface flow from upstream to downstream.

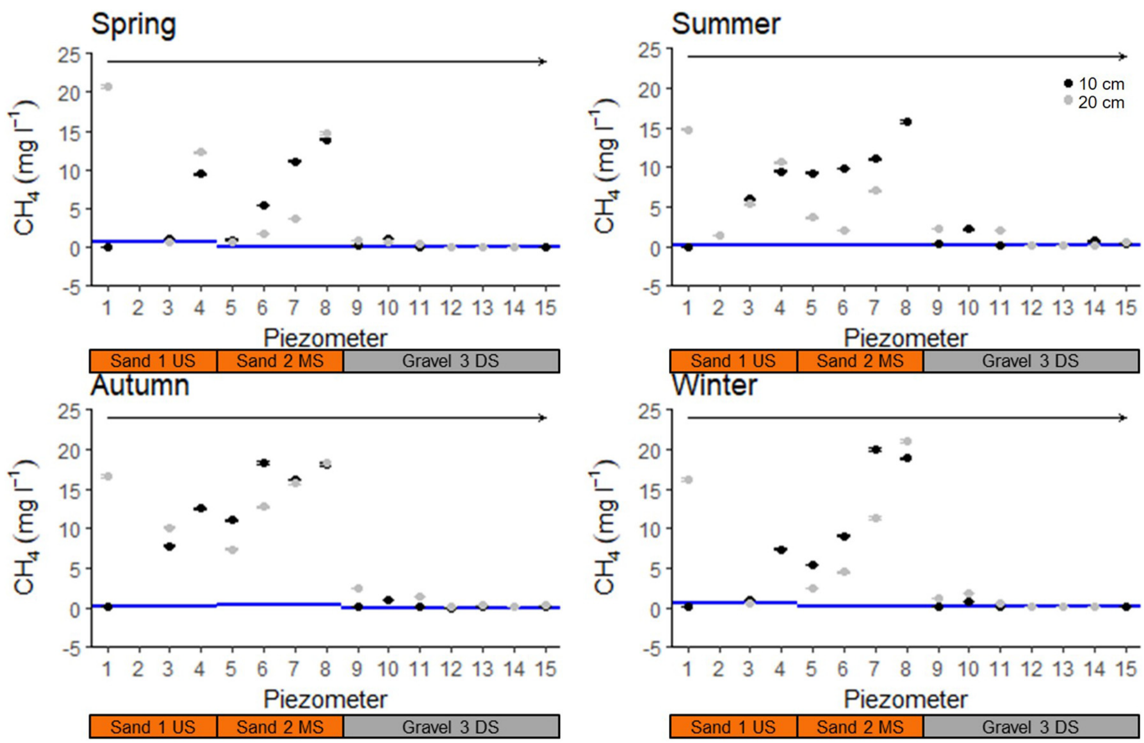

Fig. 6. Porewater CH_4 concentrations at 10 (black) and 20 (grey) cm depth, with surface water concentrations for each site shown with a blue line. The black arrow represents direction of surface flow from upstream to downstream.

produced during methanogenesis and consumed during CH_4 oxidation (Baker et al., 2000). Additionally, streambed concentrations may be due to CO_2 and CH_4 produced or consumed within these sites of the streambed, or CO_2 and CH_4 laterally transported into the streambed from groundwater (Hotchkiss et al., 2015 and Raymond et al., 2013).

4.4. The streambed as a source or a sink

CO_2 and CH_4 concentrations were consistently elevated in the sediments compared to the surface water, which is consistent with previous observations (Hlaváčová et al., 2005; Rulik et al., 2000), indicating that the streambed here is a potential source of CO_2 and CH_4 to the surface water. Further work, however, measuring benthic fluxes to the surface water is required to confirm this. DOC patterns varied seasonally, and were typically higher in porewaters than surface water at all sites in summer and autumn likely reflecting the increase in DOC production during this time (see above) and resulting in the streambed being a source of DOC during these seasons. In winter and spring, however, patterns were not consistent between sites, with porewater concentrations at sites 1 and 2 not consistently higher or lower than in the surface water. At site 3 porewater concentrations were generally similar or lower than in the surface water, indicating that the gravel-dominated sediments were a weak sink of DOC at these times.

4.5. C cycling in a wider context

The CO_2 concentrations at sites 1 and 3 and the CH_4 concentrations at site 3 were generally similar to those reported previously (Hlaváčová et al., 2005; Rulik et al., 2000; Schindler and Krabbenhoft, 1998), however, the CO_2 concentrations at site 2 and the CH_4 concentrations at sites 1 and 2 were generally higher than those previously observed (Hlaváčová et al., 2005; Rulik et al., 2000; Sanders et al., 2007; Schindler and Krabbenhoft, 1998; Wilcock and Sorrell, 2008).

Although the CH_4 concentrations at site 3 were much lower than those at sites 1 and 2 they were similar to those found in vegetated gravel sediments (Sanders et al., 2007). This is surprising, given that fine, OM-rich sediments that are ideal for methanogenesis are typically found beneath vegetation (Heffernan et al., 2008; Sanders et al., 2007; Stanley et al., 2016; Wilcock and Sorrell, 2008), and there was no vegetation in the gravel-dominated sediments of site 3.

Previous observations of streambed CO_2 and CH_4 in winter are sparse and the low seasonal variation in CO_2 and CH_4 observed here contradicts previous work showing significant increases in CO_2 and CH_4 concentrations during summer months and significant increases in CO_2 fluxes to the atmosphere in summer (Boodoo et al., 2017; Hlaváčová et al., 2005). Although the CH_4 concentrations observed here did vary significantly with season. This highlights the need for further investigation into the seasonal dynamics of streambed CO_2 and CH_4, to determine whether large differences between seasons are wide-spread.

High CO_2 and CH_4 concentrations within the sand-dominated sediments of this study site, combined with previous CH_4 observations (Crawford and Stanley, 2016; Sanders et al., 2007), suggest small agricultural streams with large amounts of fine sediment have the potential to produce significant quantities of CO_2 and CH_4. This highlights the need for further work determining the contribution of streambed CO_2 and CH_4 to overall stream emissions in agricultural streams with high OM and fine sediment inputs, especially due to recent suggestions that streambed CO_2 and CH_4 production has the potential to account for an average of 35% of the total stream flux (Romeijn et al., 2019).

Bednařík et al. (2015) determined that the contribution of the benthic flux of CH_4 from gravel sediments to overall CH_4 fluxes from the surface water was negligible (<1%). Our study, however, resulted in much larger concentrations in sand-dominated sediments, where anoxia is generally higher, and where OM content was highest. Higher OM and organic C content is associated with high CH_4 ebullition (Baulch et al., 2011; Crawford et al., 2014b), however, the OM content here was relatively low. Therefore, there may be a larger contribution of the benthic flux to overall CH_4 emissions here. Further work is required to determine the contribution of benthic CH_4 from sand-dominated sediments, as well as to determine the contribution of total benthic CO_2 and CH_4 fluxes to overall stream emissions.

5. Conclusions

We found high CO_2 and CH_4 concentrations in the streambed sediments of an agricultural river controlled by sediment type, with sand-dominated sediments characterised by significantly higher CO_2 and CH_4 concentrations than gravel-dominated sediments, despite both sediment types having relatively low OM content (<3%). This enhanced cycling resulted in high CH_4:CO_2 ratios in the sand-dominated sediments, suggesting that CH_4 production is higher in sand-dominated than gravel-dominated sediments but that CH_4 oxidation is higher in gravel-dominated sediments. The highest concentrations of CO_2 and CH_4 both found in the sand-dominated sediments suggests that CO_2 and CH_4 production may have been co-located.

High concentrations of CO_2 and CH_4 persisted year-round, with no statistically significant seasonal influence on CO_2 concentrations. This is suggested to be due to high DOC concentrations measured in the porewaters and large amounts of fine, OM-rich sediments that typically drain from agricultural watersheds. Agricultural streams are widespread across Europe, Asia and North America and the high inputs of fine, OM-rich sediment they receive are expected to increase in the future due to changes in land-use and increased weathering rates (Graeber et al., 2012; Stanley et al., 2016). Our observations of high concentrations of both CO_2 and CH_4 in fine, relatively high OM-content sediments persisting year-round in an agricultural stream, therefore, have potentially large implications for future C cycling and freshwater GHG emissions, with increases in CO_2 and CH_4 production anticipated.

Our results also have wide repercussions for agricultural stream management approaches. They suggest that the reduction of sand-dominated sediments could reduce C cycling within streambed sediments, and potentially decrease the C flux from streams, although fluxes and not just streambed concentrations (as presented here) need to be determined to verify this. Approaches for stream management to mitigate GHG production, however, are complicated by spatial patterns of streambed N_2O observed in the same study stream (Comer-Warner et al., submitted), where N cycling and nutrient attenuation were also highest in sand-dominated sediments, highlighting the increased biogeochemical cycling occurring in this sediment type. This resulted in the highest N_2O concentrations occurring in the gravel-dominated sediments of site 3, which suggests that sediment type exerts differing controls on N- versus C-based GHGs, and therefore, reducing sandy sediment at the expense of increasing gravel sediment, may decrease CO_2 and CH_4 production while increasing N_2O production.

Further work is required across additional sites of contrasting sediment type and across all seasons within agricultural streams to further constrain the influence of sediment type on C cycling and GHG production, and to determine the ubiquity of low seasonal variation in streambed GHG concentrations and emissions. Future research should also be conducted to increase the understanding of C turnover and associated CO_2 and CH_4 production in streambed sediments, as well as the contribution of the benthic flux to the overall stream flux. This is particularly important given that agricultural streams are 'hotspots' for fine sediment and organic matter loading (Stanley et al., 2016; Wood and Armitage, 2007), which are predicted to increase due to future land-use change (Stanley et al., 2016), along with increased metabolic rates (Venkiteswaran et al., 2014).

While this study did not explicitly investigate the relationship between fertiliser application, metabolism and C biogeochemistry, the C dynamics observed in this agricultural stream are expected to be affected by presumably large exogenous N inputs within the catchment. Further work is, therefore, required to constrain the direct and indirect effects of exogenous N on the C cycle and GHG production specifically.

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Author contributions

SC-W was involved in the conceptualization, data curation, formal analysis, funding acquisition, investigation and writing the original draft, DCG was involved in the conceptualization, funding acquisition, supervision, visualization, and reviewing and editing the manuscript, SU was involved in the conceptualization, funding acquisition, investigation, supervision, visualization and reviewing and editing of the manuscript, LG and AP were involved in data curation, formal analysis, investigation and visualization, NK was involved in supervision, validation, and reviewing and editing the manuscript, and SK was involved in the conceptualization, funding acquisition, supervision, visualization, and reviewing and editing the manuscript.

Declaration of Competing Interest

The authors declare no conflicts of interest, either financial or personal, that may be perceived to influence this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.317.

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