





















RESEARCH ARTICLE

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Sources, Composition, and Export of Particulate Organic Matter Across British Estuaries

Key Points:

- High interestuarine spatial and intraestuarine temporal particulate organic carbon (POC) variability
- Similar sources of particulate material throughout the year within each estuary
- Estimated average contribution of terrigenous POC from estuaries to coastal waters was 57%

E. Elena García-Martín¹ , Richard Sanders^{1,2}, Chris D. Evans³, Vassilis Kitidis⁴ , Dan J. Lapworth⁵ , Bryan M. Spears⁶, Andy Tye⁷, Jennifer L. Williamson³ , Chris Balfour⁸, Mike Best⁹, Michael Bowes⁷ , Sarah Breimann^{1,4,10} , Ian J. Brown⁴, Annette Burden³ , Nathan Callaghan³, Nancy B. Dise⁶, Gareth Farr¹¹, Stacey L. Felgate^{1,12} , James Fishwick⁴, Mike Fraser⁹, Stuart Gibb¹³, Pete J. Gilbert¹³, Nina Godsell⁹, Africa P. Gomez-Castillo¹⁰, Geoff Hargreaves⁸, Carolyn Harris⁴, Oban Jones⁴, Paul Kennedy⁹, Anna Lichtschlag¹ , Adrian P. Martin¹ , Rebecca May⁴, Edward Mawji¹ , Ian Mounteney⁷, Philip D. Nightingale^{4,14,15} , Justyna P. Olszewska⁶, Stuart C. Painter¹ , Christopher R. Pearce¹, M. Glória Pereira¹⁶ , Kate Peel¹ , Amy Pickard⁶ , John A. Stephens⁴, Mark Stinchcombe¹, Barry Thornton¹⁷, E. Malcolm S. Woodward⁴ , Deborah Yarrow¹, and Daniel J. Mayor^{1,18} 

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

E. E. García-Martín,
elencia@noc.ac.uk

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Author Contributions:

Conceptualization: Richard Sanders, Chris D. Evans, Vassilis Kitidis, Dan J. Lapworth, Bryan M. Spears, Andy Tye, Jennifer L. Williamson, Daniel J. Mayor
Data curation: Adrian P. Martin
Formal analysis: Sarah Breimann
Funding acquisition: Richard Sanders, Chris D. Evans, Vassilis Kitidis, Dan J. Lapworth, Bryan M. Spears, Andy Tye, Jennifer L. Williamson, Nancy B. Dise, Daniel J. Mayor

¹National Oceanography Centre, Southampton, UK, ²NORCE Norwegian Research Centre, Bjerknes Center for Climate Research, Bergen, Norway, ³UK Centre for Ecology & Hydrology, Environment Centre Wales, Bangor, UK, ⁴Plymouth Marine Laboratory, Plymouth, UK, ⁵British Geological Survey, Wallingford, UK, ⁶UK Centre for Ecology & Hydrology, Penicuik, UK, ⁷British Geological Survey, Environmental Science Centre, Nottingham, UK, ⁸National Oceanography Centre, Liverpool, UK, ⁹Environment Agency, Peterborough, UK, ¹⁰Ocean and Earth Science, University of Southampton, Southampton, UK, ¹¹British Geological Survey, Cardiff University, Cardiff, UK, ¹²Department of Chemistry–BMC, Uppsala University, Uppsala, Sweden, ¹³Environmental Research Institute, University of the Highlands and Islands–North Highland, Thurso, UK, ¹⁴Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK, ¹⁵Sustainable Agriculture Systems, Rothamsted Research, North Wyke, UK, ¹⁶UK Centre for Ecology & Hydrology, Lancaster Environment Centre, Lancaster, UK, ¹⁷The James Hutton Institute, Aberdeen, UK, ¹⁸School of Biosciences, University of Exeter, Exeter, UK

Abstract Estuaries receive and process a large amount of particulate organic carbon (POC) prior to its export into coastal waters. Studying the origin of this POC is key to understanding the fate of POC and the role of estuaries in the global carbon cycle. Here, we evaluated the concentrations of POC, as well as particulate organic nitrogen (PON), and used stable carbon and nitrogen isotopes to assess their sources across 13 contrasting British estuaries during five different sampling campaigns over 1 year. We found a high variability in POC and PON concentrations across the salinity gradient, reflecting inputs, and losses of organic material within the estuaries. Catchment land cover appeared to influence the contribution of POC to the total organic carbon flux from the estuary to coastal waters, with POC contributions >36% in estuaries draining catchments with a high percentage of urban/suburban land, and <11% in estuaries draining catchments with a high peatland cover. There was no seasonal pattern in the isotopic composition of POC and PON, suggesting similar sources for each estuary over time. Carbon isotopic ratios were depleted ($-26.7 \pm 0.42\%$, average \pm sd) at the lowest salinity waters, indicating mainly terrigenous POC (TPOC). Applying a two-source mixing model, we observed high variability in the contribution of TPOC at the highest salinity waters between estuaries, with a median value of 57%. Our results indicate a large transport of terrigenous organic carbon into coastal waters, where it may be buried, remineralized, or transported offshore.

Plain Language Summary Estuaries transport and process a large amount terrigenous particulate organic matter (i.e., carbon and nitrogen) prior to its export to coastal waters. In order to understand the fate of organic carbon and the role of estuaries in the global carbon cycle it is essential to improve our knowledge on its composition, origin, and amount of carbon transported. We quantified the elemental concentrations and stable isotopes composition of carbon and nitrogen to quantify the amount of terrigenous particulate organic matter transported by 13 British estuaries, which drain catchments of diverse land cover under different hydrological conditions. We found a great variability in particulate organic carbon (POC) and particulate organic nitrogen concentrations across the salinity gradient, implying inputs, and losses of material within the estuaries. Each estuary had similar sources of particulate material throughout the year. In most of the estuaries, the POC had a terrigenous origin at the lowest salinity waters. The terrigenous organic carbon contribution decreased toward coastal waters with an average contribution of 57% at the highest salinity waters, indicating a large transport of terrigenous organic carbon into coastal waters.

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Investigation: Richard Sanders, Chris D. Evans, Vassilis Kitidis, Dan J. Lapworth, Bryan M. Spears, Andy Tye, Jennifer L. Williamson, Chris Balfour, Mike Best, Michael Bowes, Sarah Breimann, Ian J. Brown, Annette Burden, Nathan Callaghan, Nancy B. Dise, Gareth Farr, Stacey L. Felgate, James Fishwick, Stuart Gibb, Pete J. Gilbert, Nina Godsell, Africa P. Gomez-Castillo, Geoff Hargreaves, Carolyn Harris, Oban Jones, Paul Kennedy, Anna Lichtschlag, Adrian P. Martin, Rebecca May, Edward Mawji, Ian Mounteney, Philip D. Nightingale, Justyna P. Olszewska, Stuart C. Painter, Christopher R. Pearce, M. Glória Pereira, Kate Peel, Amy Pickard, John A. Stephens, Mark Stinchcombe, E. Malcolm S. Woodward, Deborah Yarrow, Daniel J. Mayor

Methodology: Richard Sanders, Chris D. Evans, Vassilis Kitidis, Bryan M. Spears, Andy Tye, Jennifer L. Williamson, Nancy B. Dise, Stacey L. Felgate, Edward Mawji, Philip D. Nightingale, Justyna P. Olszewska, M. Glória Pereira, Amy Pickard, Barry Thornton, E. Malcolm S. Woodward, Daniel J. Mayor

Project Administration: Richard Sanders, Chris D. Evans, Daniel J. Mayor

Resources: Richard Sanders, Chris D. Evans, Dan J. Lapworth, Bryan M. Spears, Andy Tye, Mark Stinchcombe, Daniel J. Mayor

Validation: Mike Fraser

Writing – review & editing: Richard Sanders, Chris D. Evans, Vassilis Kitidis, Dan J. Lapworth, Bryan M. Spears, Andy Tye, Jennifer L. Williamson, Nancy B. Dise, Anna Lichtschlag, Adrian P. Martin, Stuart C. Painter, Christopher R. Pearce, M. Glória Pereira, Amy Pickard, Barry Thornton, E. Malcolm S. Woodward, Daniel J. Mayor

1. Introduction

Estuaries are part of the land ocean aquatic continuum (LOAC) and transport large amounts of terrigenous organic carbon, both particulate and dissolved (POC and DOC), to marine ecosystems. However, not all terrigenous organic carbon that enters the LOAC reaches coastal waters. There is increasing evidence that much of it is removed from the water column via accumulation in sediments (Burdige, 2005), floodplains (Hoffmann et al., 2009), or outgassed to the atmosphere via remineralization to carbon dioxide in the water column or, to a lesser extent, anaerobic decomposition to methane in bed sediments (Cole et al., 2007; Kitidis et al., 2019; Regnier et al., 2013; Tranvik et al., 2018). It has been suggested that ~70% of the particulate organic carbon (POC) transported by rivers into estuaries is transformed to carbon dioxide within estuaries (Chen & Borges, 2009), which may help to explain the low concentration of terrigenous organic matter (tOM) observed in the deep ocean compared to coastal waters (Cresson et al., 2012; Hedges et al., 1997).

Estuaries are highly dynamic ecosystems, particularly in macrotidal regions such as the UK. Spatial and temporal variability in POC concentrations can be very high, driven by changes in the physicochemical and hydrological conditions, as well as variations in land cover (Duan & Bianchi, 2006). High-rainfall events often cause soil erosion, transporting terrigenous material into estuaries (Abril et al., 2002; Arellano et al., 2019; Hope et al., 1997; Ye et al., 2017). In situ growth of autochthonous planktonic organisms, as well as marine POC transported into estuaries, may increase POC concentrations, but will reduce the proportion of terrigenous POC (TPOC) within estuaries (He et al., 2014; Liénart et al., 2017). In addition, anthropogenic pressures and changes in land cover can alter the estuarine flux of terrigenous organic carbon (Regnier et al., 2013). Estuaries with a high level of human influence, such as those with a large percentage of arable or urban/suburban land cover in their catchments, tend to have higher amounts of POC, resulting, e.g., from increased erosion of soils disturbed by agricultural activities, releases from sewage treatment works, surface runoff from urban areas, and disconnection of channelized rivers from floodplains, all reducing opportunities for sediment redeposition (Abril et al., 2002; Brookes et al., 1983). Furthermore, land cover modifications can alter the inputs of inorganic nutrients and organic substances (Harris, 2001; Wilson & Xenopoulos, 2009), which in turn can increase autotrophic and heterotrophic production within the aquatic environment, and may thus generate nonterrigenous POC within rivers and estuaries.

To quantify the amount and fate of the TPOC reaching the coastal shelf, it is necessary to understand the sources and spatiotemporal variability of the particulate organic matter present in estuaries. Carbon and nitrogen isotopic signatures ($\delta^{13}\text{C}$ -POC and $\delta^{15}\text{N}$ -PON, respectively) and stoichiometry (POC:PON) can be used to determine the origin of the organic matter present in estuaries (Kendall et al., 2001; Middelburg & Nieuwenhuize, 1998; Wu et al., 2007). In general, tOM has more depleted isotopic signatures and higher POC:PON ratio than marine organic matter (Kendall et al., 2001; Liénart et al., 2017; Meyers, 2003; Middelburg & Nieuwenhuize, 1998). The elemental composition of the particulate organic matter might be altered due to the preferential utilization of nitrogen-rich compounds during microbial degradation, and also potentially due to the seasonality of plant/algae growth rates (Elser et al., 2003; Fourqurean et al., 1997; Sterner & Elser, 2012). However, the specific isotopic fingerprints of the sources (i.e., terrigenous, marine, intertidal vegetation, wastewaters) provide a sensitive indicator of the influence of terrigenous organic carbon across estuaries (Liénart et al., 2017; Middelburg & Nieuwenhuize, 1998; Ye et al., 2017).

This paper presents an assessment of particulate organic matter concentrations and compositions from 13 British estuaries covering a wide range of hydrological conditions and land cover over the course of a year. The study had four main aims: (a) to quantify how POC and particulate organic nitrogen (PON) concentrations change across the salinity gradient in contrasting estuaries, (b) to assess the contribution of POC to total organic carbon (TOC) and its relationship with land cover, (c) to identify the different particulate organic matter (POM) sources, and (d) to quantify the amount of TPOC reaching coastal waters.

2. Materials and Methods

2.1. Study Area and Sampling Sites

Sampling campaigns were conducted in 13 estuaries distributed around Great Britain (Figure 1a). One estuary (Halladale) drains to the coast of northern Scotland, five (Tay, Forth, Humber-Trent, Thames) drain east to the

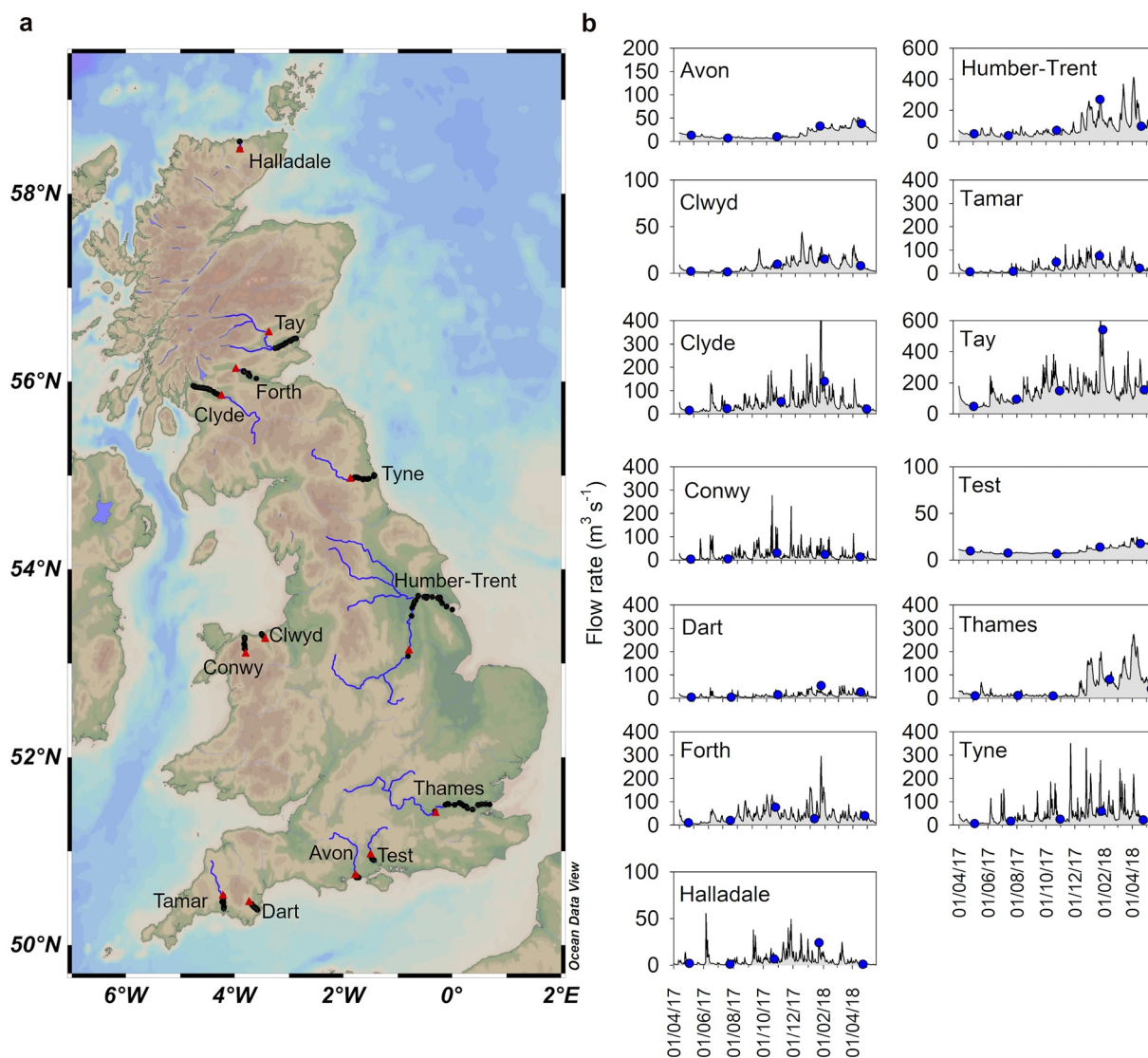


Figure 1. (a) Map of Great Britain with the sampling stations for the 13 estuaries (black dots). Red triangles indicate the sampling location where riverine water was collected to characterize the terrestrial-riverine isotopic signatures. (b) Daily mean river flow rate ($\text{m}^3 \text{s}^{-1}$) for the 13 estuaries during the period of study. Blue circles indicate estuarine sampling dates. Note the different river flow rate scales.

North Sea, four (Tamar, Dart, Avon, and Test) drain south into the English Channel, and three (Clyde, Clwyd, Conwy) drain west to the Irish Sea (Figure 1a). Catchment areas range from <200 to $>8,000 \text{ km}^2$ (Table S1 in Supporting Information S1), and hydrological regimes vary from high-rainfall, surface water dominated catchments in the north and west of Great Britain to dry, groundwater dominated catchments in the south and east (Figure 1b). Land cover ranges from predominantly seminatural land such as peatland ($\sim 67\%$ in Halladale) to intensive arable agriculture and urban/suburban land ($>46\%$ in Humber-Trent, Thames, and Test for the sum of these two land covers) (see Section 2.2 for method applied in the determination of the proportion of land cover, data in García-Martín et al. (2021) and Table S2 in Supporting Information S1). Collectively the estuaries sampled drain 16% of the mainland area of Great Britain.

2.2. Field Data Collection and Environmental Parameters

Five coordinated sampling campaigns took place in April, July, and October 2017, and January and April 2018. Surface water samples were collected, on a falling tide, from fixed land-based points, or from small boats. Samples were taken to capture as broad a salinity gradient as possible each sampling time (ranging from 0 to 32), and were therefore not necessarily collected at the same locations on each sampling campaign. Water temperature ($^{\circ}\text{C}$) and

conductivity ($\mu\text{S cm}^{-1}$) were measured in situ, and daily river flow rates ($\text{m}^3 \text{s}^{-1}$) into each estuary were obtained from the UK National River Flow Archive (www.nrfa.ceh.ac.uk). The proportion of each land cover class was calculated for each estuary catchment using land classification data supplied by the UK Centre for Ecology & Hydrology (UKCEH) based on the UKCEH Land Cover Map 2015 (Rowland et al., 2017). The UKCEH Wallingford Digital Terrain Model (Morris et al., 1990) was used to derive catchment boundaries based on the zero salinity sampling points. A full description of catchment land cover can be found in García-Martín et al. (2021).

2.3. Particulate Organic Matter Concentrations and Isotopic Analysis

Water samples to determine the concentrations of total particulate carbon, PON, and their stable isotope compositions were collected in acid-washed buckets, transferred to acid-washed carboys, and transported back to the laboratory in ice-cooled dark containers. Water samples (100–350 mL) were filtered onto precombusted (400°C overnight) 25 mm grade F glass fiber filters under gentle vacuum, dried at 50°C for 12 hr and pelleted within 33 mm tin discs prior to analysis. Concentrations of carbon and nitrogen and their isotopic signatures were determined using a Flash EA 1112 Series Elemental Analyzer connected via a ConFlo III to a Delta^{Plus} XP IRMS (Thermo Finnigan, Bremen, Germany). Samples were not acidified, avoiding artifacts associated with the resulting $\delta^{15}\text{N}$ data (Peng et al., 2018), but this means that the particulate carbon fraction will potentially contain both organic and inorganic carbon (see limitation section for further discussion). Additional analysis of 52 acidified and nonacidified samples from the Dart and Tamar estuaries was undertaken to quantify the potential uncertainty related to the presence of inorganic carbon in the total particulate carbon samples (see Text S1 and Figure S1 in Supporting Information S1 for a full description of the analysis and results). Additionally, we assessed the validity of the estimated inorganic contribution for all 13 estuaries by performing a sensitivity analysis based on assumed particulate carbon isotopic signatures (see Text S2 and Figure S2 in Supporting Information S1 for a full description of the analysis). The two independent analyses indicated that on average $84.5 \pm 9.1\%$ (standard deviation, direct measurements) and a minimum of $86.2 \pm 6.7\%$ (standard deviation, sensitivity analysis) of the total particulate carbon in the estuaries corresponded to its organic phase, and thus we refer to total particulate carbon hereafter as particulate organic carbon (POC).

TOC was estimated as the sum of POC and dissolved organic carbon (DOC) (data reported in García-Martín et al. (2021)). Briefly, water samples for DOC concentrations were collected and filtered through pre-rinsed $0.45 \mu\text{m}$ cellulose acetate filters using rubber free syringes into acid-washed HDPE bottles. Samples were acidified with 1 M HCl and analyzed by high temperature catalytic oxidation in a Shimadzu TOC-L analyzer (full description in García-Martín et al. (2021)). Filters with different pore sizes were used for POC and DOC sample collection (0.7 and $0.45 \mu\text{m}$, respectively) which implies that small quantities of POC could have been potentially lost during filtration. However, a previous study with stream waters indicated no loss in the organic carbon between samples filtered by 0.2 and $0.7 \mu\text{m}$ (Denis et al., 2017). Thus, we have assumed minimal pore size effect on our TOC concentration.

Stable isotope ratios are expressed using delta notation (δ) and in units of per mil (‰) according to the equation:

$$\delta^{13}\text{C-PC or } \delta^{15}\text{N-PON (‰)} = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1000$$

where R is the corresponding ratio $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$. Final results are expressed relative to vPDB for ^{13}C ($\delta^{13}\text{C}_{\text{vPDB}}$) and atmospheric N_2 for ^{15}N ($\delta^{15}\text{N}_{\text{Air}}$). The $\delta^{13}\text{C}_{\text{vPDB}}$ and $\delta^{15}\text{N}_{\text{Air}}$ values were normalized to their respective scales using international reference materials USGS40 and USGS41a (both L-glutamic acid) run in duplicate with every batch of 15 samples. Additionally, the USGS40 was used as a reference material for both carbon and nitrogen concentrations, measured using the area output of the mass spectrometer. Long term precisions for a quality control standard (dried milled topsoil) were: total carbon $3.69 \pm 0.08\%$, $\delta^{13}\text{C} -27.78 \pm 0.13\text{‰}$, total nitrogen $0.27 \pm 0.008\%$, and $\delta^{15}\text{N} 5.03 \pm 0.28\text{‰}$ (mean \pm sd, $n = 200$). Any two consecutive quality control values out with two standard deviations or a single value out with three standard deviations triggered repeat analysis. Data processing was performed using Isodat 2.0 (Thermo Fisher Scientific, Bremen, Germany) and exported into Excel.

2.4. Determination of Source Signatures

In order to account for the temporal and spatial variability in the isotopic signature of the 13 studied rivers discharging into the estuaries, we report supporting $\delta^{13}\text{C-POC}$, $\delta^{15}\text{N-PON}$, and POC:PON ratios measured during parallel river sampling campaigns conducted between December 2016 and December 2017 (Williamson et al., 2021).

We applied a two end-member stable isotope mixing model (Goñi et al., 2003; Jilbert et al., 2018), with riverine and marine $\delta^{13}\text{C-POC}$ as end-members, to quantify the proportion of terrestrially derived POC (POC inputs from

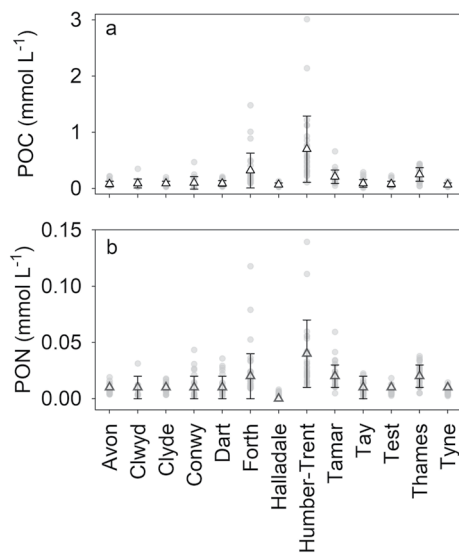


Figure 2. (a) Particulate organic carbon (POC) and (b) particulate organic nitrogen (PON) in the 13 estuaries. Individual datapoints are represented with gray circles and the average with a triangle. Error bars represent the standard deviation of the average.

3. Results

3.1. River Discharge

Annual average river discharges during the study period were highest in the Tay and Humber-Trent rivers (149 and 88 $\text{m}^3 \text{s}^{-1}$, respectively) and lowest in the Clwyd and Halladale rivers (8 and 5 $\text{m}^3 \text{s}^{-1}$, respectively) (Figure 1b). Most rivers showed a seasonal variation in their river discharges, with lower discharges from April 2017 to November 2017 and higher discharges from December 2017 to April 2018 (Figure 1b). Estimated annual average catchment water yields indicated that several small estuaries such as the Conwy and Dart had larger water yields (2.1 and 1.5 m yr^{-1} , respectively) compared to large estuaries such as the Thames (0.1 m yr^{-1}), reflecting regional rainfall patterns (Table S1 in Supporting Information S1).

3.2. Particulate Organic Matter Concentration

Concentrations of POC and PON were highly variable, with the highest concentrations measured in the Humber-Trent (3.01 mmol L^{-1} POC and 0.14 mmol L^{-1} PON) and the lowest in the Tay estuary (0.014 mmol L^{-1} POC and 0.002 mmol L^{-1} PON) (Figures 2a and 2b). The average concentration of POC and PON across all seasons differed significantly between the estuaries ($p < 0.05$ in both cases) (Figures 2a and 2b). POC and PON concentrations were significantly positively correlated within all individual estuaries ($p < 0.001$ for each of the 13 estuaries, Figure S3 in Supporting Information S1). The average (\pm standard deviation) slope of the POC:PON relationships was 12 ± 4 , with a lower slope in the Dart estuary (5.5) and higher in the Humber-Trent (21.2) and the Halladale (16.7) (Table in Figure S3 in Supporting Information S1).

The distribution of POC and PON concentrations across the salinity gradient was variable between estuaries, and without any clear seasonal trends (Figures 3 and S4 in Supporting Information S1). The Halladale was the only estuary showing a linear decrease or stable POC and PON concentrations with increasing salinity over all five sampling campaigns. We observed nonlinear variations in POC in 48 out of 62 cases. The POC:PON ratio exhibited across the salinity gradient within each estuary was complex (Figure S5 in Supporting Information S1), with increases and decreases observed across the salinity gradient. In general, the lowest salinity waters (salinity range: 0–1.8) had higher or similar POC:PON values compared to the highest salinity waters (salinity range:

the river) present at the lowest and highest salinity waters. The isotopic signatures of the individual riverine end-members corresponded to the annual average ($n = 13$) $\delta^{13}\text{C}$ -POC value measured in each river obtained from the river sampling campaigns described above. For the marine end-member signature, we assumed a value of -20‰ , which represents the average value for coastal waters (-18‰ to -22‰ , Liénart et al., 2017). TPOC concentrations at the highest salinity waters, which is likely to be exported from the estuary to coastal marine areas, were determined by multiplying the contribution of TPOC at the highest salinity waters with the bulk POC concentration measured in these waters.

2.5. Data Treatment and Statistical Analysis

Annual water yield for each estuary (m yr^{-1}) was calculated as the average annual flow divided by the catchment area.

Prior to statistical analysis, POC, PON, and POC:PON (presented as molar ratios) data were tested for normality (Shapiro-Wilkinson test) and homogeneity (Levene test). Data that were not normally distributed, and once log-transformed did not meet the assumptions of normality and homogeneity, were analyzed using the nonparametric Kruskal-Wallis test. Trends between $\delta^{13}\text{C}$ -POC, $\delta^{15}\text{N}$ -PON, and salinity were evaluated using logarithmic and linear regression models. Pearson correlation analysis was used to examine the relationships between POC and PON concentrations, POC and PON concentrations and river flow, percentage of POC to TOC and land cover, and percentage of terrestrial derived POM and river flow.

All statistical tests were performed in Sigmaplot and the R software (version 4.0.2, R Core Team, 2020).

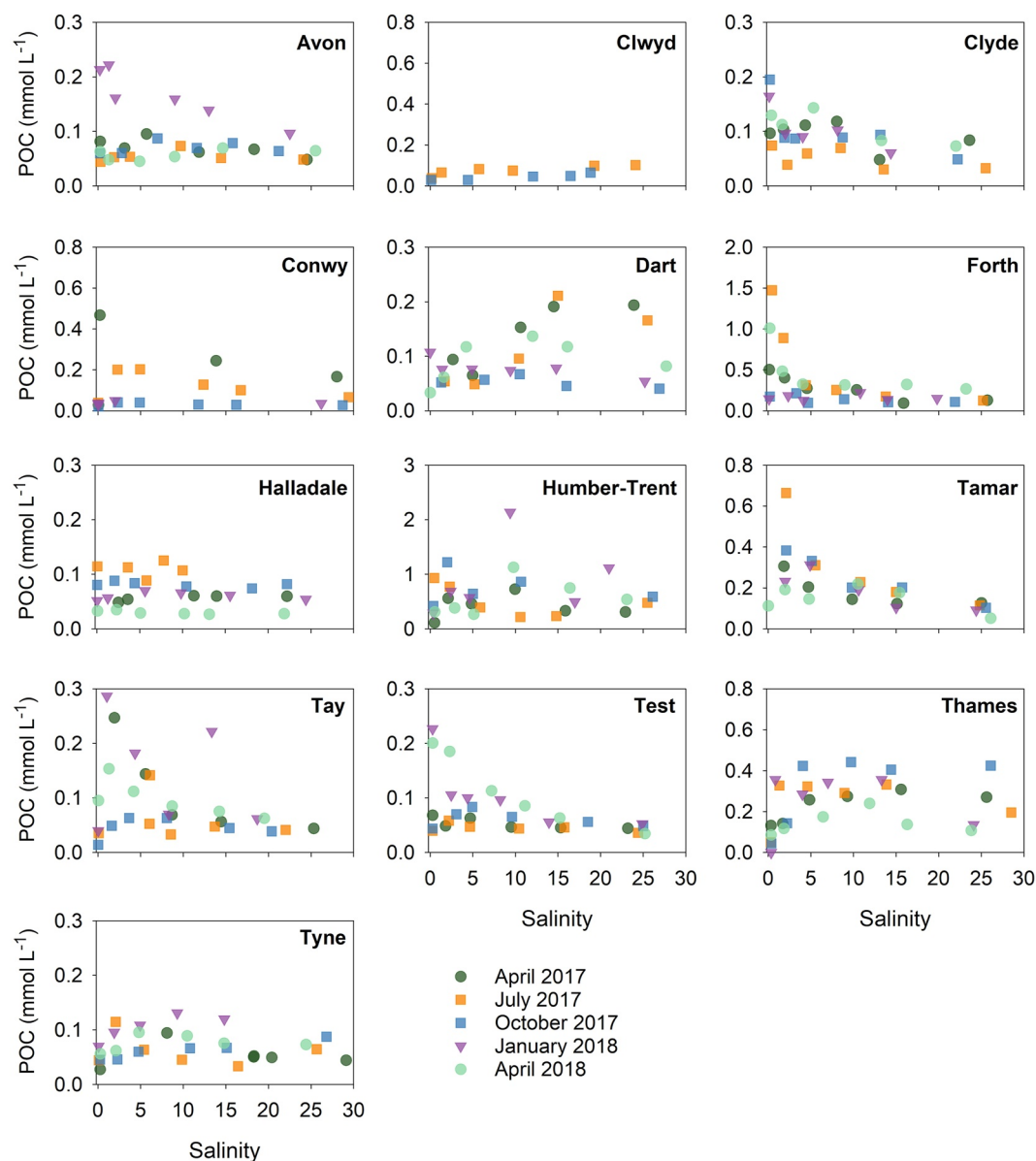


Figure 3. Particulate organic carbon concentrations versus salinity for the 13 British estuaries. The different colors correspond to five sampling campaigns: April 2017 in dark green circles, July 2017 in orange squares, October 2017 in blue squares, January 2018 in purple triangles, and April 2018 in light green circles. Note there is no data for Clwyd in April 2017 and January 2018, and for Conwy in April 2018. Note the different values on the y-axes.

20–31.9), except in the Humber-Trent and Thames where POC:PON ratio tended to increase with increasing salinities.

There was no significant correlation between POC and PON concentrations in the lowest salinity waters and the corresponding river flows ($r = -0.01$, $p = 0.91$, $n = 54$ and $r = -0.03$, $p = 0.82$, $n = 54$, respectively).

3.3. Contribution of POC to TOC

In general, POC is not the dominant organic carbon fraction in estuarine waters (Figure 4). On average POC accounted for ~25% of TOC, although lower percentages of POC (<11%) were measured in the Halladale and Tyne and higher percentages of POC (>36%) in the Forth, Humber-Trent, and Thames. There was no clear trend in the percentage contribution of POC to TOC across the salinity gradient.

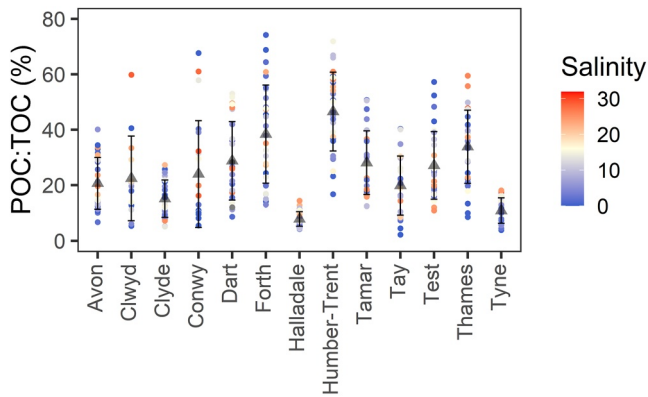


Figure 4. Contribution of particulate organic carbon (POC) to total organic carbon (TOC) (sum of dissolved and particulate organic carbon, $TOC = DOC + POC$) for the 13 estuaries. Small colored circles represent the individual datapoint within each estuary at the different salinities. Black triangles represent the mean value for each estuary and the error bars are the standard deviation.

There was a significant negative correlation between estuarine averaged POC:TOC and the proportion of peatland in the catchment ($r = -0.54$, $p = 0.04$, $n = 13$) (Figure 5a), and a significant positive correlation with the proportion of urban/suburban land cover ($r = 0.455$, $p = 0.04$, $n = 13$) (Figure 5b). In estuaries where $>10\%$ of the catchment is peatland, variations in POC:TOC were largely explained by variations in DOC concentration (Figure 5c). However, in estuaries draining catchments with a peatland coverage $<10\%$, variations in POC:TOC were related to both DOC and POC concentrations.

3.4. Isotopic Composition of Particulate Organic Matter

The isotopic signatures of POC and PON varied between different estuaries. Within estuaries, no seasonality was observed for $\delta^{13}C$ -POC and $\delta^{15}N$ -PON across the salinity range, thus, the isotopic data trends measured during the five sampling campaigns were analyzed together. In general, $\delta^{13}C$ -POC values were low (average \pm sd of $-26.7 \pm 0.42\text{‰}$) at the lowest salinity waters (salinity: 0–1.8). The Humber-Trent estuary was an exception as the $\delta^{13}C$ -POC values at the lowest salinity waters were higher (average $-16.3 \pm 3\text{‰}$, Figure 6). The lowest $\delta^{13}C$ -POC value measured in this estuary (-30.37‰), at a salinity of 0.5, was collected from the river Trent at a distance of 60 km upstream of the subsequent sampling point in this estuary (Figure 1a).

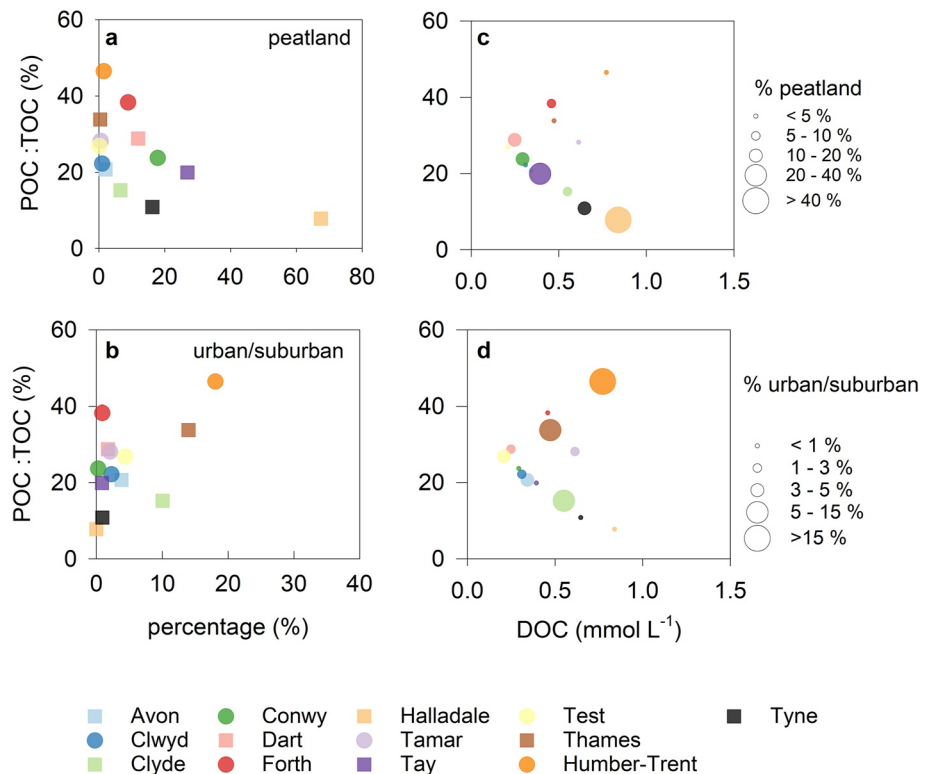


Figure 5. Relationship between the estuarine averaged contribution of particulate organic carbon (POC) to total organic carbon (TOC) ($TOC = DOC + POC$) and the percentage of (a) peatland, (b) urban/suburban land cover of the estuarine draining catchments, (c) and (d) and the averaged dissolved organic concentration (DOC). Different colors correspond to different estuaries and the size of the bubble in panels (c) and (d) to the percentage of peatland (c) and to the percentage of urban/suburban (d) land cover of the draining catchment.

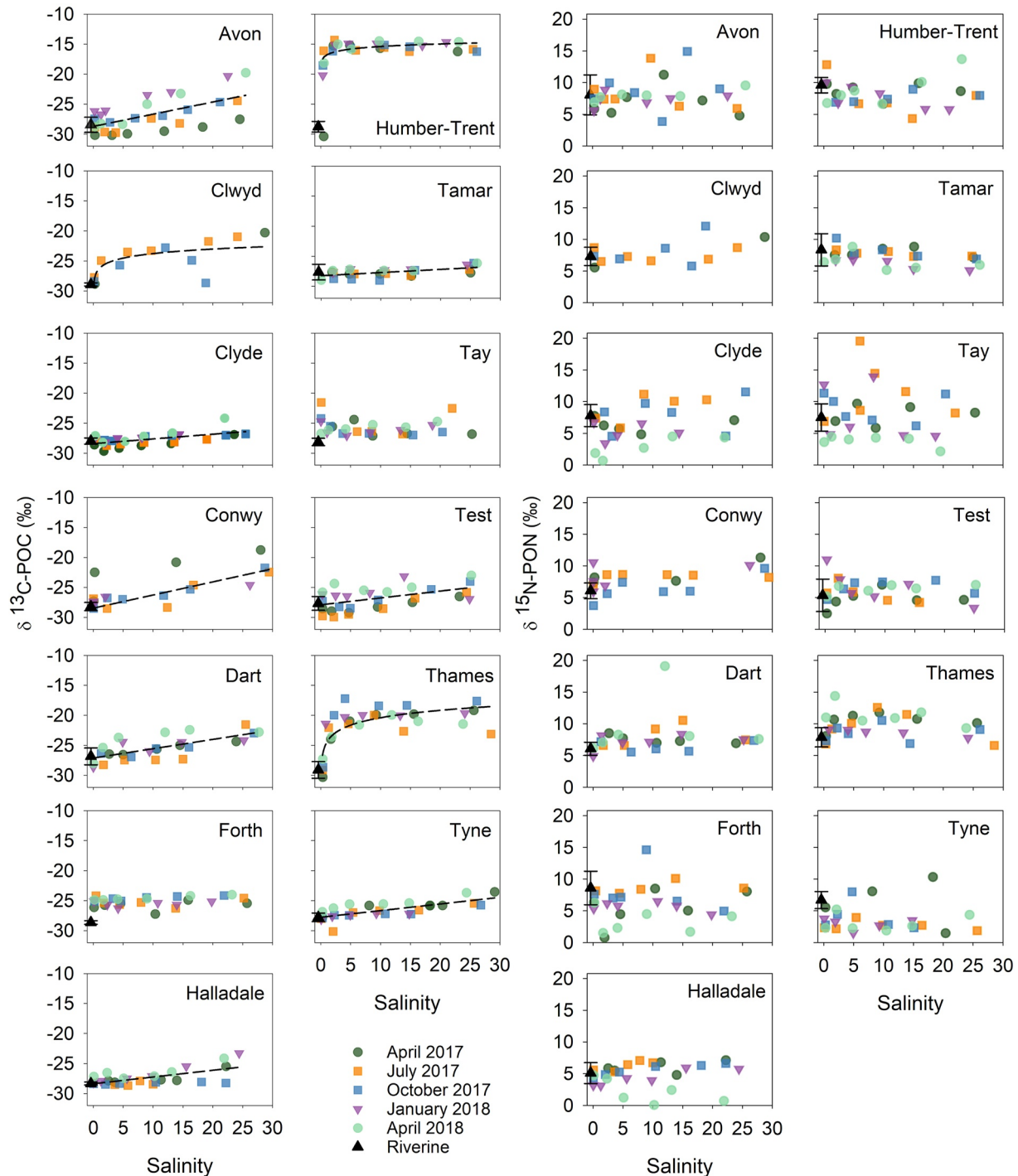


Figure 6. Variations in $\delta^{13}\text{C-POC}$ (left two columns) and $\delta^{15}\text{N-PON}$ (right two columns) across the salinity gradient of 13 British estuaries. The different colors correspond to five sampling campaigns: April 2017 in dark green, July 2017 in orange, October 2017 in blue, January 2018 in purple, and April 2018 in light green. Dotted lines in $\delta^{13}\text{C-POC}$ represent the best significant fitted regression equation (linear or logarithmic). Note that the $\delta^{13}\text{C-POC}$ relationship with salinity was not significant ($p > 0.05$) in the Forth and Tay estuaries and therefore, no regression lines are included. No significant relationship ($p > 0.05$) was found between $\delta^{15}\text{N-PON}$ and salinity. Black triangles represent the average ($n = 13$) riverine $\delta^{13}\text{C-POC}$ and $\delta^{15}\text{N-PON}$ values. Note there are no data for the Clwyd in April 2017 and January 2018 and for the Conwy in April 2018.

Seaward enrichment of $\delta^{13}\text{C-POC}$ was observed in all estuaries except the Forth and Tay, where the $\delta^{13}\text{C-POC}$ remained stable (Figure 6). This seaward enrichment followed two different patterns, with a gradual linear increase across the salinity gradient in eight estuaries (Avon, Clyde, Conwy, Dart, Halladale, Tamar, Test, and Tyne), and

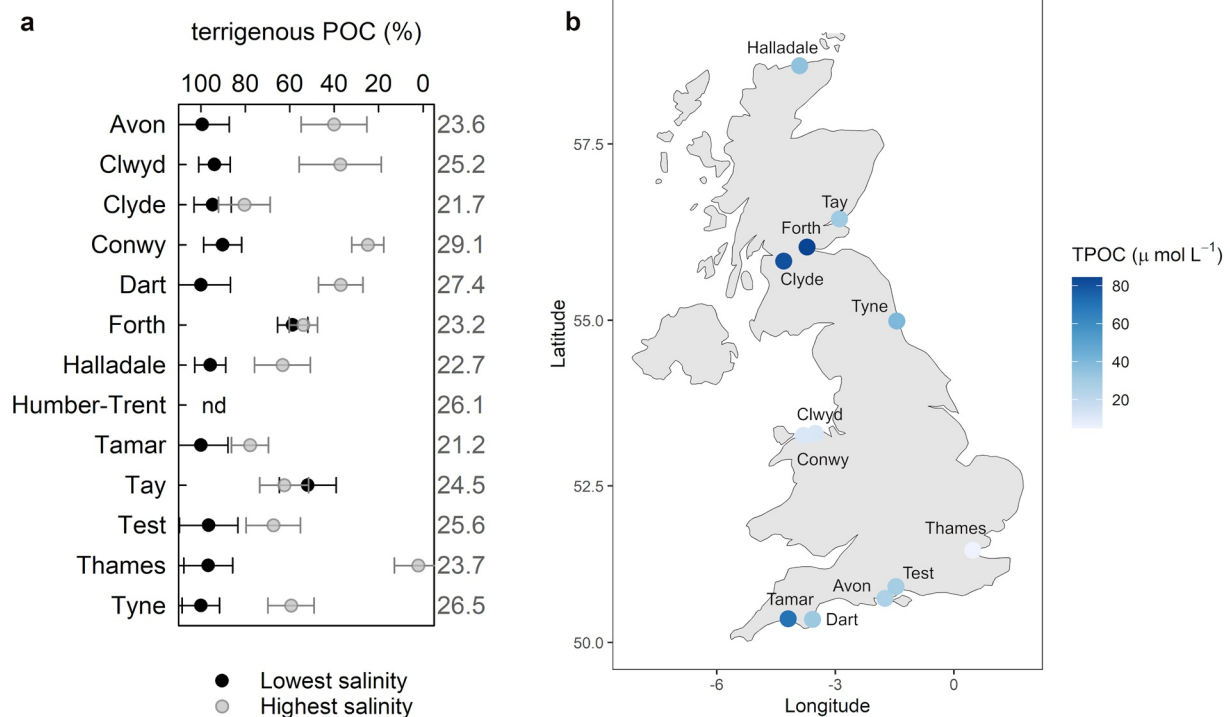


Figure 7. (a) Average of the relative contribution of terrigenous particulate organic carbon (TPOC) at the lowest salinity waters (black circles) and at the highest salinity waters (gray circles) calculated by applying a mass-balance model with two end-members (riverine and marine) for all estuaries except for Humber-Trent. Error bars represent the propagated standard error of the average, and the numbers in gray on the right-side of the vertical axis indicates the average salinity values at the highest salinity waters sampled. (b) Concentration of the TPOC calculated at the highest salinity waters for each estuary. Note that we do not report TPOC values for the Humber-Trent estuary as we could not apply the two-member mixing model as the estuarine isotopic signature was greater than the -20‰ value assumed for marine waters.

a sharper logarithmic enrichment at low salinity values (0–5) in three estuaries (Clwyd, Humber-Trent, Thames) (Figure 6).

Particulate organic matter in most of the estuaries had average $\delta^{15}\text{N-PON}$ values around 6–8‰, with lower values measured in the Halladale and Tyne (average $4.80 \pm 0.36\text{‰}$ and $3.65 \pm 0.43\text{‰}$, respectively), and greater values in the Humber-Trent and Thames estuaries (average $8.19 \pm 0.38\text{‰}$ and $9.73 \pm 0.34\text{‰}$, respectively) (Figure 6). There was a wide range of variation in $\delta^{15}\text{N-PON}$ in the Clyde, Forth, and Tay, but overall, $\delta^{15}\text{N-PON}$ values were rather uniform across salinity gradients (Figure 6).

The $\delta^{13}\text{C-POC}$ values at the lowest salinity samples (salinity: 0–1.8) were within the range of $\delta^{13}\text{C-POC}$ observations at the corresponding rivers in 10 of the 13 estuaries (Figure 6). The exceptions were the Forth, Humber-Trent, and Tay estuaries, in which $\delta^{13}\text{C-POC}$ values at the lowest salinity waters were higher than their corresponding river end-member signature.

Based on the two end-member stable isotope mixing model, the median contribution of terrigenous to estuarine POC was 96% (range 52%–100%) at the lowest salinity waters (salinity: 0–1.8, Figure 7a). At the highest salinity waters (salinity: 20–31.9), we observed a greater variability, with contributions ranging from 2% to 80% (median 57%). The constant isotopic signature observed in the Forth and Tay estuaries (Figure 6) indicated a steady contribution of terrigenous POM of $\sim 55\%$ with no significant changes along the salinity gradient in both estuaries. Estimated TPOC concentrations at the highest salinity waters ranged from $5 \mu\text{mol L}^{-1}$ in the Thames to $85 \mu\text{mol L}^{-1}$ in the Forth (Figure 7b).

4. Discussion

4.1. Bulk Particulate Organic Matter Concentrations

The diverse estuaries sampled here presented a wide range of POC and PON concentrations. The two estuaries with the highest POC and PON concentrations, Humber-Trent and Thames, are the estuaries with the largest catchment area sampled in this study. Their high POC concentrations are consistent with findings from other large, turbid European estuaries, with long water residence time (>30 days, Middelburg & Herman, 2007). Although we did not measure turbidity, previous studies in the Humber-Trent and Thames reported high turbidity related to the tidal currents (Uncles et al., 2006) and anthropogenic pressures, such as dredging of sediments, vessel navigation, and runoff from large cities (Abril et al., 2002; Pye & Blott, 2014).

Despite much evidence that catchment POC exports are flow related (Duan & Bianchi, 2006; Qu et al., 2020; Ye et al., 2017) the lack of a relationship between river flow and POC concentrations at the lowest salinity waters observed in our study suggests a limited hydrological control on the quantity of POC transported into estuaries. It is worth noting that our samples were collected mainly during low river fluxes, despite the variability presented by several estuaries (Figure 1b), which might have influenced the lack of relationship observed. High river fluxes could result in greater POC inputs from the rivers into the estuaries (Bukaveckas, 2022). However, greater POC inputs might not necessarily be related to greater POC export from the estuaries as this would depend on the organic matter retention within the estuaries (Bukaveckas, 2022). Nevertheless, riverine POC transport can be influenced by other factors not related to its flow, such as catchment characteristics or seasonal changes in human activities and variations in the biological freshwater primary productivity (Regnier et al., 2013; St. Pierre et al., 2020).

Most of the estuaries showed nonconservative mixing of POC and PON across salinity gradients. This suggests either the existence of alternative organic matter sources other than riverine inputs along the salinity gradient such as via sewage-derived POM, or a high degree of resuspension and deflocculation of organic matter within the estuary during each tidal cycle; and/or losses via flocculation, deposition to sediments, and net remineralization (Cole et al., 2007; Liénart et al., 2017; Middelburg & Herman, 2007). The linear increase in the isotopic POC signatures observed across the salinity gradient, except in the Clwyd, Thames, and Humber-Trent estuaries (Figure 6), indicates that the POC increases within the estuary, e.g., via tributaries at intermediate salinities, had a comparable POC and PON isotopic origin to that already present in the estuaries. Thus, the most plausible reason for the POC changes along the salinity gradient was a physical reworking (i.e., sediment resuspension and deposition) of the organic matter already present in the estuaries with some biological influences, as previously observed in other estuaries (Geyer et al., 2001; McCandliss et al., 2002), rather than an input of sewage-derived POM from sewage treatment plants. In contrast, decreases in POC concentration could be related to conversion between POC and DOC pools (Middelburg & Herman, 2007; Palmer et al., 2016). In this case, a negative correlation between the pools of the two fractions would be expected. However, our analysis showed significant positive correlations between POC and DOC in 3 of the 13 estuaries (Halladale, Humber-Trent, and Tamar) and no significant correlations in the other estuaries (Figure S6 in Supporting Information S1). Thus, unless there was simultaneous POC and DOC removal associated with flocculation processes, our data do not support the transformation of POC to DOC as a reason for the observed POC decrease.

4.2. Contribution of POC to TOC and Its Relationship With Land Cover

Our data, together with the estimations provided in García-Martín et al. (2021), indicate that POC is not the dominant form of organic carbon across the sampled estuaries. The average POC contribution of ~25% to the TOC pool compares well with previous worldwide estimates of 20% (Hope et al., 1994), with the 28% estimated for temperate Europe (Ciais et al., 2008) and is lower than the average value of 40% reported for nine large human-influenced estuaries along the Atlantic coastline of Europe (Middelburg & Herman, 2007). Our data showed an inverse relationship between the percentage of POC to TOC and the percentage of peatland in the catchment area. Peatlands are key reservoirs of carbon with high concentrations of DOC (Freeman et al., 2001) that can be transported from land to ocean via estuaries. Our data suggest that for estuaries draining catchments containing >10% peatland, the low percentage of POC to TOC values was primarily related to high DOC concentration—i.e., POC exports were not strongly linked to peat cover. In estuaries draining catchments with low peatland cover, the contribution of POC to TOC was more strongly influenced by variations in POC supply.

4.3. Sources of Particulate Organic Matter and Temporal Variability

The $\delta^{13}\text{C}$ -POC and $\delta^{15}\text{N}$ -PON signatures indicate that POM had a similar origin throughout the year with no seasonal variation. The lack of seasonality observed in our isotopic data contrasts with the more common pattern reported in other temperate and tropical studies, in which $\delta^{13}\text{C}$ -POC values increase during spring months due to an increase in the contribution of phytoplankton-derived organic matter (Gao et al., 2014; Liénart et al., 2017; Ye et al., 2017). In addition, temporal variability in the contribution of different POC sources has been suggested to be a result of large changes in river flow (Liénart et al., 2017; St. Pierre et al., 2020; Ye et al., 2017). However, our results suggest that the percentage of terrigenous material along the salinity gradient was independent of the hydrological conditions and was actually rather uniform over time in each of the estuaries studied. Differences in the seasonality of the isotopic signature between our results and previous studies could be explained by the riverine-estuarine hydrographic properties. Our estuaries, and their associated rivers, can be considered highly mixed and turbid, with great sediment resuspension with tidal currents, and relatively short residence times (<30 days, Uncles et al., 2002) (Uncles et al., 2006) which can limit primary production. In contrast, the work by Liénart et al. (2017) was largely carried out in coastal waters and embayments, where plankton largely contributed to POM with greater abundances during spring and summer. Furthermore, the seasonal differences observed in the tropical Pearl River Estuary (Ye et al., 2017) were related to the large differences in the river flow between the dry and wet seasons, which coincided with a fourfold seasonal change in chlorophyll-*a* concentration. Similarly, large differences in rainfall events and marine primary production drove the seasonal variability observed in a Pacific temperate coastal study (St. Pierre et al., 2020). It is likely that the impact of episodic, high river flow events on the POC isotopic signature might be more apparent in the coastal zone under these circumstances.

Most of the POM in the lowest salinity waters resembled a mix of terrestrial C3 plants, terrestrial soils, and riverine phytoplankton, which are $\delta^{13}\text{C}$ -POC depleted (-29‰ to -26‰) relative to marine POC (Middelburg & Nieuwenhuize, 1998; Thornton & McManus, 1994), have a $\delta^{15}\text{N}$ -PON between 1‰ and 8‰ (Kendall et al., 2001; Peterson & Fry, 1987) and POC:PON ratios greater than Redfield ratios (between 6.6 and 8.7, Redfield, 1934). The $\delta^{15}\text{N}$ -PON isotopic signatures (average $< 5\text{‰}$) and the POC:PON ratios above 15 measured in the Halladale estuary suggest a greater contribution of terrestrial C3 plants and soil-derived POM rather than freshwater phytoplankton. This estuary drains a peatland-dominated catchment, and therefore a C3 plant/soil and peat-derived POM signal would be expected. The Thames, and especially the Humber-Trent, exhibited more enriched $\delta^{13}\text{C}$ -POC signatures, with values in the Humber-Trent estuary $> -16\text{‰}$ and POC:PON ratios of 21.2. Enriched $\delta^{13}\text{C}$ -POC values in the Thames and Humber-Trent estuaries have been previously reported (Bristow et al., 2013), and were related to the presence of detritus from marsh plants, seagrasses, and macroalgae which were homogeneously distributed from the mouth of the estuary throughout the estuary by the flood tide. In addition, the higher nitrogen isotopic signal observed in the Thames estuary compared to the other estuaries of this study (average $\delta^{15}\text{N}$ -PON = 9.7‰) seems to reflect an enhanced anthropogenic influence that this estuary experiences and the presence of seagrasses and other macrophytes with high nitrogen isotopic values (Jones et al., 2018). It is known that macroalgae can be $\delta^{15}\text{N}$ -PON enriched by waste waters (Gartner et al., 2002), thus reflecting previous and recent sewage discharges in the estuary.

The gradual seaward increase observed in the $\delta^{13}\text{C}$ -POC values in 8 out of 13 estuaries is consistent with the dilution of TPOC with POC from marine waters. The sharp changes observed in the Clwyd, Humber-Trent, and Thames estuaries at salinities < 2 and the differences observed between the $\delta^{13}\text{C}$ -POC values at the lowest salinity samples in the Forth and its river samples, however, indicate the presence of different POC sources and/or strong internal processes which prevail over the mixing of the two end-members (Bristow et al., 2013; Fichez et al., 1993). In several estuaries, e.g., the Forth, Tamar, and Humber-Trent, a transient estuarine turbidity maximum has been reported in the vicinity of the freshwater-seawater interface (0.5, Upstill-Goddard & Barnes, 2016), generated by residual currents (Uncles & Stephens, 1993; Uncles et al., 1999), which can resuspend particles. However, surface sediments from the Thames estuary have $\delta^{13}\text{C}$ -POC values of -27‰ at low salinities (Lopes dos Santos & Vane, 2016). Thus, we suggest that the homogeneous distribution of seagrasses, marsh plants, and macroalgae along the estuary described by Bristow et al. (2013) is the most likely cause of the sharp increases at the river-estuarine transition in the Humber-Trent and Thames and not the resuspension of terrigenous particles. By contrast, the uniformity in carbon isotopic signal observed in Forth is consistent with previous observations in this estuary (Graham et al., 2001), and was explained by an efficient mixing and redistribution of its sediments.

4.4. Contribution of Terrestrial POC at the Estuary-Coastal Zone

The relative contribution of TPOC to the total POC pool at the highest salinity waters varied widely, between 2% and 80%. Our median relative contribution of TPOC (57%) is in the range of the contribution reported from a temperate estuary on the NE coast of the USA (50%–65%, Goñi et al., 2005), and higher than previous annual reports from 17 estuaries across different embayments and coastal waters of France (3%–19%, Liénart et al., 2017) and in the Pearl River, China (32%–47%, Ye et al., 2017), but lower than the contributions in the Gironde estuary in France (91%, Savoye et al., 2012).

Our data suggest that the TPOC concentrations found at the highest salinity waters (range 5–85 $\mu\text{mol L}^{-1}$, median 34 $\mu\text{mol L}^{-1}$) represent a significant contribution to overall organic carbon supply to coastal waters. The terrestrial fraction of the POC is more refractory compared to the marine POC component and it tends to become buried more easily (Burdige, 2005). It seems likely that the TPOC export from British estuaries may be redeposited in coastal marine sediments, contributing to the high POC stocks found in these sediments (Diesing et al., 2017). In addition, input signatures from the Humber river were found 50 km offshore in the North Sea during a winter period (Bristow et al., 2013), which suggest that terrestrial POC can also contribute to the POC pool of shelf seas at certain times of the year.

4.5. Limitations of Our Approach

POC and PON concentrations and isotopic composition reported in this study should be interpreted with some caution. Samples to determine the concentrations of POC, PON, and their stable isotope composition were not acidified and thus do not rule out the presence of carbonate contributions. However, we have estimated an average uncertainty of 16% associated with the contribution of particulate inorganic carbon in the water samples (see Supporting Information S1). In addition, we hypothesize that the contribution of the inorganic phase is very low based on (a) the consistency of our values compared with previous reports from several estuaries included in this study in which the samples were acidified (Bristow et al., 2013; Graham et al., 2001; Thornton & McManus, 1994); (b) the previous indication that little or no inorganic carbonate was present in particulate samples from British rivers (Adams et al., 2015); and (c) the consistency of the samples between sampling campaigns.

In addition, we acknowledge that the calculation of TPOC is subject to error. The implementation of a mixing model with two $\delta^{13}\text{C}$ -POC end-members may not be suitable in cases with multiple sources (Liénart et al., 2017; Ye et al., 2017). However, the inclusion of more than two sources increases the uncertainty of the model output (Phillips & Gregg, 2003). Furthermore, we have adopted the most common, and averaged, value of -20‰ for our marine end-member. Variability in the marine carbon isotopic signature is expected, as the amount and type of phytoplankton and the composition of their carbon compounds can all affect the isotopic signature (Fry & Wainright, 1991; Megens et al., 2001). In addition, there is a potentially large temporal and spatial variability within the North Sea (Bristow et al., 2013; Megens et al., 2001). Adopting a more positive or negative value (e.g., between -18‰ and -22‰) would lead to differences in the percentage of TPOC, especially at the highest salinity waters. Nevertheless, our average estimate of a 57% contribution by TPOC to total POC at the highest salinity waters agrees with a previous report (Goñi et al., 2005), and the interestuarine variability in TPOC concentration observed in this study reflects the benthic POC distribution observed in British coastal and shelf waters (Legge et al., 2020).

5. Conclusions

We observed heterogeneous dynamics between 13 different estuaries across Great Britain that highlight the variability in the POC and PON concentrations between estuaries. The contribution of POC to TOC was inversely related to the percentage of peatland in the surrounding catchment area. Despite the different hydrological conditions, no seasonality was observed in the POC and PON isotopic signatures of individual estuaries, thus indicating similar sources of particulate material throughout the year within each estuary. These isotopic signatures indicate a particulate carbon input representing a mix of C3-plant and freshwater phytoplankton sources at the low salinity end of most estuaries. The results of a two end-member stable isotope mixing model showed a seaward decrease in the contribution of TPOC, which ranged from 2% to 80% (average 57%) at the highest salinity waters depending on the estuary. Our study suggests that future efforts to better characterize regional contributions of TPOC to coastal waters should consider interestuarine spatial and intraestuarine temporal variability. Furthermore, in order to improve the global estimate of terrestrial carbon inputs to coastal waters it is important to include estuaries covering different catchment sizes, hydrological conditions, and land cover usage.

Data Availability Statement

All data (POC, PON, stable carbon, and nitrogen isotopes) used in this study are available in the British Oceanographic Data Centre (doi: <https://doi.org/10.5285/d111d44e-0794-28dc-e053-6c86abc0fc99>).

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