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Key Points:

- Dissolved organic carbon (DOC) mixing dynamics were mainly influenced by the DOM fluorescence components associated with land use types
- Catchments with a high percentage of arable and (sub)urban land uses tend to export more DOC to coastal areas than they receive from rivers
- Catchments with a high percentage of peatland have >5-fold greater area-specific export of DOC to coastal waters

Supporting Information:

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

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Contrasting Estuarine Processing of Dissolved Organic Matter Derived From Natural and Human-Impacted Landscapes

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Abstract The flux of terrigenous organic carbon through estuaries is an important and changing, yet poorly understood, component of the global carbon cycle. Using dissolved organic carbon (DOC) and fluorescence data from 13 British estuaries draining catchments with highly variable land uses, we show that land use strongly influences the fate of DOC across the land ocean transition via its influence on the composition and lability of the constituent dissolved organic matter (DOM). In estuaries draining peatland-dominated catchments, DOC was highly correlated with biologically refractory "humic-like" terrigenous material which tended to be conservatively transported along the salinity gradient. In contrast, there was a weaker correlation between DOC and DOM components within estuaries draining catchments with a high degree of human impact, that is, relatively larger percentage of arable and (sub)urban land uses. These arable and (sub)urban estuaries contain a high fraction of bioavailable "protein-like" material that behaved nonconservatively, with both DOC removals and additions occurring. In general, estuaries draining catchments with a high percentage of peatland (≥18%) have higher area-specific estuarine exports of DOC (>13 g C m^{-2} yr^{-1}) compared to those estuaries draining catchments with a high percentage (≥46%) of arable and (sub)urban land uses (<2.1 g C m^{-2} yr^{-1}). Our data indicate that these arable and (sub)urban estuaries tend to export, on average, ~50% more DOC to coastal areas than they receive from rivers due to net anthropogenic derived organic matter inputs within the estuary.

1. Introduction

The land ocean aquatic continuum (LOAC) consists of soils, streams, rivers, groundwater, lakes, wetlands, estuaries, and shelf seas and plays a key role in the global carbon (C) cycle. Inland waters receive ~5.1 Pg C per year from land, which is ~55% of global net ecosystem production from terrestrial ecosystems (Drake et al., 2018). This is approximately double the oceanic uptake of anthropogenic CO_2, which slows climate change and drives ocean acidification. Our understanding of what drives the export of C into the LOAC, its fate therein, and hence its export to the open ocean, remains incomplete.

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Organic C within the LOAC is derived from both allochthonous (primarily terrestrial production sourced from soils) and autochthonous (primarily aquatic production within rivers and estuaries) sources, with dissolved organic carbon (DOC) fluxes exceeding particulate organic C fluxes in most temperate rivers (Hedges et al., 1997). Within estuaries, terrigenous DOC can be modified, removed, or added through estuarine processes including flocculation (Sholkovitz et al., 1978; Uher et al., 2001), photodegradation (Hernes & Benner, 2003; Moran & Hodson, 1994), biological uptake or decomposition (Hernes & Benner, 2003; Morris et al., 1978; Søndergaard & Middelboe, 1995), and in situ production (Fisher et al., 1998). The balance of these processes influences the fate of the constituent C and its effect on the greenhouse gas balance to the atmosphere. Both photolysis and biological decomposition can increase fluxes of CO_2 to the atmosphere, whereas flocculation leads to C burial through sedimentation.

Estuarine DOC mixing displays a diversity of behavior, with some estuaries showing a linear decrease in DOC concentrations with increasing salinity (a tracer of conservative mixing) (Abril et al., 2002; Mantoura & Woodward, 1983; Osterholz et al., 2016), suggesting that removal/addition processes are minor or in balance (Cifuentes & Eldridge, 1998). Other estuaries display constant or occasional nonconservative mixing behavior suggesting inputs and/or losses of DOC (Benner & Opsahl, 2001; Li et al., 2019; Osterholz et al., 2016; Spencer et al., 2007; Uher et al., 2001). Riverine DOC concentrations have been suggested to be the dominant regulator of intraestuarine DOC behavior (Spencer et al., 2007), with high concentrations leading to DOC removal within the estuary.

Long-term changes in land use patterns, climate and atmospheric pollutant deposition have greatly altered riverine DOC concentrations and dissolved organic matter (DOM) composition in some regions during the last century, with potential consequences for DOC fluxes across the LOAC (Monteith et al., 2007). Estuaries influenced by human activities such as agriculture and urbanization, can have a higher contribution of their DOM load driven by autochthonous production as a result of higher inorganic nutrient concentrations (Wilson & Xenopoulos, 2009). Autochthonous DOM has a larger bioavailable "protein-like" fraction, which can be rapidly degraded, resulting in nonconservative DOC mixing behavior and contributing to CO_2 fluxes to the atmosphere. In contrast, estuaries draining more natural catchments, such as peatland, are dominated by biologically recalcitrant "humic-like" DOM (Moore et al., 2013) and therefore DOC from these landscapes may traverse estuaries and reach coastal areas without alteration.

The overall effect of the estuarine filter, defined as the capacity to retain material fluxes from land to sea (Bouwman et al., 2013; Lisitzin, 1997), on riverine DOC fluxes at a global scale is linked to the amount and type of DOM that individual catchments produce. Based on a comprehensive inorganic C data set in the North Sea and a consideration of riverine and estuarine data from the literature, it has been suggested that NW European estuaries convert the majority of the DOC they receive from rivers to CO_2, which can then outgas to the atmosphere (Kitidis et al., 2019). However, this assessment is based on large, anthropogenically modified rivers, and therefore may be biased toward environments with highly bioavailable DOC and overlook DOC derived from seminatural, C-rich landscapes such as those present at boreal latitudes.

A more thorough assessment of system behavior requires the study of estuaries with variable DOM inputs and quality across a range of land use types over different hydrological conditions. Here we address this issue by investigating the estuarine transport dynamics, transformation and characteristics of DOM, and the flux of DOC out of the estuary over an annual cycle in 13 British estuaries (draining 16% of the Great Britain area). These were carefully selected to represent the full range of catchment land use types across Great Britain, from those with a high proportion of peatland, to mixed catchments influenced by arable, (sub)urban areas, and intensively managed grasslands.

As DOM in estuaries draining peat-dominated and more arable catchments has different contributions of "humic-like" and "protein-like" components to the DOM pool (Asmala et al., 2013; Wilson & Xenopoulos, 2009), we hypothesize that these differences will influence the DOC mixing dynamics in small-medium size estuaries. Specifically, we suggest that estuaries draining catchments with a high percentage of peatland would have more recalcitrant "humic-like" DOM which would be transported conservatively across the salinity gradient in estuaries. By contrast, estuaries draining catchments with a high degree of human impact (i.e., relatively larger percentage of arable and (sub)urban land use) would have more bioavailable "protein-like" DOM which would be transported nonconservatively. In addition, we hypothesize that in

more human-impacted estuaries there will be losses of DOC within the estuary and therefore estuarine DOC effluxes would be lower than riverine DOC influxes.

2. Material and Methods

2.1. Study Sites

Thirteen estuaries around the Great Britain coast were studied during five sampling campaigns: three in 2017 (April, July, and October), and two in 2018 (January and April) (Figure 1). The sampling was timed so that samples were collected from high water and on a falling tide. Surface water samples were collected in acid-washed buckets at salinity intervals (ranging across all estuaries from 0 to 32) from fixed points such as bridges or from boats, depending on logistical constraints. We consider the values from the lowest salinity waters ($S < 0.5$) as the riverine end-member concentration. Fully saline offshore waters ($S > 34$) could not be sampled on every survey and so we refer to samples with the highest salinity on each sampling trip (salinity between 19 and 32) as "high-salinity" end-members. A bulk water sample was taken at each station and then split in the field into a number of subsamples for various analyses including DOC concentration and DOM fluorescence spectroscopy.

All samples for a particular determinand were sent in ice-cooled darkened containers to a single laboratory (see below) in order to ensure analytical consistency. In total, between 350 and 390 samples were collected per determinand.

2.2. Environmental Parameters and Catchment Land Use Types

Temperature (°C) and conductivity (μS cm^{-1}) of the estuarine surface water were measured in situ using a Hach HQ30D sensor. Daily river flow rates ($m^3\ s^{-1}$) were obtained from the UK National River Flow Archive (www.nrfa.ceh.ac.uk). The proportion of land use types was calculated for each estuary catchment using the land classification data supplied by the UK Center for Ecology and Hydrology (UKCEH) and 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. This data set comprises a 50 m grid of elevation values with a vertical resolution of 0.1 m. Ordnance Survey spot heights and hydrologically accurate digitized river channels were used during the development of this data set. Catchment boundaries were derived using the Hydrology Toolbox in Arc Map (v10.6) and were used to estimate the catchment area for each estuary.

2.3. Dissolved Organic Carbon Concentrations

Water samples were filtered through prerinsed 0.45 μm cellulose acetate filters using rubber free syringes into acid-washed HDPE bottles. Samples were analyzed by the UKCEH Centralized Analytical Chemistry Laboratory, Lancaster. DOC concentrations were measured using a Shimadzu TOC-L analyzer. Prior to analysis samples were acidified with 1 M HCl, then purged with Zero grade air for 6 min to remove any inorganic C. The samples were then analyzed for the remaining C, measured by infrared absorbance as CO_2 following combustion of DOC at 720 °C over a Pt-catalyst. We used two calibration ranges, 0–10 mg L^{-1} (equivalent to 0–0.83 mmol L^{-1}) and 10–50 mg L^{-1} (equivalent to 0.83–4.17 mmol L^{-1}), depending on the DOC concentration in the samples. The limit of detection for DOC analysis was 0.6 mg L^{-1} (equivalent to 0.05 mmol L^{-1}) (calculated from the mean of a series of blanks plus 3× standard deviation). Certified reference materials at concentrations of 5, 10, and 40 mg L^{-1} were measured every 30 samples or less. We checked precision on approximately 5% of the samples submitted and the calculated precision was within 10% where values were significant.

2.4. DOM Fluorescence and Absorbance

Filtered DOM fluorescence samples were analyzed at the British Geological Survey, Wallingford (Oxfordshire) laboratory within 48 h of collection. DOM fluorescence excitation-emission matrices (EEM) were measured using a Cary Eclipse fluorescence spectrophotometer with a 1 cm path length. Scan settings were

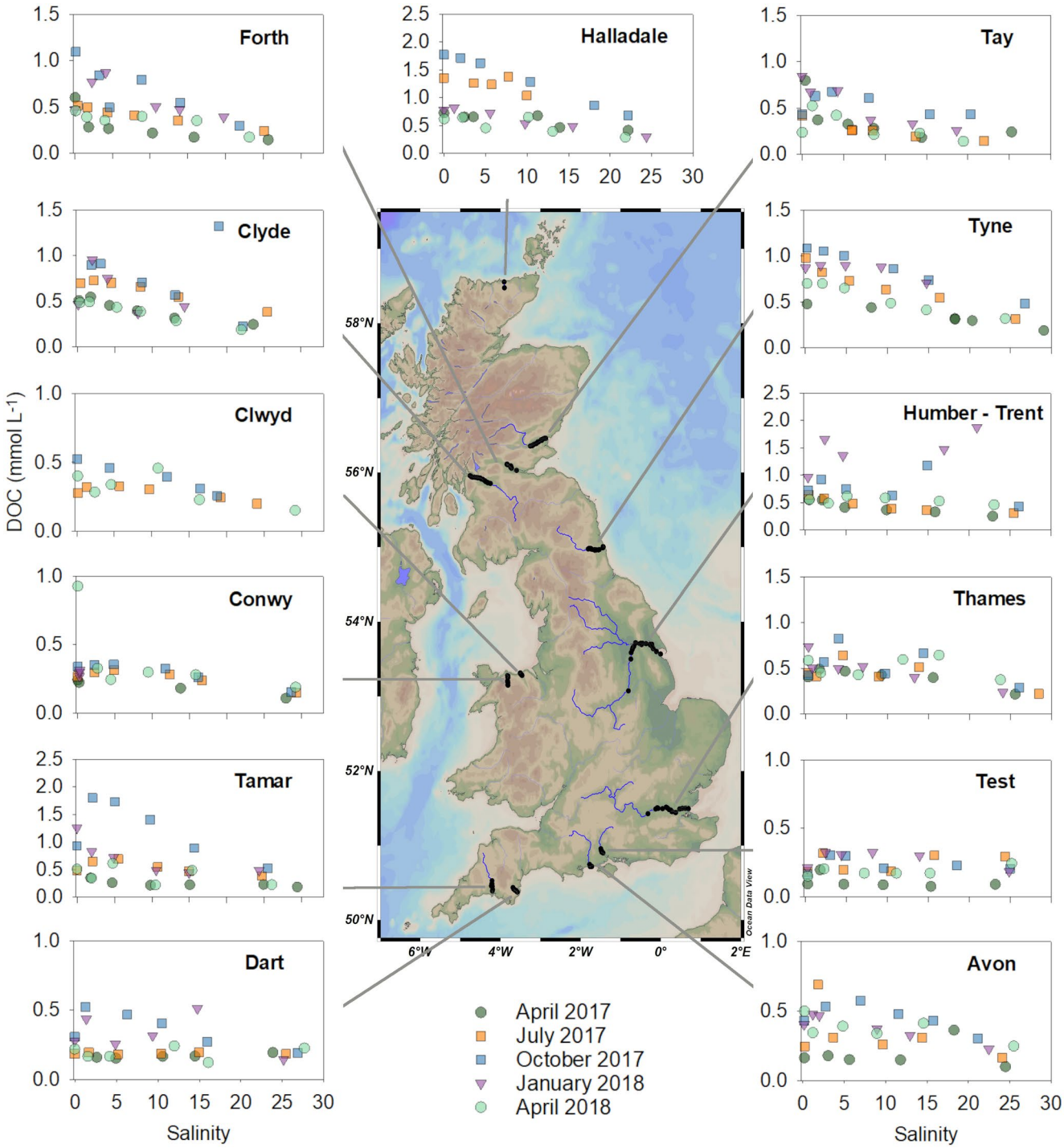

Figure 1. Dissolved organic carbon dynamics in 13 British estuaries. Geographical distribution of the 13 estuaries and the dissolved organic carbon concentration (DOC) versus salinity plots for each estuary. The black dots in the map correspond to the location where water samples were collected. In the plots, the different colors and symbols correspond to the five sampling surveys: 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.

configured for emission from 280 to 500 at 2 nm intervals, and excitation between 245 and 400 nm at 5 nm intervals. Milli-Q water was used as a blank. Absorbance was blank corrected and measured in a 1 cm cuvette on a UV-vis spectrophotometer (Varian Cary 60) at 1 nm intervals from 800 to 200 nm. The EEMs for the samples were obtained by subtracting the blank EEM and undertaking absorbance and instrument

corrections (Lakowicz, 2013) and were normalized to Raman units (Stedmon et al., 2003). Parallel factor (PARAFAC) analysis was used to obtain validated fluorescence components of the DOM using the DOM-Fluor Toolbox in Matlab (Stedmon & Bro, 2008). The complete data set used in the PARAFAC model included 418 EEMs (all the estuary samples plus samples from the river end-members collected in parallel river surveys). A 6-component model was split half validated after removing a small number of samples with large leverage (Table S1 and Figure S1). We calculated the fluorescence (FI) and beta to alpha (β/α) indices from EEMs, to better distinguish the sources and freshness of DOM (McKnight et al., 2001; Wilson & Xenopoulos, 2009) in the different estuaries. FI was calculated as the ratio of fluorescence emission intensities at 470 and 520 nm with the excitation intensity of 370 nm (Cory & McKnight, 2005). β/α was calculated as the ratio of emission fluorescence intensity at 380 nm and the maximum emission fluorescence intensity observed between 420 and 435 nm at an excitation wavelength of 310 nm. FI values around 1.2 indicate terrigenous origin, while values of 1.8 indicate a more microbial and autochthonous source (Jaffé et al., 2008; McKnight et al., 2001). Low values of β/α indicate old DOM, while values around one indicate fresh DOM (Wilson & Xenopoulos, 2009).

2.5. DOC Mixing Model Dynamics and Flux Calculations

In order to analyze the DOC dynamics along the estuaries, we modeled the conservative distribution of the DOC concentrations with salinity. The approach used was to estimate the theoretical dilution line calculated as the linear regression between the DOC concentration at the lowest and highest salinity waters (Mantoura & Woodward, 1983) for each estuary at each sampling month. The distribution of DOC was considered to be conservative when the DOC concentrations followed the theoretical linear decrease.

We allocated the trend in DOC concentration with salinity observed on each occasion in each estuary to one of five different distributions: (a) a conservative mixing (linear decrease from the low salinity waters to the high-salinity waters); (b) initial sharp decrease followed by conservative mixing; (c) initial sharp increase followed by conservative mixing; (d) nonconservative variable mixing with DOC gains and losses; and (e) nonconservative mixing with net DOC gains along the estuary, that is, DOC concentrations in high-salinity waters were greater than DOC concentrations in low salinity waters (graphical representation of the five distributions in Figure 2a).

In order to calculate the annual estuarine DOC effluxes, we calculated the "effective" freshwater DOC concentration following Raymond and Bauer (2001). We first calculated the tangent line at the highest salinity value to a quadratic, or logarithmic, equation (DOC versus salinity) for each estuary and sampling time. Then, we obtained the "effective" DOC concentration as the intercept of the tangent line with the y-axis (zero salinity). Only fitted quadratic, or logarithmic, equations with a coefficient of determination (R^2) greater than 0.5 were accepted. On this basis there was no "effective" DOC concentration data for surveys with $R^2 < 0.5$ which occurred mainly in estuaries with nonconservative variable mixing, type "d" (18 out of a total of 62 cases). In general, estuaries from Groups 1 and 2 had at least four "effective" freshwater DOC concentrations (over the five surveys per estuary), while estuaries from Group 3 had between three and four "effective" DOC concentrations (over the five surveys). As our highest salinity values were not constant for all estuaries and sampling months, we assessed the validity of the estimated "effective" freshwater DOC concentration by performing a sensitivity analysis at two fixed salinity values.

For this, we calculated the "effective" concentration at a fixed value prior to the highest salinity value ($S = 20$); and at $S = 32$, representative of marine waters. In order to obtain the DOC concentrations at salinity 32 for each estuary and at each sampling time, we extrapolated each quadratic, or logarithmic, equation up to salinity 32. Then, we compared the calculated "effective" concentrations at our highest salinity value with the "effective" concentration at the two fixed salinity values (20 and 32) applying a Wilcoxon signed paired rank test to all data together. This confirmed that the "effective" concentrations were not significantly different when adopting the two salinity points ($Z = -0.561$, $p = 0.579$, $n = 47$ for S maxima versus $S = 20$, and $Z = 0.815$, $p = 0.418$, $n = 47$ for S maxima versus $S = 32$ comparisons). Therefore, we adopted the "effective" concentration at $S = 32$ for our calculations of DOC efflux in order to give consistency between estuaries. Annual estuarine DOC effluxes were calculated as the average proportional change in DOC within the estuary (ratio of "effective" over "measured" DOC concentration at the lowest salinity) multiplied by the annual average riverine DOC export:

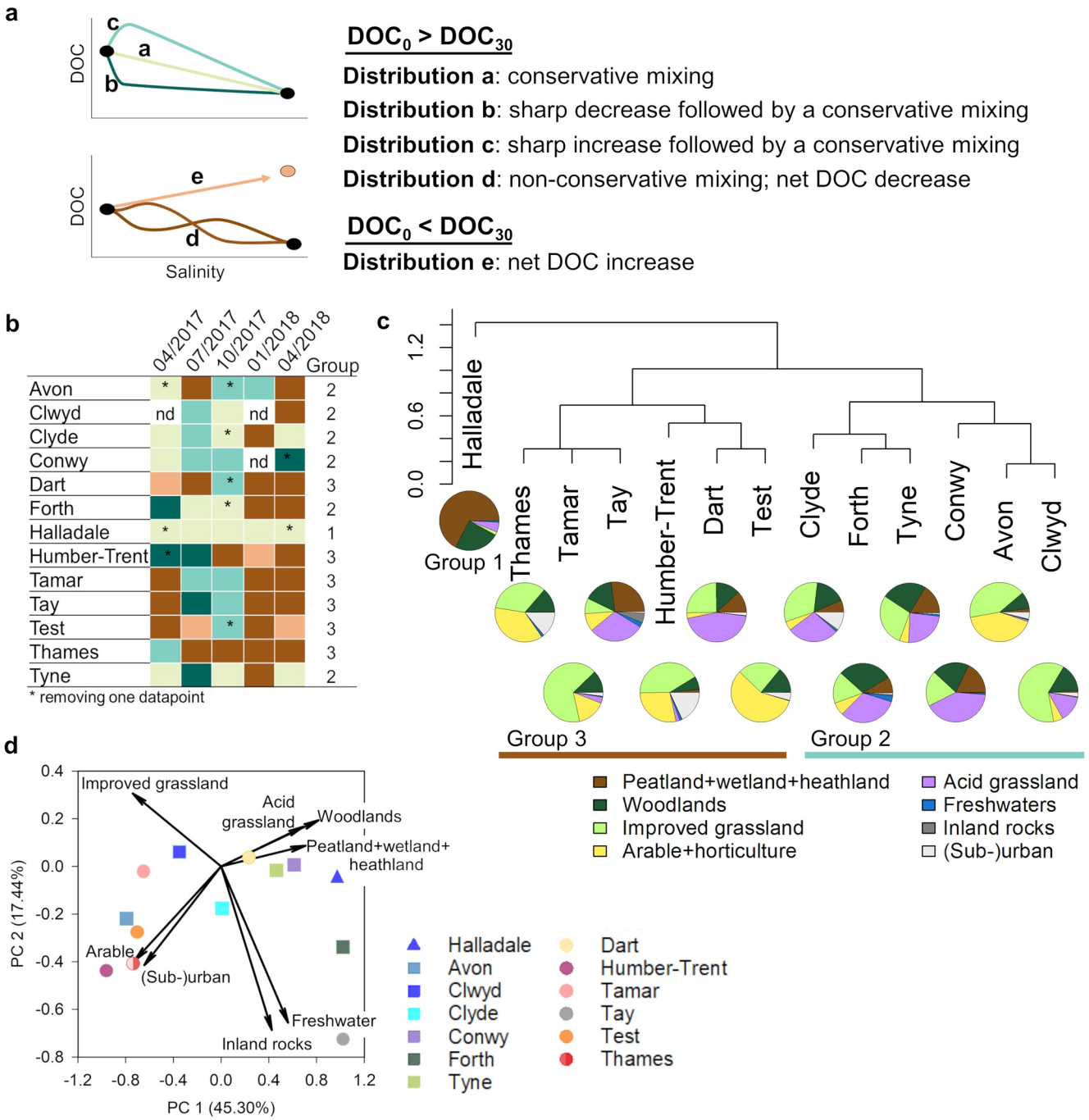

Figure 2. Classification of the different estuaries. (a) Theoretical distributions of the dissolved organic carbon concentration as a function of salinity; (b) Colored matrix summarizing the results of the dissolved organic carbon (DOC) mixing dynamics analysis (graphs in Figure 1). Color coding is according to the mixing types in panel (a) "nd" indicates no data. (c) Results from cluster analysis showing estuaries classified into three groups based on the relative frequency of their DOC mixing behavior shown in panel (b). The pie charts represent the percentage of each land use type for the 13 estuaries sampled. (d) Graphical representation of the principal component analysis results based on the percentage of land use for each estuary (shown in panel c). The black vectors represent the different land use types and individual symbols represent the estuaries. The different symbol shapes represent the three groups according to the grouping in panel (c) triangle for the estuary in Group 1, squares for estuaries in Group 2, and circles for estuaries in Group 3.

$$\text{estuarine DOC flux} = \frac{\sum_{i=1}^{n}\left(\text{DOCeff}_i/\text{DOCo}_i\right)}{n}\text{DOC}_r,$$

where DOCeff_i is the "effective" DOC concentration at the sampling time i, DOCo_i is the "measured" DOC concentration at the lowest salinity waters at the sampling time i, n is the number of sampling surveys taken, and DOC_r represents the annual average riverine DOC influx calculated for the rivers draining to our estuaries during a parallel study (Williamson et al., 2021). Areal-estuarine DOC effluxes were calculated by dividing the annual DOC effluxes by the estuarine catchment area.

2.6. Statistical Analysis

Estuaries were grouped using a hierarchical clustering analysis (Euclidean distance, complete method, hclust function implemented in the R software cluster package R Core Team, 2020) according to the relative frequency of DOC mixing distributions (a–e) presented by each estuary. Differences in the relative contribution of fluorescent components in the three groups of estuaries were tested using analysis of similarities (ANOSIM) performed with the R software vegan package. In order to perform ANOSIM on the DOM compositional data, we first analyzed potential seasonal differences in the relative contribution of the six fluorescence components at low salinity samples (riverine inputs) for the different groups of estuaries classified with the hierarchical clustering analysis. No analysis was done for Group 1 as it only includes one estuary and there was not sufficient data. The relative contribution of the six fluorescent DOM components within each group was compared for the different sampling campaigns. There were only two significant differences ($p < 0.05$) out of the 10 possible combinations in Group 2 (April 2017 versus October 2017, $p = 0.046$; and April 2017 versus January 2018, $p = 0.016$), and none in Group 3. Therefore, no clear seasonal variations in DOM composition were observed, and we analyzed together the data from the different sampling campaigns within groups. Principal component analysis (PCA) was used to group the 13 estuary catchments based on their land use data. PCA was performed with Sigmaplot software. Nonparametric correlations (Tau-Kendall and Pearson) were used to investigate the degree of relationship between DOC concentration and fluorescence DOM intensities and the contribution of the different DOM components and the percentage of land use types (α level 0.05). The map shown in Figure 1 was produced with Ocean Data View (ODV) software (Schlitzer, 2015).

3. Results

3.1. DOC Dynamics

Riverine end-member DOC concentrations (salinity (S) < 0.5) varied by an order of magnitude (0.09–1.77 mmol L^{-1}, median ± standard error 0.47 ± 0.04 mmol L^{-1}). The highest concentrations were observed in a river draining peat-dominated catchment in northern Scotland, and the lowest concentrations were observed in rivers draining groundwater dominated catchments in southern England (Figure 1). Overall, we observed a higher variability in DOC concentration in low salinity waters compared to high-salinity waters (Figure 1). Several estuaries, such as the Clyde, Forth, and Tyne had higher DOC concentrations in low salinity waters in October 2017 and January 2018 than in April 2017 and April 2018, but overall there was no clear seasonal differences in DOC concentrations. There was no significant correlation between DOC concentration in low salinity waters and river flow analyzed across the global data set ($r = 0.2$, $p = 0.11$, $n = 64$).

The relationships observed between DOC concentrations and salinity were highly variable across the different estuaries and sampling months. We assigned DOC mixing behavior on each survey to one of the five different mixing distributions (Figure 2a). The Halladale estuary, which drains a peatland-dominated catchment in northern Scotland, was the only estuary that consistently displayed conservative mixing behavior (Figures 1 and 2b). Most estuaries showed several different DOC mixing behaviors in different sampling surveys (Figures 1 and 2b). We observed conservative behavior (type "a" in Figure 2a) in 16 out of 62 surveys. From the 46 surveys presenting nonconservative mixing behavior, 24 of them showed variable DOC gains and losses (type "d" in Figure 2a) and 4 showed a net increase in DOC within the estuary (type "e" in Figure 2a), and on 18 occasions DOC mixing was characterized by sharp decreases or increases of

DOC from salinities <0.5–5, followed by a linear conservative decrease at higher salinities (type "b" and "c," respectively, in Figure 2a; 6 sharp decreases and 12 sharp increases, Figures 1 and 2b). At salinities between <0.5 and 5, the average DOC increase was equivalent to 35% of the DOC concentration at the river end-member waters (range 1%–93%, $n = 12$), while the average DOC decreases corresponded to 30% of the DOC concentration at the river end-member waters (range 0.5%–64%, $n = 6$).

Cluster analysis of the relative frequency of DOC mixing models revealed three distinct groups (Figure 2c). Group 1 comprised the Halladale; Group 2 included six estuaries (Avon, Clwyd, Clyde, Conwy, Forth, and Tyne) which presented mainly conservative mixing along the estuary or from salinities >5; and Group 3 comprised six estuaries with mainly nonconservative DOC mixing (Dart, Humber-Trent, Tamar, Tay, Test, and Thames). Seasonal analysis of DOC mixing behavior within groups indicated that Groups 2 and 3 estuaries had a higher relative frequency of nonconservative mixing in January 2018 (Figure S2) compared to the other sampling campaigns. However, there was not a clear seasonal pattern.

Land use type plays a key role in regulating DOC dynamics derived from a PCA analysis, which relates to the three groups described above (Figure 2d). The first two principal components together explained 62.7% of the variation in our data set (Figure 2d). The Halladale (Group 1) has a peatland and woodland dominated catchment (91%). Group 2 included estuaries draining seminatural (i.e., mix of peatland + wetlands + heathland, woodlands, and acid grassland) catchments. In general, estuaries from these two groups were related to positive PC1 values. Group 3 included estuaries draining improved grassland, arable, and (sub)urban catchments and were mainly related to negative PC1 values.

3.2. Fluorescence DOM Composition, Optical Indices, and Links With Land Use

The vast majority of DOM is believed to be fluorescent (Coble, 2007; Laane & Koole, 1982), with a characteristic fluorescence spectrum that depends on its composition. We used PARAFAC analysis applied to absorbance corrected EEMs to "fingerprint" the organic matter within each estuary. This yielded six components (Table S1 and Figure S1), the first three of which (C1–C3) are commonly found in estuarine and oceanic environments (Kowalczuk et al., 2013; Osburn & Stedmon, 2011; Osburn et al., 2018; Painter et al., 2018) associated with terrestrial "humic-like" fluorescence. Component C4 has been previously associated with waste water (Murphy et al., 2011). Components C5 and C6 correspond to "protein-like" components (Osburn & Stedmon, 2011; Stedmon, Markager, et al., 2007; Stedmon, Thomas, et al., 2007) which are typically associated with microbially produced DOM.

In general, "humic-like" components C1 and C2 had the highest fluorescence intensities in all estuaries and the "protein-like" components (C5 and C6) the lowest throughout the estuaries (Figure S3).

In order to evaluate the DOM composition of the three groups of estuaries identified from the DOC mixing data, we calculated the relative contribution of the six components in each group with a particular focus on the lowest and highest salinity waters as representative of the different water end-members (Figure 3a). At the lowest salinities, DOM from the Halladale (Group 1) was mainly composed of terrestrial "humic-like" components (C1–C3), which together comprised 95% of the fluorescent DOM (Figure 3a). Group 2 estuaries had a higher contribution of the waste water component C4 and the "protein-like" components C5 and C6 (sum of the relative contribution of C4–C6 = 24%) compared to Group 1, but lower than the estuaries draining catchments with greater human influence (Group 3, sum of the relative contribution of C4–C6 = 33%). Analysis of similarity (ANOSIM) based on the Bray-Curtis distance showed that the DOM composition of Group 1 was significantly different to Groups 2 and 3 (ANOSIM's $R = 0.94$ and 0.75, $p < 0.05$, respectively). Despite the nonsignificant differences observed between Groups 2 and 3 at low salinities (ANOSIM's $R = 0.02$, $p = 0.3$), there was a significant change in the DOM composition of Group 2, which was not observed in Group 3, between the low salinity riverine end-member and the high-salinity waters (ANOSIM's $R = 0.45$, $p < 0.001$ for Group 2: and $R = -0.05$, $p = 0.64$ for Group 3) (Figure 3a). These significant changes observed in Group 2 but not in Group 3 indicated that there was a differential rate of decrease of C3–C6 DOM components in estuaries draining catchments with a mix of peatlands, woodlands, and acid grasslands (Group 2); Group 3 estuaries draining arable and (sub)urban dominated catchments showed little evidence for differential rates of decrease for all components across the salinity gradient.

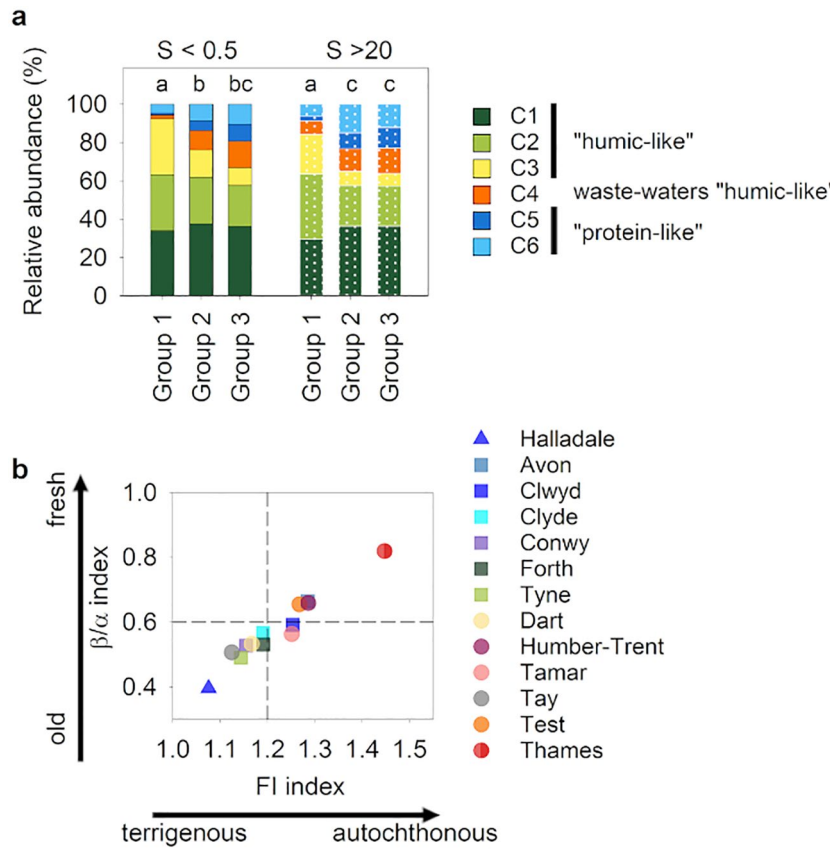

Figure 3. Fluorescent DOM characteristics. (a) Average of the relative abundance for each of the six fluorescent components in the three groups of estuaries at the river end-member ($S < 0.5$, fill bars) and at the highest salinity value ($S > 20$, dotted bars). Different letters above bars (a–c) indicate a significant difference at $p < 0.05$ level according to ANOSIM analysis; same letters indicate no difference. (b) Scatterplot of the relationship between the average fluorescence index (FI) and average beta to alpha index (β/α) for each estuary. Dashed lines indicate FI = 1.2 and $\beta/\alpha = 0.6$. The three groups of estuaries are represented with different symbols: triangle for the estuary in Group 1, squares for estuaries in Group 2, and circles for estuaries in Group 3.

The optical fluorescence index (FI) and the beta to alpha index (β/α) are indicative of the origin and freshness of the DOM (Figure 3b). In general, Group 1 and two estuaries had low FI (<1.2) and β/α indices (<0.6), indicative of older, terrigenous and more "humic-like" DOM, consistent with their catchment characteristics described earlier. Group 3 estuaries had, in general, higher values of both indices, suggesting recent microbially produced DOM, which is encouraged by agriculture and wastewater inputs in catchments significantly influenced by human activity.

The variable DOM composition observed between the three groups of estuaries is further explained by the significant correlation between the type of land use and the different DOM components (Table S2). For example, the contribution of the terrestrial "humic-like" component C2 correlated positively with peatland + wetland + heathland and woodland ($r = 0.66$ and 0.62, respectively), while the contribution of the "protein-like" component C5 was correlated to arable/horticulture and (sub)urban land use types ($r = 0.61$ and 0.83, respectively) (Table S2).

3.3. Fluorescence DOM Dynamics

There were significant positive correlations between DOC concentration and the fluorescence intensities of the three "humic-like" components (C1–C3) and the waste water component (C4) for each individual estuary (Figure S4 and table within it). The correlation coefficient was greater in estuaries from Groups 1 to 2 than in estuaries belonging to Group 3. There was also a significant positive correlation between DOC con-

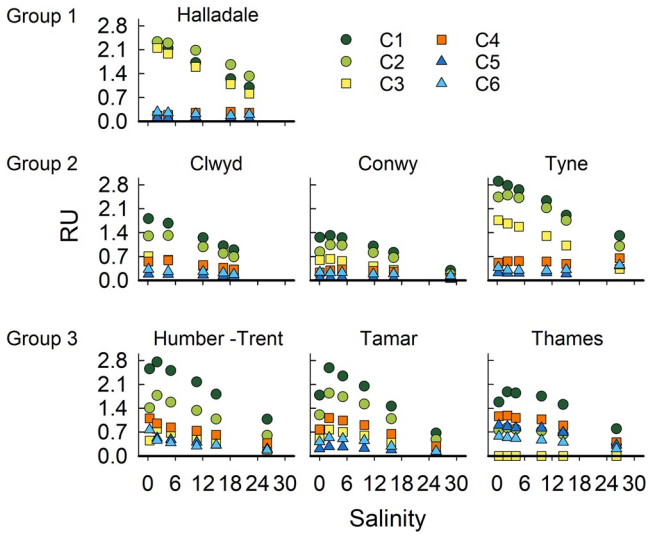

Figure 4. Fluorescent dissolved organic matter (DOM) mixing. Examples of the distribution of the normalized fluorescence intensities (RU) of the six DOM components (C1–C6) with salinity during the October 2017 sampling in estuaries from the three groups: Halladale (Group 1), Clwyd, Conwy, and Tyne (Group 2); and Humber-Trent Tamar and Thames (Group 3). All data in Figure S3.

centration and the "protein-like" component C6 in estuaries from Groups 1 to 2, although with lower correlation coefficients (<0.76) than for the correlation with "humic-like" components. The "protein-like" component C5 only showed significant correlations with DOC in 6 out of the 13 estuaries with correlation coefficients <0.7, except for the Tamar estuary whose correlation coefficient was 0.78 (Figure S4 and table within it).

There was a clear difference in the mixing behavior of the six fluorescent DOM components (examples in Figure 4, all data in Figure S3). In addition, the mixing behaviors of the fluorescent components were different between the three estuary groups. In Groups 1 and 2 estuaries, the reductions in C1–C3 fluorescence intensities were, in general, always linear when there was a conservative DOC mixing (examples in Figure 4, all data in Figures S3 and S5). Furthermore, there were sharp increases in C1–C3 fluorescence intensities in low salinity waters (<5), analogous to the increases in DOC seen in Group 2 estuaries (examples in Figure 4, all data in Figures S3 and S5). The most common mixing trend in the waste water component (C4) and the "protein-like" components (C5–C6) was a variable mixing behavior (type "d" in Figure 2a).

In Group 3 estuaries, the mixing behaviors of the six fluorescent components were highly variable between estuaries and sampling campaigns. The most frequent trend in the "humic-like" components (C1–C3) was a sharp increase in low salinity values (<5) followed by a linear decrease (type "c" in Figure 2a) (examples in Figure 4, all data in Figures S3 and S5). By contrast, the most common trend in the waste water (C4) and "protein-like" components (C5–C6) was a variable mixing trend (type "d" in Figure 2a). The Humber-Trent was an exception, wherein the "protein-like" components showed sharp decreases from salinities <0.5 to 5. Furthermore, the deviations from conservative DOC mixing behavior at intermediate salinity values seen in Group 3 estuaries (Figure 1) were, generally, not reflected in analogous increases/decreases of fluorescent components at the same salinities (examples in Figure 4, all data in Figure S3).

3.4. Organic Carbon Fluxes

Annual estuarine DOC effluxes varied by an order of magnitude (0.88–17.77 Gg C yr^{-1}; Table 1). The variability of DOC was significantly and positively correlated with annual average river flow ($r = 0.65$, $p = 0.02$, $n = 13$). A comparison of these annual estuarine DOC effluxes to the annual riverine DOC influx for each estuary presented in a parallel river study (Williamson et al., 2021) (Table 1) suggests that three estuaries show no net addition or removal of DOC within the estuary, nine estuaries had additional sources of DOC within them and one estuaries showed DOC losses (Table 1). These results agree with the patterns observed in the DOC mixing dynamics (Figure 2b), as those estuaries presenting mainly conservative mixing trends (Groups 1–2) showed estuarine DOC export to riverine DOC export ratios of ~1 (ratio between 0.9 and 1.2, Table 1). In contrast, estuaries presenting sharp increases at low salinity waters (Group 2), or nonconservative mixing behavior (Group 3), tended to have estuarine DOC export to riverine DOC export ratios >1.2, with the exception of the Tay estuary which had a ratio below 1. Group 3 estuaries showed an average increase of DOC concentrations into estuaries by ~50%, relative to the riverine flux estimates.

In order to compare the different estuaries and to study the influence of the land use type, we normalized the estuary DOC effluxes to the respective catchment area for each estuary. With the exception of the Tamar estuary, high area-specific estuarine DOC exports (>13 g C m^{-2} yr^{-1}) were estimated in estuaries which drain catchments with a high percentage of peatland (≥18%) such as Conwy and Halladale (Table 1). In contrast, the lowest exports (≤2.1 g C m^{-2} yr^{-1}) were estimated in estuaries whose catchments had a higher percentage (≥46%) of arable and (sub)urban land uses (Avon, Humber-Trent, Test, and Thames).

Table 1
Annual Riverine Dissolved Organic Carbon (DOC) Influxes Into the Estuary, Annual Estuarine DOC Effluxes Out of the Estuary, Ratio Between the Estuarine DOC Effluxes to the Riverine DOC Influxes, Total Catchment Area and the Area-Specific Estuarine DOC Effluxes

Group	Estuary	River DOC export[a] (Gg C yr^{-1})	Estuary DOC export (Gg C yr^{-1})	Estuary DOC export/river DOC export	Total catchment area (km^2)	Area-specific estuarine DOC export (g C m^{-2} yr^{-1})
Group 1	Halladale	2.52	2.55	1.01	193	13.2
Group 2	Avon	1.48	3.46	2.34	1,712	2.0
	Clwyd	2.23	4.29	1.92	431	10.0
	Clyde	12.09	11.24	0.93	2,003	5.6
	Conwy	4.13	5.17	1.25	340	15.2
	Forth	11.71	12.45	1.06	1,025	12.1
	Tyne	13.2	17.77	1.35	2,262	7.9
Group 3	Dart	1.33	1.97	1.48	257	7.7
	Humber-Trent	14.49	17.66	1.22	8,209	2.1
	Tamar	7.3	13.61	1.86	925	14.8
	Tay	24.74	13.21	0.53	5,042	2.6
	Test	0.53	0.88	1.66	1,035	0.9
	Thames	5.63	11.32	2.01	9,930	1.1

[a]Data from Williamson et al. (2021).

4. Discussion

4.1. DOC and Fluorescent DOM Dynamics

Our study provides the first analysis linking estuarine DOC dynamics, DOM composition, and land use over a broad range of estuaries and sampling times. Previous work has suggested that DOC mixing dynamics are determined by the concentration of riverine DOC (Spencer et al., 2007). However, our results show that differences in DOC mixing dynamics are not related to variation in river DOC inputs or seasonal variation, but are mainly influenced by the DOM composition, which in turn is related to the type of land use (Aitkenhead & McDowell, 2000; Kothawala et al., 2015; Lambert et al., 2017; Wilson & Xenopoulos, 2009; Yates et al., 2019). The lack of a clear seasonal variability indicates that seasonal changes in several environmental factors such as precipitation, which influences river flow, and surface irradiance, which can influence biological processes, have a low influence over DOC mixing dynamics. As expected from our hypothesis, estuaries draining catchments with relatively larger percentage of peatlands had a higher contribution of terrestrial "humic-like" components, and showed conservative DOC mixing. In contrast, estuaries draining catchments with a high degree of human impact (i.e., relatively larger percentage of arable and (sub)urban land uses) were richer in the DOM component related to waste waters (Murphy et al., 2011) and "protein-like" components, and were characterized by nonconservative mixing.

The relationship between DOC and salinity, when not linear, showed two characteristic patterns: sharp changes in low salinity (<5) waters and variable concentrations in intermediate salinity waters (5–32). The distinct pattern of an increase or decrease of DOC concentrations at salinities <5 followed by a linear decrease at higher salinities has been previously observed (Abril et al., 2002; Álvarez-Salgado & Miller, 1999; Li et al., 2019; Mantoura & Woodward, 1983; Spencer et al., 2007). However, there is no consensus on what causes these patterns. Some studies have linked them to geochemical processes, such as adsorption, flocculation, desorption or resuspension of DOC from sediments (Sholkovitz et al., 1978; Spencer et al., 2007; Uher et al., 2001) at the estuarine turbidity maxima—processes which involves a phase change, but with no loss of CO_2 to the atmosphere. Other studies have related these patterns to the presence of highly bioavailable organic matter released by phytoplankton cell plasmolysis (Morris et al., 1978) or from waste water treatment systems, which could potentially enhance the consumption of the DOC by bacteria (Li et al., 2019), the fixation of autochthonous C (Schlesinger & Melack, 1981) and impact CO_2 fluxes. We did

not observe significant alterations in the FI and β/α indices between salinities <0.5 and ~5 (paired t test $t = 0.96$, $p = 0.35$, $n = 18$ for FI and $t = -0.25$, $p = 0.80$, $n = 18$ for β/α; data not shown, available in data DOI). This suggests that the observed changes in DOC concentrations were either related to physicochemical processes (rather than biological), or represent physicochemical and biological processing of the nonfluorescent fraction of DOC. The sharp increases in DOC concentrations at salinities <5 were associated with sharp increases in "humic-like" and "protein-like" components, which indicate that both of these components were reactive when they encountered marine waters. Thus, desorption processes, DOC resuspension or inputs from lateral tributaries may be the main processes related to the observed DOC increases. Flocculation has been shown to produce sharp decreases of DOC, especially in the "humic-like" fraction in low salinities (<2) (Asmala et al., 2014; Fleming-Lehtinen et al., 2015). However, our data do not show consistent removal of "humic-like" DOM, as it was only observed in one out of six sampling occasions (Tay estuary in July 2017). The sharp DOC decreases in the Humber-Trent (April and July 2017) were associated with a sharp decrease in the "protein-like" compounds, and there was no initial reduction in any fluorescent DOM components in the other three estuaries (Conwy, Forth, and Tyne).

The variable trends observed in the mixing of DOC in estuaries draining catchments with a high percentage of arable and (sub)urban land uses suggest the production and removal of DOC in this intermediate salinity range (5–32). In general, terrestrial "humic-like" components showed a conservative linear decrease at salinities >5 with the exception of some sampling occasions in the Dart, Tamar, and Thames. Photochemical degradation can remove "humic-like" components (Del Vecchio & Blough, 2002; Spencer et al., 2009), but this was not observed in our study. The mixing dynamics of the "protein-like" components were more variable between estuaries and sampling occasions and without a clear pattern. We found linear decreases, discrete increases/decreases at a specific salinity, and even net increases across the salinity range. The "protein-like" components are likely due to microbial production of autochthonous DOM (Coble et al., 1998; Stedmon & Markager, 2005) and are related to anthropogenic sources of organic matter, such as those derived from arable and (sub)urban land use types including waste water sources (Old et al., 2019). Results from the FI and β/α indices support this idea, since the FI and β/α values of the estuaries draining arable and (sub)urban catchments indicate fresher DOM with a higher autochthonous DOM fraction, which suggest a microbial origin (Wilson & Xenopoulos, 2009). Nevertheless, the lack of or weak relationships between "protein-like" DOM components and DOC, together with the low relationship between "humic-like" DOM and DOC in estuaries draining catchments with a high percentage of arable and (sub)urban land uses suggest a low influence of both fractions in the DOC trends and can be interpreted as a higher presence of nonfluorescing DOM (Laane & Koole, 1982). This indicates that increases or decreases in DOC concentrations would be undetectable by studying only the fluorescent composition of DOM in this group of estuaries.

We observed variable mixing trends in the "protein-like" DOM despite the linear DOC decrease and the conservative mixing of the "humic-like" components in intermediate salinity waters in estuaries draining more natural catchments (Groups 1 and 2). This suggest that there is a biological production/degradation of the "protein-like" component in addition to dilution (Asmala et al., 2016). The different mixing dynamic trends in the "humic-like" and "protein-like" components resulted in a significant increase in the relative contribution of the "protein-like" components across the salinity gradient in estuaries draining a mix of peatland, woodlands, and acid grassland land uses (Group 2). This change from terrigenous to marine dominated DOM was not significant in estuaries draining catchments with a high percentage of arable and (sub) urban land uses, which further supports the lower influence of terrestrial "humic-like" components in this group of estuaries.

Overall, we found no evidence to suggest that terrestrial "humic-like" DOM was subject to consistent net removal or production despite the nonconservative behavior at salinities <5, indicating that these DOM components were moderated primarily by dilution in our estuaries (Abril et al., 2002; Álvarez-Salgado & Miller, 1999). A recent study in the North Sea showed that the C1 component was not chemically or biologically altered over 200 km from the North Sea coast, after which it showed a sharp decrease (Painter et al., 2018). This previous evidence and our results indicate that C1 can serve, in general, as an effective tracer of terrigenous DOM into coastal areas.

4.2. Estuarine DOC Efflux

The estuarine export of DOC to coastal areas agrees with previous estimates for British estuaries (Hope et al., 1997; Miller, 1999). Estuarine DOC effluxes exceed the riverine DOC influxes in 9 of the 13 estuaries, either because there is an internal generation of DOC at salinities <5, or a supply from C-rich tributaries that were not included in our estimates. Our data suggest that the DOC efflux to the ocean is enhanced by low-estuarine and midestuarine processes and external inputs. Therefore, considering DOC fluxes at the upper tidal limit as being the flux to coastal areas, without considering the low and mid-estuary, will likely underestimate the estuarine DOC export efflux. Four of the five estuaries that present the highest estuary DOC export/river DOC export ratio (Avon, Thames, Clwyd, Tamar, and Test) drain catchments with a high proportion of arable land use (≥16%), which can be an important source of inorganic nutrients that can stimulate the internal biological production of autochthonous biomass and release of DOC (Romera-Castillo et al., 2011). Furthermore, the Thames and Test catchments have a larger proportion of (sub)urban areas (>4%) which increases the likelihood of receiving DOC from anthropogenic sources such as waste water treatment works (Old et al., 2019). Thus, contrary to our initial hypothesis, estuaries draining catchments with a high proportion of arable and (sub)urban land uses do not show a loss of DOC across the salinity range.

Our results partly contradict previous results from a study of the North Sea inorganic C cycle, which suggested that estuaries remove the majority of riverine organic matter inputs through the production and outgassing of CO_2 to the atmosphere (Kitidis et al., 2019). Discrepancies between these two studies likely arise from the different type and sizes of the catchment areas of the estuaries studied. The influence of catchment size on the production of CO_2 was already speculated in the former study (Kitidis et al., 2019), and therefore, our data support their suggestion and highlight the importance of measuring DOC fluxes in both small and large, estuaries. The high fraction of bioavailable "protein-like" material exported from estuaries draining catchments with a high proportion of arable and (sub)urban land uses may stimulate remineralization processes in shelf seas, and may therefore support greater release of CO_2 to the atmosphere.

Our results indicate a clear influence of land use on the area-specific estuarine DOC efflux. They are also consistent with the conclusions of a parallel study in British rivers (Williamson et al., 2021) and resemble the spatial distribution of the DOC fluxes modeled from catchment properties, such as land use, soil type and evaporation rates (Worrall et al., 2012). Our area-specific DOC export fluxes from arable and (sub)urban dominated estuaries (<2.1 g C m^{-2} yr^{-1}) are comparable to other large European and world estuaries (i.e., 0.9 g C m^{-2} yr^{-1} for the Seine estuary, 3 g C m^{-2} yr^{-1} for the Po estuary and 2.3 g C m^{-2} yr^{-1} for the Lena estuary Worrall et al., 2012 and references therein). The higher area-specific DOC export fluxes observed in our estuaries draining catchments with relatively larger percentage of peatlands and woodlands (>13 g C m^{-2} yr^{-1}) are on average higher than the average value of 5.6 g C m^{-2} yr^{-1} reported from Finnish peatland catchments (Räike et al., 2012) and the 7.2 g C m^{-2} yr^{-1} reported from a Norwegian subarctic bog catchment (de Wit et al., 2016). Therefore, the relatively high abundance of organic C concentration contained in peatland soils (Ostle et al., 2009) is likely the dominant source of DOC fluxes across these estuaries.

4.3. Limitations

This study focusses on the large-scale distribution of DOC and DOM in the environment and was designed to cover a wide range of land use types found in this large temperate island over different hydrological conditions during a full annual cycle. Thus, we sampled five times from a single depth in order to complete the sampling survey on the falling tide in each estuary. The temporal scale of our sampling inevitably leads to the possibility that signals at lower temporal scales may not be identifiable. Our 1-D representation of the water column (water samples were only collected in surface waters) may also introduce biases on the calculation of DOC effluxes. It is known that DOC concentration can differ between depths, with higher concentrations in bottom layers as a result of resuspension of DOC from the sediments (Cauwet & Mackenzie, 1993). Furthermore, results from studies in tropical and temperate estuaries have shown semidiurnal variability in DOC and fluorescence DOM related to tides (Amaral et al., 2020; Regnier et al., 2013). High frequency DOC and online fluorescence DOM monitoring would provide further information on the transport and cycling of DOC in estuaries, but costs will be excessively high for a large-scale geographical

study such as this (Croghan et al., 2021; Khamis et al., 2020). Finally, the variable DOC mixing presented by several of the estuaries draining catchments with a high degree of human impact, such us the Dart, Humber-Trent, Test, and Thames, restricted the calculation of "effective" DOC concentrations (see Section 2). Thus, DOC fluxes reported from these estuaries have a greater amount of associated uncertainty. Despite the potential biases involved in this study, the resulting DOC effluxes are entirely comparable with previous British in situ and modeled studies (Hope et al., 1997; Worrall et al., 2012).

5. Conclusions

The latest review of terrigenous C inputs to inland waters (Drake et al., 2018), as well as the fifth Intergovernmental Panel on Climate Change Assessment Report (IPCC, 2014), recognized the importance of the processes occurring in the LOAC for improving estimates of global C budgets. This study shows how land use influences the quantity of DOC and the composition of terrigenous DOM entering estuaries and its fate therein. DOC was conservatively mixed across the salinity gradient in estuaries draining catchments with relatively larger percentages of peatlands, woodlands and acid grasslands, whereas nonconservative mixing was observed in estuaries draining catchments with a high percentage of arable and (sub)urban land uses. However, terrestrial "humic-like" components were conservatively transported across the majority of the salinity range in most estuaries. From a C cycling perspective, estuaries draining more natural catchments may be seen as transporters of terrigenous refractory DOC from land to ocean without changing the C from the dissolved to the gaseous phase (i.e., from DOC to CO_2). By contrast, the greater biogeochemical processing that occurs in estuaries draining arable and (sub)urban dominated catchments, and the bioavailability of the DOM therein, may promote microbial production and degradation, and consequently a nonconservative transfer of DOC from land to ocean. In addition, results from this study show that estuaries draining catchments with a high proportion of arable and (sub)urban land uses increase the flux of DOC exported to coastal areas by an average of 50% compared to the flux of DOC imported by the rivers. Thus, previous fluxes of DOC exported to coastal areas estimated based on riverine data without including the influence of their estuaries might be underestimates. Overall, British estuaries transfer truly terrigenous DOM conservatively, and add in anthropogenic-derived DOM, making them an overall source of DOC to coastal waters.

Data Availability Statement

All DOC, DOM fluorescence intensities data used in this study are available in the British Oceanographic Data Centre (BODC, Accession Number SOC210158).

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