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Modelling terrigenous DOC across the north west European Shelf: Fate of riverine input and impact on air-sea CO_2 fluxes

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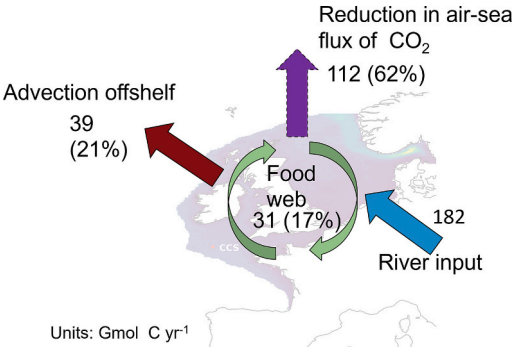
HIGHLIGHTS

- tDOC cycling is implemented in a 3D biogeochemical model for the NW European Shelf.
- Bacterial degradation is the most important process in removing tDOC on the shelf.
- 62 % of riverine tDOC input to the shelf was outgassed as CO_2 on the shelf.
- Results can help improve assumptions on fate of tDOC made by Earth System Models.

GRAPHICAL ABSTRACT



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ABSTRACT

Terrigenous carbon in aquatic systems is increasingly recognised as an important part of the global carbon cycle. Despite this, the fate and distribution of terrigenous dissolved organic carbon (tDOC) in coastal and oceanic systems is poorly understood. We have implemented a theoretical framework for the degradation of tDOC across the land to ocean continuum in a 3D hydrodynamical-biogeochemical model on the North West European Shelf. A key feature of this model is that both photochemical and bacterial tDOC degradation rates are age dependant constituting an advance in our ability to describe carbon cycling in the marine environment. Over the time period 1986-2015, 182±17 Gmol yr^{-1} of riverine tDOC is input to the shelf. Results indicate that bacterial degradation is by far the most important process in removing tDOC on the shelf, contributing to 73±6 % (132±11 Gmol yr^{-1}) of the total removal flux, while 21±3 % (39±6 Gmol yr^{-1}) of riverine tDOC was advected away from the shelf and photochemical degradation removing 5±0.5 % of the riverine flux. Explicitly including tDOC in the model decreased the air-sea carbon dioxide (CO_2) flux by 112±8 Gmol yr^{-1} (4±0.4 %), an amount approximately equivalent to the CO_2 released by the UK chemical industry in 2020. The reduction is equivalent to 62 % of the riverine tDOC input to the shelf while approximately 17 % of riverine input is incorporated into the foodweb. This work can improve the assumptions of the fate of tDOC by Earth System Models and demonstrates that the

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inclusion of tDOC in models can impact ecosystem dynamics and change predicted global carbon budgets for the ocean.

1. Introduction

Humans are greatly modifying the carbon cycle but only 44 % of anthropogenic carbon dioxide (CO_2) emissions are estimated to reside in the atmosphere (Canadell et al., 2021). To understand the fate of the missing carbon, and to increase the predictive capabilities of models, all components of the carbon cycle need to be understood. Although terrigenous dissolved organic carbon (tDOC) in aquatic systems is increasingly being recognised as an important part of the global carbon cycle (Ciais et al., 2013; Hedges et al., 1997) the fate of tDOC once it reaches the coastal ocean remains understudied (Ciais et al., 2013; Legge et al., 2020; Painter et al., 2018). This is despite the estimated global terrestrial carbon flux to the ocean of 0.6-1.4 Pg C yr^{-1} (Friedlingstein et al., 2020; Kwon et al., 2021) being on the same order of magnitude as the net anthropogenic CO_2 flux from the atmosphere into the ocean (Ciais et al., 2013; Friedlingstein et al., 2020). Remineralisation of terrestrial dissolved organic matter (tDOM) produces dissolved inorganic carbon (DIC) and nutrients in surface waters, consequently impacting air sea fluxes of CO_2 (Cai, 2011; Gustafsson et al., 2014; Polimene et al., 2022), ocean acidification (Capelle et al., 2020), and ecosystem dynamics (Polimene et al., 2022). A portion of tDOC is known to withstand remineralisation in shelf seas, as indicated by the presence of measured tDOC in the global deep ocean(Hernes and Benner, 2002; Medeiros et al., 2016, 2017; Opsahl and Benner, 1997), but the spatial distribution and magnitude of remaining tDOC is still unknown for many regions across the globe.

Currently, tDOM is either poorly constrained in Earth System Models, or not considered at all. Of those models that do include tDOM, some assume that all input from rivers is remineralised immediately (Aumont et al., 2015) whereas others do not differentiate between DOM of oceanic or terrestrial origin (Tjiputra et al., 2020). In fact, remineralisation of tDOM is not instantaneous and a number of processes determine the fate of tDOM in the ocean: these include photolysis, bacterial degradation, and flocculation (Anderson et al., 2019). The cycling of tDOM is complex with the interplay between photolysis and bacterial degradation altering the lability of tDOM (Moran and Zepp, 1997; Obernosterer and Benner, 2004). In addition, tDOM becomes more refractory as it gets degraded, leading to slower degradation rates. There is a real need for models to have realistic representation of these processes, to reduce the current uncertainties in the global carbon cycle.

Only a few regional modelling studies exist that investigate the fate of tDOM. Mass balances have been calculated for the fate of tDOC from experimental data in the Gulf of Mexico (Fichot and Benner, 2014) and Sunda Shelf Sea (Zhou et al., 2021). Other modelling studies often indirectly model tDOC though mass balance models of radiocarbon (Bauer et al., 2002) or use CO_2 as a proxy of tDOC (Capelle et al., 2020; Jiang et al., 2013) in addition to using simple techniques such as the linear decay of tDOC with time (Fransner et al., 2016, 2019; Lacroix et al., 2020). Studies of tDOC degradation using a hydrodynamic-biogeochemical mechanistic model which explicitly separates the consumption of tDOC into bacterial degradation, photodegradation and flocculation are limited in the ocean and have only been applied for the Baltic Sea (Gustafsson et al., 2014),and Yukon River delta (Clark et al., 2022). Recently, a unified model of tDOM cycling (UniDOM; Anderson et al., 2019) has been created with the aim to produce a consistent model of DOM cycling across the land-river-ocean continuum and implemented in an idealised setting. A key feature of this model is that both photochemical and bacterial degradation rates of tDOC are age dependant, with tDOC becoming more refractory the more it undergoes degradation processes.

Shelf seas have been estimated to remove up to 80 % of the tDOC (Alling et al., 2008; Amon, 2003; Benner et al., 2005; Clark et al., 2022; Fichot and Benner, 2014; Gustafsson et al., 2014; Kaiser et al., 2017; Letscher et al., 2011; Medeiros et al., 2016; Opsahl et al., 1999; Zhou et al., 2021) but no estimates exist for the north west (NW) European Shelf. Based on observational North Sea data, open ended questions regarding the fate, seasonal variability, and consumption processes acting on tDOC have been raised in addition to understanding why there is a semi constant distribution of tDOC concentrations in the North Sea over the past six decades despite changes in riverine inputs (Painter et al., 2018). In addition, questions have been raised over observed differences in tDOC concentrations in the North Sea, where concentrations were shown to be low (Painter et al., 2018) and the Central Celtic Sea where high concentrations have been estimated (Carr et al., 2019). Here, we use a modelling approach to help answer these questions. We implement UniDOM into a hydrodynamic biogeochemical model and run a 3-dimensional (3D) simulation to study, for the first time, the fate of tDOC on the NW European shelf. In particular, we show the spatial distribution of tDOC across the NW European shelf and identify the key consumption processes for tDOC and proportion of riverine tDOC advected to Atlantic Ocean. Finally, we also investigate how the inclusion of tDOC in hydrodynamic-biogeochemical models impacts the strength of the shelf as a carbon sink through changes in ecosystem dynamics.

2. Methods

2.1. Model description

The hydrodynamics are represented using the Nucleus for European Modelling of the Ocean (Madec and the NEMO team, 2016) and ecosystem dynamics by the European Regional Seas Ecosystem Model (ERSEM; Butenschön et al., 2016). These are coupled together using the Framework for Aquatic Biogeochemical Models (FABM; Bruggeman and Bolding, 2014), herein called NEMO-FABM-ERSEM. NEMO-FABM-ERSEM is run for the Atlantic Meridional Margin 7 km (AMM7) domain (e.g. EU Copernicus Marine Service, 2021; Lessin et al., 2020; Wakelin et al., 2020) which covers part of the North Atlantic and NW European shelf, spanning 40°N to 65°N and from 20°W to 12°E (Fig. S1). The model is run on an approximately 7 km grid corresponding to a latitudinal and longitudinal spatial resolution of 1/9th and 1/6th degree respectively. Vertically, a z*-σ coordinate system of 51 layers has been used, with layers thinner on the shelf where the water column is shallower, and thicker in the open ocean, especially close to the seafloor.

ERSEM is a complex lower trophic ecosystem model for both pelagic and benthic systems, representing the biogeochemical cycling of 5 elements – carbon, nitrogen, phosphorus, silicon and oxygen by primary producers, consumers and decomposers (Fig. S2). ERSEM uses a functional type approach to represent the various organisms. The pelagic food web is represented by four phytoplankton groups (producers), three zooplankton groups (consumers) and a group of bacteria (decomposers). The latter metabolizes three pools of dissolved organic matter characterised by different labilities and three pools of particulate organic carbon characterised by different size. We use the same model setup and boundary conditions as in previous simulations (Lessin et al., 2020; excluding N_2O) except for the differences described below.

2.1.1. Representing tDOM in ERSEM

A module for tDOM has been added to ERSEM using equations adapted from UniDOM (Anderson et al., 2019) (Fig. 1). Terrestrial DOM within UniDOM is split into two different variables: one which represents a coloured, humic-like substance, is photolabile and relatively

unavailable to bacterial degradation (T1) and one which is resistant to photochemical degradation and has relatively high bacterial degradation (T2). Here we explicitly model tDOC and calculate terrestrial dissolved organic nitrogen (tDON) and terrestrial dissolved organic phosphorus (tDOP) implicitly using constant molar carbon:nitrogen and carbon:phosphorus ratios of 19.8 and 833 respectively (Mackay et al., 2020; Yates et al., 2019) for both T1 and T2.

A unique feature of UniDOM is the continuous age dependence on degradation rates of tDOM: this represents a key challenge in adding UniDOM to ERSEM in a Eulerian context. A theory on how to model the age of water parcels has been proposed where the age of the parcel of water resulting from mixing waters of different age is equal to the mass weighted average of the age of the single parcels (Deleersnijder et al., 2001; Delhez et al., 1999). This approach has been successfully implemented to simulate the dispersion of radioactive tracers (Delhez and Deleersnijder, 2002) and to estimate residence time of water (Placke et al., 2018). However extending this approach to the case of tDOM would add significant uncertainty because when tDOM of significantly different ages mix, their degradation rate would depend on their average age resulting in a potentially significant overestimation of consumption of the older tDOM and an underestimation of the younger one. For this reason, we adopted an age class approach where, for each type of tDOC, multiple pools of fixed age were added.

In UniDOM "aging" represents the decrease in lability of the tDOM due to the change in the pool as consequence of physio-chemical processes (e.g. DOC left in a sterile and dark bottle would not age). While Anderson et al. (2019) used time as a measure of age, in our fixed-age classes approach we assume that each time a fraction of tDOM is transformed by a particular process, an additional fraction of less labile tDOM is added to the older age class. Here we have added 6 additional state variables to ERSEM to represent discrete ages of tDOM– 3 variables for T1 and T2 each representing 30 days, 8 years and 70 years old tDOM. Age classes were defined by comparing outputs from UniDOM using discrete age classes of tDOM rather than a continuous parameter and manually adjusting the age classes and aging parameters (ω_{photo} and ω_{bio}; see supplementary material) to achieve a good comparison with the original UniDOM outputs. While it is possible to add numerous age classes in this way, we limited it at three due to the computational cost this adds to a 3D simulation with 3 age classes.

The sinks of T1 are photo-oxidation ($T1_{photo}$), flocculation ($T1_{flocc}$) and bacterial degradation ($T1_{bac}$). T2 instead can only be consumed by bacterial degradation ($T2_{bac}$) with T2 assumed to be three times more bioavailable to bacteria than T1. T2 is also produced when T1 is photo-oxidized ($T1T2_{photo}$) through photopriming, that is, the process by which photolysis breaks down tDOM into smaller fractions which become more bioavailable to bacteria. Note in the model photopriming is parameterised to be a fraction of the total photolysis flux. Both T1 and T2 are added to the shelf through river inputs ($T1_{riv}$, $T2_{riv}$) which are assigned only to the 30 day age class. The governing equations for T1 and T2 are:

$$\frac{dT1_{age}}{dt} = T1_{riv\ (age)} - T1_{photo(age)} - T1_{flocc(age)} - T1_{advection\ (age)} - T1_{diffusion\ (age)} \quad (1)$$

$$\frac{dT2_{age}}{dt} = T2_{riv\ (age)} - T2_{bac(age)} + T1T2_{photo(age)} - T2_{advection\ (age)} - T2_{diffsuion\ (age)} \quad (2)$$

where *age* is the age of T1 or T2 (30d, 8y or 70y).

Dissolved inorganic carbon, ammonium and phosphate are produced directly through the photodegradation of tDOM, while flocculation produces medium sized particulate organic matter (Fig. 1). Although bacterial degradation does not directly produce DIC or nutrients, this still indirectly produces DIC and nutrients through bacteria metabolising the tDOM and thus producing DIC and nutrients through respiration (Fig. S2).

A key assumption for photodegradation is that photolysis only occurs in the surface layer since UV light is not explicitly included within ERSEM and due to UV light having a faster attenuation rate within the water column than the modelled photosythentic active radiation (PAR) (Tedetti and Sempere, 2006). This may result in an underestimation of photolysis with 10 % penetration depths for UV light in North European coastal water reported being between 0 and 13 m (Smyth, 2011; Tedetti and Sempere, 2006). It is also important to note that tDOC in the model setup used here does not contribute to the attenuation of visible light in the water column. Instead, a satellite product is used to estimate the spatially varying attenuation coefficient as it is not only dependant on allochthonous DOM but also autochthonous DOM and suspended

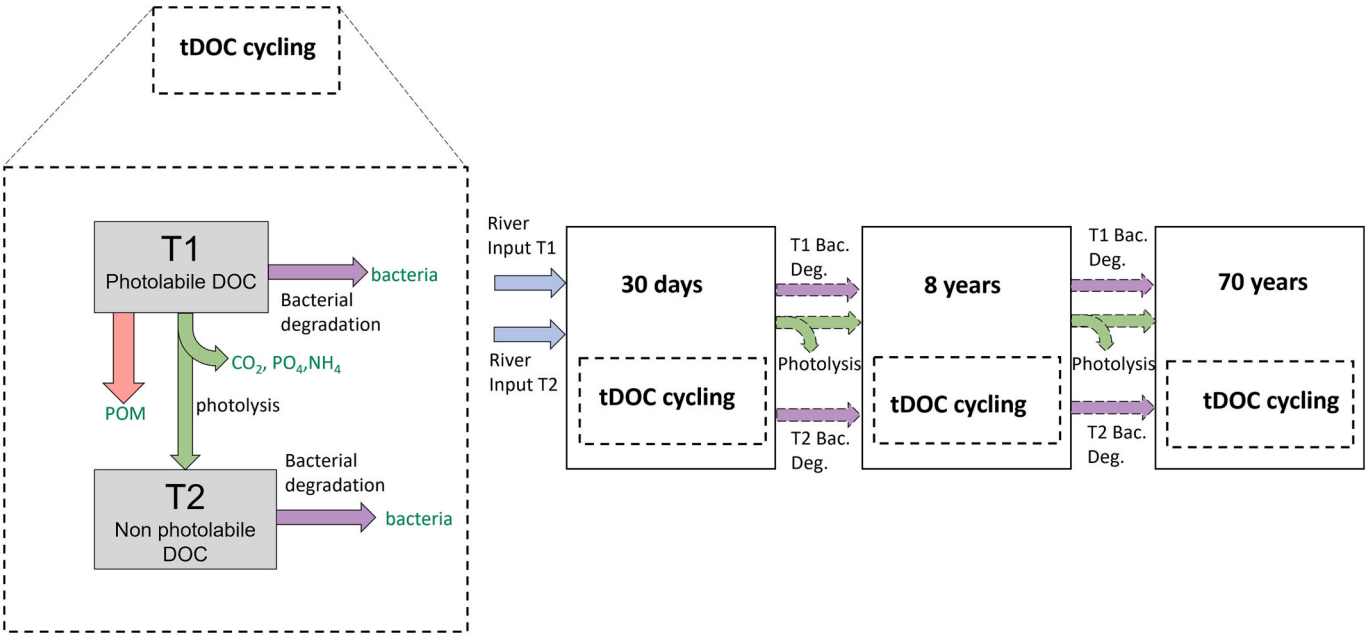

Fig. 1. Schematic showing additional module for tDOC cycling added to ERSEM. The tDOC cycling module is applied to all age classes. When bacterial degradation (Bac. Deg.) or photolysis occurs a fraction of tDOC goes into the next age class, where the degradation/photochemical rates are lower than the previous age class.

particulate matter. Finally, flocculation has been modelled to peak at 2 salinity units (Asmala et al., 2014). The tDOC model parameters are taken as far as possible from uniDOM (Anderson et al., 2019) with rates for each age class within our model matching those predicted by uniDOM for the corresponding age class. A comprehensive description and equations for fluxes described in Eqs. (1) and (2) can be found in the supplementary material in addition to all justification and values of all new parameters used in this version of the model.

2.2. Model setup

2.2.1. Rivers

2.2.1.1. Great Britain. British river inputs to the domain were provided by outputs of the Long Term Large Scale (LTLS) Integrated Model (Bell et al., 2021), which provides high spatial and daily temporal resolution of riverine tDOC inputs to the ocean, along with other biogeochemical variables, along the entire coast of Great Britain. The original LTLS model representation of (total) DOC was updated to split tDOC into T1 and T2 based on land use and field measurements (Anderson et al., 2019). Here, the new LTLS model version provides estimates for river discharge, tDOC (T1 + T2), nitrate, total dissolved phosphorus, and ammonium. Total dissolved phosphorus was converted to phosphate by removing the tDOP implicitly added to the ocean when adding tDOC using a tDOC:tDOP ratio of 833:1. DIC and total alkalinity were assigned following trends in Artioli et al. (2012).

2.2.1.2. Ireland and continental Europe. For rivers in Ireland and continental Europe, a temporally constant concentration of tDOC was assigned to individual rivers based upon literature estimates (Table S1). When no literature estimates were available for an individual river, the nearest river with a DOC concentration was used. The exceptions are for the rivers Rhine, Weser, Ebro and Elbe. For these rivers we use river concentrations of DOC taken from the GLORICH dataset (Hartmann et al., 2019). To assign the contribution of T1 and T2 to DOC we used the average T1:tDOC and T2:tDOC ratio in GB rivers of 0.48 and 0.52 respectively. River inputs for all other variables, including discharge, were produced from an updated version of the river dataset used in Lenhart et al. (2010) combined with climatology of daily discharge data from the Global River Discharge Data Base (Vorosmarty et al., 2000) and from data prepared by the Centre for Ecology and Hydrology as used by (Young and Holt, 2007), as used in the Copernicus Marine Environment Monitoring Service reanalysis (EU Copernicus Marine Service, 2021). The locations of river discharge and mean tDOC loads and concentrations within the model can be found in Fig. S3.

2.2.2. Boundary conditions

Zero concentration boundary conditions were applied for tDOC in both the open ocean and for the Baltic boundary. While we acknowledge this is unrealistic, especially along the Baltic boundary, our focus here is to understand the fate to tDOC discharged from rivers to the NW European Shelf. In initial runs that included tDOC from the Baltic Sea, the Baltic input (Seidel et al., 2017) was the largest contributor of tDOC to the domain and masked the fate of the riverine inputs to the shelf (results not shown).

Marine autochthonous semi-labile and semi-refractory DOC were applied as open ocean and Baltic boundary conditions. In the Atlantic Ocean, the total surface DOC concentration is 70 μM of which we assume 40 μM is refractory, 20 μM is semi-labile and 10 μM is semi-refractory (Carlson and Hansell, 2015). We further assume that the semi-labile and semi-refractory DOC exponentially decays with depth to almost zero (to avoid numerical instability) by 500 m with all DOC below this representative of the refractory pool (not modelled). We designate the Baltic outflow as having a DOC concentration of 325 μM of which 78 % is of terrestrial origin (Seidel et al., 2017) leaving 71.5 μM coming from autochronthous DOC. Assuming that 40 μM of the autochronthous DOC is refractory and assigning the same portion of semi-labile to semi refractory DOC as the Atlantic Ocean, gives us 21 and 10.5 μM of semi-labile and semi refractory DOC, respectively, outflowing from the Baltic.

In addition, we have updated the nutrients (nitrate, phosphate and silicate) and oxygen boundary conditions using the World Ocean Atlas (Boyer et al., 2018).

2.2.3. Initial conditions

The simulation was started using the same restart file as the CMEMS NW European Shelf reanalysis (EU Copernicus Marine Service, 2021), updated for nutrients and oxygen (Boyer et al., 2018) and assigning a zero concentration for each class of tDOC. The model was spun up for 20 years using a 5 year repeating cycle of forcing data from 1981 to 1985 until a quasi-steady state of tDOC, and all other variables on the shelf were reached. The simulation was restarted in 1981 with results presented here limited to 1986–2015 to allow an additional 5 year spinup.

2.3. Simulation experiments

In addition to the main simulation as described above, three additional simulations were run. 1) *no-tDOC sim*: A simulation was run without tDOC input from rivers to enable the quantification of the impact of tDOC on the air-sea gas exchange of CO_2 with all other parameters in this simulation remaining the same as the main simulation. 2) *tracer-sim*: A tracer experiment for the river tDOC inputs with no degradation processes acting on the tDOC was undertaken to determine the concentrations and spatial distribution of tDOC due to only advection and diffusion. 3) *discharge-sim* A simulation where all river discharge was effectively assigned a concentration of 1 mg/l and run as a passive tracer. Scenarios were undertaken for all rivers and then only GB, Irish, Scandinavia and Western European rivers respectively (Fig. S4) to determine the contribution of each region of river inputs to different areas of the shelf, in addition to the dilution rate of rivers across the shelf.

3. Results

3.1. Mass balance of tDOC on the NW European Shelf

On average, 182±17 Gmol C yr^{-1} (mean ± standard deviation of each year) of riverine tDOC entered the NW European Shelf between 1986 and 2015 of which 46±0.2 % is as T1 and 54±0.2 % as T2 (Fig. 2). Bacterial degradation is by far the most dominant degradation process of tDOC, responsible for up to 73±6 % (132±11 Gmol yr^{-1}) of the removal flux of tDOC on the shelf, of which 34±0.4 % is T1 and 66±0.4 % is T2. Photolysis and flocculation only represent 5±0.5 % and 0.5±0.1 % of total degradation of tDOC respectively. Altogether, 21±3 % (39±6 Gmol C yr^{-1}) of the riverine flux onto the shelf is predicted to be advected offshelf. The remaining imbalance reflects the change in the shelf mass between the start and end of our run, in addition to numerical error accounting for 1 % of the budget. The higher availability of T2 to bacteria allows T2 to be degraded faster, and the fact photolysis is confined to the surface layer and is highly seasonal, results in the mass of T2 on the shelf being approximately half of the mass of T1 on the shelf. This is despite higher riverine inputs of T2 to the shelf than T1 and there being more degradation processes acting on T1 than T2. Consequently, the residence time of T2 on the shelf is approximately half that of T1 (Fig. 2).

3.2. Temporal trends and seasonality of tDOC concentrations and degradation processes on shelf

In this section, everything is reported in units of per year to enable comparison between all values given in the manuscript. High inter- and intra- annual variability of tDOC is predicted in both the riverine loads of tDOC to the shelf and tDOC concentrations on the shelf (Fig. 3). The

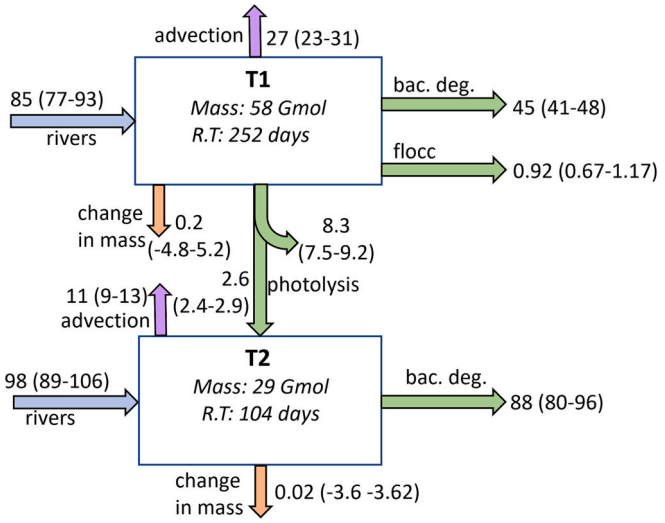

Fig. 2. Mass balance diagram for T1 (photolabile tDOC) and T2 (non photolabile tDOC) on the NW European Shelf averaged over 1986-2015 with ±1 standard deviation reported in brackets. Units: Fluxes - Gmol C yr^{-1}, mass Gmol. R.T = residence time of tDOC on the NW European shelf (total flux in/total mass on shelf), advection = advection to the Atlantic. Note numbers may slightly differ than that recorded in the text due to rounding errors.

interannual variability of river loads varied between 162 and 222 Gmol C yr^{-1} while monthly river loads are predicted to vary between 91 and 450 Gmol C yr^{-1}. Over the course of 1986-2015 river loads of tDOC were greatest during winter months (January and December) and lowest in August (Fig. 4) reflecting the patterns of river discharge. The interannual mass of total tDOC on the shelf varied between 78 and 102 Gmol (Fig. 3B) while on a seasonal basis varied between 67 and 121 Gmol. No substantial long-term trends in either river loads or mass of tDOC on the shelf were observed in the model simulations.

Bacterial degradation is the dominant loss process for tDOC throughout the year contributing between 85 and 98 % (99-138 Gmol yr^{-1}) of total DOC consumption (bacterial degradation+photolysis +flocculation) on an intra-annual timescale with highest relative contribution in winter months when photolysis is low (Fig. 4). Photolysis contributes to 1-14 % (1-22 Gmol yr^{-1}) of consumption and unsurprisingly is most important during summer months while flocculation only has minor contribution to the fate of tDOC throughout the entire year. The total degradation of tDOC was highest in April and May which reflects the balance between high riverine inputs to the shelf, high bacterial biomass due to initiation of the spring phytoplankton bloom and relatively high photodegradation rates.

3.3. Spatial distribution of tDOC concentrations and fluxes 1986–2015

The mean spatial distribution of tDOC over 1986-2015 (Fig. 5A–C) is comparable to observational data for the North Sea (Painter et al., 2018). Unsurprisingly the highest tDOC concentrations occur near the coast (maximum concentration of 372 μM) and decrease towards the middle of the shelf and the open ocean. Depleted tDOC concentrations are predicted in the northern and central North Sea with high tDOC concentrations in the German Bight and to the East of England following the plume of river water from the River Thames. These trends are also clearly seen in nutrient concentrations (EU Copernicus Marine Service, 2021). T1 concentrations are greater than T2, especially towards the shelf edge and central North Sea whereas T2 is depleted in these areas due to its higher biodegradation rate (Table S2; Figs. 2 and 4). While model concentrations of tDOC along the Norwegian coast are of a similar magnitude to those along the UK coast, observational tDOC concentrations along the Norwegian coast (Painter et al., 2018) are higher than what we predict here due to the zero concentration boundary conditions applied at the Baltic boundary.

As demonstrated in the mass balance, bacterial degradation is the most important removal flux of tDOC and occurs throughout the shelf (Fig. 5D). Similar to tDOC concentrations, bacterial degradation is greater towards the coast due to the younger, and more labile tDOC entering the ocean from rivers in addition to there being more tDOC to process. Photolysis is also important in coastal areas but is minimal in areas of the shelf far away from the coastal ocean (Fig. 5E). Finally, flocculation is only substantially present in a small area of the German Bight where the salinity of the sea is relatively low (Fig. 5F). As a consequence flocculation only minorly contributes to the mass balance budget.

3.3.1. Validation of spatial distribution of tDOC

Obtaining quantitative observational measurements of tDOC is difficult given the uncertainty in separating tDOC from autochthonous DOC produced in the ocean (Painter et al., 2018). Consequently only a semi-quantitative validation of our tDOC results is possible. The similarity of the simulated tDOC distribution to that observed in Painter et al., (2018) is demonstrated by a strong positive correlation (R^2 = 0.83) between observed proxy for terrestrial DOC in the North Sea (fluorophore 2) and modelled terrestrial DOC (Fig. 6). A taylor diagram for the validation of salinity, temperature and nutrients against ICES (ICES Data Portal, 2023) and North Sea Biogeochemistry Climatology (Hinrichs et al., 2017) observational data and can be found in the supplementary material (Fig. S5).

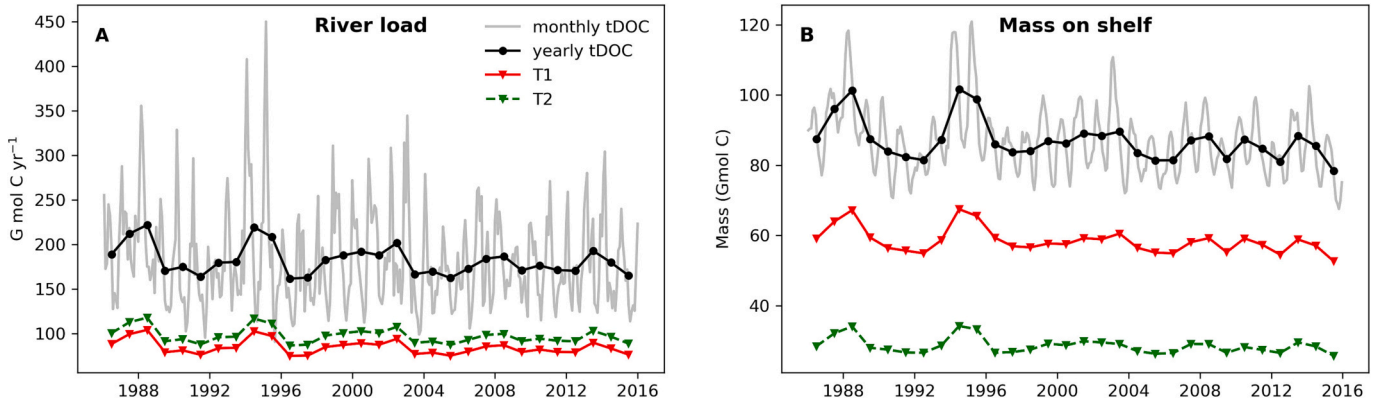

Fig. 3. A) Total river load of tDOC to the NW European Shelf and B) total mass of tDOC on the shelf on yearly (black line) and monthly (grey line) timescales, and corresponding contribution of T1 (red line) and T2 (green line) to tDOC.

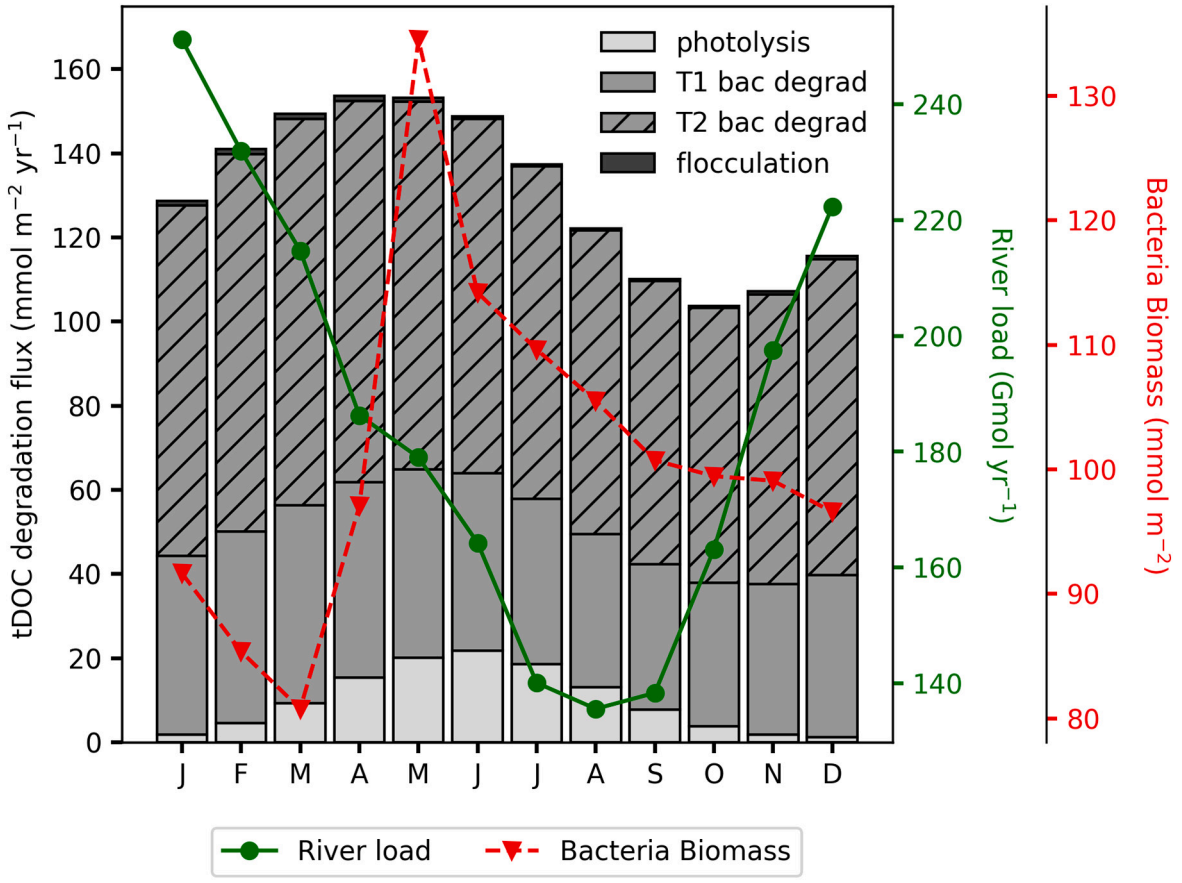

Fig. 4. Climatological mean monthly depth-integrated degradation fluxes for tDOC (bars; left y axis), river loads of tDOC (green line; right y axis) and bacteria biomass (red dashed line, far right axis) on the North West European Shelf from 1986 to 2015. Bars depict the contribution of each degradation process for tDOC.

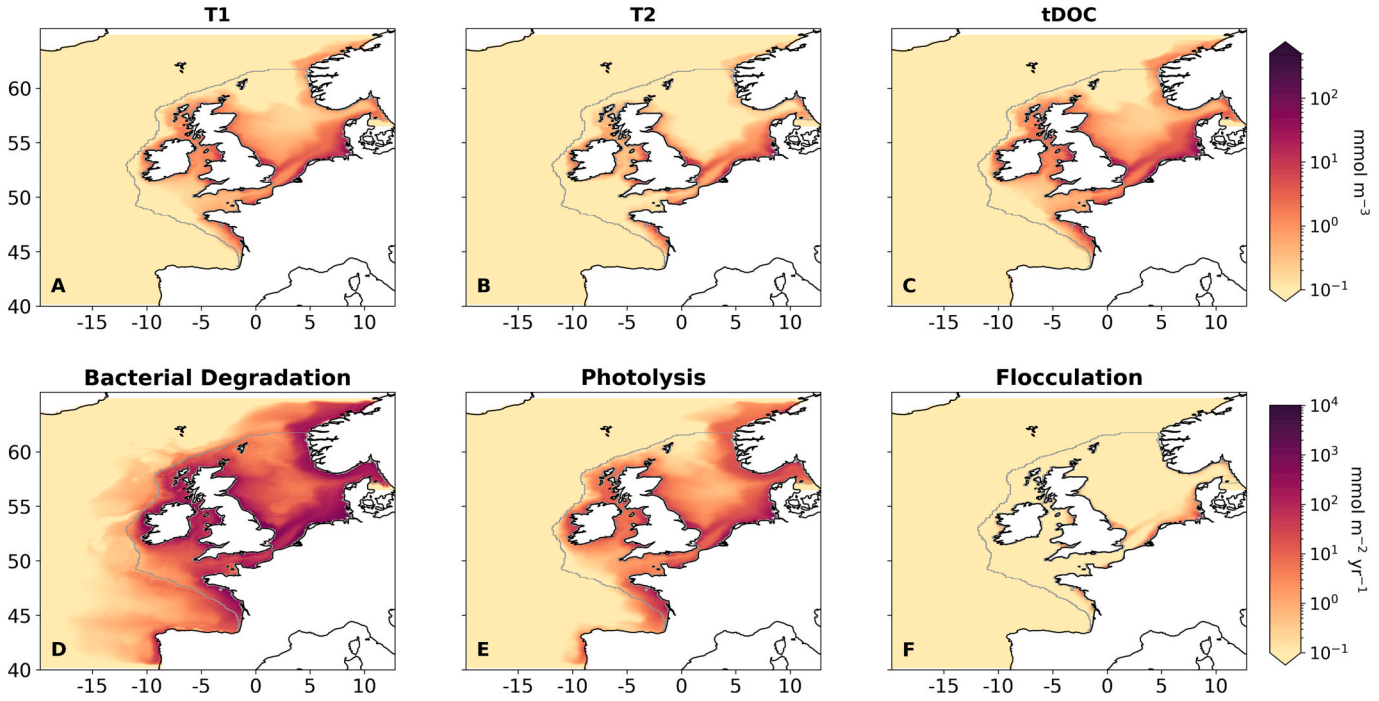

Fig. 5. Mean spatial distribution of tDOC concentrations (A–C) and tDOC degradation fluxes (D–F) over the period 1986–2015. Grey line depicts the North West European shelf edge.

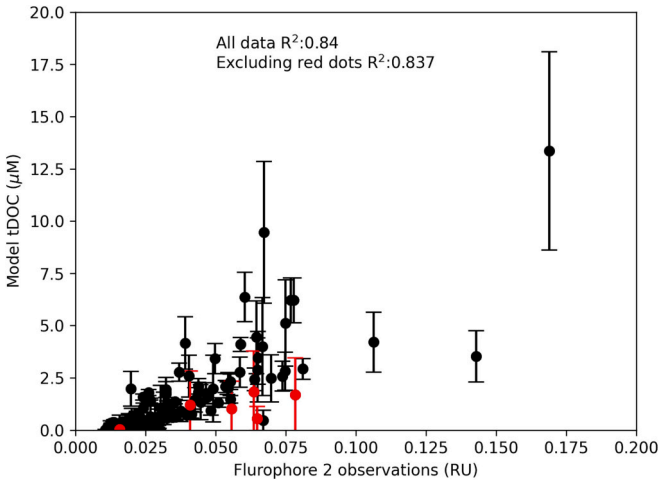

Fig. 6. Correlation between model predicted tDOC (μM; sum of all T1 and T2 across all age classes) and observation Flurophore 2 data (Raman Units (RU)), a proxy for terrestrial DOC in the North Sea for August-September 2016 (Painter et al., 2018). Due to the model simulation finishing in 2015 the data for model tDOC represent the mean over 2011–2015 of daily mean predictions for the date of the corresponding observation, while error bars represent the standard deviation. Red dots represent data close to the Norwegian coast where there is a sharp front of tDOC and discrepancies partially lie due to the location of this front and due to no Baltic input being included. R^2 represents the Spearman correlation coefficient.

3.4. Changes in air-sea CO_2 flux

The inclusion of tDOC in models impacts ecosystem dynamics and ultimately the air-sea flux of CO_2 (Fig. 7). Comparisons of the main simulation against the model run without tDOC (*no-tDOC sim*) shows that the inclusion of tDOC in the model decreases the net air-sea flux of CO_2 across the NW European Shelf by 4±0.4 %(112±8 Gmol yr^{-1}) to give a total air-sea flux of 2855±203 Gmol yr^{-1}. The decrease represents approximately 62±4 % of mean annual riverine DOC input to the NW European Shelf (182 Gmol yr^{-1}). In addition, not only does the air-sea flux decrease, but some cells also changed from the ocean being a net sink of CO_2 to a net source resulting in those areas changing from net autotrophic to net heterotrophic. These cells generally occurred along Dutch and German coastline, Irish Sea and Severn Estuary in the UK (Fig. 7c).

4. Discussion

The fate of terrestrial DOC once it reaches estuaries, shelf seas and the open ocean is poorly understood with very few studies investigating this. Although inputs of tDOC from rivers are included in mass balances for the NW European shelf (Kitidis et al., 2019; Legge et al., 2020), its fate and contribution to carbon fluxes on the shelf is unknown. The model results presented here are a first attempt at filling in this knowledge gap and understanding tDOC cycling in shelf seas.

4.1. Inputs of tDOC to the North West European Shelf

Previous estimates for tDOC inputs onto the NW European Shelf exhibit high uncertainties. Kitidis et al. (2019) estimate that estuaries provide 200 ± 25 Gmol DOC yr^{-1} to the NW European Shelf while Legge et al. (2020) predict that organic matter from rivers contribute 200–2400 Gmol C yr^{-1} to the NW European Shelf. Our modelled input of tDOC to the NW European Shelf of 182±17 Gmol yr^{-1} is at the lower end of these estimates. Although river inputs from Great Britain in this study include tDOC inputs from streams and small rivers to the shelf, they excluded the direct contribution from submarine groundwater discharge (SGD) which is estimated to contribute to approximately 15 % of the total tDOC input from Great Britain to the coastal ocean (Bell et al., 2021). Kwon et al. (2021) also indicate that SGD is likely to be small on the North West European Shelf as although on a global scale SGD contributes up to 57 % of tDOC inputs from land, this is largely confined to the Pacific and Indian Oceans.

The previous estimates of riverine DOC to the NW European Shelf (Kitidis et al., 2019; Legge et al., 2020) also include the impact of estuaries. Estuaries are highly dynamic environments and can be both a source and sink of DOC (Abril et al., 2002; García-Martín et al., 2021). Overall, UK estuaries are estimated to become enriched in DOC relative to what enters the estuary due to additional anthropogenically derived DOM such as from arable areas or wastewater sources (Garcia-Martin et al., 2021; Kitidis et al., 2019). Our estimates do not include the impact of estuaries on tDOC loads, nor can the model adequately resolve the impact of estuaries on tDOC fluxes due to the coarse model resolution with respect to estuaries (7 km). Nonetheless Garcia-Martin et al. (2021) found that in general tDOC behaved conservatively as it was transported through estuaries indicating that our estimates may only be missing the additional inputs from estuaries themselves rather than impacts of internal biogeochemical processing.

Terrestrial DOC may also be added to the ocean through atmospheric deposition which is not included in our budget here. Globally atmospheric deposition of DOC is estimated to be approximately half of that through rivers (Lønborg et al., 2020) although not all deposited DOC will be of terrestrial origin (Iavorivska et al., 2016; Lønborg et al., 2020; Meskhidze et al., 2011). Factors such fossil fuel, biofuel, and biomass burning, and land use changes, enhance the atmospheric deposition of DOC (Bond et al., 2004; Lamarque et al., 2010). The tDOC entering the oceans through atmospheric deposition is likely to behave differently to that delivered to the coastal ocean due the different sources of atmospheric versus river tDOC with altered processes also acting on the tDOC in the atmosphere leading to different chemical properties of atmospheric tDOC entering the ocean than that of riverine tDOC (Lønborg et al., 2020). Thus, for the purpose of this study it is not prudent to add atmospheric deposition of tDOC to our model designed for riverine inputs of tDOC but it nonetheless remains an uncertainty for tDOC cycling on the NW European Shelf.

Finally, the lack of tDOC input from the Baltic Sea in our model limits the spatial distribution and quantification of tDOC along the Norwegian coast. However, this enables quantification of the fate of riverine tDOC on the shelf which is generally younger, and thus more reactive than the Baltic input. Inputs of terrestrial DOC to the NW European Shelf from the Baltic are substantial (Seidel et al., 2017) due to the high freshwater inputs the Baltic receives, and the fact that it is an estuarine basin resulting in the export of surface water containing high quantities of tDOC. Approximately 60-70 % of total DOC in the Kattegat outflow is of terrestrial origin, resulting in a tDOC concentration in the Danish Straits of approximately 250 μM (Seidel et al., 2017) and a flux towards the North Sea of 67–175 Gmol C yr^{-1} (Gustafsson et al., 2014; Osburn and Stedmon, 2011; Seidel et al., 2017). Our modelled riverine input to the NW European Shelf is the same as the top-end estimate of Baltic estimates, indicating that by not including the Baltic input in the mass balances, we are substantially underestimating the input of tDOC to the shelf by up to 50 %. This should be included if inputs or total export of total tDOC on/away from the NW European Shelf are required.

Despite the large quantity of tDOC entering the NW European Shelf from the Baltic, the net impact of the Baltic Sea on the tDOC budget maybe small due to 1) The tDOC entering the NW European Shelf from the Baltic is likely to be already substantially degraded (Painter et al., 2018; Seidel et al., 2017) due to the Baltic Sea having a water residence time on the order of 10-30 years (Döös et al., 2004; Voss et al., 2011) and therefore more refractory than the riverine inputs directly to the shelf, and 2) the Baltic input is mostly constrained to the Norwegian coast/trench with minimal interaction with the rest of the shelf (Painter et al., 2018). Thus, it is possible that only a minor fraction of tDOC from the

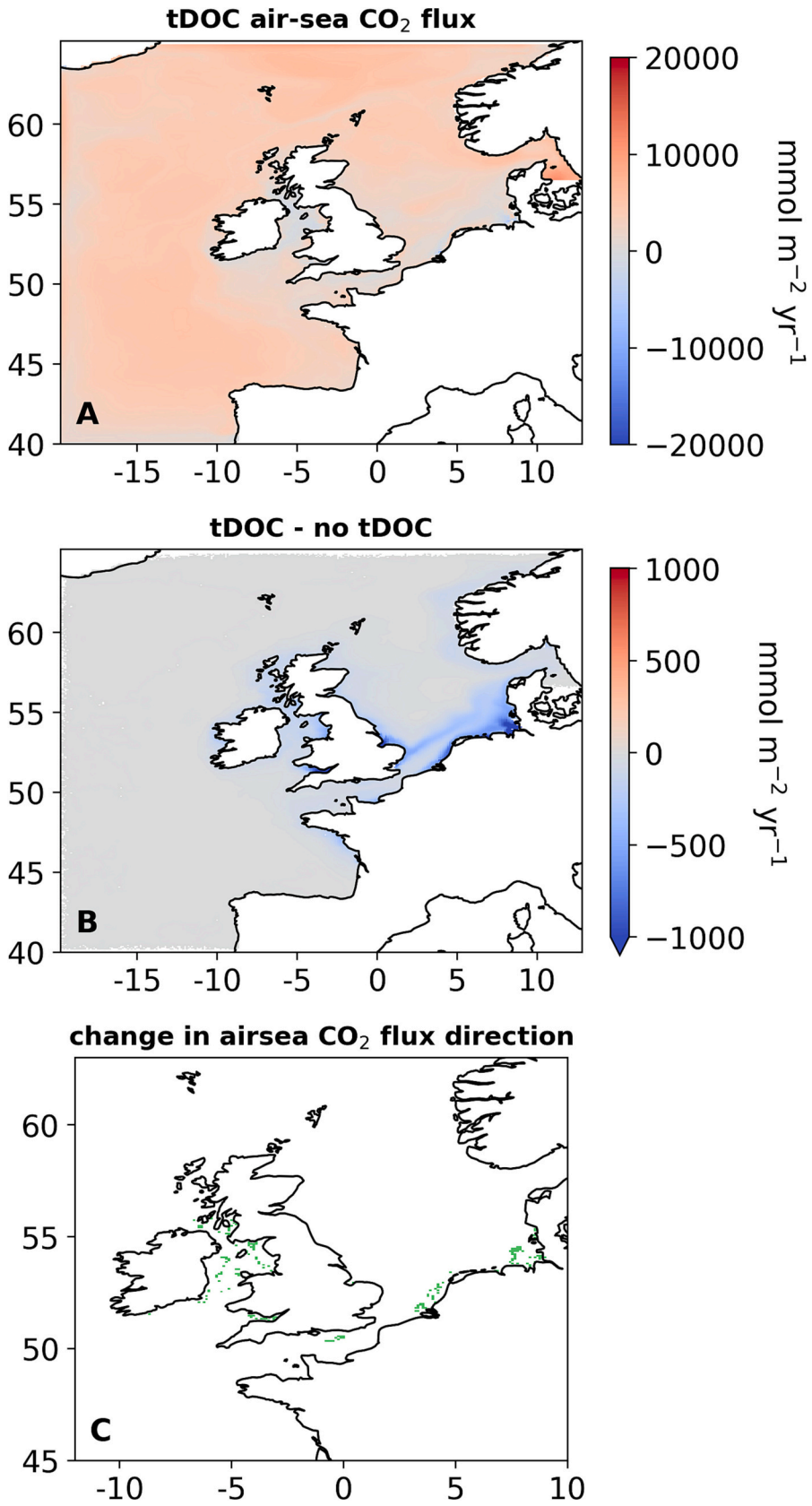

Fig. 7. Air-sea CO_2 flux in (A) tDOC simulation, (B) difference in air-sea CO_2 flux between simulations with and without tDOC and C) cells which change from net sink of CO_2 to net source of CO_2 to the atmosphere (no scale). Note that positive values in A means the sea is a net sink of atmospheric CO_2, while the negative values in B indicate that the air-sea CO_2 flux is smaller in the tDOC simulation than no tDOC simulation.

Baltic gets degraded on the NW European Shelf and thus the net effect of the Baltic input could be rather small. Nevertheless, this remains a key uncertainty currently in our budget.

4.2. What is the fate of tDOC on the NW European shelf?

Our results highlight the dominance of bacterial degradation in mineralizing tDOC input on the NW European Shelf. A key reason for the dominance of bacterial degradation is that it can occur throughout the water column whereas photolysis in this work is confined to the surface due to the fast decay of UV light in the water column. Thus, generally photolysis becomes relatively more important as the water depth gets shallower although in the open ocean photolysis may become relatively more important than in coastal areas due to clearer waters inducing higher light penetration which is not accounted for in this model setup. The increasing importance of photolysis as water depth gets shallower may partially explain the higher relative importance of photolysis in freshwater systems than here (Dempsey et al., 2020; Hernes and Benner, 2003; Spencer et al., 2009). However, multiple studies investigating the entire river/estuarine system also indicate photodegradation may only contribute to a minor part of the fate of tDOC (Amaral et al., 2013; Maavara et al., 2021; Stubbins et al., 2011) although these studies tend to ignore the potential of photopriming stimulating bacterial degradation which could also be a significant factor. Similar to our results, direct photodegradation was also shown to be a minor contribution to tDOC degradation in shelf seas (Bélanger et al., 2006; Fichot and Benner, 2014; Osburn et al., 2009; Reader and Miller, 2012; Table 1). Flocculation is an insignificant flux as it reaches a maximum in low salinity conditions (2 salinity units), which are rare in the AMM7 domain as estuaries are not resolved and salinity is generally high. Consequently, flocculation contributes to a very minor portion of the budget presented here. The minor role of flocculation is consistent with estimates of flocculation in the Yukon River delta contributing to an approximately 2 % loss of DOC even though salinity was much lower (Clark et al., 2022). In contrast flocculation was estimated to contribute to 22 % of removal of tDOC in the Baltic Sea (Gustafsson et al., 2014; Table 1). However, this value should be considered as a theoretical maximum since in the model used by Gustafsson et al. (2014) flocculation was tuned to keep the model close to observational data. This suggests that other processes not included in their model such as photopriming could potentially contribute to the observed loss of tDOC.

Our results are consistent with a previous study focussing on the Louisiana Shelf (Fichot and Benner, 2014). These authors found that bacterial degradation was responsible for up to 94 % of total tDOC remineralisation with the contribution of photodegradation only accounting for a minor fraction (2 %) of tDOC removal. However, despite the small photodegradation contribution on the Louisiana Shelf, Fichot and Benner (2014) found that photo-induced biomineralization potentially contributed to 25 % of total biodegradation flux by assuming the difference between total loss, biomineralization loss in the dark and photodegradation, was a result of photo-induced biomineralization. Here, photopriming is modelled as a fraction (0.24) of the photolysis flux and therefore its contribution to the total tDOC remineralisation cannot exceed that of photolysis. Although based on a single study, this comparison suggests that photopriming could be underestimated in our model and that the description of this process needs to be better developed.

Not all budgets for tDOC in the coastal ocean, however, indicate that bacterial degradation is important. In South East Asia, direct bacterial degradation is shown to play a minor role in tDOC remineralisation (Nichols and Martin, 2021; Zhou et al., 2021),with photolysis and/or photopriming contributing up to 74 % of remineralisation (Zhou et al., 2021). The high peat content of tDOC (=T1) is hypothesized to cause the low bioremineralisation rates although the role of photopriming still needs further investigation in these areas.

The dominance of bacterial degradation in our tDOC budget highlights the importance to constrain the biological lability of tDOC entering the ocean and how it varies with age once reaching the marine system. The rates we use in this study, are based on compilation of bioassay experiments from inland waters (Anderson et al., 2019; Catalán

Table 1
Fate of tDOC in the ocean, expressed as a % of the tDOC river input received to the study area. *Input includes riverine and atmospheric DOC,**Total loss does not add to 100 % and likely indicate additional ecosystem processes acting on DOC in the river plume.

Study Area	Total remin	Photo-degradation	Bacterial degradation	Flocculation	Photopriming	Advection	Method	Ref
North West European Shelf	78 %	5±0.5 %	73±6 %	0.5±0.1 %	1±0.2 %	21±3 %	Model	This study
Baltic Sea*	40 %			22 %		40 %	Model	(Gustafsson et al., 2014)
Louisiana Shelf	>40 %	~2 %	~35 %	–	~8 %	<60 %	Experiment/mass balance model	(Fichot and Benner, 2014)
Sunda Shelf	70–80 %	Up to 74 %				20–30 %	Isotope mass balance/ incubation experiments	(Zhou et al., 2021)
Amazon shelf						50–76 %	Lab – molecular composition	(Medeiros et al., 2016)
Gulf of Bothnia						47 %	Isotope and mass balance	(Alling et al., 2008)
Arctic Basin						21–40 %	Observation/Ra isotopes	(Letscher et al., 2011)
Arctic DOC exported to Fram strait						12–41 %	Lignin content	(Opsahl et al., 1999)
						20–50 %	DOM fluorescence	(Amon, 2003)
Arctic						25–33 %	Isotopes/lignin phenol composition	(Benner et al., 2005)
Eurasian shelf	~50 %						Field sampling/bioassay experiments	(Kaiser et al., 2017)
Southeastern Beaufort Sea		3-5 %					Model+experimental data	(Bélanger et al., 2006)
Yukon River Delta**		5 %	17 %	1.7 %		50 %	Model	(Clark et al., 2022)
McKenzie Shelf		<1 %					Photodegradation experiments	(Osburn et al., 2009)
South Atlantic Bight		2.9–3.2 %					Photodegradation experiments/ model	(Reader and Miller, 2012)

et al., 2016; Evans et al., 2017). More studies are required to further constrain tDOM lability in regard to how they vary with age and source of tDOC to further improve our estimates of bacterial degradation. In addition, the contrasting results on the importance of bacterial degradation depending on source of tDOC highlight the need to also improve predictions of type of tDOC (T1 vs T2) entering the ocean, and indeed the need in ocean models to separate tDOC into different sources.

A large portion (79 %) of riverine tDOC is remineralised on the NW European shelf with the remaining 21 % exported off the shelf. The advection flux is lower than the 50 % arbitrarily assumed for post-estuarine tDOC by Kitidis et al. (2019) in their carbon budget for the shelf. This suggests the NW European Shelf may play a larger role than initially thought in the reworking of tDOC, which impacts the air-sea CO_2 flux across the shelf (Section 4.4). In comparison ~50 % of arctic river input is processed/removed on the Eurasian Shelf (Kaiser et al., 2017) with 12-41 % estimated to be transported to the Atlantic (Benner et al., 2005; Hansell et al., 2004; Opsahl et al., 1999). In the Baltic, 36-51 % of total riverine input is advected out to the North Sea through the Kattegat (Gustafsson et al., 2014; Seidel et al., 2017). The comparatively lower fraction of tDOC advected away from the NW European Shelf highlights the key role of the NW European shelf in remineralising tDOC.

The results reported in this manuscript all come with a level of uncertainty associated with them both though parameter uncertainty associated with degradation rates and transfer across age classes and uncertainty in the model structure. A full uncertainty analysis such as in Ciavatta et al. (2016) for bottom oxygen using 100 member ensembles is not feasible for this work. The parameters used in this study are taken as much as possible from the UniDOM model. The photochemical degradation rates in UniDOM are likely to be overestimated because they are taken from laboratory experiments where usually DOM is exposed to levels of UV light which are unrealistically high compared to those observed in the water column. However, such overestimation is likely to be balanced by the assumption that UV light does not penetrate below the surface layer. Likewise bacterial degradation rates are formulated differently to that in uniDOM because ERSEM includes an explicit representation of bacteria, however the rates used in ERSEM were set so that the resulting mineralisation rates of tDOC were as close as possible to the UniDOM values. Future work may concentrate on improving model equations and parameterisation for both photochemistry and bacterial degradation.

4.3. Spatial and temporal distributions of tDOC

Observational data for tDOC suggests little tDOC reaches the central North Sea. The depleted tDOC signature observed in the central and Northern North Sea was hypothesized to be a consequence of significant degradation of tDOC and/or mixing with autochronthous DOC masking the terrestrial signature (Painter et al., 2018). Our results suggest that small amounts of tDOC are present in the Central and Northern North Sea and lie mostly in the 8 year age fraction (Fig. S6). In addition, the results of the *tracer sim* suggests that even if no degradation takes place tDOC concentrations would still be low in the central and northern North Sea due to conservative mixing (Fig. S7).

Little tDOC is also predicted in the Central and Southern Celtic Sea. This contrasts with results of Carr et al. (2019) who estimated tDOC concentrations of ~25 μM at the Central Celtic Sea station (see Fig. S1), based on observational data and linear regressions of salinity, DOC and fluorescence component identified as tDOC. At this station, our model predictions are two orders of magnitude lower than that predicted by Carr et al. (2019) (Fig. S8a). Maximum daily tDOC concentrations at this station in the *tracer sim* are simulated to not exceed 2.2 μM which is still an order of magnitude lower than that estimated by Carr et al. (2019) (Fig. S8b). The *discharge sim* suggests that riverine water is diluted by a minimum of 99.4 % (Fig. S9) by the time it reaches the Central Celtic Sea station further suggesting a minimal influence of riverine discharge at this station. Differences between the model and the inferred observational values may be due to the high end member of tDOC used by Carr et al. in freshwater due to their extrapolation of DOC (fluorescence component) from observed salinity ranges of 34.6-35.6. Thus given the evidence provided here, we suggest that tDOC in the Celtic Sea is lower than previously indicated.

A key uncertainty in our results is the different methods used for calculating riverine inputs, with a relatively high-resolution river model used for GB rivers and a literature search with constant concentration/interpolation of observed data for the rest of Europe. The results from the *discharge sim* suggest that the majority of riverine water in the North Sea is from UK rivers (Fig. S4). Hence the distribution of tDOC in the North Sea is largely due to UK river inputs. Thus the discrepancies between the spatial resolution of rivers from GB and that of the rest of Europe should not greatly influence concentrations or temporal trends of tDOC within the North Sea. Freshwater inputs from the large European rivers such as the Elbe and Rhine are confined to the German Bight and Norwegian coast indicating that the trends in tDOC seen in these areas are due to European/Scandinavian rivers. Therefore predicted temporal trends in these regions are likely lacking due to the prescribed constant tDOC concentrations from some of these rivers in this area.

4.3.1. Why is there a constant spatial distribution of tDOC on the shelf for the last 60 years?

A key question highlighted by Painter et al. (2018) is why there is a semi-constant spatial distribution in tDOC concentrations in the North Sea over the last 60 years despite observed increases in riverine DOC concentrations during varying time periods (Asmala et al., 2019; Monteith et al., 2007; Worrall et al., 2004). However, long term model estimates from 1950 to 2020 suggest that DOC loads from rivers in fact show a decreasing or non-significant trend in Europe, although rivers from the UK were not included in this analysis (Li et al., 2019). This agrees with recent observational data for UK rivers highlighting a substantial portion are in fact showing a decreasing DOC trend, with UK rivers reaching a peak in DOC concentrations in 2005 and decreasing thereafter (Worrall et al., 2018) although DOC concentrations in lake and stream headwaters across Europe have increased over 1990-2016 (de Wit et al., 2021). These contrasting trends are a balance between improved technology in wastewater treatment plants (Worrall et al., 2018) reducing DOC inputs to rivers and changes in air quality and climate increasing DOC inputs(de Wit et al., 2021). The riverine input of tDOC to the NW European Shelf used here does not show a significant trend in the river load of tDOC over time, nor do our results show any obvious trend in the mass of tDOC on the shelf over 1986-2015. While the assumption of constant DOC concentration for most of the Irish and continental European rivers could have affected this result, as discussed in Section 4.3, its impact is largely constrained to the German Bight, English Channel and Celtic Sea (Fig. S4) and therefore has limited impact within the North Sea.

4.4. Influence of tDOC processing on air-sea fluxes of CO_2

tDOM influences ecosystem dynamics as it is a carbon source to bacteria and supplies an additional source of nutrients to the ocean through the remineralisation of dissolved organic nitrogen and phosphorus associated with the tDOM. As a consequence of including riverine inputs of tDOC, bacterial biomass increases enhancing bacterial respiration, CO_2 production and nutrients. At the same time, photodegradation of T1 directly produces CO_2, as well as nutrients. It should be noted that the increased CO_2 production due to bacterial respiration is not always counterbalanced by an increase in gross primary production (GPP) from the inorganic nutrients released by remineralisation of tDOM (Fig. S10). Indeed, in some coastal areas with high tDOC concentrations, GPP tends to decrease in the tDOC simulation relative to the *no-tDOC sim* likely due to the increased zooplankton grazing triggered by the enhanced bacterial biomass from river DOM input. Overall, our simulations suggest that the main impact of tDOM on the air-sea CO_2

fluxes is triggered by the increase in heterotrophic biomass (bacteria and zooplankton) and the consequent decoupling between respiration and primary production, as recently suggested for the Arctic Shelf (Polimene et al., 2022). Indeed, this process dominates over the potential increase in primary production due to the nutrients associated with tDOM (Polimene et al., 2022).

The inclusion of tDOC influences the magnitude of the oceanic carbon sink. Although the 4 % (112 Gmol yr^{-1}) reduction in the air-sea CO_2 flux on the NW European Shelf is well within the uncertainty estimates of the air-sea CO_2 flux for the NW European Shelf (1300-3300 Gmol yr^{-1}; Legge et al., 2020), this is still equal to the amount of CO_2 emitted by the UK chemical industry (NAEI, 2023). Furthermore, in some regions the inclusion of tDOC in the model simulation results in some areas of the shelf changing from a net sink of atmospheric CO_2 to a net source of CO_2. This indicates the sensitivity and uncertainty in our knowledge of oceanic uptake of CO_2. It is thought that in pre-industrial times coastal oceans were net heterotrophic and a source of carbon to the atmosphere (Bauer et al., 2013). Anthropogenic influences have increased the flux of nutrients to the oceans making coastal seas net autotrophic. Here we show that in addition to the influence of nutrients it is also important to consider the organic matter flux of rivers in the discussions for net autotrophy versus heterotrophy.

This substantial change in the air-sea CO_2 flux on the NW European Shelf indicates that the influence of tDOC in the oceans needs to be considered on a global scale and in climate models. The change in the CO_2 flux of 112 Gmol yr^{-1} between the main simulation and *no-tDOC sim* suggests that on the NW European Shelf, 62±4 % of riverine inputs (182 Gmol yr^{-1}) is remineralised into CO_2. Of the remaining 38 %, 21±2 % is advected off the shelf which leaves ~17 % of the riverine inputs to enter the food web on the shelf itself. These results highlight the overestimation of reminerlisation of tDOC and consequent underestimation of air-sea flux of CO_2 in ESMs which assume all tDOC from rivers is immediately remineralised in shelf seas, in addition to the overestimation of the air-sea CO_2 flux in those which do not consider tDOC from rivers. In addition, the inclusion of tDOC in our model results in coastal acidification mostly due to the increase in DIC (from mineralisation of tDOC). At the shelf scale the mean difference in pH over 1986-2015 is lower than the uncertainty in model predictions (-0.0023 units), however near the coast the difference can be as high as -0.10 units (Fig. S11), comparable to the decrease projected in the NW European Shelf in the next 30 years under the RCP8.5 climate scenario (McGovern et al., 2022).

Despite some river catchments on the NW European Shelf having high DOC yields (Li et al., 2019; Williamson et al., 2021), the total tDOC flux reaching the shelf was relatively small compared to other rivers globally (Li et al., 2017, 2019), due to the small catchment sizes of rivers on the NW European Shelf. In contrast, the high tDOC yields and large catchment areas of rivers in both Arctic and tropical regions, result in substantially greater tDOC loads from rivers in these areas than the NW European shelf. Hence the potential for including tDOC in models and influencing air-sea exchanges of CO_2 is much greater in these areas (Terhaar et al., 2019). This also suggests that net autotrophy vs heterotrophy of these areas has the potential to change with the inclusion of tDOC in models. With climate change likely to thaw permafrost, and increase storminess, further increasing the tDOC flux reaching the ocean (Bauer et al., 2013; Bruhn et al., 2021; Mann et al., 2022), in addition to speeding up degradation processes (Polimene et al., 2022 and citations therein), the role of tDOC impacting air-sea CO_2 fluxes in shelf seas is likely to become even more important in these regions in the future.

5. Conclusions

For the first time, a comprehensive budget for tDOC on the NW European Shelf was achieved using a coupled model system. Our results highlight the major role of the NW European Shelf as a sink of tDOC with only 21±3 % of riverine tDOC exported away from the shelf. Bacterial remineralisation is shown to be the most important degradation flux on the shelf. Thus, further work should concentrate on refining the rates of the bacterial degradation on tDOC in the ocean in addition to improving the modelling of photodegradation, including the role of photopriming in increasing degradation rates. In addition, further understanding on characterising tDOC from rivers and estimating the portion of T1 and T2 from rivers, in addition to the continued improvements in estimates of fluxes of DOC from rivers to the ocean are required to accurately model the fate of tDOC in the ocean.

Implementing tDOC in the model resulted in a 4±0.4 % reduction in the strength of the shelf as a net sink of atmospheric CO_2 which is equivalent to 62±4 % of the riverine tDOC input to the shelf. This highlights the uncertainties in climate models that assume all tDOC from rivers is immediately remineralised as CO_2 (i.e. Aumont et al., 2015) or do not consider tDOC at all (i.e. Tjiputra et al., 2020). It is important to consider the impact of tDOC on a global scale, where riverine fluxes of tDOC are much greater, for example in the Arctic and tropical oceans. In addition, these regions are likely to be greatly influenced by climate change, resulting in higher tDOC fluxes to the ocean, and greater remineralisation of tDOC which both may further reduce the ability of the ocean to absorb anthropogenic CO_2, and increase coastal acidification. Consequently, further studies are required to understand the influence tDOC on global carbon cycling.

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CRediT authorship contribution statement

Helen R. Powley: Formal analysis, Investigation, Software, Validation, Visualization, Writing – original draft. **Luca Polimene:** Conceptualization, Methodology, Software, Writing – review & editing. **Ricardo Torres:** Conceptualization, Methodology, Writing – review & editing. **Muchamad Al Azhar:** Software, Writing – review & editing. **Victoria Bell:** Conceptualization, Methodology, Writing – review & editing. **David Cooper:** Conceptualization, Methodology, Software, Writing – review & editing. **Jason Holt:** Conceptualization, Funding acquisition, Project administration. **Sarah Wakelin:** Conceptualization, Formal analysis, Writing – review & editing. **Yuri Artioli:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Software, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The ERSEM code is available from the doi: https://doi.org/10.5281/zenodo.10185314. Model output data is available from authors upon request.

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