LIMNOLOGY and OCEANOGRAPHY

ASLO

Limnol. Oceanogr. 68, 2023, 1802–1820

doi: 10.1002/lno.12387

Marine nutrient subsidies promote biogeochemical hotspots in undisturbed, highly humic estuaries

Chris D. Evans [1,2*] **Stacey L. Felgate,** [3,4,5] **Steffi Carter,** [1,6] **Mark Stinchcombe,** [4] **Edward Mawji,** [4] **Andrew P. Rees,** [7] **Inma Lebron,** [1] **Richard Sanders,** [3,8] **Paul Brickle,** [6,9] **Daniel J. Mayor** [4,10]

[1]UK Centre for Ecology and Hydrology, Bangor, UK
[2]Swedish Agricultural University, Uppsala, Sweden
[3]Ocean and Earth Science, University of Southampton, Southampton, UK
[4]Ocean Biogeosciences, National Oceanography Centre (NOC), Southampton, UK
[5]Department of Chemistry–BMC, Uppsala University, Uppsala, Sweden
[6]South Atlantic Environmental Research Institute (SAERI), Stanley, Falkland Islands
[7]Plymouth Marine Laboratory (PML), Plymouth, UK
[8]Norwegian Research Centre (NORCE), Bergen, Norway
[9]School of Biological Sciences (Zoology), University of Aberdeen, Aberdeen, Scotland, UK
[10]Biosciences, University of Exeter, Exeter, UK

Abstract

The land-ocean dissolved organic carbon (DOC) flux represents a significant term within the global carbon budget, with peatland-dominated regions representing the most intense sources of terrestrial DOC export. As the interface between freshwater and marine systems, estuaries have the potential to act as a filter of the land-ocean carbon flux, removing terrestrially derived DOC, which is present at low concentrations in the oceans, via a combination of physicochemical and biological processes. However, the fate of peat-derived DOC within estuaries remains poorly quantified, partly due to the complicating influences of heterogeneous soils, land-use, point sources, and upstream modification of organic matter. To minimize these modifying factors, we studied DOC and inorganic nutrients in four small, peat-dominated, minimally disturbed, and oligotrophic Falkland Island estuaries. Contrary to expectations, we found limited evidence of physicochemical estuarine DOC removal, and instead observed apparent "hot zones" of biogeochemical activity, where terrestrially-derived silicate mixed with inorganic nitrogen and phosphorus entering the estuaries from the nutrient-rich marine ecosystem. In two estuaries, this coincided with apparent in situ DOC production. We suggest that the observed phenomena of marine nutrient subsidy of estuarine productivity, and flexible utilization of multiple nutrients within the oligotrophic system, may once have been widespread in temperate estuaries. However, this function has been lost in many ecosystems due to catchment eutrophication by agricultural and urban development. We conclude that the estuaries of the Falkland Islands provide a valuable pre-disturbance analogue for natural biogeochemical functioning in temperate estuaries receiving high organic matter inputs.

*Correspondence: cev@ceh.ac.uk

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

Author Contribution Statement: C.D.E. conceived and designed the study, with support from S.L.F., S.C., R.S., and D.J.M. C.D.E., S.L.F., S.C., R.S., D.J.M., and A.P.R. undertook estuary surveys. P.B. collected additional marine samples. S.C. derived catchment spatial data. M.S., E.M., I.L., and R.S. undertook chemical analyses. C.D.E. drafted the manuscript with support from all authors.

The aquatic transport of carbon (C) between the land and the ocean represents an important, but comparatively poorly understood, component of the global carbon (C) cycle (Cole et al. 2007; Tranvik et al. 2009; Raymond et al. 2013; Drake et al. 2018). The IPCC's 6th Assessment Report (Canadell et al. 2021) and a recent review by Battin et al. (2023) give best estimates of 2.5 and 3.2 Pg C yr^{-1}, respectively, for the transfer of carbon from terrestrial to freshwater ecosystems, and 1.7 and 2.3 Pg C yr^{-1}, respectively, for the amount of C lost from the freshwater system via degassing of CO_2 and (to a lesser extent) burial in sediments. The remaining 0.8 Pg C yr^{-1} is exported from freshwater to marine systems. Although this

value, based on large river C concentration and discharge measurements, is considered to be comparatively well-constrained (Drake et al. 2018; Battin et al. 2023), the processing and fate of terrestrially derived organic carbon (OC) as it passes into the marine system via estuaries remains uncertain (e.g., Evans et al. 2016; Bogard et al. 2020; Zhou et al. 2021).

The land-to-ocean C flux comprises a spatially and temporally variable mixture of dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC). Global aquatic fluxes of organic and inorganic C are approximately equal, but around 40% of the DIC flux is transported in groundwater, whereas most OC is transported via rivers (Cole et al. 2007). In most rivers, the OC flux is dominated by the DOC, for example, Ciais et al. (2008) estimated that around three quarters of the European OC flux was in the form of DOC. The riverine DOC flux thus represents the largest transfer of reduced carbon between the continents and the ocean (Hansell et al. 2004). At a global scale, the largest inputs of DOC to rivers on an areal basis occur in areas of high peat cover, both in the high latitudes and in the humid tropics (Aitkenhead and McDowell 2000; Raymond and Spencer 2015; Williamson et al. 2021).

Despite the magnitude of the land-ocean DOC flux, there is little evidence that terrestrial inputs enter the large marine DOC pool, which is believed to be largely of marine planktonic origin (Hedges et al. 1997; Opsahl and Benner 1997). This has led to the proposed existence of a "marginal filter" for terrigenous OC at the land-ocean boundary (Lisitsyn 1995), although the removal processes remain difficult to characterize or quantify (Hedges et al. 1997; Hansell et al. 2004; Bauer et al. 2013; Dittmar 2015).

One possible sink for riverine DOC is removal in the estuary, via a range of potential physico-chemical and biological mechanisms. These include flocculation or adsorption to mineral particles as dissolved organic matter (DOM) becomes less soluble at higher salinities, which could contribute to the burial of terrigenous OC in continental margin sediments. Mineralization via biological and/or photochemical degradation convert DOC to DIC, and can lead to degassing of CO_2 to the atmosphere (Zhou et al. 2021). Estuaries provide favorable environments for flocculation due to the rapid increase in ionic strength across the freshwater–seawater interface, which may reduce DOM solubility. Sholkovitz et al. (1978) observed strong flocculation of the "humic" (high molecular weight, aromatic, and soil-derived) fraction of DOM in both Amazonian and UK river waters during mixing with seawater at low salinities. Similar preferential removal of humic DOM has been observed in other rivers draining peaty catchments (Forsgren et al. 1996; Spencer et al. 2007; Asmala et al. 2014; Kritzberg et al. 2014), and may be enhanced by photodegradation where estuarine residence times are long (Anderson et al. 2019). On the other hand, studies in less peat-influenced catchments have recorded approximately conservative mixing of total DOC across salinity gradients, implying little or no net removal (e.g., Mantoura and Woodward 1983; Álvarez-Salgado and Miller 1998; Abril et al. 2002) or in some cases apparent net DOC production (Abril et al. 2002; García-Martin et al. 2021).

Overall, existing evidence suggests that: (1) DOC represents the largest riverine flux of terrigenous carbon from land to ocean; (2) peatlands generate the highest inputs of DOC to rivers on an areal basis; and (3) peat-derived DOC is comparatively susceptible to estuarine removal via flocculation and photodegradation, but not biodegradation. The estuarine processing of peat-derived DOC is, however, difficult to determine in many parts of the world because peatlands often occur within mosaic landscapes of mixed soils and land-use (e.g., Ågren et al. 2014; García-Martin et al. 2021), as well as lakes and reservoirs, which can act as DOM "reactors" (e.g., Tranvik et al. 2009; Catalán et al. 2016; Evans et al. 2017). Fluxes of DOC in many rivers are also subject to heavy modification by nutrient and organic matter loadings from areas of farmland and human habitation (e.g., Spencer et al. 2007; Noacco et al. 2017). However, Vieillard et al. (2020) argue that estuarine research is strongly biased toward highly eutrophic European and North American catchments, leading to a distorted understanding of estuarine biochemical processes in general, and call for more research on oligotrophic estuaries. Childers et al. (2006) describe the phenomenon of "upside down" estuaries, in which oligotrophic (and often DOC-rich) catchments drain into more eutrophic coastal marine systems, to the extent that nutrients limiting estuarine production are provided by the sea rather than the land. It is likely that such conditions were more common in the past than they are today (Jickells et al. 2014).

Our understanding of the controls on transport and processing of peat-derived DOM through estuaries is currently reliant on comparatively few studies. Working in a large Indonesian river draining a peat-dominated catchment, Moore et al. (2011) observed nonlinear variation in DOC across the salinity gradient, with DOC removal rates of 12% to 27%. In peat-influenced UK catchments, Palmer et al. (2016) observed nonconservative DOC mixing in one of five estuary transects (giving an estimated removal of 40% in this case) while Spencer et al. (2007) observed clear non-conservative mixing on four out of nine occasions, with maximum removal of 58%. In both studies, high rates of DOC removal were associated with summer high flow events, when unmodified peat-derived DOM was entering the estuary. At other times, the peat signal appeared to be masked by mixing with other water types, upstream modification, and wastewater inputs. This complexity was also evident in a recent study of 13 UK estuaries spanning a broad soil and land-use gradient, which showed highly variable DOC variations in both time and space, and evidence of net DOC production in some estuaries with high arable and urban influence (García-Martin et al. 2021). In line with the observations of Vieillard et al. (2020), we found that most

studies of estuarine DOC processing were from northern temperate estuaries, one exception being a study of four subtropical, land-use impacted estuaries in Australia by Looman et al. (2019).

In order to examine the controls on estuarine processing of peat-derived DOM without these confounding influences, we studied a set of exceptionally peat-rich and relatively unmodified catchments in the Falkland Islands, which lie off the Atlantic coast of South America. The Falkland Islands are among the most peat-dominated regions in the world, with the majority of the land area occupied by peat or other organic soils (Carter et al. 2020). Coastal marine ecosystems here are also notably carbon-rich (Bax et al. 2022). River lengths are short, there are no lakes or reservoirs along the main river channels, and population density is extremely low. Prior to European settlement in the late 18th century there were no herbivorous mammals on the islands, and the introduction of livestock led to large-scale vegetation changes (Armstrong 1994). Present-day agriculture is limited to low-intensity sheep grazing, and away from the coastal fringe soils are acidic and nutrient-poor, leading to highly oligotrophic conditions in most surface waters (Carter et al. 2022). We therefore anticipated that the Falkland Islands would provide an effective model ecosystem in which to determine the extent of estuarine processing of peat-derived DOM in the absence of confounding human impacts, and a proxy for the biogeochemical conditions and processes that would have prevailed in peaty temperate estuaries more widely prior to human disturbance. We hypothesized that high inputs of relatively unmodified peat-derived DOM to the estuaries would lead to strong net removal, supporting the concept of estuaries as "marginal filters" for terrigenous OC. To interpret observed DOM processes and mixing in the context of wider biogeochemical processes, we analyzed DOC and light absorbance (as a measure of DOM quality) alongside salinity and inorganic forms of the major nutrients nitrogen, phosphorus, and silica.

Materials and methods

Study area

The Falkland Islands (52°S, 59°W) have a total land area of 12,170 km^2, split across two main islands and numerous smaller ones. Maximum elevation is 705 m. Annual precipitation is low (mean recorded precipitation 585 mm yr^{-1} at Mount Pleasant, East Falkland; Upson 2012). Annual mean temperature is around 6°C, and the islands are characterized by high average wind speeds. There is no natural tree cover, and the vegetation is dominated by the tussock grass *Cortadelia pilosa* and dwarf shrub *Empetrum rubrum* (Moore 1968). Recent soil mapping of the islands suggests that 38% of the total land area is occupied by peat, giving them one of the highest proportions of peat cover on Earth, with most of the remaining land having a peaty topsoil (Carter et al. 2020). Peat occurs on both plateaus and hillslopes in the uplands, and along river valleys in the lowlands. The majority of inland peat is fairly shallow (0.4–2 m), with widespread presence of erosional features. While it physically resembles the blanket bogs of hyperoceanic regions such as the British Isles, peat in the Falkland Islands has formed under much lower rainfall, ostensibly at the edge of the climate envelope of peat formation, for reasons that remain incompletely understood (e.g., Payne et al. 2019). Like blanket bogs elsewhere, however (e.g., Holden and Burt 2003) it appears to have a very low lateral hydraulic conductivity at depth, so that water either percolates vertically to the mineral soil or moves laterally near the peat surface. Rock outcrops and periglacial "stone runs" occur in upland areas, but occupy only a small part of the overall land area.

We surveyed four of the largest rivers in East Falkland, the largest island. The San Carlos River, Malo River and Swan Inlet drain the central upland region, while the smaller Murrell River catchment drains to the east coast, close to the small capital city of Stanley (population ~ 2100). All four catchments have high peat cover, and broadly similar catchment characteristics, but vary in their connectivity to the open sea; the Murrell and San Carlos Rivers connect directly to deep water, whereas the Malo River and Swan Inlet drain to long, poorly connected shallow inlets (Fig. 1; Table 1). Figure 2 provides an example of the visual appearance of the estuaries. The tidal range of the Falklands is relatively small (maximum 1.9 m in Stanley; Bax et al. 2022), but estuaries tend to be shallow and are therefore effectively flushed during each tidal cycle.

Sample collection and analysis

Samples were collected during two field campaigns, the first from 05 November 2017 to 08 November 2017, and the second from 16 November 2019 to 19 November 2019. Each river was sampled in a single day, and on a falling tide. Samples were mostly collected from the shore, using a galvanized steel bucket and nylon rope to sample as close as possible to mid-channel. For the Murrell River (2017) and Swan Inlet (both campaigns) a boat was used to sample the lower part of the estuary. For each river transect, we started at the seaward end of the estuary, sampling as close as possible to full salinity, then proceeded upstream, sampling at approximately equal salinity intervals, until we reached nontidal freshwater. The number of samples collected per transect ranged from 5 to 10 (average 8) depending on time available and accessibility. At each sampling location, we measured salinity and temperature in situ using a Hach HQ40D handheld multiparameter sonde. At all sites, a 60 mL sample was syringe-filtered through 0.45 μm cellulose acetate filters into amber glass bottles. This sample was analyzed for DOC and absorbance. A second filtered 40 mL sample was collected in a centrifuge tube for analysis of all inorganic nutrients. All bottles were acid-washed, and bottles and filters were prerinsed with sample

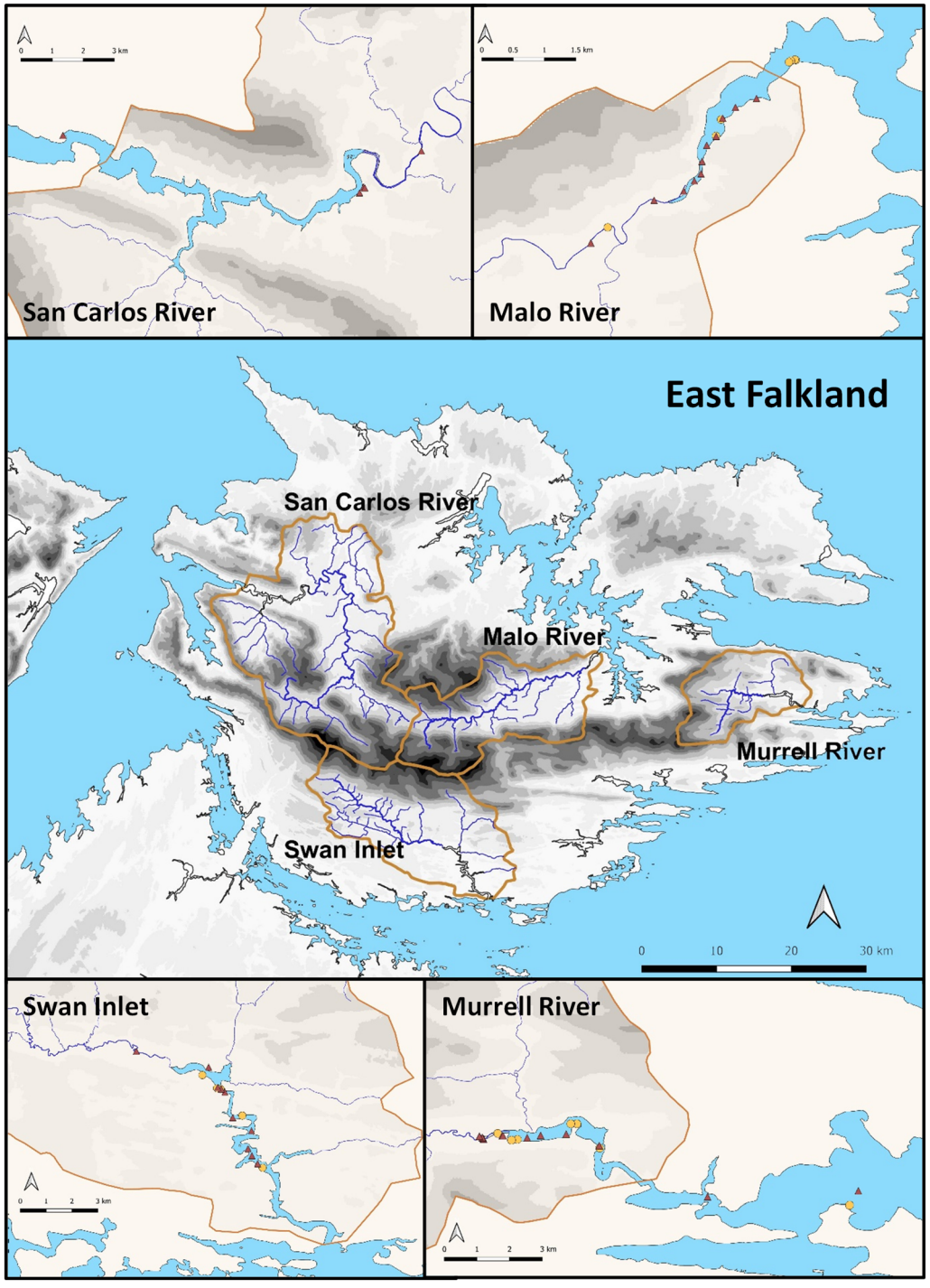

Fig. 1. Sampling catchments overlaid on a digital elevation model of East Falkland (darker shading indicates higher elevation). Inset figures show points at which samples were collected in each river-estuary transect (red triangles show 2017 survey points and yellow circles 2019 survey points—differences in location reflect differences in the salinity gradient at the time of sampling).

before use. On return from each survey, samples were stored at 4°C in the dark prior to analysis.

For the 2017 campaign, samples were transferred onto the RRS Discovery, a UK Natural Environment Research Council research vessel, which was berthed in Stanley at the time, and analyzed on board for dissolved nutrients including nitrite (NO_2^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and silica (SiO_2) by colorimetry using a four-channel SEAL QuAAtro

Table 1. Summary characteristics of the four surveyed catchments.

Catchment	Area (km^2)	Maximum elevation (m)	Estimated peat cover (%)	Proximity to open ocean
Malo River	257	637	43	Low
Swan inlet	316	660	20	Intermediate
Murrell River	143	469	15	High
San Carlos River	547	705	43	High

Peat cover estimates are derived from the soil map of Carter et al. (2020), based on a 40 cm minimum depth threshold. Shallower peaty soils occupy much of the remaining land area. The estimated peat extent for the Murrell catchment is believed to be an under-estimate (S. Carter, personal observation).

Fig. 2. Tidal section of the Malo River (looking upstream) and individual samples ordered from upstream (peat seepage sample, salinity < 0.01, top left) to most saline sample collected (salinity 28.5, bottom right).

39 analyzer. Nitrate was calculated by difference between total oxidized nitrogen (i.e., $NO_3^- + NO_2^-$) and NO_2^- measured separately. Detection limits (calculated using SEAL analytical software by running the lowest standard 20 times) were 0.05 μmol L^{-1} for $NO_3^- + NO_2^-$, 0.01 μmol L^{-1} for NO_2^-, 0.01 μmol L^{-1} for PO_4^{3-} and 0.02 μmol L^{-1} for SiO_2. We did not have access to instrumentation for analysis of ammonium (NH_4^+), and expected that concentrations would be negligible in the aerated, unpolluted Falkland estuaries. It is possible that NH_4^+ was present in estuarine sediment porewaters (e.g., Vieillard and Thrush 2021) but any leached to the water column was assumed to be rapidly oxidized to NO_x, and therefore captured by our measurements.

Light absorbance was measured across the visible and ultraviolet spectrum (0.5 nm increments from 200 to 800 nm) using a Cary 60 UV–visible spectrophotometer (Agilent Technologies, Cheadle, UK), also located on Discovery. A quartz cuvette with a 1 cm path length was used, and higher-DOC samples were diluted by a factor of 2 or 4 using Milli-Q water to avoid saturation of absorbance at lower wavelengths.

Absorbance measurements were Milli-Q blank-corrected, and expressed in absorbance units per meter path length. Samples for DOC analysis were returned to the UK and analyzed at the UK Centre for Ecology and Hydrology Bangor laboratory on a Thermalox analyzer, using the nonpurgable organic carbon method. This involved first sparging samples with hydrochloric acid for 60 s to remove inorganic carbon, then analyzing total carbon concentrations by thermal oxidation. The same samples were also analyzed for pH with a Metrohm 888 Titrando, and conductivity with a Jenway 4320 m and Jencons 223–018 probe.

For the 2019 campaign, all samples were returned to the UK for analysis. Samples for nutrient analysis were frozen during transit, while samples for DOC and absorbance analysis were refrigerated based on previous work for high-DOC waters suggesting that extended cold storage has less effect on DOC concentrations and optical properties than freezing (Peacock et al. 2015) or acidification (Tfaily et al. 2011). All 2019 measurements were made using the same instruments and methods described for 2017. Detection limits, measuring using the same method as above, were 0.01 μmol L^{-1} for $NO_3^- + NO_2^-$, 0.01 μmol L^{-1} for NO_2^-, 0.02 μmol L^{-1} for PO_4^{3-} and 0.02 μmol L^{-1} for SiO_2.

Data analysis

Estuary transect data

For each of the nutrients analyzed (DOC, SiO_2, NO_3^-, and PO_4^{3-}) we plotted concentrations against salinity for each river-estuary transect. In each case, we defined a conservative mixing line by linearly connecting the freshwater sample with the most saline sample collected at each site. Consistent deviation below this line (i.e., a "concave" concentration-salinity relationship) indicates net removal of that solute within the estuary, with larger deviations indicating greater removal. In solutes with higher concentrations in the freshwater end-member, this implies that this solute is being exported from the terrestrial ecosystem and removed in the estuary, whereas higher concentrations in the saline end-member imply removal of material from a marine source. If observed solute concentrations deviated positively from the conservative mixing line drawn from the highest to the lowest salinity measurement (a "convex" concentration-salinity relationship) we interpreted this as evidence of net production of that solute within the estuary. In order to quantify the extent of apparent removal or production of each solute at each location, we compared the observed concentration to that which would be predicted by the conservative mixing line at the observed salinity. A negative difference between observed and predicted concentrations (termed ΔX, where X is the solute under investigation) was taken to indicate net removal, while a positive ΔX net production.

To evaluate the potential role of limiting nutrients on autotrophic production across the estuary, we compared calculated molar ratios of inorganic nutrients at the freshwater and seaward end of each estuary. Since diatoms are a potentially important primary producer in these ecosystems we compared molar ratios to the Redfield-Brzezinski C : Si : N : P of 106 : 15 : 16 : 1 (Brzezinski 1985). For primary producers, the availability of OC is not relevant, so we focused solely on the critical ratios for inorganic nutrients, namely Si : N = 0.94, Si : P = 15, and N : P = 16. We included measured NO_2^- in the sum of available N, but assumed that (unmeasured) ammonium was negligible in these highly aerated waters). We also omitted organic N and P, which are potentially high in high-DOC freshwater inputs, but likely to be of low bioavailability (Stutter et al. 2018). In relation to heterotrophic production, we also considered ratios of DOC to N and P, again based on Redfield-Brzezinski ratios, but recognizing that only a fraction of the total DOM pool is bioavailable.

For samples collected at the freshwater end of each estuary, salinity levels were too low to be measured using the field salinity probe. For consistency, we therefore used laboratory measured conductivity to derive salinity using an empirical calibration (quadratic equation with zero intercept; Eq. 1) derived from all samples where both salinity and conductivity were measured. Salinity is expressed in PSU and conductivity in mS cm^{-1}.

$$\text{Salinity} = 0.570\,\text{Conductivity} + 0.0032\,\text{Conductivity}^2 \quad R^2 = 0.993, n = 44 \tag{1}$$

Analysis of absorbance data

As an indicator of DOM quality, we calculated the specific UV absorbance of samples at 254 nm ($SUVA_{254}$), calculated as the ratio of absorbance at 254 nm and measured DOC concentration in mg L^{-1}. $SUVA_{254}$ is a widely used proxy measure of DOM aromaticity (Weishaar et al. 2003) and reactivity. High-$SUVA_{254}$ DOM is typically derived from soils with a high organic content and is relatively resistant to biological degradation, but susceptible to photodegradation (e.g., Jones et al. 2016; Berggren et al. 2018; Anderson et al. 2019). Low-$SUVA_{254}$ DOM tends to be produced from more mineral soil dominated catchments (e.g., Carter et al. 2012), or by autochthonous production in freshwater and marine environments (Nguyen et al. 2005; Henderson et al. 2008; Adams et al. 2018). Low-$SUVA_{254}$ DOM is typically less colored, less aromatic, more biodegradable, and less photodegradable (e.g., Anderson et al. 2019). Although we measured absorbance across a broad spectrum of wavelengths, and derived a range of other absorbance-based metrics, these did not add substantively to the interpretation of results, and for the sake of brevity we only report $SUVA_{254}$ results here.

Results

Meteorological conditions

For the 2017 survey, mean air temperature at Mount Pleasant in the 30 d prior to the start of sampling was 6.8°C, and

total rainfall during the same period was 44 mm. In 2019, 30 d mean air temperature prior to the first sampling day was 7.4°C, and total rainfall 49 mm. Rainfall during both sampling periods was negligible (< 2 mm in total). The only notable difference in meteorological conditions between surveys was that significant rain occurred prior to the start of sampling in 2019 (12 mm on 15 November, the day before the first estuary transect); whereas in 2017, the last significant rainfall was 6 d prior to the start of sampling (11 mm on 30 October).

Water temperatures ranged from 8.9°C to 16.1°C in freshwater end-member sampling points, and from 8.9°C to 13.5°C at the seaward sampling point of each estuary (Table 2). With the exception of the Murrell River in 2017, temperatures were higher in freshwater inputs than in seawater, and where estuaries were sampled in both years, mean freshwater temperatures were 3.4°C higher in 2019 than in 2017, and seawater temperatures were 2.0°C higher.

Concentration variations across salinity gradients

Summary chemical data for all freshwater and seawater end-member concentrations are shown in Table 2, and full transect data in Supplementary Table S1. Of the inorganic nutrients, Si (Fig. 3a–d) tended to be highest in freshwater inputs to the estuary, and lower at the seaward end (< 12 μmol L^{-1} for all rivers on both sampling occasions). Freshwater Si concentrations were notably higher in the 2017 survey (> 90 μmol L^{-1} in all rivers), declining steadily through the estuary. The decline was near-linear in the Malo River, but clearly nonlinear in the other three. The pattern in 2019 was markedly different, with much lower concentrations (10–24 μmol L^{-1}) at the freshwater end of all three resampled estuaries. There was some evidence of a dilution gradient at salinities > 20 PSU, and seaward end-member Si concentrations were similar to the 2017 survey. Below 20 PSU, however, there was no clear pattern of Si variation in any estuary. At both the Malo River and Swan Inlet, peak Si concentrations in the upper estuary exceeded those in freshwater inputs.

In contrast to Si, PO_4^{3-} was consistently higher at the seaward end of all estuaries than at the freshwater end for all rivers and on both sampling occasions (Fig. 3e–h). Concentrations of PO_4^{3-} at the seaward end were notably higher in the Murrell and San Carlos Rivers in 2017, and mixing lines were non-linear at this time for all rivers except the Malo. In 2019, PO_4^{3-} concentrations were higher in the seaward end member at the Malo River and Swan Inlet, but lower in the Murrell River. However in 2017, it was possible to sample the seaward end of the Murrell River from a boat; whereas in 2019, we were only able to sample from the shore, in an area of giant kelp (*Macrocystis pyrifera*) beds, so this value may not be representative of conditions in open water. At the Murrell, we also observed higher PO_4^{3-} concentrations at the freshwater end of the estuary, which were not observed previously or in other estuaries.

Table 2. Measured water quality variables in the freshwater and seawater end-member samples from each surveyed estuary in both study years (November 2017 and 2019).

Site	Year	End-member	Temp. (°C)	Salinity (PSU)	SiO_2 (μ mol L^{-1})	PO_4^{3-} (μ mol L^{-1})	NO_3^- (μ mol L^{-1})	DOC (μ mol L^{-1})	Abs_{254} (m^{-1})	$SUVA_{254}$ (L mg^{-1} m^{-1})
Malo River	2017	Freshwater	–	0.06	90.9	0.11	0.00	842	0.62	6.12
		Seawater	–	31.38	3.5	0.27	0.08	149	–	–
	2019	Freshwater	16.1	2.40	10.9	0.12	0.78	2407	0.96	3.34
		Seawater	11.7	27.30	11.3	0.50	0.35	1316	0.19	1.22
Swan inlet	2017	Freshwater	13.3	0.09	145.8	0.15	0.14	515	0.33	5.37
		Seawater	10.1	28.68	7.9	0.26	0.13	185	0.11	4.86
	2019	Freshwater	15.8	2.32	14.3	0.10	0.27	1057	0.43	3.43
		Seawater	13.5	29.40	5.5	0.47	0.22	285	0.10	2.22
Murrell River	2017	Freshwater	8.9	0.16	95.7	0.11	0.00	1250	0.96	6.42
		Seawater	9.5	32.41	1.1	0.76	7.49	106	0.06	4.47
	2019	Freshwater	13.2	0.10	23.7	0.22	0.93	2132	1.38	5.40
		Seawater	10.0	33.20	3.7	0.30	0.54	246	0.03	0.94
San Carlos River	2017	Freshwater	12.1	0.12	133.0	0.14	0.00	1833	1.70	7.71
		Seawater	8.9	29.94	5.8	0.83	10.52	159	–	–

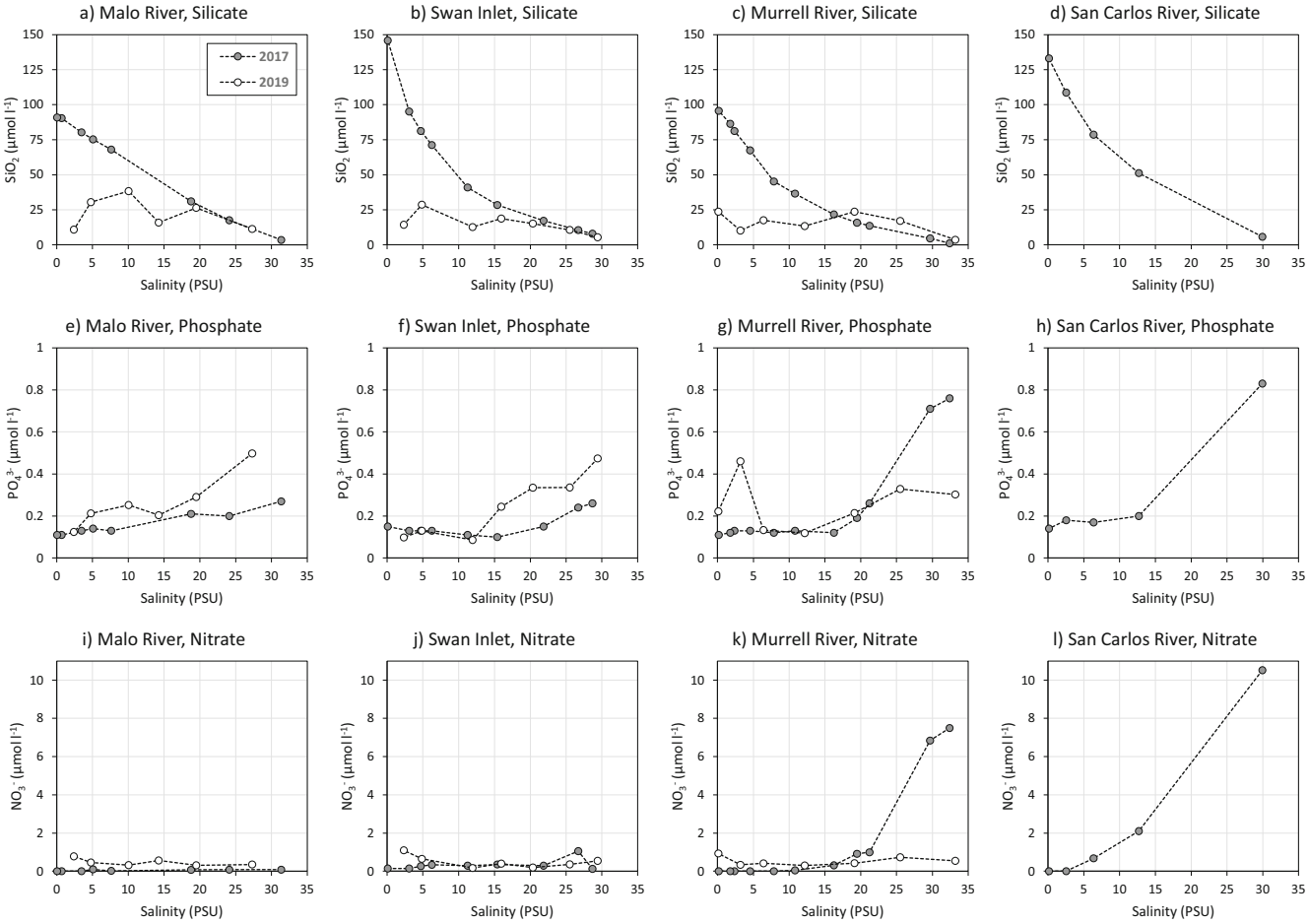

Fig. 3. Measured concentrations of inorganic nutrients vs. salinity in the four surveyed rivers and in both study years (note no data from the San Carlos River in 2019). Concentrations are plotted on a common y axis for each nutrient.

Concentrations of NO_3^- (Fig. 3i–l) were consistently ≤ 1 μmol L^{-1} in the Malo River and Swan Inlet. In the Murrell and San Carlos Rivers, NO_3^- concentrations were similarly low in the freshwater end of the estuary, but in 2017 concentrations > 6 μmol L^{-1} were found at the seaward end. Increases across the salinity gradient were clearly nonlinear. In the three estuaries resampled in 2019, NO_3^- concentrations were slightly higher in freshwater inputs and declined in the upper estuary. At Swan Inlet and the Murrell River, NO_3^- concentrations then rose slightly at the seaward end of the estuary, albeit not to the relatively high concentrations observed at the seaward end of the Murrell in 2017.

Variations in DOC, absorbance at 254 nm and $SUVA_{254}$ are shown in Fig. 4. In all cases, DOC concentrations were highest at the freshwater end of the estuaries, but with considerable variation between rivers. In 2017, the highest concentrations were observed in the San Carlos River (1830 μmol L^{-1}) and lowest in Swan Inlet (510 μmol L^{-1}). In 2019, freshwater concentrations were higher than in 2017 for all three resurveyed rivers, exceeding 2000 μmol L^{-1} in both the Malo and Murrell Rivers, and 1000 μmol L^{-1} at Swan Inlet. Higher DOC concentrations in the Malo River extended to the seaward end of the estuary, but in the other two estuaries concentrations declined to values similar to those observed in 2017 at high salinities. In both Swan Inlet and the Murrell River, peak DOC concentrations (i.e., higher than freshwater input concentrations) were observed at salinity values between 3 and 16 PSU. This pattern was also weakly evident in the Malo River. At higher salinities, the relationship between DOC and salinity frequently had a concave non-linear form (Malo in 2019, Swan Inlet in 2019, Murrell River in both years), indicative of net DOC removal.

Variations in Abs_{254} (Fig. 4e–h) were broadly similar to those for DOC, but in general lacked the peak values observed in the upper estuary, with variations conforming more closely to a conservative mixing line. Variations in $SUVA_{254}$ (Fig. 4i–l) were not consistent over the salinity gradient, although lower values were observed at the seaward end of the Malo and Murrell Rivers in 2019. For the two rivers where data were available from both surveys, $SUVA_{254}$ was notably higher on average in 2017 than in 2019.

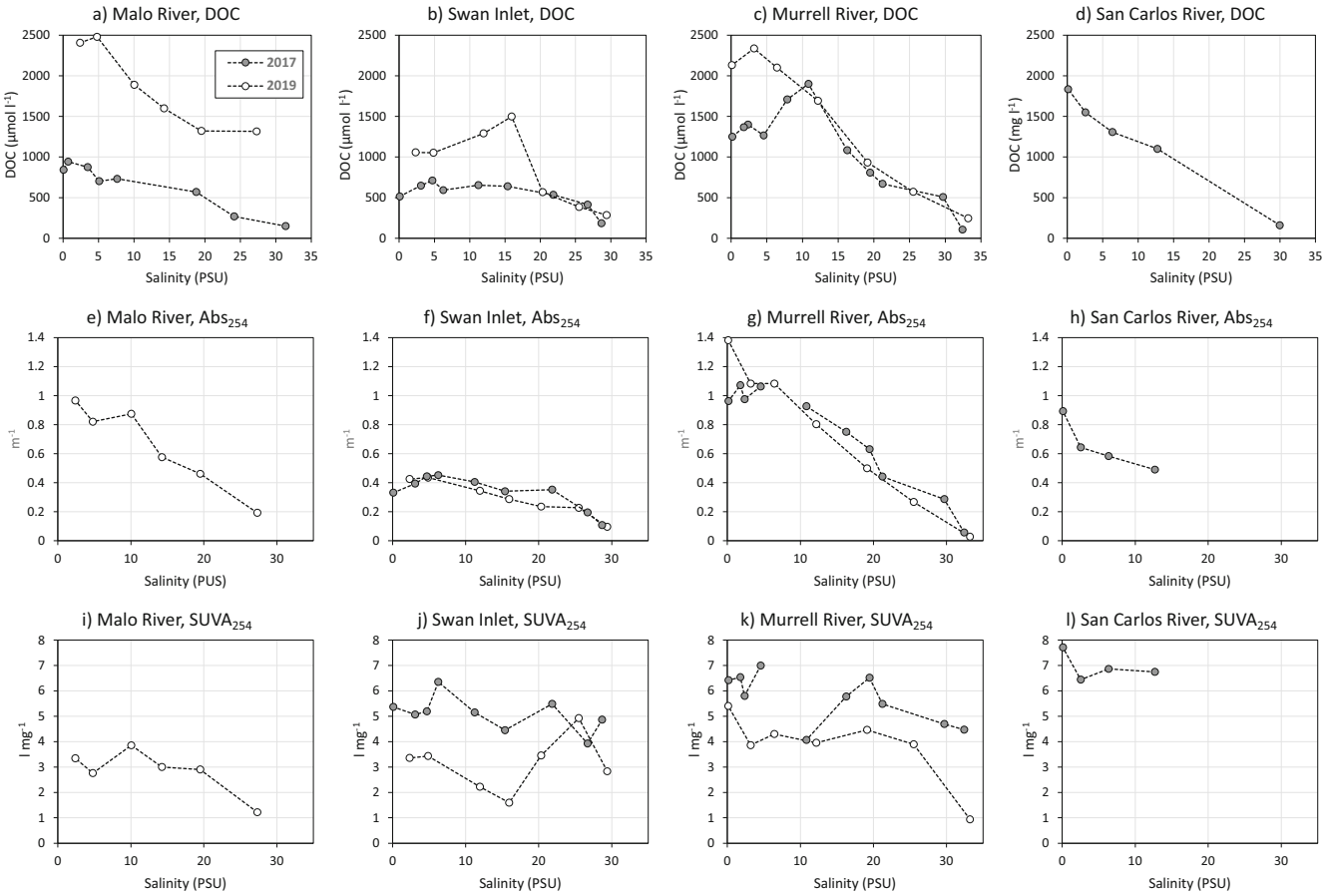

Fig. 4. Measured concentrations of DOC, absorbance at 254 nm and $SUVA_{254}$ vs. salinity in each surveyed estuary in both study years (note that the San Carlos River was not surveyed in 2019, and that optical analyses were not available for the Malo River or for the seaward end of the San Carlos River in 2017).

Deviations from conservative mixing relationships

Observed variations from conservative mixing lines are shown for the four measured solutes in Fig. 5. In 2017, we observed consistent SiO_2 removal in all estuaries. Estimated removal (ΔSiO_2) was smallest for the Malo River, where it peaked at 8 μmol L^{-1} (26%) below the predicted conservative mixing value. At Swan Inlet, peak removal was larger in both absolute and proportional terms (48 μmol L^{-1}, 58%). At both the Murrell and San Carlos Rivers, peak removal was 28 μmol L^{-1}, but due to higher freshwater concentrations in the San Carlos River this represented a smaller percentage removal here (35% vs. 43%). The salinity at which peak absolute Si removal occurred was greatest in the Malo River (19 PSU), and lowest in the Murrell River (8 PSU). In 2019, a similar but more subdued pattern of SiO_2 removal was observed in the Murrell River, but in the Malo River and Swan Inlet we observed apparent net release of SiO_2, with ΔSiO_2 peaking at 27 μmol L^{-1} in the Malo River. At a number of points in both of these estuaries, SiO_2 concentrations were more than double the values predicted from conservative mixing.

For PO_4^{3-} (Fig. 5e–h), we observed a pattern of net estuarine removal in all estuaries other than the Malo in 2017, with maximum removal of around 0.3 μmol L^{-1} at mid salinity in the Murrell River. Given the generally low estuarine PO_4^{3-} concentrations (mostly < 0.2 μmol L^{-1}) this indicates that a high proportion of the PO_4^{3-} entering the estuary (primarily from the seaward end) was being removed (maximum > 50% in all estuaries other than the Malo). In 2019, with higher PO_4^{3-} inputs at the seaward end of the Malo River and Swan Inlet, we observed higher rates of peak PO_4^{3-} removal. In the Murrell River, removal was apparently lower, although this may have been confounded by the different sampling point of the seaward end-member (see above). Apparent net PO_4^{3-} release at the top of the estuary in 2019 was reliant on a single sample.

Mixing relationships for NO_3^- (Fig. 5i–l) were similar to those for PO_4^{3-}, with strong net removal at the Murrell and San Carlos Rivers in 2017. Removal at the Murrell River peaked at 4 μmol L^{-1} and around 90% removal, while at the San Carlos River the equivalent figures were 2.4 μmol L^{-1}% and 66% removal. At the Malo River, NO_3^- concentrations were near

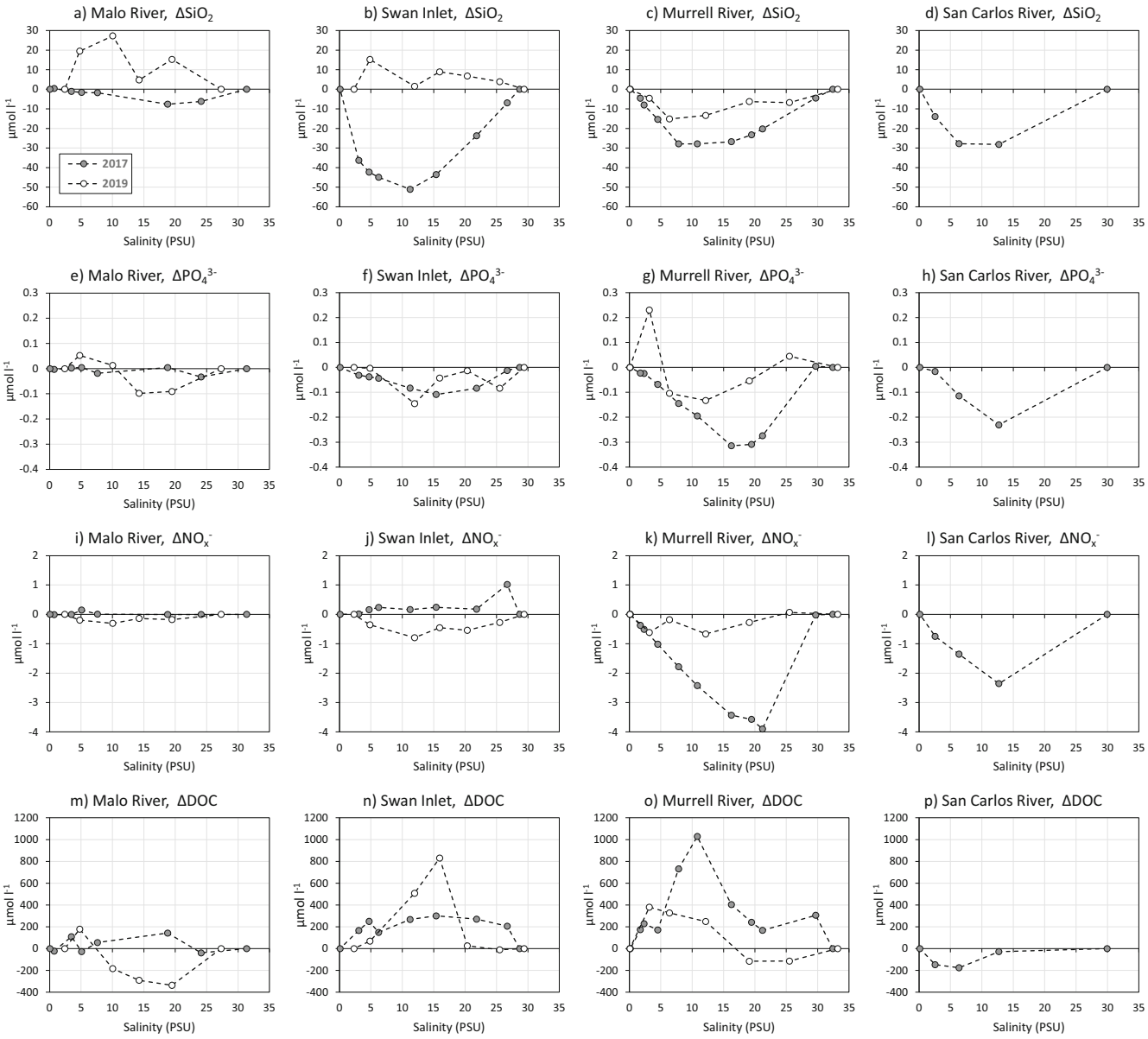

Fig. 5. Deviation of observed SiO_2, PO_4^{3-}, oxidized N (NO_x^-), and DOC concentrations from a conservative mixing line. Concentrations are plotted on a common y axis for each of the determinands.

zero throughout the salinity gradient, so there was no deviation from a theoretical mixing line. At Swan Inlet, with similarly low NO_3^- concentrations, there is some evidence of net production in 2017; however, this result is highly dependent on the selection of seawater endmember; using the second highest-salinity sample, which had higher NO_3^-, would suggest slight net removal. In 2019, NO_3^- concentrations were again uniformly low at the Malo River, while a small amount of net removal ($< 1\ \mu mol\ L^{-1}$) was apparent at mid-salinity values in Swan Inlet and the Murrell River.

For DOC, estuarine mixing varied greatly between estuaries and between surveys. At the Malo River, there was little deviation from a conservative mixing line in 2017, but in 2019 (when freshwater input concentrations were higher) we observed net removal, peaking at $340\ \mu mol\ L^{-1}$ (20% removal). At Swan Inlet, on the other hand, we observed apparent net DOC production during both years, with a relatively sharp ΔDOC peak of $830\ \mu mol\ L^{-1}$ at a salinity of 16 PSU in 2019. This implies a doubling of concentrations vs. the conservative mixing model. A more subdued peak spanning more of the salinity range was observed in 2017 (peak ΔDOC of $300\ \mu mol\ L^{-1}$ at salinity 15 PSU). A sharp peak of DOC production was also observed in the Murrell River in 2017 (maximum ΔDOC of $1000\ \mu mol\ L^{-1}$ at salinity 11 PSU). However in 2019, a small peak of DOC production in the upper estuary (maximum ΔDOC $380\ \mu mol\ L^{-1}$ at salinity

Table 3. Stoichiometry of DOC, nitrate, phosphate, and silicate for freshwater and seawater end-member samples from each surveyed estuary, compared to Redfield-Brzezinski ratios for marine organisms.

Site	Year	End-member	DOC : N	DOC : P (mol mol^{-1})	N : P (mol mol^{-1})	Si : N	Si : P
Malo River	2017	Freshwater	4951	7652	**1.5**	534.7	826.4
		Seawater	1356	552	**0.4**	31.5	**12.9**
	2019	Freshwater	1850	19,411	**10.5**	8.4	88.3
		Seawater	2809	2646	**0.9**	24.2	22.8
Swan inlet	2017	Freshwater	2861	3433	**1.2**	810.0	972.0
		Seawater	1321	712	**0.5**	56.3	30.3
	2019	Freshwater	846	10,787	**4.3**	33.8	146.4
		Seawater	469	602	**0.6**	19.3	**11.5**
Murrell River	2017	Freshwater	8333	11,364	**1.4**	637.7	869.5
		Seawater	14	139	**10.0**	**0.1**	**1.5**
	2019	Freshwater	1252	9603	**7.7**	13.9	106.7
		Seawater	377	814	**2.2**	5.6	**12.2**
San Carlos River	2017	Freshwater	6548	13,095	**2.0**	475.1	950.1
		Seawater	15	192	**12.9**	**0.5**	**6.9**
Redfield-Brzezinski ratios			6.6	106	16	0.94	15

Values shown in bold are below the critical thresholds for growth derived from Redfield-Brzezinski ratios, implying that the first nutrient may be limiting.

3 PSU) was effectively reversed in the lower estuary, so that from salinity 19 to 25 PSU we observed modest net DOC removal (ΔDOC around $-115\ \mu mol\ L^{-1}$ at both sampling points). We also observed apparent net removal of DOC at low salinities in the San Carlos River in 2017.

Nutrient stoichiometry

Molar ratios for bulk DOC, oxidized N ($NO_3^- + NO_2^-$), PO_4^{3-} and SiO_2 are shown in Table 3. In general, total DOC : N and DOC : P ratios were very high (≥ 846 and ≥ 3433, respectively) at the freshwater end of all estuaries, but lower at the seaward end, notably at the Murrell and San Carlos Rivers in 2017 when DOC : N ratios were ≤ 15 and DOC : P ≤ 192, both approaching Redfield values. Among the inorganic nutrients, N : P ratios were consistently below Redfield ratios at both the freshwater and marine end of the all estuaries, and on both sampling occasions. In most cases, the N : P ratio was higher in the freshwater input than in the seaward end-member, but this was not the case for the Murrell and San Carlos Rivers in 2017. Freshwater N : P was higher in 2019 than in 2017 for all resurveyed rivers.

Si : P and Si : N ratios were higher in the freshwater end of the estuary than the seaward end on almost all occasions, the sole exception being Si : N at the Malo River in 2019. Freshwater Si : P and Si : N ratios were invariably higher in 2017 than in 2019. However, both ratios fell to low levels at the seaward end of the estuary, falling below Redfield-Brzezinski ratio values for Si : P in the Malo (2017), Swan Inlet (2019), Murrell (both years), and San Carlos (2017), and for Si : N in the Murrell and San Carlos in 2017.

For the estuary transects where there was evidence of in situ DOC production (Murrell River and Swan Inlet in both years, Malo River in 2019), we calculated the ratio of maximum DOC increases to the maximum reduction in inorganic nutrients, where observed. Ratios of maximum $\Delta DOC : \Delta PO_4^{3-}$ ranged from 1780 to 5533, while for $\Delta DOC : \Delta NO_3^-$ the range was 259 to 1051, and for ΔDOC : ΔSi it was 6 to 37.

Discussion

Our results indicate that, even without major local anthropogenic influences, biogeochemical processes in estuaries are highly variable. Despite the similarity and proximity of our study catchments, we observed striking differences in DOC and nutrient concentrations between estuaries surveyed on successive days, and between the same estuaries sampled under very similar conditions in different years. We recognize that the data presented represent two snapshots of biogeochemical gradients that can be expected to vary over tidal cycles, in response to weather conditions, and over seasons. Spatial variations are undoubtedly greater than we were able to capture by sampling just four estuaries. Nevertheless, a number of consistent patterns did emerge from the data, and the stability of many of the mixing relationships obtained (Figs. 3, 4) suggest that temporal variations in end-member composition were not sufficient to affect results in these rapidly flushed estuaries. Our results should therefore provide some useful insights into the nature of biogeochemical processes in DOC-rich temperate estuaries, in the absence of large-scale human influence.

Nutrient sources to Falkland estuaries

High concentrations of DOC at the freshwater end of all estuaries confirmed that, as expected, the peaty terrestrial

ecosystems of the Falkland Islands are the dominant source of estuarine DOC. This is consistent with many previous studies from different river-estuary systems in the UK (e.g., Spencer et al. 2007; García-Martin et al. 2021) and Fennoscandia (Asmala et al. 2014; Kritzberg et al. 2014). However, DOC concentrations entering Falkland Islands estuaries are exceptionally high in global terms, exceeding 2300 μmol L^{-1} ($\sim$ 25 mg L^{-1}) in two of the rivers in 2019. These concentrations exceed those observed in other studies of peat-influenced high-latitude rivers at their tidal limit, for example, a maximum flow-weighted mean of 1100 μmol L^{-1} in a set of 40 UK rivers (Williamson et al. 2021), 1750 μmol L^{-1} among a set of 30 large Finnish rivers (Räike et al. 2016), and 733 μmol L^{-1} for the six largest Arctic rivers (Cooper et al. 2008). Indeed, observed concentrations are similar to those measured at the mouth of an Indonesian "blackwater" river draining peat swamp forest (2350 μmol L^{-1}; Moore et al. 2011). These high DOC concentrations, and their subsequent impacts on aquatic light and energy regime, have the potential to profoundly influence the ecology of estuarine and coastal waters.

It is also clear that the land provides the overwhelming source of Si to Falkland Islands estuaries, with weathering of silicate rocks the likely source. The marked difference in freshwater Si concentrations in the two surveys, despite ostensibly similar seasonal, tidal and meteorological conditions, was however unexpected. One possibility is that differences in antecedent weather conditions led to differences in the proportion of Si-enriched groundwater between surveys. In an Oregon estuary, Sigleo and Frick (2007) observed dilution of Si to near-zero levels during peak flows, and studies of UK blanket bogs show rapid dilution of weathering-derived solutes in response to relatively small changes in stream discharge (e.g., Tipping et al. 2010). While the lack of hydrological monitoring in the Falkland Islands makes this hypothesis difficult to test, there was a modest (12 mm) rain event 1 d before the first estuary survey in 2019, whereas no significant rainfall was recorded in the 5 d before sampling commenced in 2017, so it is possible that Si concentrations were diluted in the second survey. Higher freshwater DOC concentrations in 2019 are consistent with this explanation, because terrestrial DOC export tends to be higher during wetter periods, when more flow is passing through shallow organic horizons rather than deeper mineral soils (e.g., Raymond and Saiers 2010). An alternative explanation for lower freshwater Si in 2019 is that biological activity was higher in the upstream terrestrial or aquatic ecosystems in 2019, to the extent that most Si was retained before reaching the estuary (Woodruff et al. 1999; Bowes et al. 2005; Carey and Fulweiler 2013). Average freshwater temperatures were around 3°C higher in 2019 than 2017, consistent with this hypothesis. However stoichiometric constraints make this explanation unlikely, because the biological removal of (in some cases) > 100 μmol L^{-1} of Si would require similar uptake of N, along with > 6 μmol^{-1} of P, both of which far exceed any of the measured concentrations in our freshwater samples. A final possibility is that differences in sample handling between surveys (rapid analysis of unfrozen samples in 2017 vs. freezing for analysis in the UK in 2019) could have affected results. In particular, reactive silica in samples with high concentrations (> 120 μmol L^{-1}) and low salinity may polymerize on freezing, affecting measured concentrations after thawing (Dore et al. 1996; MacDonald and McLaughlin 1982). However, differences in measured concentrations between the surveys (at least a factor of four in all freshwater end-members) far exceeded reported reductions in Si concentrations due to this issue (e.g., 5%–25%; MacDonald and McLaughlin 1982) so we consider it unlikely that this issue could explain observed differences.

With regard to NO_3^- and PO_4^{3-}, our data suggest that catchment exports were negligible. On the other hand, seawater end-member concentrations of both solutes were frequently higher than mid-estuary or freshwater concentrations. It appears therefore that coastal seas are the main sources of both these inorganic nutrients to Falkland estuaries. We did not measure organic nutrient concentrations, but based on a conservative DOC : DON ratio of 30 mol mol^{-1} for peaty oligotrophic freshwaters (Yates et al. 2019), we estimate that freshwater DON inputs would likely have been in the region of 17 to 71 μmol L^{-1}. This is several orders of magnitude higher than freshwater NO_3^- concentrations, so even allowing for a high uncertainty it is clear that DON dominates the land-ocean N flux. In contrast, if we apply a typical DOC : DOP ratio of 8000 mol mol^{-1} based on the values reported for peat-dominated streams by Yates et al. (2019), this gives freshwater DOP concentrations in the region of just 0.06 to 0.27 μmol L^{-1}. This is similar in magnitude to measured PO_4^{3-} concentrations, suggesting a more even split of catchment inorganic and organic P exports.

The dominance of marine sources of inorganic N and P to the estuary is in marked contrast to the majority of previously published studies of estuarine and coastal nutrient processing, in which human-modified terrestrial catchments are the dominant source (e.g., Howarth 2008; Beusen et al. 2022). While the development of agriculture and urban areas within many catchments mean that this situation is now commonplace, Vieillard et al. (2020) argue that over-representation of populated (mostly temperate) catchments, and therefore highly eutrophic estuaries, in the literature has led to a somewhat biased understanding of estuarine biogeochemical functioning. In the Falkland Islands, with very low populations and low-intensity land-use, catchments and rivers are oligotrophic, whereas the surrounding marine ecosystem is naturally productive as a result of the Falkland Current, which transports nutrient-rich waters from the Antarctic Circumpolar Current (Arkhipkin et al. 2013; Groff et al. 2020). This situation, in which the sea rather than the land provides the source of limiting nutrients to estuaries, appears unusual but not unique; Childers et al. (2006) referred to the estuaries of the Florida Everglades as "upside-down," because the main source of the limiting nutrient here (in this case P) was the ocean, rather

than the oligotrophic ($p < 0.25$ μmol L^{-1}) waters draining the Everglade peat swamps. Further, both Jickells et al. (2014) and Vieillard et al. (2020) suggest that this pattern, of estuaries receiving a large proportion of their nutrient supply from the sea, was once far more widespread, but that it has now been largely reversed in developed areas such as Europe and North America. Despite their lack of physical resemblance to the Everglades, it appears that Falkland estuaries also remain "upside down" in relation to both N and P.

Estuarine macronutrient cycling

Our results showed clear deviation from conservative mixing in the majority of transects for all measured solutes. For SiO_2, we observed clear evidence of net removal in 5 out of 7 estuary transects, including all four 2017 surveys. Given that SiO_2 concentrations were almost always higher in freshwater inputs compared to the seaward end of the estuary (markedly so in 2017), and that mixing was highly nonconservative across salinity gradients, we infer that Si exported from the catchments was being removed during transport through the estuary. The likeliest sink for Si in the estuaries is diatoms, which have siliceous skeletons and can drive high rates of Si uptake (Brzezinski 1985; Leynaert et al. 2009; Bondoc et al. 2016). This could include planktonic diatoms, although the shallow, stony nature of the Falkland estuaries suggest that benthic diatoms may be more important. Given that the estuary beds were largely exposed at low tide, and water was mostly shallow even at high tide, light availability was considered unlikely to limit benthic productivity despite the high DOC concentrations. Exceptions to the general pattern of estuarine Si uptake were the Malo River and Swan Inlet in 2019, where we observed evidence of Si release, possibly due to the remineralisation/dissolution of biogenic Si following a spring diatom bloom.

Concentrations of PO_4^{3-} were highest at the seaward end of all estuaries on both sampling occasions, and we observed active estuarine removal in all transects except the Malo River in 2017. The behavior of NO_3^- was generally similar where it was present in sufficiently high concentrations at the seaward end of the estuary (notably the Murrell and San Carlos Rivers in 2017). Where NO_3^- concentrations were uniformly low across the salinity gradient (Malo River and Swan Inlet on both sampling occasions) there was little scope for further processing, although we did observe apparent NO_3^- removal in Swan Inlet in 2019 (Fig. 5j). Assuming that higher seawater NO_3^- concentrations observed at the other sites in 2017 were representative of coastal ocean values at the time, we infer that N uptake had likely already occurred between true seawater and the lowest estuarine sampling point (possible reasons for differences between estuaries are discussed below). In any case, it is clear that marine inputs of N and P in these "upside-down" estuaries were being actively utilized by the estuarine biota where available.

Our hypothesis that high inputs of highly humic and unmodified DOM would result in active estuarine removal via physicochemical processes such as flocculation was not strongly supported. We observed DOC removal in the estuary on only three occasions: in the San Carlos estuary in 2017, and in the lower part of the Malo and Murrell estuaries in 2019. It is notable that these were the three transects in which freshwater DOC inputs were highest (1833, 2407, and 2132 μmol L^{-1} respectively, compared to ≤ 1250 μmol L^{-1} in all other transects). It is therefore possible either that DOC concentrations were sufficiently high to trigger flocculation at these times, or that higher concentrations are associated with weakly soluble, aromatic-rich organic compounds that are more prone to flocculation (Anderson et al. 2019). However, with the exception of the San Carlos River, freshwater $SUVA_{254}$ values were not particularly high, casting some doubt on this explanation. Furthermore, we observed very little nonlinearity in Abs_{254}, and few consistent changes in $SUVA_{254}$ across the salinity gradient, arguing against preferential removal of terrestrially-derived high-$SUVA_{254}$ DOM. Nevertheless, it does appear that a proportion of terrestrially derived DOM is removed in the estuary when inputs are high, and indeed this interpretation is supported by visual observations of brown staining on rocks in parts of these estuaries (Fig. 6).

While we found limited evidence of net DOC removal, we did observe apparent net DOC production over some or all of the salinity gradient in both the Murrell River and Swan Inlet, on both sampling occasions. This was unexpected given the high freshwater DOC inputs and the oligotrophic nature of all estuaries, but repeated evidence of higher DOC in the low to mid salinity range at these sites suggests a genuine production or release mechanism. We cannot completely rule out a physicochemical mechanism, such as aggregation/adsorption/settling and disaggregation/desorption/resuspension of organic molecules in response to changes in salinity, turbulence and suspended sediments over a tidal cycle (e.g., Eisma 1986). However, the congruence of DOC production with evidence of active N, P, and Si uptake in the same parts of the estuary suggest a biological mechanism. Previous studies have shown that elevated nutrients favor DOC production over removal in lakes and reservoirs (Evans et al. 2017) and several studies have reported DOC production in eutrophic estuaries (e.g., Abril et al. 2002; Looman et al. 2019; García-Martin et al. 2021). We therefore hypothesize that the combination of Si supply from the terrestrial system, and N and P supply from seawater, may be driving a "hot zone" of biological activity in the mid-salinity zone of oligotrophic estuaries such as those of the Falklands, leading to the production of autochthonous DOC. Given the shallow and highly dynamic nature of the estuaries, production is likely to be mainly by benthic microalgae and bacteria (microphytobenthos), which is present on the rocky substrate. The strong uptake of Si argues for an important role of diatoms within the benthic community, and is consistent with evidence that benthic diatoms can

Fig. 6. Brown staining of rocks in the middle of the Malo Estuary, possibly due to removal of DOC from the water.

respond dynamically in order to exploit localized and short-lived hotspots of Si availability in estuarine sediments (Bondoc et al. 2016).

Based on the stoichiometric data shown in Table 3, it appears that N may be limiting to growth in most cases. This might not be the case if some of the DON present in the rivers is bioavailable, or mineralized to inorganic N by biotic or abiotic processes; given high inferred concentrations, only a small fraction of this DON would need to be bioavailable to substantially alter overall N availability. Previous work has shown that marine phytoplankton, including diatoms, are able to utilize more labile forms of both DON and DOP (Fitzsimons et al. 2020). However, in the absence of consistent evidence of DOC removal in most of our estuary transects, it seems likely that the majority of the freshwater DON input is transported conservatively to the sea. Furthermore, the near-total depletion of any NO_3^- entering estuaries from the sea suggests intense demand for N, which is not being met by any mineralization of DON that is occurring. In the case of P, freshwater inputs of both PO_4^{3-} and DOP appear low, so marine PO_4^{3-} inputs are almost certainly influencing estuarine productivity, as suggested by strong depletion of this PO_4^{3-} within most estuaries. For Si, freshwater inputs are clearly well in excess of biological demand, but as a result of efficient removal within the estuary it falls close to or below limiting concentrations (relative to P) at the seaward end of most of estuaries. Overall, therefore, it appears that all three nutrients are to some extent influencing biological production in the Falkland estuaries, with the specific limiting nutrient element varying in space and time. It could also indicate some stoichiometric plasticity, i.e., that different constituents of the ecosystem are able to utilize different nutrients depending on their relative availability (e.g., Glibert et al. 2013; Mäkelin and Villnäs 2022).

Microalgae are known to exude DOC in the form of simple polysaccharides that do not contain nutrient elements, a phenomenon that increases with the severity of nutrient-limitation (Azam et al. 1983). The coincidence of DOC production and low macronutrient concentrations in the mid-estuary regions may therefore suggest that nutrient-stressed algae in these locations were exuding DOC via photosynthetic overflow production (reviewed by Thornton 2014). The observed Si uptake within this section of the estuaries is consistent with the inferred importance of diatoms, although direct observation of the microphytobenthic community composition would be required to confirm this interpretation. It could also occur if the amount of biomass in the estuaries was declining following a spring algal bloom, leading to DOC release via decomposition. On the other hand, observed ratios of ΔDOC to ΔSi (6 to 37) are more similar to the Redfield-Brzezinski C : Si ratio of 7.1, and might imply a tighter link between Si uptake and DOC production, consistent with the inferred importance of diatoms in the system. However, without direct measurements of algal community composition, growth and turnover, as well as macronutrient consumption and release, this interpretation remains speculative.

Causes of variability between estuaries

We observed a surprising degree of spatial and temporal variability in the biogeochemistry of the four estuaries sampled, despite their broadly similar soils and land-use. The rivers had uniformly low NO_3^- and PO_4^{3-} concentrations, while DOC concentrations were more variable (both spatially and temporally), but consistently high by global standards. Freshwater Si concentrations differed sharply between the two sampling campaigns, but to a lesser extent between sites during each campaign. The lower DOC and higher Si concentrations in freshwater inputs to Swan Inlet are consistent with a lower proportion of peat cover in this catchment, and higher weathering inputs. More generally, however, differences in estuarine biogeochemistry cannot be explained by differences

in catchment properties or freshwater nutrient inputs. Instead, they appear to be related to differences in NO_3^- and PO_4^{3-} concentrations in the seaward end-member samples. Both the Murrell and San Carlos Rivers connect fairly directly to deep coastal waters which, as noted earlier, are high in nutrients as a result of the Falkland Current. Conversely, Swan Inlet comprises a long, shallow estuary, while the Malo River flows into the southern, inland end of Salvador Water, an extensive network of shallow inlets extending 30 km inland from the open ocean. In both estuaries, and especially the Malo, we speculate that marine-derived N and P is removed from the water column before reaching the lower end of the estuary, for example, through uptake by kelp beds, which are extensive around the coast of East Falkland and can act as strong nutrient sinks (Bayley et al. 2021). As a result, these poorly-connected estuaries appear to be naturally oligotrophic throughout their salinity gradients, and estuarine diatoms are less able to exploit high rates of freshwater Si input. In contrast, the better-connected Murrell and San Carlos receive larger inputs of marine N and P, along with freshwater Si, and are thus able to maintain a higher level of biogeochemical activity and productivity.

The Falklands in a global context: Toward a conceptual understanding of DOC and nutrient cycling in oligotrophic estuaries

As highlighted by Vieillard et al. (2020), studies of estuarine nutrient cycling have been heavily weighted toward eutrophic and hypereutrophic systems in North America and Europe. Our study adds to the smaller body of work that has been undertaken in oligotrophic temperate systems, which may provide useful insights into the biogeochemical functioning of higher-latitude estuarine systems prior to human disturbance, and thereby help to enhance understanding of target conditions for estuary restoration.

DOC concentrations in these estuaries are notably high by global standards, due to extensive peat cover in the catchments. However, these high concentrations do not dictate the overall biogeochemical functioning of the estuary, with the majority of terrigenous DOC apparently passing through the system without being subject to biological or physicochemical removal. This DOC, exported to the coastal ocean, may ultimately transfer to long-term C sinks such as sediments or the marine DIC pool, although evidence from tropical shelf seas receiving high freshwater peat-derived DOC inputs suggests that a high proportion is mineralized and degassed as CO_2 (Zhou et al. 2021).

In the more nutrient-rich estuaries, we observed zones of apparent in situ DOC production. This was unexpected, because previous studies have suggested that DOC production typically occurs in eutrophic estuaries and inland water bodies (e.g., Evans et al. 2017; García-Martin et al. 2021). Our results suggest that even naturally low-nutrient estuaries have the potential to act as net sources of DOC to the marine system when and where rates of primary production are high. Autochthonous DOC production and physicochemical removal (presumably of allochthonous DOC) appear to be largely decoupled, with evidence of both occurring in different parts of the salinity gradient on at least one occasion (Fig. 5o).

To a large extent, observed DOC production occurred within "hot zones" of biological activity, typically in the upper to middle estuary, where terrestrially derived Si mixes with marine-derived N and P (Fig. 7). In our estuaries, biological activity appeared to occur mainly in the benthic zone, but in deeper, longer residence time systems planktonic uptake and production may be more significant. Estuarine "hot zones" are likely to be highly dynamic, with the peak of activity varying temporally and spatially over every tide, and in response to changes in terrestrial and marine nutrient supply. For example, the marked difference in freshwater Si concentrations

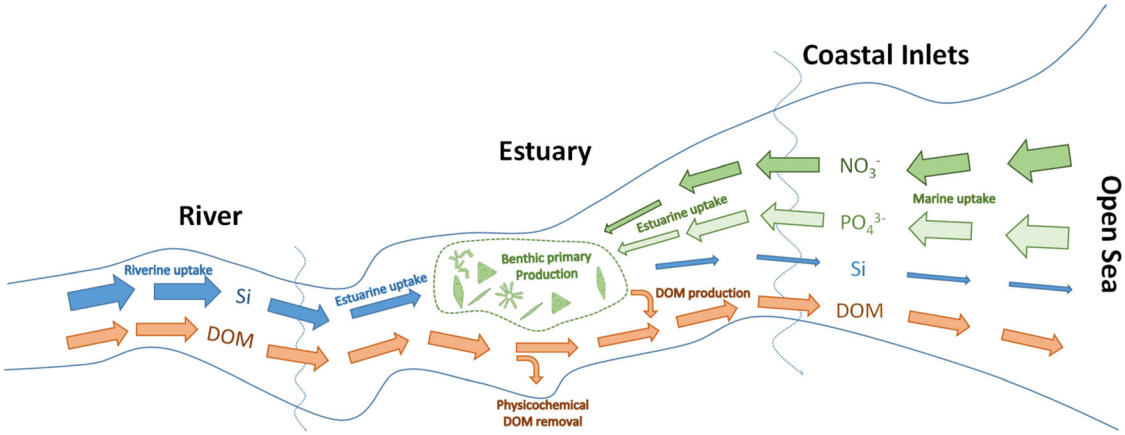

Fig. 7. Conceptual illustration of nutrient flows, uptake, and production processes for the "upside down" estuaries of the Falkland Islands. Colored arrows indicate dominant direction of flows for each nutrient, with widths illustrating concentrations and fluxes relative to their (riverine or marine) sources. "Coastal inlets" are zones of high salinity but poor connectivity to the open ocean, which affect marine nutrient supply to the estuary where present. The "DOM" flux encompasses both DOC and associated DON and DOP.

between our two surveys suggests variable inputs to the estuaries, possibly linked to hydrological conditions. While productivity at our study sites appears to be most strongly limited by low concentrations of mineral N, widespread evidence of the active removal of NO_3^-, PO_4^{3-}, and Si, as well as localized examples of both removal and production of DOC, suggest that these naturally oligotrophic estuarine ecosystems are well-adapted to flexibly use scarce resources, derived from both terrestrial and marine sources, depending on temporal and spatial variations in nutrient concentrations and stoichiometry. This flexible ecological functioning may have been characteristic of many estuaries in the past, but has now in many places been replaced by ecosystems adapted to continuously exploit an excess of terrestrially-derived nutrients. This has had detrimental impacts for ecosystem condition and function such as harmful algal blooms, hypoxia, loss of water clarity, decline of fish and shellfish populations (e.g., Kemp et al. 2005; Wurtsbaugh et al. 2019), and emissions of greenhouse gases such as nitrous oxide (Seitzinger et al. 2000).

Conclusions

We found limited evidence to support our original hypothesis that estuaries receiving high inputs of relatively unmodified peat-derived riverine DOM would act as efficient "marginal filters" for land-ocean carbon transport through physical and biological removal processes. Instead, we found that the majority of freshwater DOC input was transported through the estuary without substantial modification, with localized DOC removal peaking at around 20%. However, and despite extremely low terrestrial N and P export, we observed active nutrient uptake in several estuaries, apparently driven by the convergence of terrestrially-derived Si and marine-derived N and P in the middle estuary. The shallow nature of the estuaries and the observed Si uptake strongly point to a role for benthic diatoms in these processes. On some occasions this zone of high biological activity appears to have resulted in net generation of DOC within the estuary, further augmenting the already high land-to-ocean DOC flux. Given the apparent importance of marine N and P supply, the degree of connectivity between individual estuaries and the open sea appeared to exert a strong influence on estuarine biogeochemical processes. The dynamic flexibility of nutrient usage in these relatively undisturbed, oligotrophic ecosystems may offer clues to the natural reference state of high-latitude estuaries in other parts of the world, where agricultural and urban nutrient exports have now to a large extent overwhelmed natural biogeochemical processes.

Data availability statement

All data presented in this article are included in Supporting Information Table S1.

References

Abril, G., M. Nogueira, H. Etcheber, G. Cabeçadas, E. Lemaire, and M. J. Brogueira. 2002. Behaviour of organic carbon in nine contrasting European estuaries. Estuar. Coast. Shelf Sci. **54**: 241–262.

Adams, J. L., E. Tipping, H. Feuchtmayr, H. T. Carter, and P. Keenan. 2018. The contribution of algae to freshwater dissolved organic matter: Implications for UV spectroscopic analysis. Inland Waters **8**: 10–21.

Ågren, A. M., I. Buffam, D. M. Cooper, T. Tiwari, C. D. Evans, and H. Laudon. 2014. Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements? Biogeosciences **11**: 1199–1213.

Aitkenhead, J. A., and W. H. McDowell. 2000. Soil C: N ratio as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochem. Cycles **14**: 127–138.

Álvarez-Salgado, X. A., and A. E. Miller. 1998. Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation: Conditions for precise shipboard measurements. Mar. Chem. **62**: 325–333.

Anderson, T. R., and others. 2019. Unified concepts for understanding and modelling turnover of dissolved organic matter from freshwaters to the ocean: The UniDOM model. Biogeochemistry **146**: 105–123.

Arkhipkin, A., P. Brickle, and V. Laptikhovsky. 2013. Links between marine fauna and oceanic fronts on the Patagonian shelf and slope. Arquipelago Life Mar. Sci. **30**: 19–37.

Armstrong, P. H. 1994. Human impact on The Falkland Islands environment. Environmentalist **14**: 215–231.

Asmala, E., R. Autio, H. Kaartokallio, C. A. Stedmon, and D. N. Thomas. 2014. Processing of humic-rich riverine dissolved organic matter by estuarine bacteria: Effects of predegradation and inorganic nutrients. Aquatic sciences **76**: 451–463.

Azam, F., T. Fenchel, J. G. Field, J. S. Gray, L. A. Meyer-Reil, and F. Thingstad. 1983. The ecological role of water-column microbes in the sea. Mar Ecol Prog Ser **10**: 257–263.

Battin, T. J., and others. 2023. River ecosystem metabolism and carbon biogeochemistry in a changing world. Nature **613**: 449–459.

Bauer, J. E., W. J. Cai, P. A. Raymond, T. S. Bianchi, C. S. Hopkinson, and P. A. Regnier. 2013. The changing carbon cycle of the coastal ocean. Nature **504**: 61–70.

Bax, N., and others. 2022. Towards incorporation of blue carbon in Falkland Islands marine spatial planning: A multitiered approach. Front. Mar. Sci. **9**: 872727.

Bayley, D., P. Brickle, P. Brewin, N. Golding, and T. Pelembe. 2021. Valuation of kelp forest ecosystem services in The Falkland Islands: A case study integrating blue carbon sequestration potential. One Ecosystem **6**: e62811.

Berggren, M., M. Klaus, B. P. Selvam, L. Ström, H. Laudon, M. Jansson, and J. Karlsson. 2018. Quality transformation of

dissolved organic carbon during water transit through lakes: Contrasting controls by photochemical and biological processes. Biogeosciences **15**: 457–470.

Beusen, A. H. W., J. C. Doelman, L. P. H. Van Beek, P. J. T. M. Van Puijenbroek, J. M. Mogollón, H. J. M. Van Grinsven, E. Stehfest, D. P. Van Vuuren, and A. F. Bouwman. 2022. Exploring river nitrogen and phosphorus loading and export to global coastal waters in the shared socioeconomic pathways. Glob. Environ. Chang. **72**: 102426.

Bogard, M. J., B. A. Bergamaschi, D. E. Butman, F. Anderson, S. H. Knox, and L. Windham-Myers. 2020. Hydrologic export is a major component of coastal wetland carbon budgets. Global Biogeochem. Cycles **34**: e2019GB006430.

Bondoc, K. G. V., J. Heuschele, J. Gillard, W. Vyverman, and G. Pohnert. 2016. Selective silicate-directed motility in diatoms. Nat. Commun. **7**: 1–7.

Bowes, M. J., D. V. Leach, and W. A. House. 2005. Seasonal nutrient dynamics in a chalk stream: The river Frome, Dorset, UK. Sci. Total Environ. **336**: 225–241.

Brzezinski, M. A. 1985. The Si:C:N ratio of marine diatoms: interspecific variability and the effect of some environmental variables. J. Phycol. **21**, 347–335.

Canadell, J.G., Monteiro, P.M.S., Costa, M.H. Cotrim da Cunha, L., Cox, P.M. Eliseev, A.V., Henson, S. Ishii, M., Jaccard, S., Koven, C., Lohila, A., Patra, P.K., Piao, S., Rogelj, J., Syampungani, S., Zaehle, S., Zickfeld, K. 2021. Climate change 2021: The physical science basis. Contribution of Working Group I to the Sixth assessment report of the intergovernmental panel on climate change. Cambridge Univ. Press 673–816.

Carey, J. C., and R. W. Fulweiler. 2013. Watershed land use alters riverine silica cycling. Biogeochemistry **113**: 525–544.

Carter, H. T., E. Tipping, J.-F. Koprivnjak, M. P. Miller, B. Cookson, and J. Hamilton-Taylor. 2012. Freshwater DOM quantity and quality from a two-component model of UV absorbance. Water Res. **46**: 4532–4542.

Carter, S., M. Aitkenhead, C. Evans, A. Jungblut, J. McAdam, and M. McNee. 2020. Soil map and online database as climate change mitigation tools. Darwin Plus **83**. Dataset available at http://dataportal.saeri.org/dplus083–chemical–and–physical–soil–properties

Carter, S., and D. Stroud. 2022. Falklands wetlands and aquatic habitats: Baselines for monitoring future change. *In* Project DPLUS 116 final report to Darwin plus overseas territories and environment fund. South Atlantic Environment Research Institute.

Catalán, N., R. Marcé, D. N. Kothawala, and L. Tranvik. 2016. Organic carbon decomposition rates controlled by water retention time across inland waters. Nat. Geosci. **9**: 501–504.

Childers, D. L., J. N. Boyer, S. E. Davis, C. J. Madden, D. T. Rudnick, and F. H. Sklar. 2006. Relating precipitation and water management to nutrient concentrations in the oligotrophic "upside-down" estuaries of the Florida Everglades. Limnol. Oceanogr. **51**: 602–616.

Ciais, P., A. V. Borges, G. Abril, M. Meybeck, G. Folberth, D. Hauglustaine, and I. A. Janssens. 2008. The impact of lateral carbon fluxes on the European carbon balance. Biogeosciences **5**: 1259–1271.

Cole, J. J., and others. 2007. Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems **10**: 172–185.

Cooper, L. W., J. W. McClelland, R. M. Holmes, P. A. Raymond, J. J. Gibson, C. K. Guay, and B. J. Peterson. 2008. Flow-weighted values of runoff tracers (δ18O, DOC, Ba, alkalinity) from the six largest Arctic rivers. Geophys. Res. Lett. **35**: L18606.

Dittmar, T. 2015. Reasons behind the long-term stability of dissolved organic matter, p. 369–388. *In* Biogeochemistry of marine dissolved organic matter. Academic Press.

Dore, J. E., T. Houlihan, D. V. Hebel, G. Tien, L. Tupas, and D. M. Karl. 1996. Freezing as a method of sample preservation for the analysis of dissolved inorganic nutrients in seawater. Mar Chem **53**: 173–185.

Drake, T. W., P. A. Raymond, and R. G. Spencer. 2018. Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. Limnol Oceanogr Lett **3**: 132–142.

Eisma, D. 1986. Flocculation and de-flocculation of suspended matter in estuaries. Neth J Sea Res **20**: 183–199.

Evans, C. D., M. N. Futter, F. Moldan, S. Valinia, Z. Frogbrook, and D. N. Kothawala. 2017. Variability in organic carbon reactivity across lake residence time and trophic gradients. Nat. Geosci. **10**: 832–835.

Evans, C. D., F. Renou-Wilson, and M. Strack. 2016. The role of waterborne carbon in the greenhouse gas balance of drained and re-wetted peatlands. Aquat Sci **78**: 573–590.

Fitzsimons, M. F., I. Probert, F. Gaillard, and A. P. Rees. 2020. Dissolved organic phosphorus uptake by marine phytoplankton is enhanced by the presence of dissolved organic nitrogen. J. Exp. Mar. Biol. Ecol. **530**: 151434.

Forsgren, G., M. Nilsson, and P. Janssen. 1996. Aggregation and sedimentation of iron, phosphorus and organic carbon in experimental mixtures of freshwater and estuarine water. Estuar. Coast. Shelf Sci. **43**: 259–268.

García-Martín, E. E., and others. 2021. Contrasting estuarine processing of dissolved organic matter derived from natural and human-impacted landscapes. Global Biogeochem. Cycles **35**: GB007023.

Glibert, P. M., T. M. Kana, and K. Brown. 2013. From limitation to excess: The consequences of substrate excess and stoichiometry for phytoplankton physiology, trophodynamics and biogeochemistry, and the implications for modeling. J. Mar. Syst. **125**: 14–28.

Groff, D. V., K. M. Hamley, T. J. Lessard, K. E. Greenawalt, M. Yasuhara, P. Brickle, and J. L. Gill. 2020. Seabird

establishment during regional cooling drove a terrestrial ecosystem shift 5000 years ago. Sci Adv **6**: eabb2788.

Hansell, D. A., D. Kadko, and N. R. Bates. 2004. Degradation of terrigenous dissolved organic carbon in the western Arctic Ocean. Science **304**: 858–861.

Hedges, J. I., R. G. Keil, and R. Benner. 1997. What happens to terrestrial organic matter in the ocean. Org. Geochem. **27**: 195–212.

Henderson, R. K., A. Baker, S. A. Parsons, and B. Jefferson. 2008. Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms. Water Res. **42**: 3435–3445.

Holden, J., and T. P. Burt. 2003. Hydraulic conductivity in upland blanket peat: Measurement and variability. Hydrol. Process. **17**: 1227–1237.

Howarth, R. W. 2008. Coastal nitrogen pollution: A review of sources and trends globally and regionally. Harmful Algae **8**: 14–20.

Jickells, T. D., J. E. Andrews, D. J. Parkes, S. Suratman, A. A. Aziz, and Y. Y. Hee. 2014. Nutrient transport through estuaries: The importance of the estuarine geography. Estuar. Coast. Shelf Sci. **150**: 215–229.

Jones, T. G., C. D. Evans, D. L. Jones, P. W. Hill, and C. Freeman. 2016. Transformations in DOC along a source to sea continuum; impacts of photo-degradation, biological processes and mixing. Aquat Sci **78**: 433–446.

Kemp, W. M., and others. 2005. Eutrophication of Chesapeake Bay: Historical trends and ecological interactions. Mar. Ecol. Prog. Ser. **303**: 1–29.

Kritzberg, E. S., A. B. Villanueva, M. Jung, and H. E. Reader. 2014. Importance of boreal rivers in providing iron to marine waters. PLoS One **9**: e107500.

Leynaert, A., S. N. Longphuirt, P. Claquin, L. Chauvaud, and O. Ragueneau. 2009. No limit? The multiphasic uptake of silicic acid by benthic diatoms. Limnol. Oceanogr. **54**: 571–576.

Lisitsyn, A. P. 1995. The marginal filter of the ocean. Russ Acad Sci Oceanol **34**: 671–682.

Looman, A., I. R. Santos, D. R. Tait, J. Webb, C. Holloway, and D. T. Maher. 2019. Dissolved carbon, greenhouse gases, and $\delta^{13}C$ dynamics in four estuaries across a land use gradient. Aquat Sci **81**: 22.

MacDonald, R. W., and F. A. McLaughlin. 1982. The effect of storage by freezing on dissolved inorganic phosphate, nitrate and reactive silicate for samples from coastal and estuarine waters. Water Res **16**: 95–104.

Mäkelin, S., and A. Villnäs. 2022. Food sources drive temporal variation in elemental stoichiometry of benthic consumers. Limnol. Oceanogr. **67**: 784–799.

Mantoura, R. F. C., and E. M. S. Woodward. 1983. Conservative behaviour of riverine dissolved organic carbon in the Severn estuary: Chemical and geochemical implications. Geochim. Cosmochim. Acta **47**: 1293–1309.

Moore, D.M. 1968. The vascular flora of The Falkland Islands. British Antarctic Survey Scientific Reports No. 6. British Antarctic Survey.

Moore, S., V. Gauci, C. D. Evans, and S. E. Page. 2011. Fluvial organic carbon losses from a Bornean Blackwater river. Biogeosciences **8**: 901–909.

Nguyen, M.-L., P. Westerhoff, L. Baker, Q. Hu, M. Esparza-Soto, and M. Sommerfield. 2005. Characteristics and reactivity of algae produced dissolved organic carbon. J Environ Eng **131**: 1574–1582.

Noacco, V., T. Wagener, F. Worrall, T. P. Burt, and N. J. Howden. 2017. Human impact on long-term organic carbon export to rivers. J. Geophys. Res. Biogeo. **122**: 947–965.

Opsahl, S., and R. Benner. 1997. Distribution and cycling of terrigenous dissolved organic matter in the ocean. Nature **386**: 480–482.

Palmer, S. M., and others. 2016. Sporadic hotspots for physico-chemical retention of aquatic organic carbon: From peatland headwater source to sea. Aquat Sci **78**: 491–504.

Payne, R. J., F. Ring-Hrubesh, G. Rush, T. J. Sloan, C. D. Evans, and D. Mauquoy. 2019. Peatland initiation and carbon accumulation in The Falkland Islands. Quat Sci Rev **212**: 213–218.

Peacock, M., C. Freeman, V. Gauci, I. Lebron, and C. D. Evans. 2015. Investigations of freezing and cold storage for the analysis of peatland dissolved organic carbon (DOC) and absorbance properties. Environ. Sci. Process Impacts **17**: 1290–1301.

Räike, A., P. Kortelainen, T. Mattsson, and D. N. Thomas. 2016. Long-term trends (1975–2014) in the concentrations and export of carbon from Finnish rivers to the Baltic Sea: Organic and inorganic components compared. Aquat Sci **78**: 505–523.

Raymond, P. A., and others. 2013. Global carbon dioxide emissions from inland waters. Nature **503**: 355–359.

Raymond, P. A., and J. E. Saiers. 2010. Event controlled DOC export from forested watersheds. Biogeochemistry **100**: 197–209.

Raymond, P. A., and R. G. M. Spencer. 2015. Riverine DOM, p. 509–533. *In* D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter. Academic Press.

Seitzinger, S. P., C. Kroeze, and R. V. Styles. 2000. Global distribution of N_2O emissions from aquatic systems: Natural emissions and anthropogenic effects. Chemosphere **2**: 267–279.

Sholkovitz, E. R., E. A. Boyle, and N. B. Price. 1978. The removal of dissolved humic acids and iron during estuarine mixing. Earth Planet. Sci. Lett. **40**: 130–136.

Sigleo, A. C., and W. E. Frick. 2007. Seasonal variations in river discharge and nutrient export to a northeastern Pacific estuary. Estuar. Coast. Shelf Sci. **73**: 368–378.

Spencer, R. G., J. M. Ahad, A. Baker, G. L. Cowie, R. Ganeshram, R. C. Upstill-Goddard, and G. Uher. 2007. The estuarine mixing behaviour of peatland derived dissolved organic carbon and its relationship to chromophoric dissolved organic matter in two North Sea estuaries (UK). Estuar. Coast. Shelf Sci. **74**: 131–144.

Stutter, M. I., D. Graeber, C. D. Evans, A. J. Wade, and P. J. A. Withers. 2018. Balancing macronutrient stoichiometry to alleviate eutrophication. Sci. Total Environ. **634**: 439–447.

Tfaily, M. M., D. C. Podgorski, J. E. Corbett, J. P. Chanton, and W. T. Cooper. 2011. Influence of acidification on the optical properties and molecular composition of dissolved organic matter. Anal. Chim. Acta **706**: 261–267.

Thornton, D. C. O. 2014. Dissolved organic matter (DOM) release by phytoplankton in the contemporary and future ocean. Eur. J. Phycol. **49**: 20–46.

Tipping, E., M. F. Billett, C. L. Bryant, S. Buckingham, and S. A. Thacker. 2010. Sources and ages of dissolved organic matter in peatland streams: Evidence from chemistry mixture modelling and radiocarbon data. Biogeochemistry **100**: 121–137.

Tranvik, L. J., and others. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. **54**: 2298–2314.

Upson, R. 2012. Important plant areas of The Falkland Islands. Falklands Conservation, p. 80.

Vieillard, A. M., S. E. Newell, and S. F. Thrush. 2020. Recovering from bias: A call for further study of underrepresented tropical and low-nutrient estuaries. Journal of geophysical research. Biogeosciences **125**: e2020JG005766.

Vieillard, A. M., and S. F. Thrush. 2021. Ecogeochemistry and denitrification in non-eutrophic coastal sediments. Estuaries Coasts **44**: 1866–1882.

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Tech. **37**: 4702–4708.

Williamson, J. L., and others. 2021. Landscape controls on riverine export of dissolved organic carbon from Great Britain. Biogeochemistry: 1–22. doi:10.1007/s10533–021–00762–2

Woodruff, S. L., W. A. House, M. E. Callow, and B. S. Leadbeater. 1999. The effects of a developing biofilm on chemical changes across the sediment-water interface in a freshwater environment. Int Rev Hydrobiol **84**: 509–532.

Wurtsbaugh, W. A., H. W. Paerl, and W. K. Dodds. 2019. Nutrients, eutrophication and harmful algal blooms along the freshwater to marine continuum. Wiley Interdiscip. Rev. Water **6**: e1373.

Yates, C. A., and others. 2019. Variation in dissolved organic matter (DOM) stoichiometry in UK freshwaters: Assessing the influence of land cover and soil C:N ratio on DOM composition. Limnol. Oceanogr. **64**: 2328–2340.

Zhou, Y., C. D. Evans, Y. Chen, K. Y. Chang, and P. Martin. 2021. Extensive remineralization of peatland-derived dissolved organic carbon and ocean acidification in the Sunda Shelf Sea, Southeast Asia. J. Geophys. Res. Oceans **126**: e2021JC017292.

Acknowledgments

This study was supported by the UK Natural Environment Research Council (NERC) LOCATE and BIOPOLE projects (NE/N018087/1 and NE/W004933/1), the Defra Darwin Plus programme (projects DPLUS083 and DPLUS116), and the NERC COMICS project NE/M020835/1 for access to lab facilities on the RRS Discovery. Stacey Felgate was supported by the NERC-funded SPITFIRE Doctoral Training Programme (grant number NE/L002531/1) and a grant from the Shackleton Scholarship Fund. We are grateful to the staff of South Atlantic Environment Institute and Falklands Conservation for their support during field campaigns, to Steve Cartwright (Shallow Marine Surveys Group) for support with boat surveys, to Glen Tarran and Ian Brown for sample collection in 2017, and to local landowners for access to field sites and for sharing their knowledge of land-management on the Islands. We also appreciate the time and effort of the reviewers and editors.

Conflict of Interest

None declared.

Submitted 14 November 2022
Revised 20 May 2023
Accepted 29 May 2023

Associate editor: Robinson W. Fulweiler