Marine Pollution Bulletin 207 (2024) 116828

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Nitrogen isotope variability of macroalgae from a small fishing village, Staithes Harbour, Yorkshire, UK

Freya C. Alldred [a,*], Darren R. Gröcke [a], Samuel E. Jackson [b]

[a] Department of Earth Sciences, Durham University, South Road, Durham DH1 3LE, UK
[b] Department of Mathematical Sciences, Durham University, Stockton Road, Durham DH1 3LE, UK

ARTICLE INFO

Keywords:
Nitrogen isotopes
Macroalgae
Pollution
Harbours
Mixing

ABSTRACT

Macroalgal nitrogen isotope analysis ($\delta^{15}N$) is a reliable method for the identification of nitrogen pollutant sources. Understanding $\delta^{15}N$ geospatial variation within small bays and/or harbour environments can help identify point sources of nitrogen pollution. This study sampled over 300 *Fucus vesiculosus* and *Ulva* sp. specimens in September 2022 and May 2023 from Staithes Harbour, North Yorkshire, England. $\delta^{15}N$ values for Staithes Beck were elevated when compared to sites in Staithes Harbour and the North Sea: this is attributed to sewage effluent and/or agricultural manure. Few sites within Staithes Harbour were significantly different from one another in terms of $\delta^{15}N$, suggesting a relatively homogenous nitrogen isotope record of the harbour. Simple harbour environments like Staithes may be relatively well mixed, and thus, sampling one harbour site may be enough to represent the entire harbour. Of course, more complex harbours may require more sample locations to ascertain point sources and mixing in the harbour.

1. Introduction

Anthropogenic activity has accelerated the rate of biologically available nitrogen that is added to the coastal environment, increasing the frequency of algal blooms, red tides, and eutrophication worldwide (Howarth, 2008; Howarth and Marino, 2006; Smith and Schindler, 2009; Wurtsbaugh et al., 2019). Sewage effluent (and influent) is a significant cause of excess nutrients, specifically nitrogen. Sewage pollution has almost become the norm in the UK: in 2022 alone over 1.7 million hours of sewage release was recorded for Combined Sewer Overflows (CSOs) into UK rivers and estuaries (Environment Agency, 2023). No waterbodies in England are of 'Good Overall Status' according to the most recent report by the Rivers Trust, and high volumes of sewage effluent is a driving factor in this (The Rivers Trust, 2024). Over 90 % of UK estuaries fail to meet the 50 mg/l Water Framework Directive (WFD) nitrogen standard (Drinking Water Inspectorate, 2023). Excess nutrients either from sewage and/or agricultural pollution has contributed to 16 English estuarine environments being classified as eutrophic and hence, designated as Nitrogen Vulnerable Zones (NVZs) (Environment Agency, 2018a, 2019a). Nutrient inputs have prolonged residence times in estuaries due to coastal morphology, tidal changes, oceanic currents and oceanic fronts (Maier et al., 2009; Zhou et al., 2024). Therefore, understanding the amount and types of nutrients (e.g., sewage, agricultural manure and/or fertilizers) into an estuary will help to evaluate and improve basin-wide environmental management strategies.

Traditionally, sewage pollution is monitored through water analysis including, *Escherichia coli* (*E. coli*), total nitrogen (TN) and biochemical oxygen demand (BOD) (Environment Agency, 2019b, 2022a). These tests are carried out sporadically for coastal environments in England; some sites are tested only 12–24 times a year during summer and winter testing is not undertaken at all (Environment Agency, 2019b). These types of analyses also do not directly identify sewage, for example TN and BOD may also become elevated due to agricultural runoff (Crowther et al., 2002; Environment Agency, 2018a). Water testing however, only represents a snapshot in time and is costly to generate (Environment Agency, 2019b). In addition, nitrogen isotope analysis ($\delta^{15}N$) of water dissolved nitrate $\delta^{15}NNO_3^-$ (Bronders et al., 2012; Ohte, 2013) can provide a good alternative to identifying nitrogen sources, but this method is also time consuming, costly and again only represents a snapshot in time.

Nitrogen isotope analysis of photosynthetic organic matter (e.g., macrophytes, macroalgae, microalgae) can be used as an alternative method for determining nitrogen sources (see Gröcke et al., 2017, and

* Corresponding author.
E-mail address: freya.alldred@durham.ac.uk (F.C. Alldred).

https://doi.org/10.1016/j.marpolbul.2024.116828
Received 19 April 2024; Received in revised form 30 June 2024; Accepted 5 August 2024
Available online 5 September 2024

references therein): it is inexpensive and these proxies record an average $\delta^{15}N$ value of the nitrogen source during the growing period (Cohen and Fong, 2005; García-Seoane et al., 2018; Gröcke et al., 2017; Samper-Villarreal, 2020). Anthropogenic and artificially derived nitrogen sources in aquatic environments have been successful measured for several decades using nitrogen isotope analysis (e.g., Heaton, 1986; Aravena et al., 1993; Savage, 2005; Lapointe et al., 2015). Anthropogenic sewage nitrogen sources typically exhibit more elevated $\delta^{15}N$ values (Costanzo et al., 2001; Dailer et al., 2010; Heaton, 1986). Denitrification of nitrate in the sewage treatment process favours the reduction of ^{14}N from nitrate to N_2 (g) compared to ^{15}N, which leads to an enrichment in ^{15}N in the residual pool (Dailer et al., 2010; Heaton, 1986; Risk et al., 2009). Other processes such as ammonia (NH_4^+) volatilisation will further elevate the $\delta^{15}N$ value of remaining wastewater (Heaton, 1986; Risk et al., 2009)(Heaton, 1986; Risk et al., 2009)(Heaton, 1986; Risk et al., 2009). Prolonged denitrification can elevate $\delta^{15}N$ values to > +18 ‰ in certain environmental conditions (Barr et al., 2013; Dailer et al., 2010; Gartner et al., 2002; Riera et al., 2000). Untreated and/or raw sewage may be less elevated in $\delta^{15}N$ (~ +8 ‰) since it has not undergone denitrification (Barr et al., 2013; Risk et al., 2009). Industrially-sourced nitrogen products (i.e., chemical fertiliser) have lower $\delta^{15}N$ values since atmospheric N_2 (g) is used in the making process (Heaton, 1986). Baseline coastal $\delta^{15}N$ values or "natural", unpolluted environments have been proposed to range between +4 ‰ and +6 ‰ for the north-east Atlantic Ocean by Savage and Elmgren (2004). This "natural" isotopic range agrees with limited UK data: Jones et al. (2018) suggested that +6 ‰ in seagrass was the upper boundary range for unpolluted water and Gröcke (2022, unpublished data) recorded $\delta^{15}N$ values of +5 ‰ ± 0.3 ‰ from macroalgae in the outer-most coastline of the Hebrides, northwest Scotland.

Macroalgae $\delta^{15}N$ has been used as a reliable tracer of nitrogen pollution in coastal environments (e.g., Dailer et al., 2010; Gröcke et al.,

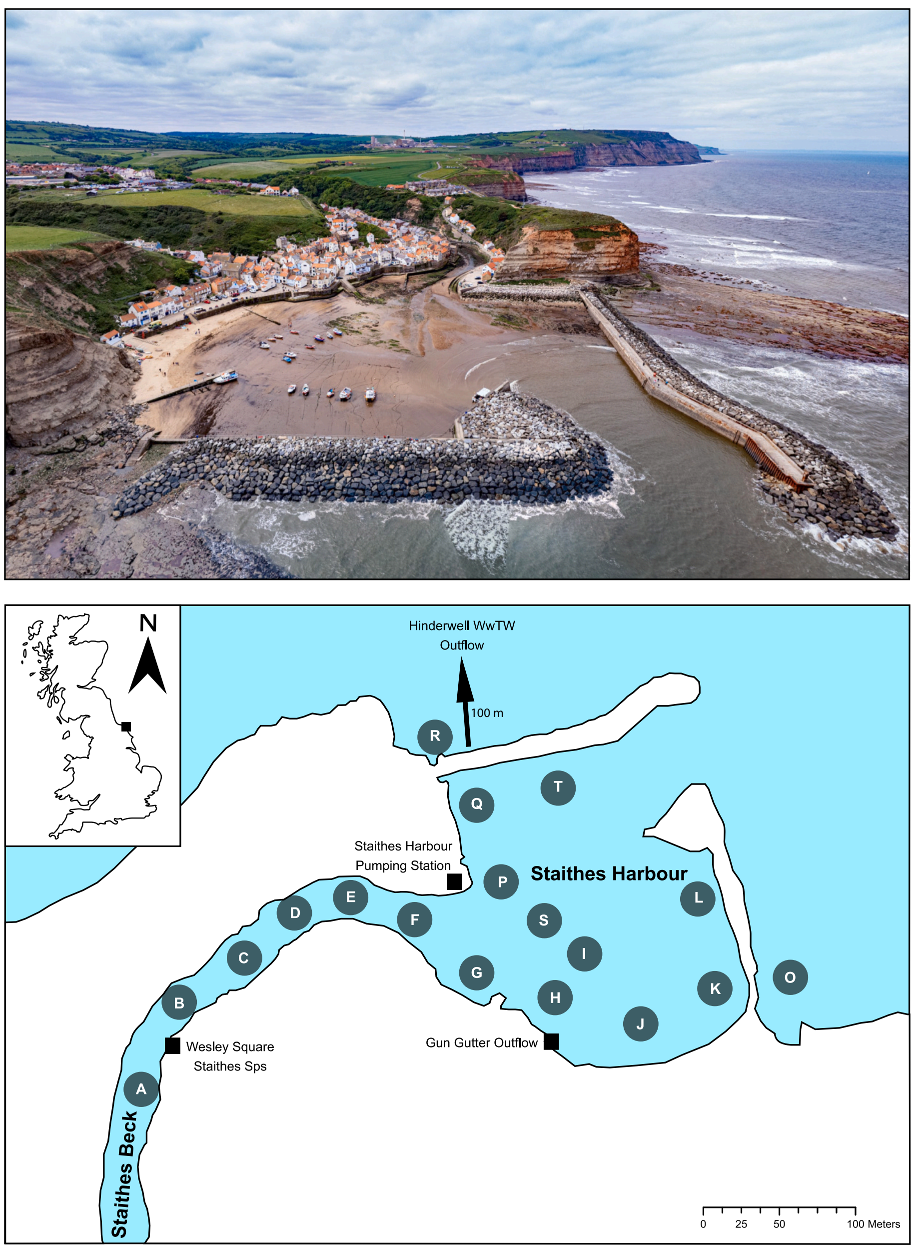

Fig. 1. Top: Aerial drone photograph of Staithes in 2022 (courtesy of Chris Riddell). Bottom: Map sampling locations for Staithes Beck, Staithes Harbour and the North Sea. ArcGIS Pro 3.0 was used to produce the map, with subsequent editing in Adobe Illustrator (this applies to all map figures). WwTW = wastewater treatment works. Sps = sewage pumping station.

2017; Risk et al., 2009). Studies vary from using a single species (e.g., Barr et al., 2013; Orlandi et al., 2017), whereas other studies have analysed the three dominant types – red (Rhodophyta), brown (Phaeophyceae), and green (Chlorophyta) (Lemesle et al., 2016). Most nitrogen isotope studies on macroalgae in Europe have dominantly focused on using *Fucus* sp. and *Ulva* sp. (hereafter, *Fucus* and *Ulva*, respectively) due to their ubiquitous distribution and ease of identification (Bunker et al., 2017; García-Seoane et al., 2018; Samper-Villarreal, 2020). Nitrogen assimilation rates and nitrogen isotopic fractionation are well understood for these species (Bailes and Gröcke, 2020; Cohen and Fong, 2005; Swart et al., 2014). Assimilation rates are distinctly different for these two species: for example, ~48 h for *Ulva* (Budd and Pizzola, 2008; Lemesle et al., 2016) 14–30 days for *Fucus* ((Bailes and Gröcke, 2020; Gröcke et al., 2017; White, 2008) and 1–7 months for *Ascophyllum nodosum* (Hill and White, 2008; Viana et al., 2015).

Since no standardised survey design exists for macroalgae stable isotope research a variety of approaches have been employed (e.g., García-Seoane et al., 2018; Samper-Villarreal, 2020). Simple field collections of macroalgal growing in situ are common and restricted to the intertidal zone, typically <2 m water depth (e.g. Thornber et al., 2008; Titlyanov et al., 2011). In locations where macroalgae distribution and presence is limited, translocation/deployment of isotopically labelled macroalgae can be used for assessing nitrogen pollution (Bailes and Gröcke, 2020; Costanzo et al., 2001). Translocated macroalgae also enables sampling of open oceans/deeper water as demonstrated by Howarth et al. (2019) to trace salmon farm effluent in Nova Scotia, Canada.

Investigations that sample macroalgae across a large spatial area have also been undertaken: Viana and Bode (2013) collected macroalgae from 10 sites >80 km apart, whereas Savage and Elmgren (2004) sampled 19 sites along a 36-km stretch of coastline. However, changes in coastal morphology are known to impact macroalgae $\delta^{15}N$ due to increased nutrient retention times in bays/lagoons (Raimonet et al., 2013; Titlyanov et al., 2011). Therefore, in studies such as Titlyanov et al. (2011), where 9 sites spanning >300 km, all nitrogen sources and impacts affecting that ecosystem are unlikely to be captured. Similar problems may arise when sampling estuarine environments: a few studies have investigated small bays (e.g. (Gartner et al., 2002) and/or ports/harbours ((Dudley and Shima, 2010) to determine the geospatial variation of nitrogen isotopes on a localised scale.

In this study, we selected a simple structured small fishing harbour in the north-east of England, Staithes, North Yorkshire, and collected seaweed geospatially over two periods of the year (May = Spring, September = Autumn). During each collection trip *Fucus* and *Ulva* were collected from 18 field plots for nitrogen isotope analysis to understand the source and distribution of nitrogen pollution in the harbour. The results of this study indicates that a minimum number of 10 samples (from a central area) from each species is adequate enough to determine the $\delta^{15}N$ value of a simple (single river and single exit to the open ocean), small port/harbour.

2. Materials & methods

2.1. Study site

Staithes is a small fishing harbour/village located on the north-east coast of North Yorkshire, England (Fig. 1A). The Staithes Beck is a 25 km-long river draining a catchment of ~32 km^2 before discharging into the small harbour (0.03 km^2) and the North Sea (Environment Agency, 2022b). Three small other becks drain into the Staithes Beck, including the Borrowby Dale Beck draining from the village of Hinderwell (Crowther et al., 2002). Wastewater treatment in the region is managed by the private water company, Yorkshire Water. In 2001 the Hinderwell Sewage Treatment Works were constructed to redirect sewage from Hinderwell and Easington to the Staithes Long Sea Outfall (Environment Agency, 2022a). The Staithes Long Sea Outfall (Fig. 1A) discharges

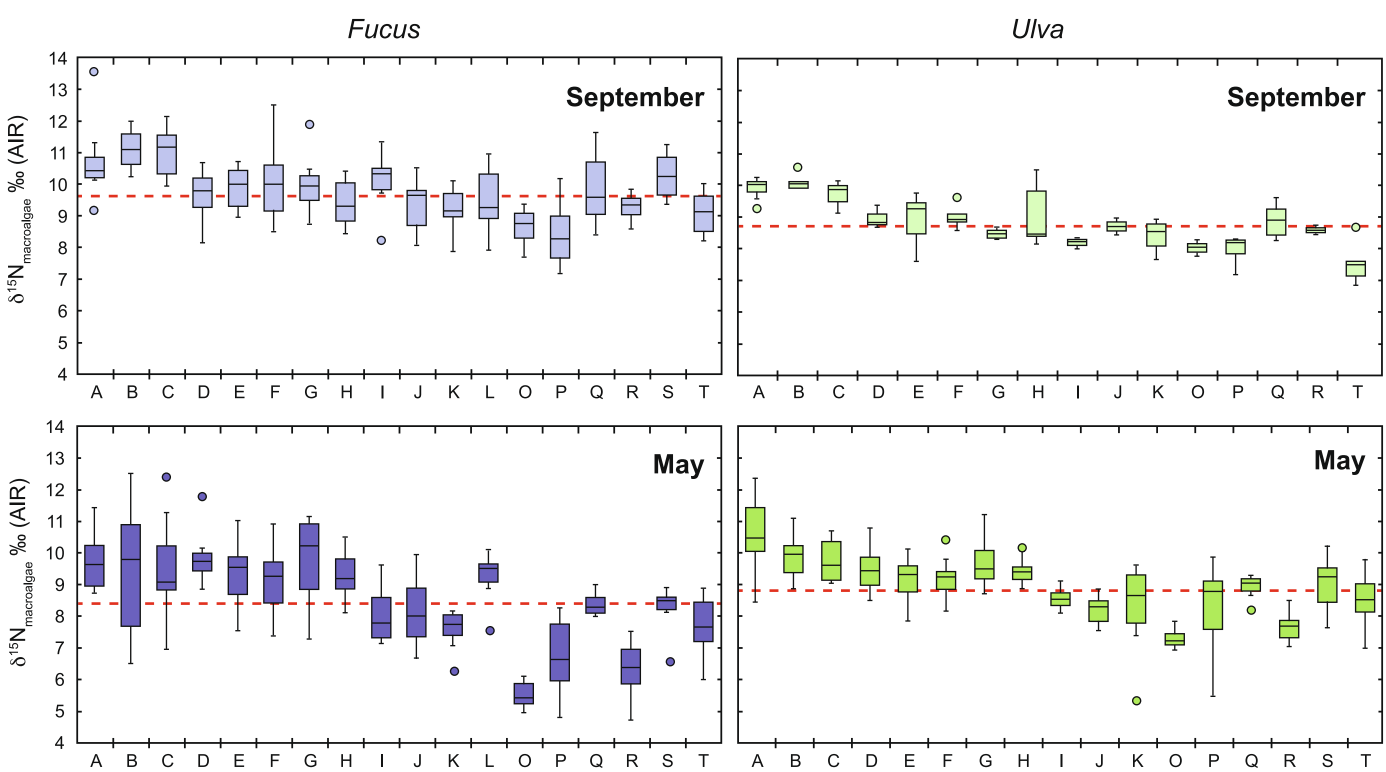

Fig. 2. $\delta^{15}N$ values recorded for *Fucus* (left) and *Ulva* (right) for September 2023 and May 2023. The red dash line represents the average for each species for each collection month. *Fucus*: September +9.7 ‰ ± 1.0 ‰ ($n = 235$) and in May +8.4 ‰ ± 1.6 ‰ ($n = 184$). Ulva: September +8.8 ‰ ± 0.9 ‰ ($n = 70$) and in May +8.9 ‰ ± 1.1 ‰ ($n = 197$). Note the change in site scale for *Ulva* between September and May: Site S did not contain any *Ulva* in September 2022. $\delta^{15}N$ scale for each plot is identical. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

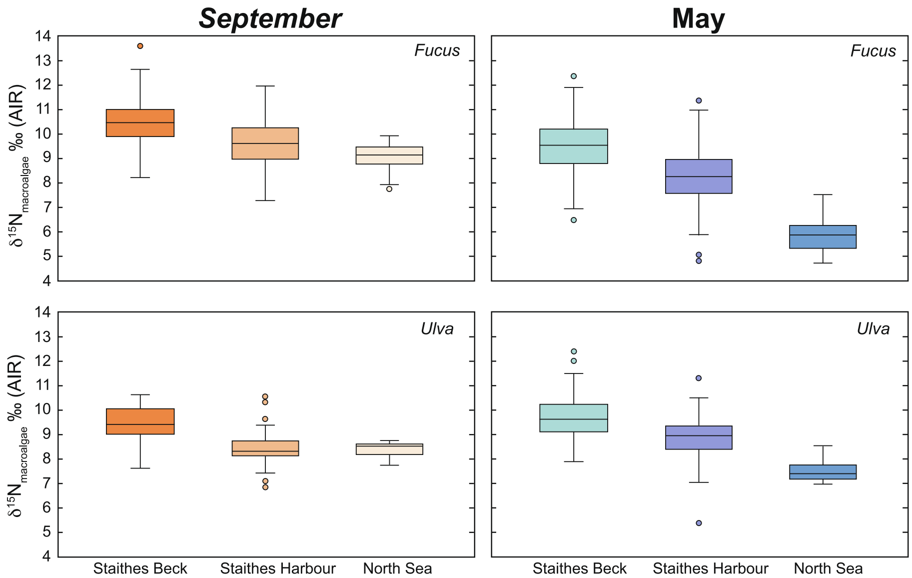

Fig. 3. Average $\delta^{15}N$ values recorded for each region of this study (e.g., Staithes Beck, Staithes Harbour and the North Sea) for September 2022 (left) and May 2023 (right) for *Fucus* (top) and *Ulva* (bottom). Note, the general decreasing $\delta^{15}N$ trend from Staithes Beck to the North Sea.

Table 1
Student t-test p-value results showing of nitrogen isotope values between Fucus and Ulva for the three major sampling locations. All tests were performed at the 95% confidence level.

All seaweed

September	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck		1.73×10^{-8}	1.98×10^{-13}
Staithes Harbour			5.6×10^{-4}
May	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck		1.34×10^{-12}	3.35×10^{-25}
Staithes Harbour			7.2×10^{-16}

Fucus

September	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck		2.1×10^{-7}	8.7×10^{-13}
Staithes Harbour			5.5×10^{-5}
May	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck		8.88×10^{-7}	3.39×10^{-21}
Staithes Harbour			7.72×10^{-15}

Ulva

September	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck		6.5×10^{-7}	1.5×10^{-5}
Staithes Harbour			0.79
May	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck		1.9×10^{-7}	1.65×10^{-23}
Staithes Harbour			1.65×10^{-12}

~100 m north of the harbour into the North Sea (The Rivers Trust, 2022; Yorkshire Water, 2023). Staithes has two Combined Sewer Overflows (CSOs); one discharges directly in the harbour (the Gun Gutter or Slipway) and the second directly into Staithes Beck (Fig. 1A) (Crowther et al., 2002; The Rivers Trust, 2022; Yorkshire Water, 2023). The Staithes Pumping Station is located on the western harbour wall (Fig. 1A) (The Rivers Trust, 2022).

Staithes Beck has a history of poor water quality: ecological status was rated Poor or Moderate until 2014 (Environment Agency, 2022b). Since 2015 Staithes Beck has been rated as 'Good Ecological Status', but has consistently failed to reach 'Good Chemical Status' (Environment Agency, 2022b). The Staithes Beck has limited chemical data, for example, TN has not been reported since 2015 (Environment Agency, 2021, 2022b). The Hinderwell Sewage Treatment Works was not fit for purpose upon completion in 2001, and sewage leaks to Staithes Beck and Gun Gutter were a regular occurrence (Hinderwell Parish Council, Ms. C. Barker, email pers. comm. 2023). In 2015 a major leak caused a reduction in dissolved oxygen, high ammonia concentrations and foul discoloured water into the harbour, killing at least 100 fish in Staithes Beck (Environment Agency, 2018b). Yorkshire Water were fined £600,000 over the incident due to poor maintenance of rusted sewage tanks (Environment Agency, 2018b; Minting, 2017). Since then, public opinion over water quality has been low, with concerns over faecal pollution, poor water quality and dissatisfaction that Staithes Harbour was removed as a designated bathing site in 2016 (DEFRA, 2016). Since 2015, Staithes Harbour has seen minimal improvement, with over 1000 discharge hours of raw sewage from the Staithes Long Sea Outfall in 2020 (The Rivers Trust, 2022; Yorkshire Water, 2023).

3. Methods

Macroalgae was collected from 18 sites (sites) divided into three geographical zones: Staithes Beck (A – F), Staithes Harbour (G – L, P, Q, S, T) and North Sea (O, R) (Fig. 1A). Sites were chosen for accessibility, macroalgal cover and to produce good coverage of the harbour. Macroalgae was sampled on 26th September 2022 and 19th May 2023 to understand seasonal changes in $\delta^{15}N$ between Autumn and Spring. In each area at least 20 random macroalgae samples were collected, with a minimum of 10 *Fucus* samples. In September there was less *Ulva* present and so a minimum of 5 samples was set; this was increased to 10 samples in May due to abundant *Ulva* present. For *Fucus* the most recent growth was sampled, and fertile tips were ignored since they do not rapidly assimilate nitrogen (Viana et al., 2015). Sections of in-place *Ulva* between 3 and 5 cm^2 were sampled and squeezed to remove seawater. All samples were placed into individual lunch-money sized envelopes and subsequently dried in an oven set at 60 °C for between 48 and 72 h. The tips of *Fucus* are assumed to record $\delta^{15}N$ values that represent the previous 2–4 weeks, whereas we have assumed that for *Ulva* it would represent ~2 days based on varying nitrogen assimilation rates (Gröcke et al., 2017; Viana et al., 2015).

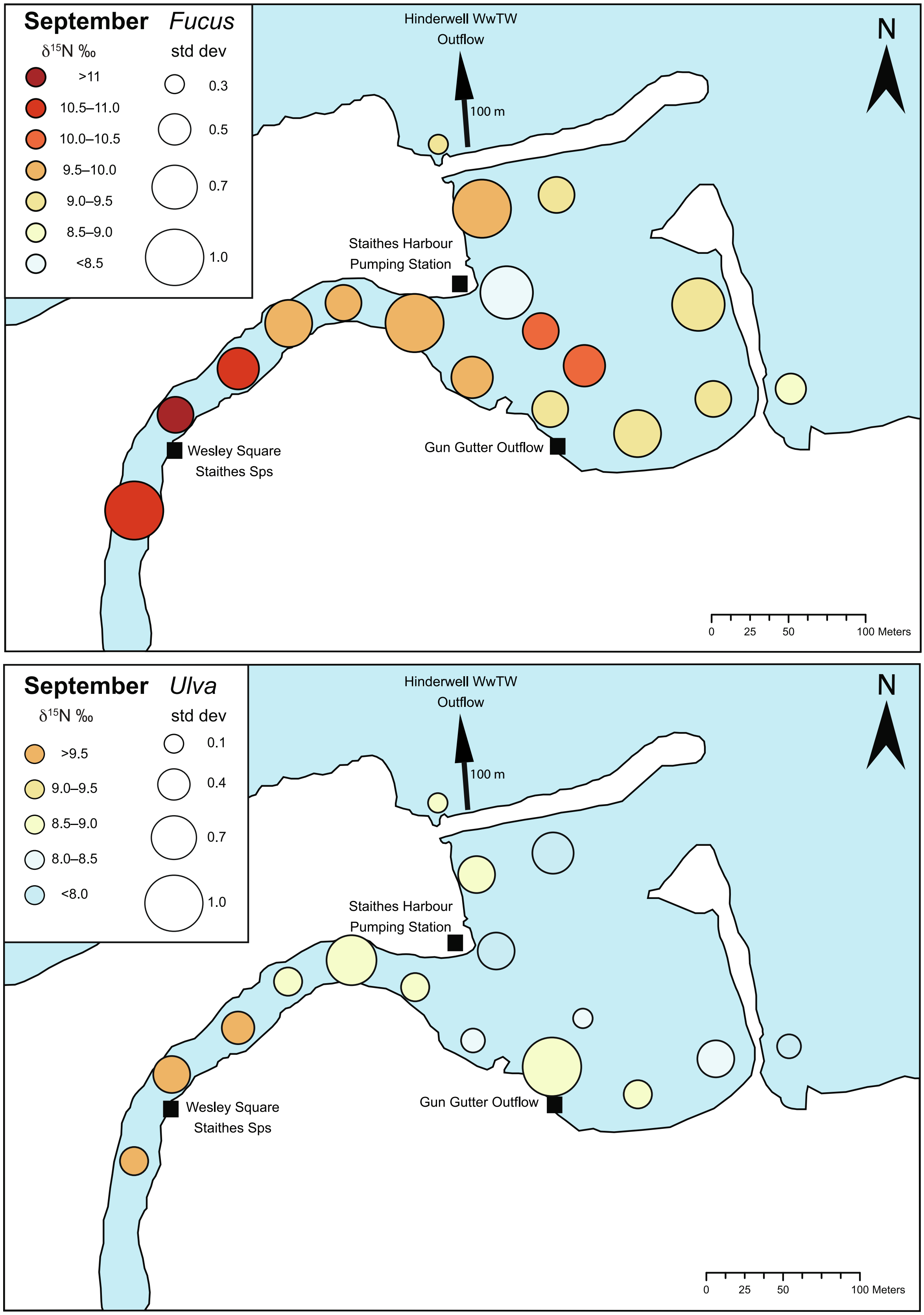

Fig. 4. Geospatial representation of average $\delta^{15}N$ values for *Fucus* (top) and *Ulva* (bottom) for each site (see Fig. 1) during September 2022. Note, the size of the circle represents the amount of standard deviation (std dev) for each site.

Table 2
Student t-test p-value results showing of nitrogen isotope values between Fucus and Ulva and the three major sampling locations between September and May. All tests were performed at the 95% confidence level.

All seaweed

	May				
September	Fucus	Ulva	Staithes Beck	Staithes Harbour	North Sea
Fucus	1.33×10^{-18}				
Ulva		0.097			
Staithes Beck			86×10^{-4}		
Staithes Harbour				6.55×10^{-12}	
North Sea					7.38×10^{-18}

Fucus

	May		
September	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck	1.65×10^{-5}		
Staithes Harbour		0.705	
North Sea			2.14×10^{-16}

Ulva

	May		
September	Staithes Beck	Staithes Harbour	North Sea
Staithes Beck	0.132		
Staithes Harbour		0.018	
North Sea			1.27×10^{-4}

All samples were weighed into tin capsules (weight range between 1.0 and 1.5 mg) and analysed using a Costech Elemental Analyser (ECS 4010) connected to a Thermo Scientific Delta V Advantage in the Stable Isotope Biogeochemistry Laboratory (SIBL), Durham University. Nitrogen isotope ratios are reported against atmospheric nitrogen (AIR). Routine analyses of in-house standards are calibrated against international standards (e.g., IAEA-600, IAEA-N-1, USGS24) to ensure isotope accuracy. Analytical uncertainty was typically ±0.1 ‰ (1 sd) for replicate analyses. In total, 305 individual macroalgae samples were analysed from September, and 351 from the May fieldtrip.

All maps were produced using ArcGIS Pro 3.0, a colour-blind key was used to depict average $\delta^{15}N$ plot values and the point size represents the standard deviation in $\delta^{15}N$ for that plot location. Figures and statistical tests generated using Excel and R Studio. A Tukey pairwise comparison *t*-test (Tukey test) was performed to statistically assess how similar each site was to one another in terms of mean $\delta^{15}N$ values; for this test we removed Site L since it was an area that did not contain any *Ulva* during both fieldtrips. Levene's test for homogeneity (Fox, 2015; Levene, 1960) provided evidence of heterogeneity of isotopic values across groups. Tukey test results are often presented in the form of a compact number display, which attributes a shared group number between any two groups for which there is no evidence (at the 95 % significance level) of a difference between their group means (Piepho, 2004). Therefore, the Tukey test was based on constructing a generalised linear model for isotopic values, with Site as the regressor, and for each isotope type-month pairing.

4. Results

In September 2022, *Fucus* produced an average of +9.7 ‰ ± 1.0 ‰ (n = 235) whilst *Ulva* was slightly less positive at +8.8 ‰ ± 0.9 ‰ (n = 70). Staithes Beck averaged +10.4 ‰ ± 1.0 ‰ (n = 63) (*Fucus*) and +9.4 ‰ ± 0.7 ‰ (n = 26) (*Ulva*). Staithes Harbour recorded a lower average: +9.6 ‰ ± 0.9 ‰ (n = 144) and +8.4 ‰ ± 0.8 ‰ (n = 37), for *Fucus* and *Ulva* respectively. *Fucus* averaged +9.0 ‰ ± 0.5 ‰ (n = 28) and *Ulva* averaged +8.3 ‰ ± 0.3 ‰ (n = 7) for the North Sea. $\delta^{15}N$ values range between +7.2 ‰ (Site T) and +13.5 ‰ (Site A) for *Fucus* and between +6.8 ‰ (Site P) and +10.6 ‰ (Site B) for *Ulva*. Site B was the most elevated site for *Fucus* and *Ulva* with a $\delta^{15}N$ average of +11.1 ‰ ± 0.6 ‰ (n = 15) and +9.9 ‰ ± 0.5 ‰ (n = 5), respectively. The lowest average $\delta^{15}N$ was recorded at Site P for *Fucus* (+8.4 ‰ ± 0.9 ‰, n = 10) and at Site T for *Ulva* (+7.5 ‰ ± 0.6 ‰, n = 5). Fig. 2 illustrates the $\delta^{15}N$ range across all sites for September: Site F (*Fucus*) and H (*Ulva*) exhibited the largest $\delta^{15}N$ range whereas Site R had the smallest range for both species. All sites for Staithes Beck plot above the respective mean for both species. Staithes Harbour sites show some variation around the mean while Sites R and O plot below the Staithes Harbour mean (Fig. 2A, B). Fig. 3 illustrates the range for each designated zone, all zones recorded significantly $\delta^{15}N$ values except between the Staithes Harbour and North Sea *Ulva* (p value >0.05) (Table 1).

May 2023, recorded a lower average $\delta^{15}N$ value than September 2022 in both *Fucus* (+8.4 ‰ ± 1.6 ‰, n = 184) and *Ulva* (+8.9 ‰ ± 1.1 ‰, n = 167) (Fig. 2A, B). Staithes Beck averaged +9.5 ‰ ± 1.3 ‰ (n = 61) and +9.7 ± 0.9 ‰ (n = 59), for *Fucus* and *Ulva* respectively. Staithes Harbour records a lower average: +8.3 ‰ ± 1.2 ‰ (n = 103) and +8.8 ‰ ± 0.9 ‰ (n = 88), for *Fucus* and *Ulva* respectively. *Fucus* averaged +5.9 ‰ ± 0.8 ‰ (n = 20) and *Ulva* averaged +7.5 ‰ ± 0.4 ‰ (n = 20) for the North Sea. $\delta^{15}N$ values range between +4.7 ‰ (Site R) to +12.5 ‰ (Site B) for *Fucus* and +5.3 ‰ (Site K) and +12.4 ‰ (Site A) for *Ulva* (Fig. 2A, B). In line with the results from September 2022, the most elevated $\delta^{15}N$ values are recorded in Staithes Beck with Sites D and G recording the highest average for *Fucus* (+9.8 ‰ ± 1.3 ‰, n = 10 and +9.8 ‰ ± 1.6 ‰, n = 10, respectively). Site A recorded the highest $\delta^{15}N$ average for *Ulva* (+10.6 ‰ ± 1.1 ‰, n = 10). Site O recorded the lowest average $\delta^{15}N$ for both *Fucus* and *Ulva*: +5.5 ‰ ± 0.4 ‰ (n = 10) and +7.3 ‰ ± 0.3 ‰ (n = 10), respectively (Fig. 2A, B). Macroalgae $\delta^{15}N$ values for Staithes Harbour (G – L, Q, S and T) exhibit a range of 5.1 ‰ in September 2022, compared to 6.4 ‰ in May 2023.

Of all the data generated in this study Site P produced anomalous results in September 2022 and May 2023 suggesting a difference in nitrogen pollution source or amounts compared to the other sites. September *Fucus* at Site P had significantly lower $\delta^{15}N$ averages compared to all other Staithes Harbour sites (Fig. 4A). *Ulva* $\delta^{15}N$ averages were generally lower but not significantly different from other Staithes Harbour sites (Fig. 4B) although in May 2023 there was significantly variability at this site. The $\delta^{15}N$ values from Site P were similar to the North Sea sites (Sites R and O) during September and May. Neighbouring sites S and Q are significantly different to Site P for *Fucus* in both collection periods.

5. Discussion

5.1. Seasonal $\delta^{15}N$ variation

Fucus $\delta^{15}N$ is more positive across all three environmental zones in September 2022 compared to May 2023 (Table 2, Fig. 3A, B). On the other hand, *Ulva* shows no significant difference between September and May (Table 2), although more spatial variation is observed with more elevated $\delta^{15}N$ values in September (Fig. 2A). Lower $\delta^{15}N$ in May differs to seasonal trends observed by Raimonet et al. (2013) and Lemesle et al. (2016) where $\delta^{15}N$ was elevated in warmer months. The Staithes Harbour data more closely reflects findings for the County Durham coast (England) where more elevated $\delta^{15}N$ values occurred in September in comparison to May (Bailes, 2022). To generate a more thorough understanding of seasonal changes in $\delta^{15}N$ a study composed of monthly sampling would be required for all 17 sites. Although this would produce a very extensive dataset it would also come at a cost in terms of time and analyses (> 3500 samples). This scientific approach would not,

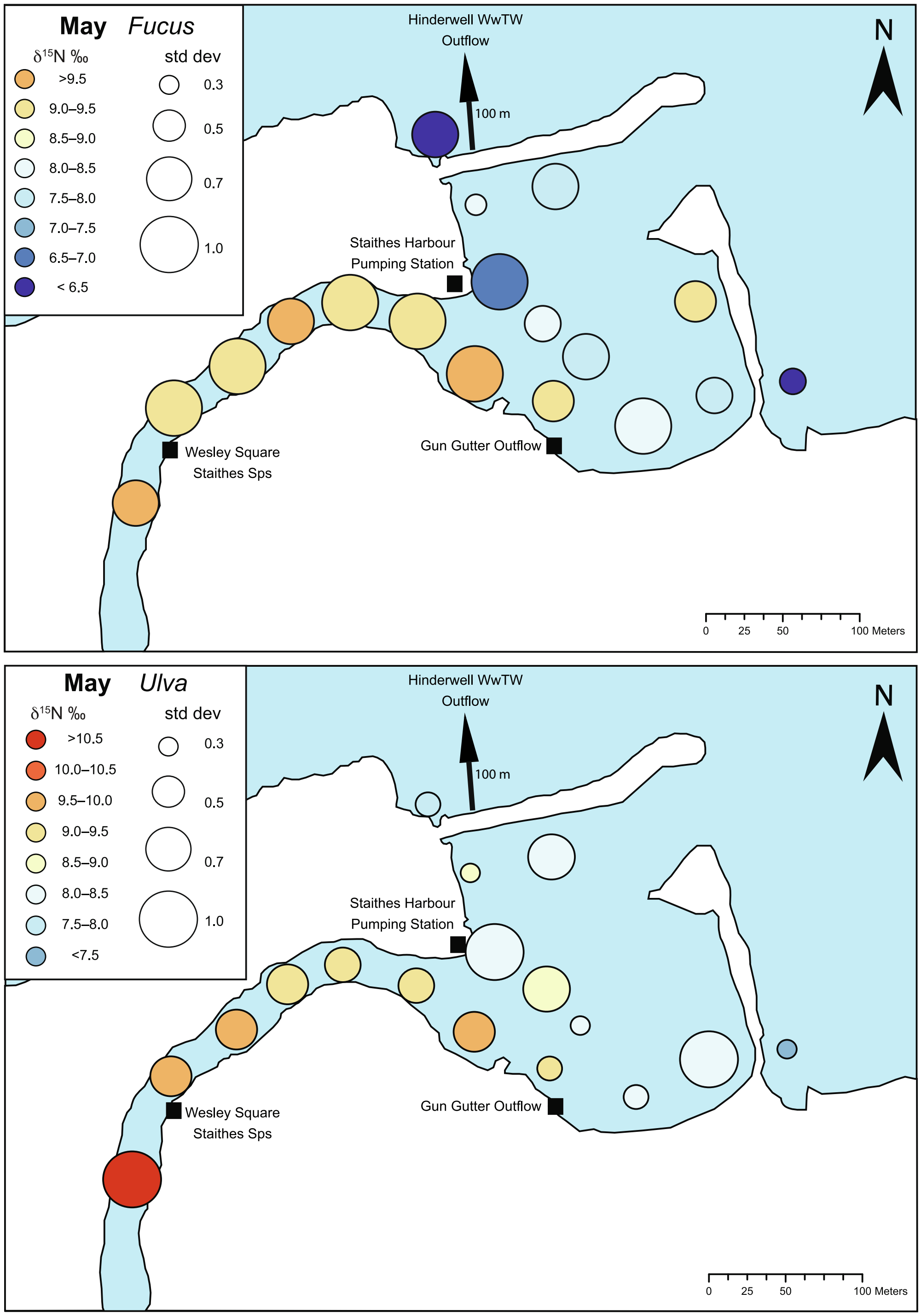

Fig. 5. Geospatial representation of average $\delta^{15}N$ values for *Fucus* (top) and *Ulva* (bottom) for each site (see Fig. 1) during May 2023. Note, the size of the circle represents the amount of standard deviation (std dev) for each site.

in our opinion, show anything significantly different to what is presented in this study: other, more complex geospatial environments may require seasonal and/or monthly records depending on the scientific question to be investigated.

The seasonal difference in $\delta^{15}N$ for *Fucus* and *Ulva* between September 2022 and May 2023 indicates that the nitrogen pollution source into Staithes Harbour is not significantly different between these seasons. Elevated $\delta^{15}N$ values (> +6 ‰) suggest an input from anthropogenic effluent (raw and/or treated) and/or animal manure, and thus, chemical fertilizers are not the dominant nitrogen source (Deutsh and Voss, 2006; Kroeger et al., 2006). Staithes Beck is known to receive sewage effluent from the Hinderwell Facility and from two holding tanks which regularly overflow after heavy rainfall (Hinderwell Parish Council, Ms. C. Barker, email pers. comm. 2023). Organic fertiliser, such as animal manure, can also produce elevated $\delta^{15}N$ values > +6 ‰ (Jones et al., 2018; Xue et al., 2009). In England the spreading of anthropogenic effluent/animal manure predominantly occurs in September in preparation for winter-sown crops (Kynetec, 2023). Since *Fucus* records a longer uptake of nitrogen pollution (i.e., slower assimilation rate) and thus a more elevated $\delta^{15}N$ average compared to *Ulva* that may only be recording the last few days of nitrogen input into Staithes Harbour (Gröcke et al., 2017; Kynetec, 2023). However, no information is

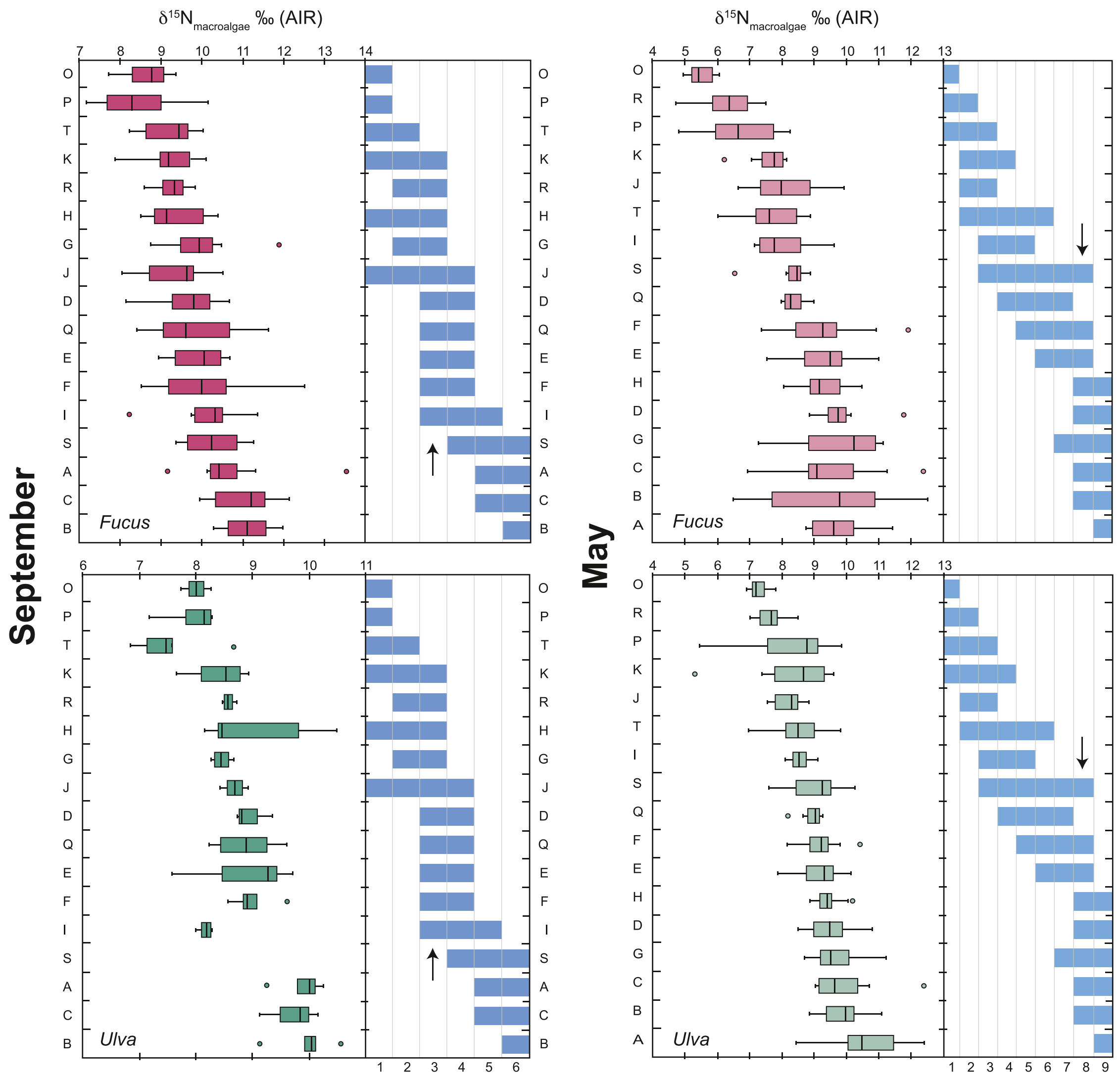

Fig. 6. Box and whisker plots of δ^{15}N for September 2022 (left) and May 2023 (right) for *Fucus* (top) and *Ulva* (bottom). To the right of each box and whisker plot is a graphical representation of the pairwise site groupings based on the Tukey test output. The blue horizontal bar indicates that two sites have no evidence of a difference between their group mean δ^{15}N, thus sharing that group number (horizontal axis). This implies that the sites that fall into more groups will give a similar mean to the majority (indicated by black arrows). Therefore, September 2022 *Fucus* would indicate that collecting >10 samples from any sites in Group 3 would produce an average δ^{15}N value within error of the δ^{15}N mean of the majority of sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

publicly available on the amounts and type of fertiliser application in the surrounding farming area to support this interpretation.

5.2. *Spatial δ^{15}N variation*

Figs. 4 and 5 show spatial variation, with elevated δ^{15}N values in Staithes Beck compared to the Staithes Harbour and North Sea. Staithes Beck records the highest δ^{15}N average of > +11 ‰, suggesting denitrified sewage as the dominant source for the nitrogen pollution. Since it is reported that Staithes Beck receives treated sewage effluent from the Hinderwell Facility, this is supported by the macroalgae δ^{15}N data. Reduced mixing between freshwater and seawater may be a mechanism that concentrates the effluent upstream, allowing the macroalgae more time to incorporate the treated sewage effluent δ^{15}N signature (Barr et al., 2013): at least during periods of high tide. Although on a much smaller spatial area this may also represent a nutrient front that is limiting dilution between the mixing of seawater and freshwater: this has been shown to be a mechanism in more large-scale, open estuary environments such as (Zhou et al., 2024).

Macroalgae δ^{15}N values gradually decline from Staithes Beck into the Staithes Harbour in both collection periods (see Figs. 4, 5). There is a general δ^{15}N decrease on the order of ~3 ‰ in *Fucus* and *Ulva* from Site A to the open ocean sites (R and O) representing the North Sea (Figs. 4, 5), however, the magnitude is less in September *for Ulva,* ~1.5 ‰ (Fig. 4). During May 2023, *Ulva* recorded significantly more elevated δ^{15}N values in comparison to *Fucus* in Staithes Harbour. This also corresponded with considerably more growth of *Ulva*, especially along Staithes Beck and the outflow pathway in Staithes Harbour (see Fig. 1). Increased runoff of nutrients and warmer temperatures during May are interpreted to promote *Ulva* growth and nutrient uptake. There is no significant difference for *Ulva* between these areas in September (*p* value = 0.79, Table 1) and it is interpreted to be caused by increased wave activity and mixing between Staithes Harbour and the North Sea, reduced growth rates and thus uptake of nutrients.

Fig. 6 graphically represents the Tukey test results: 6 groups are required to categorise the sites in September (Fig. 6A), whereas 9 groups are required for May (Fig. 6B). Both months show considerable overlap between sites within Staithes Harbour: 10 for September (Group 3) and

6 for May (Group 3). The $\delta^{15}N$ data suggests that Staithes Harbour exhibits less $\delta^{15}N$ variation between sites indicating that the harbour has relatively well-mixed the nitrogen pollution inputs from Staithes Beck and the open ocean (North Sea). More Tukey test groups overlap between sites for September 2022 thus more homogenous in terms of nitrogen pollution mixing. There are more Tukey test groups for May 2023, and in particular, fewer site pairs sharing any group number, which may represent differential uptake and assimilation in *Ulva* in comparison to *Fucus*. In addition, it may represent the different nitrogen strategies between *Fucus* and *Ulva*. During the winter months when *Fucus* is growing slowly it can take up nitrogen and store it for subsequent use in Spring (Lehvo et al., 2001; Young et al., 2007) and thus, not have to compete with opportunistic, faster assimilating macroalgae species, such as *Ulva*. Therefore, the Tukey test results suggest that to produce a representative $\delta^{15}N$ value for Staithes Harbour more sites may need sampling in Spring in comparison to Autumn.

5.3. Staithes sewage infrastructure

From this study, we hypothesise that the pumping station is still leaking and releasing raw sewage and/or household chemicals that are lowering the $\delta^{15}N$ average value (Barr et al., 2013; Risk et al., 2009) at Site P in comparison to the other sites in Staithes Harbour (Figs. 4 and 5). During both sampling fieldtrips, trickling water could be heard from under the rocks of the retaining wall opposite the Staithes Harbour Pumping Station (Fig. 1), which transfers wastewater from local properties to the nearest wastewater treatment works. Clearly this specific site requires investigation by local authorities and private water company. This result highlights the potential of macroalgae $\delta^{15}N$ to locate point sources that may be impacting an area in comparison to a less detailed approach.

Other infrastructures in Staithes Harbour, such as the Gun Gutter Outflow (Site H), indicate minimal impact during either sampling trip (Figs. 4, 5). The $\delta^{15}N$ average for both *Fucus* and *Ulva* at Site H falls within the range of $\delta^{15}N$ recorded from Staithes Harbour and Staithes Beck. This suggests that Site H was not influenced by the Gun Gutter Outflow during these fieldtrips and/or mixing in this part of the harbour is strong, thus dissipating any influence. A cautionary note: during other periods of the year the impact of this outflow may be greater.

6. Conclusions

Spatial variation in macroalgae $\delta^{15}N$ was investigated from a small fishing harbour, Staithes, on the North Yorkshire coast of England. Over 300 macroalgae samples were collected in September 2022 (Autumn) and May 2023 (Spring). No significant difference was documented between these two sampling time intervals, although there is significant spatial variation in $\delta^{15}N$ between Staithes Beck, Staithes Harbour, and the open sea (North Sea). The dominant nitrogen pollution source as identified by $\delta^{15}N$ is raw and/or treated sewage that entered Staithes Harbour via Staithes Beck. The nitrogen pollution source (isotopically) is well-mixed in Staithes Harbour suggesting that 10 macroalgae samples from the central part of the harbour would accurately represent the overall average $\delta^{15}N$ value. Thus, if the purpose of the study is to generate large-scale patterns along the coastline it is suggested that macroalgae collection should occur in the centre of bays and harbours, away from point sources. Detailed sampling strategies in harbours can be used to define mixing patterns and potentially identify unknown point-sources as illustrated in this study (i.e., Site P).

Future research aims and questions will drive the type of sampling procedure to be undertaken, for example: (1) a broad coastal study will only require a minimum of 10 samples, of each macroalgae species being collected, from within the central portion of the bay, estuary and/or harbour to identify the average $\delta^{15}N$ value for that site; and (2) more detailed investigations, potentially seasonally, to pin-point nitrogen pollution sources and mixing in a harbour and/or estuary. Each of these studies has it merits. A broad coastal study could be used to discriminate major changes in nitrogen pollution, for example, between agricultural and highly-populated regions. Very details estuary studies can be used to help understand mixing patterns, but also identify previous unknown point sources.

This study highlights the strength of using macroalgae nitrogen isotope ratios ($\delta^{15}N$) as a tool for identifying the dominant nitrogen pollution source, mixing patterns of the nitrogen pollution and the identification of additional or unknown point-source nitrogen pollution inputs (i.e., Site P).

CRediT authorship contribution statement

Freya C. Alldred: Writing – review & editing, Writing – original draft, Methodology, Investigation. **Darren R. Gröcke:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Samuel E. Jackson:** Writing – review & editing, Formal analysis, Data curation.

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

Data is fully available in the supplementary data file.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2024.116828.

References

Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. Groundwater 31, 180–186. https://doi.org/10.1111/j.1745-6584.1993.tb01809.x.

Bailes, I., 2022. Using Nitrogen Isotopes in Macroalgae to Determine and Monitor Sources of Nitrogen Pollution in Estuarine and Coastal Areas: An In-Vitro Study and Case Study in North East England. Durham University, UK.

Bailes, I.R., Gröcke, D.R., 2020. Isotopically labelled macroalgae: a new method for determining sources of excess nitrogen pollution. Rapid Commun. Mass Spectrom. 34 https://doi.org/10.1002/rcm.8951.

Barr, N.G., Dudley, B.D., Rogers, K.M., Cornelisen, C.D., 2013. Broad-scale patterns of tissue-$\delta^{15}N$ and tissue-N indices in frondose *Ulva* spp.; developing a national baseline indicator of nitrogen-loading for coastal New Zealand. Mar. Pollut. Bull. 67, 203–216. https://doi.org/10.1016/j.marpolbul.2012.11.033.

Bronders, J., Tirez, K., Desmet, N., Widory, D., Petelet-Giraud, E., Bregnot, A., Boeckx, P., 2012. Use of compound-specific nitrogen ($\delta^{15}N$), oxygen ($\delta^{18}O$), and bulk boron ($\delta^{11}B$) isotope ratios to identify sources of nitrate-contaminated waters: a guideline to identify polluters. Environ. Forensics 13.

Budd, G., Pizzola, P., 2008. Gut Weed (*Ulva intestinalis*) [WWW Document]. MarLIN: Marine Information Network. URL. https://www.marlin.ac.uk/species/detail/1469 (accessed 3.25.24).

Bunker, F.StP.D., Brodie, J., Maggs, C., Bunker, A., 2017. Seaweeds of Britain and Ireland, Second. ed. Wild Nature Press, Plymouth.

Cohen, R., Fong, P., 2005. Experimental evidence supports the use of $\delta^{15}N$ content of the opportunistic green macroalga Enteromorpha intestinalis to determine nitrogen sources to estuaries. J. Phycol. 41, 229–448.

Costanzo, S.D., Oõdonohue, M.J., Dennison, W.C., Loneraganà, N.R., Thomas, M., 2001. A new approach for detecting and mapping sewage impacts. Mar. Pollut. Bull. 42, 149–156.

Crowther, J., Kay, D., Wyer, M., 2002. Faecal-indicator concentrations in waters draining lowland pastoral catchments in the UK: relationships with land use and farming practices. Water Res. 36, 1725–1734.

Dailer, M.L., Knox, R.S., Smith, J.E., Napier, M., Smith, C.M., 2010. Using $\delta^{15}N$ values in algal tissue to map locations and potential sources of anthropogenic nutrient inputs on the island of Maui, Hawai'i, USA. Mar. Pollut. Bull. 60, 655–671. https://doi.org/10.1016/j.marpolbul.2009.12.021.

DEFRA, 2016. Consultation on the Proposal to Remove Staithes from the List of Designated Bathing Waters.

Deutsh, B., Voss, M., 2006. Anthropogenic nitrogen input traced by means of δ^{15}N values in macroalgae: results from in-situ incubation experiments. Sci. Total Environ. 366, 799–808.
Drinking Water Inspectorate, 2023. Nitrate [WWW Document]. UK Government. URL. https://www.dwi.gov.uk/consumers/learn-more-about-your-water/nitrate/#:~:text=The%20UK%20standard%20is%20based,as%20a%20safeguard%20against%20methaemoglobinaemia (accessed 7.24.23).
Dudley, B.D., Shima, J.S., 2010. Algal and invertebrate bioindicators detect sewage effluent along the coast of Titahi Bay, Wellington, New Zealand. N. Z. J. Mar. Freshw. Res. 44, 39–51. https://doi.org/10.1080/00288331003641687.
Environment Agency, 2018a. The State of the Environment: Water Quality.
Environment Agency, 2018b. Annual Fisheries Report 2017 to 2018 Yorkshire. Bristol.
Environment Agency, 2019a. 2021 River Basin Management Plan.
Environment Agency, 2019b. Waste Water Treatment Works: Treatment Monitoring and Compliance Limits.
Environment Agency, 2021. Staithes Beck - U/S Dalehouse Pub [WWW Document]. Water Quality Archive. URL. https://environment.data.gov.uk/water-quality/view/sampling-point/NE-49000325 (accessed 10.27.23).
Environment Agency, 2022a. 2022 Bathing Water profile for Runswick Bay [WWW document]. UK Government. URL. https://environment.data.gov.uk/data/bathing-water-profile/uke2206-06900/2022:1.
Environment Agency, 2022b. Staithes Beck from source to Newton Beck Water body [WWW document]. Department for Environment Food & Rural Affairs. URL. https://environment.data.gov.uk/catchment-planning/WaterBody/GB104027068770?cycle=3.
Environment Agency, 2023. Storm Overflow Spill Data Shows Performance Is Totally Unacceptable.
Fox, J., 2015. Applied regression analysis and generalised linear models. Sage Publications.
García-Seoane, R., Fernández, J.A., Villares, R., Aboal, J.R., 2018. Use of macroalgae to biomonitor pollutants in coastal waters: optimization of the methodology. Ecol. Indic. 84, 710–726. https://doi.org/10.1016/j.ecolind.2017.09.015.
Gartner, A., Lavery, P., Smit, A.J., 2002. Use of δ^{15}N signatures of different functional forms of macroalgae and filter-feeders to reveal temporal and spatial patterns in sewage dispersal. Mar. Ecol. Prog. Ser. 235, 63–73.
Gröcke, D.R., Racionero-Gómez, B., Marschalek, J.W., Greenwell, H.C., 2017. Translocation of isotopically distinct macroalgae: a route to low-cost biomonitoring? Chemosphere 184, 1175–1185. https://doi.org/10.1016/j.chemosphere.2017.06.082.
Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. Chemical Geology (Isotope Geoscience Section) 59, 87–102.
Hill, J., White, N., 2008. Knotted Wrack (*Ascophyllum nodosum*) [WWW Document]. MarLIN: Marine Information Network. URL. https://www.marlin.ac.uk/species/detail/1336 (accessed 3.25.24).
Howarth, R.W., 2008. Coastal nitrogen pollution: a review of sources and trends globally and regionally. Harmful Algae 8, 14–20. https://doi.org/10.1016/j.hal.2008.08.015.
Howarth, R.W., Marino, R., 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. In: Limnology and Oceanography. American Society of Limnology and Oceanography Inc., pp. 364–376. https://doi.org/10.4319/lo.2006.51.1_part_2.0364
Howarth, L.M., Filgueira, R., Jiang, D., Koepke, H., Frame, M.K., Buchwald, C., Finnis, S., Chopin, T., Costanzo, S.D., Grant, J., 2019. Using macroalgal bioindicators to map nutrient plumes from fish farms and other sources at a bay-wide scale. Aquac. Environ. Interact. 11, 671–684. https://doi.org/10.3354/AEI00340.
Jones, B.L., Cullen-Unsworth, L.C., Unsworth, R.K.F., 2018. Tracking nitrogen source using δ^{15}N reveals human and agricultural drivers of seagrass degradation across the British Isles. Front. Plant Sci. 9 https://doi.org/10.3389/fpls.2018.00133.
Kroeger, K.D., Cole, M.L., York, J.K., Valiela, I., 2006. Nitrogen loads to estuaries from waste water plumes: modelling and isotopic approaches. Ground Water 44, 188–200. https://doi.org/10.1111/j.1745-6584.2005.00130.x.
Kynetec, 2023. The British Survey of Fertiliser Practice: Fertiliser Use on Farm Crops for Crop Year 2022. London.
Lapointe, B.E., Herren, L.W., Debortoli, D.D., Vogel, M.A., 2015. Evidence of sewage-driven eutrophication and harmful algal blooms in Florida's Indian River lagoon. Harmful Algae 43, 82–102. https://doi.org/10.1016/j.hal.2015.01.004.
Lehvo, A., Bäck, S., Kiirikki, M., 2001. Growth of *Fucus vesiculosus* L. (Phaeophyta) in the northern Baltic proper: energy and nitrogen storage in seasonal environment. Botanica Marina 44, 345350.
Lemesle, S., Erraud, A., Mussio, I., Rusig, A.M., Claquin, P., 2016. Dynamics of δ^{15}N isotopic signatures of different intertidal macroalgal species: assessment of bioindicators of N sources in coastal areas. Mar. Pollut. Bull. 110, 470–483. https://doi.org/10.1016/j.marpolbul.2016.06.006.
Levene, H., 1960. Robust Tests for Equality of Variances. Contributions to Probability and Statistics: Essays in Honor of Harold Hotelling, pp. 278–292.
Maier, G., Nimmo-Smith, R.J., Glegg, G.A., Tappin, A.D., Worsfold, P.J., 2009. Estuarine eutrophication in the UK: current incidence and future trends. Aquat. Conserv. 19, 43–56. https://doi.org/10.1002/aqc.982.
Minting, S., 2017. Water Firm Fined £600k over Sewage Sludge Pollution at Staithes. Northern Echo.
Ohte, N., 2013. Tracing sources and pathways of dissolved nitrate in forest and river ecosystems using high-resolution isotopic techniques: a review. Ecol. Res. 28, 749–757. https://doi.org/10.1007/s11284-012-0939-3.
Orlandi, L., Calizza, E., Careddu, G., Carlino, P., Costantini, M.L., Rossi, L., 2017. The effects of nitrogen pollutants on the isotopic signal (δ^{15}N) of *Ulva lactuca*: microcosm experiments. Mar. Pollut. Bull. 115, 429–435. https://doi.org/10.1016/j.marpolbul.2016.12.051.
Piepho, H.-P., 2004. An algorithm for a letter-based representation of all-pairwise comparisons. J. Comput. Graph. Stat. 13, 456–466. https://doi.org/10.1198/1061860043515.
Raimonet, M., Guillou, G., Mornet, F., Richard, P., 2013. Macroalgae δ^{15}N values in well-mixed estuaries: Indicator of anthropogenic nitrogen input or macroalgae metabolism? Estuar. Coast. Shelf Sci. 119, 126–138. https://doi.org/10.1016/j.ecss.2013.01.011.
Riera, P., Stal, L.J., Nieuwenhuize, J., 2000. Heavy δ^{15}N in intertidal benthic algae and invertebrates in the Scheldt estuary (the Netherlands): effect of river nitrogen inputs. Estuar. Coast. Shelf Sci. 51, 365–372. https://doi.org/10.1006/ecss.2000.0684.
Risk, M., Lapointe, B., Sherwood, O., Bedford, B., 2009. The use of δ^{15}N in assessing sewage stress on coral reefs. Mar. Pollut. Bull. 58, 793–802.
Samper-Villarreal, J., 2020. Strengths and challenges of δ^{15}N to identify anthropogenic nutrient loading in coastal systems. Isotopes Environ. Health Stud. 56, 700–712. https://doi.org/10.1080/10256016.2020.1809389.
Savage, C., 2005. Tracing the influence of sewage nitrogen in a coastal ecosystem using stable nitrogen isotopes. AMIBO: Journal of the Human Environment 34, 145–150. https://doi.org/10.1579/0044-7447-34.2.145.
Savage, C., Elmgren, R., 2004. Macroalgal (Fucus vesiculosus) δ^{15}N values trace decrease in sewage influence. Ecol. Appl. 14, 517–526. https://doi.org/10.1890/02-5396.
Smith, V.H., Schindler, D.W., 2009. Eutrophication science: where do we go from here? Trends Ecol. Evol. https://doi.org/10.1016/j.tree.2008.11.009.
Swart, P.K., Evans, S., Capo, T., Altabet, M.A., 2014. The fractionation of nitrogen and oxygen isotopes in macroalgae during the assimilation of nitrate. Biogeosciences 11, 6147–6157. https://doi.org/10.5194/bg-11-6147-2014.
The Rivers Trust, 2022. Sewage in our Rivers [WWW document]. The Rivers Trust. URL. https://theriverstrust.org/sewage-map.
The Rivers Trust, 2024. State of Our Rivers.
Thornber, C.S., DiMilla, P., Nixon, S.W., McKinney, R.A., 2008. Natural and anthropogenic nitrogen uptake by bloom-forming macroalgae. Mar. Pollut. Bull. 56, 261–269. https://doi.org/10.1016/j.marpolbul.2007.10.031.
Titlyanov, E.A., Kiyashko, S.I., Titlyanova, T.V., Van Huyen, P., Yakovleva, I.M., 2011. Identifying nitrogen sources for macroalgal growth in variously polluted coastal areas of southern Vietnam. Bot. Mar. 54, 367–376. https://doi.org/10.1515/BOT.2011.041.
Viana, I.G., Bode, A., 2013. Stable nitrogen isotopes in coastal macroalgae: geographic and anthropogenic variability. Sci. Total Environ. 443, 887–895. https://doi.org/10.1016/j.scitotenv.2012.11.065.
Viana, I.G., Bode, A., Bartholomew, M., Valiela, I., 2015. Experimental assessment of the macroalgae *Ascophyllum nodosum* and *Fucus vesiculosus* for monitoring N sources at different time-scales using stable isotope composition. J. Exp. Mar. Biol. Ecol. 466, 24–33. https://doi.org/10.1016/j.jembe.2015.01.014.
White, N., 2008. Bladder wrack (*Fucus vesiculosus*) Marine Life Information Network Biology and Sensitivity Key Information Reviews [online]. https://doi.org/10.17031/marlinsp.1330.1.
Wurtsbaugh, W.A., Paerl, H.W., Dodds, W.K., 2019. Nutrients, eutrophication and harmful algal blooms along the freshwater to marine continuum. Wiley Interdiscip. Rev. Water 6. https://doi.org/10.1002/WAT2.1373.
Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. Water Res. 43, 1159–1170. https://doi.org/10.1016/j.watres.2008.12.048.
Yorkshire Water, 2023. Yorkshire Water Event Duration Monitoring Dashboard [WWW Document]. URL. https://yorkshirewater.maps.arcgis.com/apps/dashboards/c293a15e5d4d454ebe7c65f2aba35dac (accessed 7.3.23).
Young, E.B., Dring, M.J., Savidge, G., Birkett, D.A., Berges, J.A., 2007. Seasonal variations in nitrate reductase activity and internal N pools in intertidal brown algae are correlated with ambient nitrate concentrations. Plant Cell Environ. 30, 764–774. https://doi.org/10.1111/j.1365-3040.2007.01666.x.
Zhou, X., Zhang, S., Liu, S., Chen, C., Lao, Q., Chen, F., 2024. Thermal fronts in coastal waters regulate phytoplankton blooms via acting as barriers: A case study from western Guangdong, China. J. Hydrol. (Amst.) 636.