Chemosphere 184 (2017) 1175–1185

Contents lists available at ScienceDirect

Chemosphere

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

Translocation of isotopically distinct macroalgae: A route to low-cost biomonitoring?

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HIGHLIGHTS

- *Fucus* sp. can be used to monitor nitrogen pollution in rivers and estuaries.
- Nitrogen isotopes in *Fucus* sp. respond faster to high concentrations of nitrate and ammonia.
- *Fucus* sp. change their $\delta^{15}N$ values within 7 days of being relocated by 50% from the background value.
- Depth position, i.e. 0.2 m or 1 m from surface, of relocated macroalgae respond differently.

ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form
14 June 2017
Accepted 18 June 2017
Available online 19 June 2017

Handling Editor: Keith Maruya

Keywords:
Nitrogen
Isotopes
Pollution
Environmental monitoring
Macroalgae
Seaweed

ABSTRACT

Nitrogen stable isotope ratios ($\delta^{15}N$) in macroalgae are often used to identify sources of nitrogenous pollution in fluvial and estuarine settings. This approach assumes that the macroalgal $\delta^{15}N$ is representative of the sources of the pollution averaged over a timespan in the order of days to weeks. The preferential uptake of a particular nitrogen compound or potential for fractionation in the water column or during uptake and assimilation by the macroalgae could make this assumption invalid. Laboratory studies were therefore performed to investigate the uptake and assimilation of both nitrate and ammonium at a variety of concentrations using the vegetative (non-fertile) tips of the brown macroalgae, *Fucus vesiculosus*. Nitrate appeared to fractionate at high concentrations, and was found to be taken up more rapidly than ammonia; within 13 days, the macroalgae tips were in isotopic equilibrium with the nitrate solution at 500 μM. These experiments were complemented by an investigation involving the translocation of macroalgae collected from a site enriched in ^{15}N relative to natural levels (Staithes, UK), to the River Tees, Middlesbrough (UK), a site depleted in ^{15}N relative to natural levels. The nitrogen isotope signature shifted by ~50% within 7 days, with samples deployed nearer the surface subject to greater change. These findings suggest that the translocation of macroalgae with isotopically distinct signatures can be used as a rapid, cost-efficient method for nitrogen biomonitoring in estuarine environments.

1. Introduction

Stable isotope ratios are an excellent tool to discern, or ascertain, biological, ecological and environmental processes. The modern nitrogen cycle has been heavily influenced by human activity. Waste products, such as sewage and fish farm effluent, are normally more enriched in ^{15}N than seawater (Vizzini and Mazzola, 2004), whereas agricultural waste products are normally more depleted in ^{15}N (Heaton, 1986). This has led to the application of using nitrogen stable isotope ratios ($\delta^{15}N$) of marine sediments, marine organisms and macroalgae to monitor nitrogen pollution/contamination (e.g., McClelland et al., 1997; Savage, 2005).

$\delta^{15}N$ can also be measured in dissolved inorganic nitrogen (DIN: $\delta^{15}N_{DIN}$) taken directly from the water (Deutsch et al., 2006; Korth et al., 2014). Unfortunately, in systems such as estuaries with very complex flow regimes, spot sampling does not always represent the true average concentrations because of high temporal variability; it is also more time-consuming and costly to do isotopic analysis of DIN. To address this difficulty, nitrogen isotope ratios in macroalgal tissues are often utilised to discern sources of excess nutrients (Costanzo et al., 2001, 2005; Savage and Elmgren, 2004; Derse et al., 2007; Dailer et al., 2012).

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http://dx.doi.org/10.1016/j.chemosphere.2017.06.082
0045-6535/

However, this methodology assumes that macroalgal $\delta^{15}N$ values are representative of an integrated $\delta^{15}N$ value of nitrogen inputs over a time period, which implies that the $\delta^{15}N$ values of the source(s) are the sole contributors to the $\delta^{15}N$ of the macroalgae. This does not account for the potential for fractionation during nitrogen transformations in the water column, or in the processes of uptake and assimilation, which can lead to $\delta^{15}N$ values in algal biomass different to that of the ambient nitrogen source (Viana et al., 2011; Swart et al., 2014). Nitrogen uptake by macroalgae is influenced by morphological factors, metabolism, tissue type, age and nutrition (e.g., Rosenberg and Ramus, 1984; Pedersen, 1994; Neori et al., 2004). During this process, nitrogen is transported from the water through the cell membrane and assimilated into organic compounds, such as proteins (McGlathery et al., 1996). Macroalgal $\delta^{15}N$ values are also significantly influenced by the enrichment of ammonium in a river, as originally documented by Minagawa and Wada (1984), and more recently by Savage and Elmgren (2004), Savage (2005) and Viana et al. (2011). To more accurately interpret macroalgae $\delta^{15}N$, a good understanding of the fractionation processes taking place is required (Viana et al., 2011).

It has therefore been suggested that variability in $\delta^{15}N$ due to isotopic fractionation may be an important factor controlling macroalgal tissue $\delta^{15}N$ (e.g., Viana and Bode, 2015; Swart et al., 2014), as macroalgal $\delta^{15}N$ could be modified by environmental parameters such as oxygen concentration, microbe concentration, pH, temperature, light and DIN concentration (Raimonet et al., 2013; Jona-Lasinio et al., 2015). Furthermore, reduced N, as NH_4^+, is preferred to NO_3^- as a nitrogen source by some macroalgal species (Cohen and Fong, 2005), thus the $\delta^{15}N$ of the macroalgae could be strongly influenced by a NH_4^+ signal independent of NO_3^-. Bacterial populations could therefore affect $\delta^{15}N_{DIN}$ (Korth et al., 2014; Ochoa-Izaguirre and Soto-Jiménez, 2015).

Riera (1998) and Riera et al. (2000) reported that *Fucus* from natural (uncontaminated) sites have $\delta^{15}N$ values of around +6‰. Savage and Elmgren (2004) and Savage (2005) reported significant increases in $\delta^{15}N$ (greater than 7‰) from *Fucus* that were impacted by sewage pollution. Notwithstanding the subtle difference between each site, this could be explained simply by background oceanographic factors independent of human activity (Viana and Bode, 2013); thus, every site being investigated should be treated independently. Deutsch and Voss (2006) indicated that *in situ* incubation experiments in an unpolluted brackish location could be suitable as a simple monitoring tool, but their data were inconclusive for *Fucus vesiculosus*. Viana et al. (2011) measured $\delta^{15}N$ in macroalgal tissues in coastal areas between 1990 and 2007 and found a decrease in $\delta^{15}N$ from ~ +8‰ to ~ +5‰, which they related to a reduction in human activities and the level of contamination, and/or other environmental factors.

In the present study, we aim to assess the usefulness of $\delta^{15}N$ in the macroalgae, *Fucus vesiculosus* (hereafter, *Fucus*) as a low-cost, easily deployed biomonitor for nitrogen pollution. We use *Fucus* as it is near ubiquitous in United Kingdom coastal waters, and has been shown to be a species where the isotopic composition of the tissues is linked to that of the environment (e.g. Viana et al., 2015). In the first instance, laboratory incubation experiments of vegetative *Fucus* tips, in the presence of different concentrations of nitrate and ammonia, were undertaken to determine the nitrogen isotope response. In addition, this study involved the novel translocation of vegetative tips of *Fucus* from one site (Staithes, UK) that has an enriched ^{15}N signature, to an industrial site (River Tees, UK) which has a depleted ^{15}N signature. In this case, the nitrogen isotope response of vegetative *Fucus* tips was used to determine whether short-term or long-term field experiments are required to assess nitrogen pollution. The usefulness of $\delta^{15}N$ in macroalgae as a pollution biomonitor has been argued by different authors, but until now, it has not hitherto been proven that translocation of vegetative tips of *Fucus* could be a useful tool for nitrogen monitoring. Therefore, we aim to determine whether the isotopic signal of seaweed can be modified to give a signature significantly shifted from any environment where we may wish to deploy environmental monitoring.

2. Material and methods

2.1. Macroalgae selection

Macroalgae of the genus *Fucus* belong to the brown macroalgae family Phaeophyceae. *Fucus* is commonly found along sheltered shores of the North Sea, Baltic Sea, Atlantic Ocean and Pacific Ocean. *Fucus* is a tethered macroalgae, with a growth rate ranging between 0.05 and 0.80 cm/day and a life span on the order of 3–5 years (Strömgren, 1977; Carlson, 1991). The species is annually episodic, gonochoristic and highly fecund (i.e., prolific). Gametes are released into the seawater and the eggs are fertilized externally to form a zygote that starts to develop as soon as it settles into a substrate. The gametes are released from receptacles found in the fertile tips of the macroalgae. However, *Fucus* also have vegetative tips that do not contain these structures and are composed of a parenchymatous thallus (Hiscock, 1991). The meristematic zones of the vegetative tips of *Fucus* have a significantly greater uptake of nitrogen than in older parts of the macroalgae tissue (Savage and Elmgren, 2004; Viana et al., 2015), and hence vegetative tips of *Fucus vesiculosus* were used in this study.

2.2. Study area

Two sites were chosen for this study: Staithes, North Yorkshire,

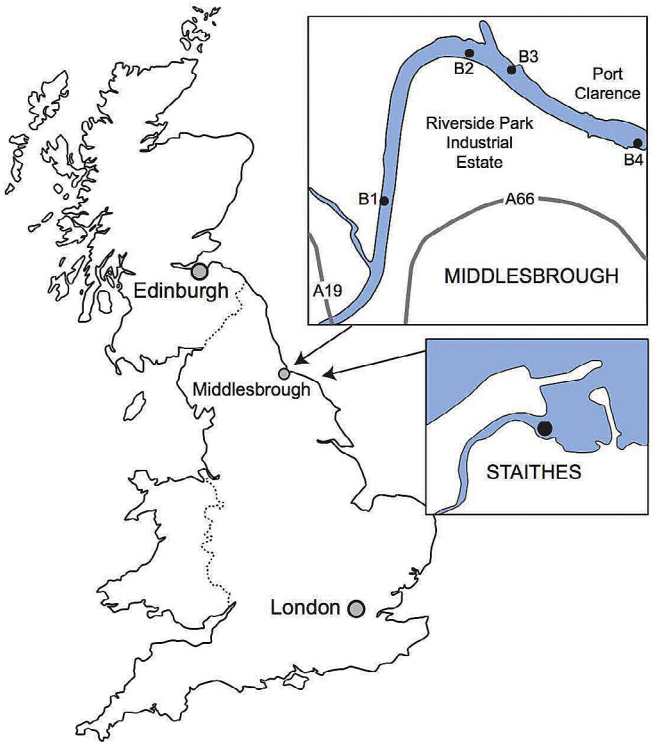

Fig. 1. Part map of the United Kingdom showing the two locations discussed in this study, River Tees, Middlesbrough (top insert), and Staithes, North Yorkshire (bottom insert). Buoy locations are labelled; buoy 1 (B1), buoy 2 (B2), buoy 3 (B3) and buoy 4 (B4). Sample collection of macoralgae from Staithes are represented by the large dot.