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$\delta^{15}N$ and $\delta^{13}C$ in the Mondego estuary food web: Seasonal variation in producers and consumers

Alexandra Baeta [a,*], Rute Pinto [a], Ivan Valiela [b], Pierre Richard [c], Nathalie Niquil [c], João C. Marques [a]

[a] IMAR – Institute of Marine Research, Department of Zoology, University of Coimbra, 3004-517 Coimbra, Portugal
[b] The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543, USA
[c] Centre de Recherche sur les Ecosystèmes Littoraux Anthropisés – UMR6217 CNRS, IFREMER, Université de La Rochelle, Avenue Michel Crépeau 17042 La Rochelle, France

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ABSTRACT

Assessments of temporal variation in stable carbon and nitrogen ratios were used to examine seasonal trends of the water column and benthic food webs in the Mondego estuary (Portugal). There was a marked seasonality in weather and water column conditions, including nutrient supply and chlorophyll concentrations. In spite of the pronounced environmental changes, we found little evidence of seasonal variation in $\delta^{13}C$ and $\delta^{15}N$ of producers and consumers in the Mondego estuary, with a few notable exceptions. Nitrogen isotope ratios in macrophytes (*Zostera noltii*, *Ulva* sp., *Enteromorpha* sp., and *Gracilaria* sp.), and in two grazers (*Idotea chelipes* and *Lekanesphaera levii*) increased during late summer, with the highest $\delta^{15}N$ values being measured in July, during a period of elevated temperatures and drought, which may have favored high rates of denitrification and heavier $\delta^{15}N$ values. The results suggest that stable-isotope values from macrophytes and selected grazers are useful as tracers of seasonal changes in nitrogen inputs into estuaries, and that those of consumers reflect other factors beyond seasonal variations in N and C sources.

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1. Introduction

Increased anthropogenic delivery of nutrients to water bodies, both freshwater and estuarine, has caused detrimental changes in habitat, food web structure, and nutrient cycling (Valiela et al., 1997; Cole et al., 2004). The resulting eutrophication has many adverse effects within the estuaries (D'Avanzo et al., 1996; Hauxwell et al., 2003). Increased N loading can lead to the loss of important estuarine habitats such as seagrass meadows (Hauxwell et al., 2003). Eutrophic estuaries can also suffer from hypoxia and anoxia (Zimmerman and Canuel, 2000), and phytoplankton and macroalgal blooms (Hauxwell et al., 2003).

To better understand management of water quality, it is important to know the sources, as well as the amount of inputs of the nutrient limiting production. In the Mondego estuary, as in most estuarine ecosystems, there is evidence that at least for macroalgal growth, nitrogen is the limiting factor (Teichberg et al., submitted for publication). $\delta^{15}N$ has proven useful as a tracer of the major source of nitrogen entering coastal waters. Joint use of $\delta^{15}N$ and $\delta^{13}C$ has further shown promise as a tool that helps to explain how the external N sources, as well as the C sources, move up into estuarine food webs. Application of these isotopic ratios has largely remained an item of research rather than a management tool (Peterson and Fry, 1987; Cole et al., 2004). The practical utility of stable-isotopic ratios to some degree depends on the relative sensitivity of $\delta^{15}N$ and $\delta^{13}C$ to seasonal variation.

Stable-isotopic N ratios might, in addition, change with increased temperatures as we might find seasonally, but also as might be forced by global atmospheric warming. Microbial processes such as denitrification are strongly affected by temperatures (Valiela, 1995), and higher denitrification could result in notable fractionation of $\delta^{15}N$. This indirect linkage could furnish heavier N that is taken up by producers.

Some studies reported that $\delta^{15}N$ and $\delta^{13}C$ of producers showed seasonal variation (Riera and Richard, 1996, 1997; Fourqurean et al., 1997; Kang et al., 1999; Adin and Riera, 2003; Machás et al., 2003; Riera and Hubas, 2003; Pruell et al., 2006), while others did not (McClelland and Valiela, 1998; Cole et al., 2004). Similarly, some studies showed variation in consumers (Goering et al., 1990; Riera and Richard, 1996, 1997; Buskey et al., 1999; Kang et al., 1999; Carman and Fry, 2002; Kibirige et al., 2002; Moens et al., 2002; Adin and Riera, 2003; Machás et al., 2003; Riera and Hubas, 2003; Vizzini and Mazzola, 2003, 2005), and others did not (Goering et al., 1990). Knowledge of seasonal variation in stable-isotopic ratios is important as a reflection of biogeochemical and ecological processes, as well as in regard to sampling schedules and expected variability for applied monitoring schedules.

In this paper, we examine the seasonal variation in N and C stable-isotopic ratios of producers and consumers within the food

* Corresponding author. Tel.: +351 239 837797; fax: +351 239 823603.
E-mail address: asbaeta@ci.uc.pt (A. Baeta).

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web of the Mondego estuary, and compare the changes in ratios in organisms to the seasonal changes in temperature, precipitation, dissolved nutrients, and in phytoplankton chlorophyll we measured in the Mondego ecosystem. This comparison aims to discern the degree to which seasonally varying driving factors might be manifest in the isotopic ratios of the food web, as well as identify the components of the food web that might be reasonably reliable indicators of changes in nutrient enrichment and warming.

2. Methods

2.1. Study site

The Mondego estuary is a relatively small (1600 ha), warm-temperate, polyhaline, intertidal system located on the Atlantic coast of Portugal, and consists of two arms, north and south (Fig. 1). The southern arm is characterised by large areas of intertidal mudflats (almost 75% of the area) exposed during low tide. The system receives agricultural runoff from 15,000 ha of upstream cultivated land (mainly rice fields) and supports a substantial population, industrial activities, salt-works, and aquaculture farms, and is also the location of the Figueira da Foz city harbour, which constitutes a tourism centre. All these activities have imposed a strong anthropogenic impact. A mixture of inputs from sewage effluent, agricultural runoff, as well as releases from maricultural activity contributes to the nutrient loads entering the Mondego estuary.

In the early 1990s, the southern arm was almost silted up in the upstream areas, causing the river discharge to flow essentially through the northern arm. Consequently, the water circulation in the southern arm became mostly dependent on the tides and on the small freshwater input from a tributary, the Pranto River, artificially controlled by a sluice (Marques et al., 2003). In 1990–1992, the communication between the two arms of the estuary became totally interrupted in the upstream area due to the completion of stonewalls in the northern arm banks. Following this interruption, the ecological conditions in the southern arm suffered a rapid deterioration. The combined effect of an increased water residence time and of nutrient concentrations became major driving forces behind the occurrence of seasonal blooms of *Ulva* sp. and a concomitant severe reduction of the area occupied by *Zostera noltii* beds, previously the richest habitat in terms of productivity and biodiversity (Marques et al., 1997, 2003). The shift in benthic primary producers affected the structure and functioning of the biological communities, and through time such modifications started inducing the emergence of a new selected trophic structure, which has been analysed in abundant literature (e.g. Dolbeth et al., 2003; Cardoso et al., 2004a,b; Patrício et al., 2004).

From 1998 to 2006 several interventions were carried out to ameliorate the condition of the system, namely, by improving water circulation, which was followed by a partial recovery of the area occupied by *Z. noltii* and the cessation of green *Ulva* sp. blooms (Lillebø et al., 2005, 2007).

2.2. Sample collection and preparation

To assess water quality of the Mondego waters, we collected water samples on a monthly basis at two sites (*Zostera* site and bare sediment site; Fig. 1), from November 2005 to July 2006. In a companion paper (Baeta et al., submitted for publication) we established that there were no differences in nutrients or chlorophyll concentrations in samples taken from the two sites, and so here we treat the samples as replicates. In each sample, we measured concentrations of nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}), and the concentration of chlorophyll *a*. Samples

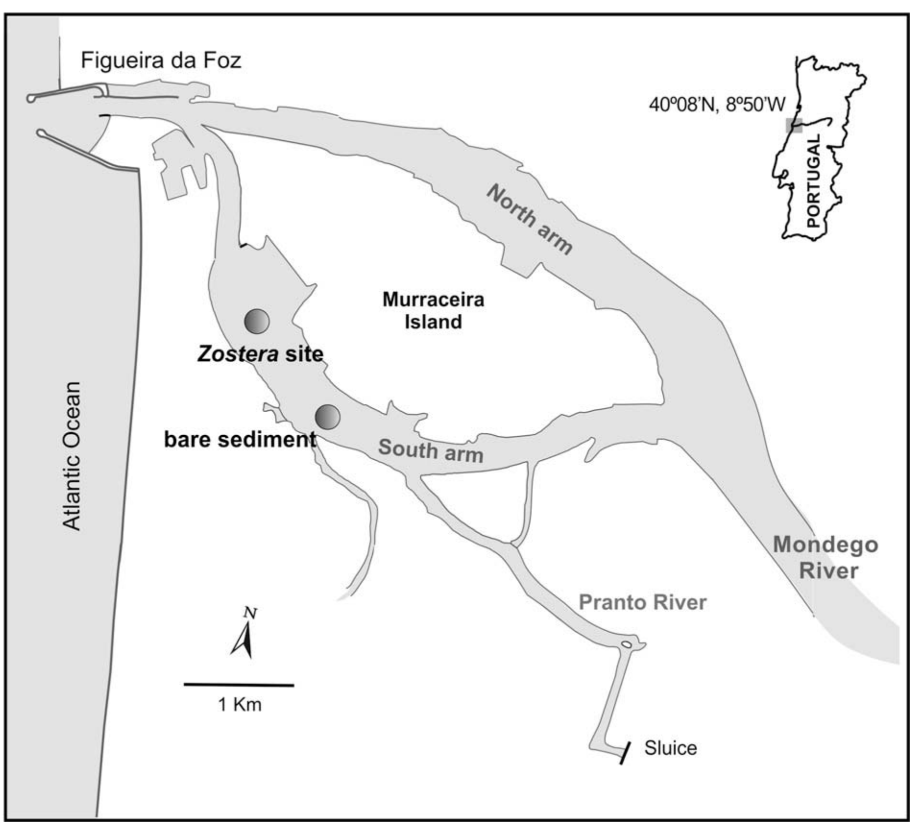

Fig. 1. Mondego estuary map showing sampling sites: *Zostera* and bare sediment sites (grey circles).

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