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Tissue Cu, Fe and Mn concentrations in different-aged and different functional thallus regions of three brown algae from western Ireland

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Abstract

Copper and iron concentrations in three brown algae, *Ascophyllum nodosum*, *Fucus vesiculosus* and *Laminaria digitata* (and additionally Mn in *L. digitata*) from the Irish west coast were determined using flame atomic absorption spectrophotometry. Metal concentrations in the three species were indicative of prevailing bioavailable metal concentrations in situ but varied greatly between functional tissue parts, between sites and over time. Cu concentrations in actively growing tips of *A. nodosum* decreased over a 4-month period during autumn/winter, while Fe concentrations increased. Both Fe and Cu concentrations in different thallus sections of *A. nodosum* and *F. vesiculosus* increased with increasing age of thallus part in a clean site, but there was no consistent trend for *F. vesiculosus* from an industrialized site. Within sites, concentrations of all Cu and Fe were similar in both fucoids, but concentrations at the industrialized site were about twice as high as at the pristine site. In *L. digitata*, all three metals were highest in holdfasts, but had distinctly different distribution patterns in stipes and blade sections, which were most likely related to growth pattern and tissue function. Fe was lowest in meristematic and young blade regions, suggesting small-scale Fe limitation in actively growing tissue. Mn concentrations were higher in distal blade sections than in stipes, and Cu concentrations were highest in meristematic and young thallus parts.

Keywords: *Ascophyllum*; *Fucus*; Ireland; *Laminaria*; metals; Phaeophyta; thallus section

1. Introduction

Several trace metals are required by macroalgae as micronutrients and fulfil essential metabolic functions at low concentrations. Amongst these, copper (Cu) and manganese (Mn) are required for enzyme activation and photosynthetic electron transport, respectively (Falkowski and Raven, 1997). Also, iron (Fe) is involved in photosynthetic electron transport and in nitrogen metabolism, and thus, represents an essential micronutrient for algal growth (e.g. Raven, 1988; Martin and Fitzwater, 1988; Martin et al., 1990; Falkowski and Raven, 1997). However, at high concentrations, these metals can become toxic, e.g. Cu at higher concentrations can inhibit photosynthesis (Overnell, 1976; Gledhill et al., 1997) and restrict the growth of algae (e.g. Steemann Nielsen and Wium-Andersen, 1970; Coelho et al., 2000).

Ionic forms of metals in seawater are controlled by environmental variables such as pH, temperature, ionic strength, salinity, alkalinity, presence of organic and particulate matter, metal complexation, and the chemical characteristics of individual metal species (Rai et al., 1981; Gledhill et al., 1997). Although metals may be

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present in seawater in colloidal and particulate phases at high concentrations, levels of dissolved forms (bio)-available for algal uptake may be low (Suzuki et al., 1995; Gledhill et al., 1997).

Marine macroalgae mostly accumulate metals from the dissolved ionic phase in seawater (Phillips, 1977, 1994). Thus, metal concentrations in seaweed tissue are most likely to reflect the dissolved concentration present in the surrounding seawater, and the use of macroalgae in biomonitoring of metals in the marine environment is well documented (e.g. Bryan and Hummerstone, 1973; Amado Filho et al., 1999; Daka et al., 2003). In particular, brown algae have been considered good indicators of bioavailable metals, due to the high binding capacity of their polysaccharides for divalent metal species (e.g. Haug, 1961; Giusti, 2001).

When applying macroalgae in marine biomonitoring, some problems may arise due to differences in metal accumulation rates by different-aged thallus parts and under different environmental conditions (Phillips, 1977). Only few studies have examined intra-specific or even intra-thallus variation in metal concentrations in situ (Myklestad and Eide, 1978; Munda, 1986; Higgins and Mackey, 1987). Fluctuations in growth rates and metabolic activity between plants collected at different times of the year and from different environments can lead to variation in tissue metal concentrations controlled by factors other than bioavailable concentrations in the seawater. Increased accumulation of metals can occur during slow growth and/or during passive uptake/adsorption (Markham et al., 1980); on the other hand, a dilution of metals accumulated may occur due to high growth rates and fast tissue expansion, resulting in low tissue metal concentrations (Bryan, 1969; Fuge and James, 1973; Villares et al., 2002). However, the accumulation of essential metals is also reported to increase during periods of fast growth (Rice and Lapointe, 1981).

The aims of this study were to assess natural (or anthropogenic) temporal fluctuations and intraspecific variation in concentrations of metals in different tissue parts of three species of brown macroalgae, *Ascophyllum nodosum*, *Fucus vesiculosus* and *Laminaria digitata*, from western Ireland. Cu and Fe concentrations were monitored in apical tips of *A. nodosum* over a 4-month period, and in different-aged thallus sections of *F. vesiculosus* and *A. nodosum*, and Cu, Fe and Mn in different functional thallus parts of *L. digitata*.

2. Materials and methods

2.1. Study sites

Algae were collected from three sites in Galway Bay, western Ireland, Galway Docks in Galway City, Spiddal and Ballyconneely (Fig. 1). 'Galway Docks' (53°16′W; 9°3′N) is a well-developed, industrialised region of Galway City; 'Ballyconneely' (10°2′W; 56°24′N) is a remote site in Connemara characterised by little anthropogenic influence, and 'Spiddal' (9°18′W; 53°15′N) is located 12 km west from Galway City near a village with little heavy industry. Salinity, seawater temperature and pH were determined in situ with a YSI 556mps probe on 14 October 2003 (Ballyconneely: salinity 33.53, pH 7.45, temperature 13.2 °C; Galway Docks: salinity 16.11, pH 8.08, temperature 15.5 °C; Spiddal: salinity 30.25, pH 7.67, temperature 14.0 °C).

2.2. Sample collection and preparation

2.2.1. Temporal variation in Cu and Fe concentrations in tips of Ascophyllum nodosum from Spiddal

Tips of five plants of *Ascophyllum nodosum* Le Jolis (L.) were collected from the centre of its vertical distribution on the shore (to avoid potential effects of shore height on metal concentration; Nickless et al., 1972) at Spiddal fortnightly between 13/10/2003 and 19/2/2004. Three tips from the same plants were placed in a clean polyethylene plastic bag, kept in a cool dark place and, on return to the lab, stored at −20 °C until processing. For analysis, the three tips from each of the five plants were pooled to give one sample ($n = 5$).

2.2.2. Intra-thallus variation in Cu and Fe concentrations in A. nodosum, F. vesiculosus and Laminaria digitata and variation between sites

For *F. vesiculosus* and *A. nodosum*, five whole plants, including the holdfasts, of *A. nodosum* and *Fucus vesiculosus* (Linnaeus) were collected from Ballyconneely (13/10/03) and Galway Docks (14/10/03). Again, all plants were collected from the centre of their vertical distribution on the shore. Plants were placed in individually labelled polyethylene bags, transported to the laboratory and stored as described above until subdividing and further processing.

In *Ascophyllum nodosum*, the main axes were identified and material (excluding laterals) was chosen that exhibited little or no herbivore-induced or physical damage. Thalli were subdivided into sub-samples at the base of air bladders as these represented annual growth segments (David, 1943). In Ballyconneely, plants were generally older and healthier, and 7-year-old thallus segments (3-year-old at Galway Docks) were identified and used for metal analyses.

In *Fucus vesiculosus*, the main axis was identified and thalli were dissected into samples at the base of every second pair of air bladders along the thallus. Again, plants from Ballyconneely were larger and could be subdivided into five regions and the holdfast. Plants from Galway Docks were divided into three subsections and the holdfast.