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Trace element seasonality in marine macroalgae of different functional-form groups

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ABSTRACT

Novel information on the seasonality of element accumulation in seaweeds is provided. Seasonal patterns of As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, U, V and Zn concentrations in macroalgae belonging to different functional-form groups (*Ulva intestinalis, Ulva rigida, Codium fragile, Gracilaria gracilis*) from the Thessaloniki Gulf, Aegean Sea were determined and compared. Uni- and multivariate data analyses were applied. Element concentrations generally decreased during spring and/or summer, probably due to the growth effect, but a reverse trend, particularly in *Ulva* species, was also observed. Most elements (Cd, Co, Cr, Cu, Mo, Ni, Pb, Sr) in *Ulva* species displayed a comparatively low monthly variability, indicating that the extent of seasonal variation is closely related to thallus morphology and growth strategy. In particular, these data suggest that Cd, Co, Cr, Cu, Mo, Ni, Pb and Sr contents in fast-growing, sheet-like macroalgae are less influenced by the season, compared to their contents in coarsely-branched and thickleathery macroalgae; therefore, sheet-like macroalgae may be more appropriate to be used in biomonitoring of coastal waters. The data presented could be utilized in the development of biomonitoring programmes for the protection of coastal environments.

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1. Introduction

The accumulation of trace elements by certain organisms has been demonstrated to be useful in the assessment of trace element contamination in coastal environments; in particular, two groups of organisms, namely seaweeds and filter-feeding mollusks, have been considered to be especially valuable in biomonitoring studies. Seaweeds, which primarily accumulate elements from solution, have been widely employed in field studies of trace element contamination at various coastal areas (Phillips, 1994). Especially, over the last two decades, both the number of seaweed species used as biomonitors and the trace elements involved in the analyses have been markedly expanded (e.g. Malea and Kevrekidis, 2014; Pérez et al., 2007; Rodriguez-Castañeda et al., 2006). In addition, new evidence suggests that the accumulation of some elements such as As and Sr is closely related to species phylogeny, while that of several other elements to thallus morphology and growth strategy, irrespective of phylogenetic relationships (Malea and Kevrekidis, 2014; Stengel et al., 2004).

monitoring data, to avoid misleading conclusions. Information on seasonal variation in trace element contents in seaweeds is more available for a small number of trace elements,

variations in growth rates, high growth rates in the warmer months

of the year serving to dilute the accumulated elements and reduce

their concentrations (e.g. Phillips, 1994; Villares et al., 2002).

Thereby, the potential influence of growth rates on tissue element

concentrations should be seriously considered in the design of biomonitoring programmes and the interpretation of bio-

Trace element concentrations in seaweed tissues appear to be influenced by season. This tissue element seasonality is due to environmental factors, metabolic factors or interactions between both kinds of factors; variations in ambient element concentrations, in interactions between elements, in growth rates, in the production and release into the environment of organic substances by seaweeds having the capacity to bind dissolved elements and other factors may contribute to this seasonal variation (e.g. Vasconcelos and Leal, 2001; Villares et al., 2002). Seasonal patterns in fluvial inputs and terrestrial inputs (e.g. run-off from the land, wastewater discharges), leading to changes in bioavailable element loads in the seawater/sediment, have been suggested to markedly influence tissue element seasonality (e.g. Villares et al., 2002). However, tissue element seasonality (as the transmitted to the tissue element seasonality (as the transmitted to the transmitted to the tissue element seasonality (as the table terms terms terms the table terms terms terms the table terms terms

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mainly Zn, Cu, Cd, Pb and seaweed species of a few genera, particularly Ulva; data for other elements including Mn, Ni, Co and Cr are less frequent, while data for several elements of environmental importance, such as As, Ba, Mo, Se, Sr, U and V, are scarce or missing (e.g. Akcali and Kucuksezgin, 2011; Burdon-Jones et al., 1982: Malea and Haritonidis, 1999, 2000: Riget et al., 1995: Villares et al., 2002). In addition, comparative data on the extent of tissue element variation with season and, evenmore, data on the critical component in interspecific variation as for this extent are lacking. Logically, the extent of the seasonal variation would be expected to be closely related to species growth strategy, in particular to be higher in fast-growing sheet-like and filamentous macroalgae than in seaweeds of the remaining functional-form groups, as proposed by Littler et al. (1983). Such information could be of major importance for the design of biomonitoring programmes, as it could allow the identification of species and, evenmore, groups of species, the use of which as biomonitors is less influenced by season.

The present study aims to provide novel information on seasonality of trace element accumulation in marine macroalgae. The patterns of monthly variation in concentrations of a wide set of elements (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, U, V and Zn) in four widespread and abundantly available seaweed species, belonging to the sheet group (Ulva intestinalis, Ulva rigida), the coarsely-branched group (Codium fragile) and the thick-leathery group (Gracilaria gracilis), from the Gulf of Thessaloniki, Northern Aegean Sea, in the Mediterranean Sea, were determined and compared. The relation of tissue element seasonality with (a) environmental variables closely related to fluvial and terrestrial inputs (salinity), (b) seawater and sediment element concentrations, and (c) environmental variables closely associated with seaweed growth (water temperature, solar irradiance), was also investigated. According to those mentioned earlier, we predict that (1) trace element concentrations in seaweeds will generally display a seasonal pattern, mainly characterized by a decrease in element loads during spring and/or summer with increasing water



Fig. 2. Monthly variation in water temperature (°C) and salinity (psu) at station V and in mean monthly total solar irradiance (kWh m^{-2}) in the wider area. The occurrence of seaweed species at station V during the sampling period is also indicated by horizontal lines.

temperature and solar irradiance, (2) relatively lower salinity values will be concurrent with markedly elevated element loads in seawater/sediment and seaweed tissues and (3) trace element concentrations in sheet-like macroalgae will display a wider seasonal variation, compared to their concentrations in coarsely-branched and thick-leathery macroalgae.

2. Materials and methods

2.1. Study area

Thermaikos Gulf is a water mass located in the northwestern Aegean Sea at $40^{\circ}30'N$ and $22^{\circ}55'E$ (Fig. 1). To the north, the Gulf



Fig. 1. Geographical location of the study site and map of the Gulf of Thessaloniki indicating the sampling station V.

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