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Trace element patterns in marine macroalgae

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HIGHLIGHTS

- Trace element patterns in several seaweed species were determined and compared.
- Element accumulation is closely related to species morphology and growth strategy.
- Filamentous algae showed the highest concentrations and CFs for several elements.
- As and Sr accumulation is largely related to species biochemical composition.
- As and Sr concentrations and CFs were the highest in brown seaweeds.

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ABSTRACT

Novel information on interspecific variation in trace element accumulation in seaweeds is provided. Concentrations and concentration factors (CFs) of a wide set of elements (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, U, V and Zn) in 26 dominant macroalgae from the Gulf of Thessaloniki, Aegean Sea were determined and compared. Uni-and multivariate data analyses were applied. Phaeophyceae showed higher concentrations and CFs of As and Sr than Rhodophyta and Chlorophyta, indicating that the accumulation of these elements is closely related to species biochemical composition. Filamentous macroalgae displayed higher concentrations and CFs of several elements, particularly Cd, Co, Cr, Cu, Mn and V than sheet-like, coarsely-branched and/or thick-leathery macroalgae, irrespective of phylogenetic relationships, indicating that the accumulation of several elements is largely related to thallus morphology and growth strategy. On a species basis, *Cystoseira* spp. showed both the highest concentrations and CFs of As, *Padina pavonica* of Sr and U, *Ceramium* spp. of Mn, *Ceramium* and *Cladophora* species of Co and Cu, *Cladophora prolifera* of Cr and *Polysiphonia deusta* and *Ulva clathrata* of Cd. Se concentration in *Ulva rigida* correlated positively with seawater Se concentration, and As concentration in this species with sediment As concentration. Thereby, these seaweeds could be regarded as potential biomonitors for the respective elements. A literature review was performed and global element concentrations and CFs were presented for seaweeds from genera collected during this survey. The data presented can contribute to the interpretation of biomonitoring data and the design of biomonitoring programs for the protection and management of coastal environments.

1. Introduction

In the monitoring of coastal environmental quality, emphasis has been placed on the use of selected biological species, termed biomonitors, as it allows the evaluation of biological available levels of trace elements in the ecosystem. Biomonitors should have several desirable characteristics, most importantly to be strong net accumulators of trace elements and to reflect their ambient bioavailabilities (e.g. Rainbow, 2006). Marine macroalgae have been considered excellent biomonitors of the bioavailable trace element in seawater, as they accumulate elements from solution several times their levels of surrounding seawater and meet many of the other desirable characteristics of an ideal biomonitor (e.g. Rainbow, 2006).

Numerous studies, generally in situ, have been carried out concerning trace element accumulation in seaweeds. However, data are more available for species of a few genera, such as *Ulva* and a small number of elements, mainly Cd, Cu, Cr, Mn, Ni, Pb and Zn (e.g. Haritonidis and Malea, 1999; Malea and Haritonidis, 1999; Villares et al., 2002; Żbikowski et al., 2007). References concerning widespread and abundantly available macroalgae, for instance species of the genus *Hypnea* (see Bouzon et al., 2012), that could potentially be used as biominitors, are scarce

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(as for *Hypnea* species see Karez et al., 1994; Sánchez-Rodríguez et al., 2001; Schintu et al., 2010). Less frequently reported elements in macroalgae include As and Co, while published data about elements that have also gained special interest for their adverse effects, such as Ba, Mo, Se, Sr, U and V (e.g. Bonanno, 2011) are sparse (e.g. Sánchez-Rodríguez et al., 2001; Rodríguez-Castañeda et al., 2006; Gaudry et al., 2007; Farias et al., 2007; Pérez et al., 2007). Thereby, considering that accumulation rates are trace element- and seaweed species-specific (Wang and Dei, 1999; Baumann et al., 2009), research needs to be extended to several elements and seaweed species for which data are scarce or missing.

Interspecific variation in trace element concentrations in seaweeds has usually been attributed to species phylogeny, which determines the biochemical composition (van den Hoek et al., 1995) and, thus, the availability of binding sites for elements (Stengel et al., 2004); however, no consistent trends of higher or lower levels of different elements have been reported across several field studies for certain taxonomic groups (Phaeophyceae, Rhodophyta, Chlorophyta) (e.g. Sánchez-Rodríguez et al., 2001; Rodríguez-Castañeda et al., 2006; Strezov and Nonova, 2009). On the other hand, Stengel et al. (2004) noted that the functional-form model by Littler et al. (1983), which holds that physiological processes of macroalgae are related to form characteristics, largely applies to Zn accumulation, with sheet-like and filamentous macroalgae accumulating higher element amounts than coarsely-branched, thick-leathery and calcareous macroalgae. Results of a laboratory study (Baumann et al., 2009), concerning Cd, Cr, Cu, Pb and Zn accumulations in several seaweeds belonging to different taxonomic and functional-form groups, were to some extent in agreement with the findings of Stengel et al. (2004), as accumulation was highest in sheet-type seaweeds but lowest in a filamentous species. However, earlier laboratory studies have not shown any consistent trends for representatives of certain taxonomic or functional-form groups to accumulate higher or lower amounts of elements (e.g. Amado Filho et al., 1997; Wang and Dei, 1999). Therefore, more knowledge and understanding of interspecific variation in trace element accumulation in seaweeds are needed.

The present study aims to provide novel information on the accumulation of trace elements in seaweeds. The patterns of concentrations of a wide set of elements (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, U, V and Zn) in twenty six dominant seaweed species from the Gulf of Thessaloniki, Northern Aegean Sea, the Mediterranean Sea were determined and compared; element concentrations in seawater and sediments were also determined and concentration factors based on seaweed to seawater element concentrations were additionally calculated and compared. Our data could reveal seaweed species with the strongest accumulation of particular elements and, thus, allow the identification of potential cosmopolitan biomonitors for several elements. Our data could also provide evidence for the critical component in interspecific variation in trace element accumulation in seaweeds; such information could allow the comparison of levels of element contamination over large geographical areas using similar species.

2. Materials and methods

2.1. Study area

Thermaikos Gulf is a water mass located in northwestern Aegean Sea (Fig. 1). The rivers Axios, Aliakmon, Loudias, Galikos flow into the Gulf. To the north, the Thermaikos Gulf becomes narrow and continues into the Gulf of Thessaloniki, on the northern coast of which the city of Thessaloniki is located. In the Gulf of Thessaloniki currents have a cyclonic direction (Ganoulis and Krestenitis, 1982). The Thessaloniki Gulf receives industrial, partially treated domestic and agricultural effluents (Christophoridis et al., 2009). In particular, effluents from food industries, leather tanning, chrome painting, petrochemical distilleries and electrolytic manganese dioxide factories are being discharged in the northwestern part of the Gulf. The harbor of Thessaloniki is widely used by cargo ships.

The Kalochori area (K) is situated near the industrial area, the harbor and the pump room of the main wastewater treatment plant of Thessaloniki. The Viamyl area (V) receives local effluents of a small wastewater treatment plant and a small starch treatment factory, direct urban discharges and freshwater inputs from a stream (Anthemoundas stream); this area has been considered as a polluted one. Agia Triada (A) is located relatively far from the harbor facilities and industrial activities; however, high metal levels have been detected in this area probably due to the transport of industrial seawage by sea currents (e.g. Haritonidis and Malea, 1995). At these areas, water temperature, salinity and pH near the bottom varied between 10.4 and 26.8 °C, 34.1 and 37.0 psu and 7.64 and 9.4, respectively during March, June, September and December 2007.

2.2. Sample collection and sample pretreatment

Samples of the dominant seaweed species were collected in the Gulf of Thessaloniki in March, June, September and December 2007 at three sampling stations considered to be contaminated (Kalochori, K, 40° 36′ N and 22° 51′ E, Viamyl, V, 40° 33′ N and 22° 58′ E, Agia Triada, A, 40° 30′ N and 22° 52′ E; Fig. 1). Each time, several seaweeds (entire thalli) within each species, and three samples of seawater and surface sediments were randomly collected from each station. The seaweeds were collected by hand wearing plastic gloves directly from the substrate; algal samples were washed in seawater at the sampling site and placed in plastic bags; seawater samples were then acidified (1.5 mL L^{-1} conc. HNO_3). Samples were taken seasonally from different stations in order for the number of collected seaweed species to be increased and the magnitude of seasonal intraspecific variation in comparison to that of interspecific variation to be assessed.

In the laboratory, seaweeds were identified to the lowest possible taxon. Seawater samples, sediment samples and algal samples of the same species collected from a common sampling date and station were pooled, offering a normalization option towards spatial variability within the sampling station. Seawater samples were filtered through an acid-washed grass-fiber (0.45 μm). Algal samples were washed in distilled water and any epiphyte and sediments were carefully removed with nylon brushes. All samples were then frozen (−20 °C) until analysis.

Sixty-three seaweed samples comprising 26 different species, 12 seawater samples and 11 sediment samples were analyzed. After being dried to a constant weight (60 °C), sediment samples were sieved through a nylon net with a mesh of 63 μm; the <63 μm sediment fraction (silt and clay) was used in the procedures that followed (e.g. Dassenakis et al., 1995). Algal samples were freeze-dried to constant weight and ground in an agate mill. Three sub-samples of each powdered algal and sediment sample were wet digested with $HNO_3/HClO_4$ (4/1); this mixture of oxidizing acids has been frequently used in previous studies for the digestion of marine macrophytes and the corresponding sediment samples (e.g. Brix and Lyngby, 1983; Tiller et al., 1989; Malea and Haritonidis, 2000; Storelli et al., 2001). As for these sediment samples, the moderate acidic extractants like 1 M HCL have been commonly used (e.g. Richir et al., 2013); the use of the oxidizing acids allows us to obtain also element fractions that can be dissolved under oxidative conditions.

2.3. Analytical procedures

Total As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, U, V and Zn concentrations in sediments and seaweeds were determined with an X-series inductively coupled plasma-mass spectrometer (ICP-MS; Thermo Fischer Scientific, Winsford, UK) and concentrations of dissolved