On Background Levels of Heavy Metals in Agarophytes of the Black Sea

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Abstract—Ecological standards for commercial seaweeds are very important due to anthropogenic pollution of the marine sublittoral. The content of heavy metals in agarophyte red algae, seawater, and sediments are investigated by the method of atomic absorption spectroscopy. The level of Cd, Pb, and Ni in Gelidium verrucosa was low, while the level of Zn, Pb, and Nu was comparatively higher in Gelidium latifolium and Phyllophora nervosa, especially in the Caucasus nearshore zone. There is no relationship between the concentration of metals in the environment and the concentration of metals in agarophytes. Background levels of dangerous metals are discussed in connection with commercial exploitation of red algae.

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The problem of ecological standards of commercial hydrobionts is becoming very urgent due to increasing anthropogenic pollution of marine coastal ecosystems. First of all, this is true of benthic algae owing to their high capacity for concentration of heavy metals, including toxic ones—lead, cadmium, and nickel. Therefore, determination of background levels of these metals in agar-containing red algae and in potential objects of mariculture is highly important.

In the Black Sea, over 130 species of red algae are present. Among them there are potential sources of phycocolloids: Gelidium latifolium (Grev.) Born. et Thur., Gelidium crinale (Turn.) Lamour., Gracilaria verrucosa (Huds.) Parenf., Phyllophora nervosa (DC.) Grev., Laurencia obtusa (Huds.) Lamour, etc. Agar and carrageenans are the most valuable products of processing of red algae. Isolated from different algae, they significantly differ in chemical properties. High-quality agar used in the microbiological industry is obtained from algae of the genus Gelidium (Santos, 1980). Up to the present, carrageenans are isolated from over more than 80 species of red algae. The principal types are represented by the forms β-, κ-, λ- and Ω-carrageenans. Depending on the growth stage of algae and technology of their processing, different types of carrageenans may be obtained (Abbott and Chapman, 1981; Mollion et al., 1988). Recently, in production of agar and carrageenans, the mariculture of agarophyte red algae is used, as a higher content of heavy metals significantly changes physicochemical properties of phycocolloids and decreases their capacity of gel formation (Hansen et al., 1981; Kapkov et al., 1987).

In the present study, the content of heavy metals was determined in thalli of principal agarophytes in the sublittoral zone of the northeastern area of the sea. This information may make a basis for elaboration of ecological standards of the content of toxic metals in commercial algae of the Black Sea.

MATERIAL AND METHODS

The algae for analyses were selected in the near-shore zone of the northeastern coast of the sea. The algae were identified using the key by A.D. Zinova (1967). The samples were prepared by the method of wet combustion by means of the “Digestor System.” The weight of 0.5–1.0 g was treated with concentrated HNO₃ and 30% H₂O₂, by the following scheme: 20 min at 30°, 5 h at 75°, and 30 min at 150°. Then the samples were filtered through an ash-free filter and the volume of the samples was made up to 10 ml.

Water for analyses was taken from the surface and at the bottom with a 5-l plastic water bottle. Samples of water were consecutively filtered through membrane filters with different pore size with a final filter of 0.23 μm and fixed with HNO₃ until a final concentration of the acid 0.5% by volume. The samples were stored in plastic vessels preliminarily washed with 25% HCl. Metals were extracted from water with solution of 0.01 M hexamethylenammonium hexamethyl dithiocarbminate in methyl isobutyl ketone in 4 N acetate buffer at pH 6.0. Samples of sediment were taken using a corer with teflon tubes to avoid contact of the ground with metal parts of the device. The core (ca 10 cm) was divided into parts, separated the silt component, dried, and made up to constant weight at 105°. Metals were extracted from sediment by the modified method of consecutive fractionation (Ageman and Chan, 1977; Kapkov and Trichina, 1990).

The content of metals was determined by the AAC method in devices “Perkin Elmer” (Model 403) and “Hitachi” (Model 207) using CRM standards for calibration (Kapkov and Kartitsev, 1998).
RESULTS AND DISCUSSION

The seasonal dynamics of concentrations of heavy metals in water, sediment, and thallome of *Gracilaria verrucosa* in the sublittoral zone of the northeastern areas of the Black Sea is shown in Fig. 1. The content of cadmium and lead in water of the sublittoral zone is characterized by a double-peak curve with spring and autumn maximums of concentrations, and that of nickel—with summer and winter, respectively. The highest content of these metals in the thallome of *Gracilaria* occurs in September when this tropical–boreal alga grows intensively. It follows from these results that in this period the peaks of the investigated metals in water and in the thallome of this alga coincide.

![Fig. 1. The dynamics of concentrations of heavy metals in water, sediments, and thallome of *Gracilaria verrucosa* in the sublittoral zone of the northeastern areas of the Black Sea: (1) concentration of metal in sediments (µg/g dry weight); (2) content of metal in thallome of the alga (µg/g dry weight); (3) concentration of metal in water (µg/l).](image-url)