

ABSTRACT

The main objective of the PhD thesis was to assess heavy metal/oligoelement contamination of the surface sediments and bivalve molluscs (mussels) *Mytilus galloprovincialis* from the Romanian Black Sea area in 2018-2019. Determination of elemental concentrations in marine sediments and mussels, relevant indicators of marine environmental quality, assessment of their contamination status, factors controlling contaminant distribution and potential sources of contamination are essential for the development/improvement of pollution control strategies.

Surface sediments were collected during the multidisciplinary research cruise with the *RV Mare Nigrum*, which took place in August-September 2018 and August-September 2019. Concentration values of the analyzed elements (As, Cr, Cu, Hg, Ni, Pb and Zn) in surface sediments (0-2 cm depth) collected from 34 stations located at water depths between 12.7 m and 149 m were in the following ranges: 3.4-57.1 mg/kg for As, 26.3-114.0 mg/kg for Cr, 6.9-62.9 mg/kg for Cu, 0.02-0.45 mg/kg for Hg, 15.0-118.0 mg/kg for Ni, 11.4-50.8 mg/kg for Pb and 28.0-135.0 mg/kg for Zn.

PCA and correlation analysis results revealed that As, Cu, Ni, Hg, Pb and Zn were associated with finer carriers (i.e., clay, silt and organic matter), suggesting that these elements originate mainly from Danube discharges contaminated with various effluents, but also from local anthropogenic sources (e.g., port and construction activities, coastal tourism, petrochemical industry, wastewater discharges, offshore oil/gas extraction), and Al and Cr come from rock/soil erosion. The indices used to assess the degree of contamination of surface sediments, i.e., enrichment factor (EF), contamination factor (CF) and geo-accumulation index (I_{geo}), generally indicated natural levels of the analyzed element concentrations.

The values of concentrations of some heavy metals (Cd, Co and Hg) in the soft tissue of *M. galloprovincialis* mussels (related to the dry mass of the mussel without shell) collected from 5 sampling stations in the northern part of the Romanian shelf (St. Gheorghe area), located at water depths in the range 43.2-54.2 m, during a research cruise on board *RV Mare Nigrum* (May 2019), ranged between the following limits: 1.69-5.37 mg/kg for Cd, 0.72-3.00 mg/kg for Co and 0.06-0.12 mg/kg for Hg.

The Cd concentration values exceeded the limit set by the European Commission Regulation (No 1881/2006), i.e. 1 mg/kg. The PCA showed a discrimination between molluscs

samples collected from shallow stations (43.2 m), characterized by higher Cd, Co and Hg concentrations, and samples collected from deeper stations (49.4-54.2 m), characterized by lower heavy metal concentrations. Also, the strong direct correlation ($r = 0.84$) between Cd and Co concentrations suggests common sources for these 2 heavy metals.

Values of some heavy metals/oligoelements concentrations (As, Br, Cu, Hg, Se and Zn) in the soft tissue of *M galloprovincialis* mussels, manually collected with the help of a team of professional divers from an artificial rocky substrate in the southern part of the Romanian Channel (Port of Agigea area) during February-June 2019, were as follows: 9.22-19.3 mg/kg for As, 124-309 mg/kg for Br, 7.32-15.5 mg/kg for Cu, 0.01-0.07 mg/kg for Hg, 1.71-5.92 mg/kg for Se and 118-241 mg/kg for Zn. The values for As, Cu, Hg and Zn are within the ranges reported for mussels from low/moderate pollution areas. There is very little information in the literature on Br and Se accumulation in mussels from the Black Sea.

According to length, mussels have been classified into the following classes: A (3-5.9 cm), B (6-8.9 cm) and C (9-12 cm). Higher element concentrations were generally determined for mussels in classes A and B compared to larger mussels in class C. Element concentrations, seawater properties, i.e., temperature (4-24°C), salinity (10.4-19 PSU), pH (8.20-8.40), chlorophyll a concentration (0.1-6 mg/m³) and dissolved oxygen concentration (289-357 mmol/m³), meat yield index (34.1-69.5%) were the variables for the PCA. Multivariate statistical analysis suggested the following relevant aspects: (i) phytoplankton was an important source of As and Br for the smaller mussels collected in February (when temperature levels were lower and pH and water salinity higher) compared to the higher mussels collected in June; (ii) Cu, Se, Zn and Br came from similar sources (e.g., port activities, wastewater discharges) and the higher concentrations of these reported in February and June were obtained at lower water salinity levels (corresponding to higher Danube flows).

The information provided in the thesis may be useful for complementing existing data on heavy metal/oligoelement pollution of sediments and mussels in the Black Sea, for developing new pollution control strategies and/or improving existing strategies. The research undertaken so far can be continued/developed in future studies on the assessment of contamination/pollution of the aquatic ecosystem (sediment, water and different food chain species) with heavy metals/oligoelements/radionuclides and organic compounds.