Bioaccumulation of heavy metals in marine organisms from the Romanian sector of the Black Sea

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The aim of this research was to study the accumulation of heavy metals (cadmium – Cd, lead – Pb, chromium – Cr, nickel – Ni, and copper – Cu) from water and sediments into living tissues of relevant marine species from different trophic levels of a food web, representative for shallow waters of the Romanian Black Sea Coast where the main anthropogenic impacts exist. The heavy metals concentrations were analysed by using an Atomic Absorption Spectrometer with graphite furnace, the results being further used to calculate the bioconcentration factors for a few key taxa like green and red algae, molluscs and fishes.

Seven sampling sites influenced by anthropogenic pollution sources (municipal wastewater treatment plants and diffuse sources) were considered and a total of 300 samples were analysed for the period 2011–2012, this being the first unitary study for the Romanian Black Sea marine ecosystem.

In 2011 and 2012 there were no significant differences between the sampling areas considering the heavy metals concentrations in water. For the sediments significant differences were observed between sampling sites for some heavy metals, namely Pb in 2011 and Pb, Cu and Cd in 2012, the highest concentrations being registered in the southern sector of the Romanian Black Sea shore, where the anthropogenic pollution sources are represented by the harbour and wastewater treatment plants. The values of the bioaccumulation factors (BCF_{sed}) shows that algae are good accumulators for Cu > Pb > Ni > Cr > Cd, in comparison with BCF_{water} where the order of heavy metal accumulation was different: Cr > Ni > Pb > Cd > Cu. Molluscs have higher bioconcentration factors for Cu and Cd for sediments and for Cu and Ni for water. *Rapana venosa* accumulated more Cd and Cu. For fishes, Pb, Cu and Ni had the highest values in the tissues of benthonic species *Mullus barbatus*. In bivalve molluscs and fishes, in the majority of cases, there were not recorded exceeding mean concentrations as compared to the maximum allowed concentrations for Cd and Pb.

Introduction

During the last two centuries the freshwater and marine environments faced severe threats from human activities such as: extensive mining, industry and agriculture development [1–3]. The contamination of aquatic ecosystems with nutrients (synthetic) organic compounds and heavy metals and their consequences on human health and biodiversity conservation are important topics of debate among environmental scientists. More generally, the organic pollution does affect marine key taxa like benthic invertebrates and fish, affecting the marine ecosystems

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by changing the population structure of dominant taxa and the replacement of sensitive species to pollution with more ubiquitous organisms.

The heavy metals represent the major type of pollutants in the marine environment because they easily can be assimilated and accumulated in the living tissues and food webs. The bioaccumulation and biomagnification of heavy metals in aquatic food webs not only threatens directly the biodiversity, but sometimes may impact humans as well, as proven by the well documented Minamata case, where humans were directly exposed to the harmful effects of mercury after consuming tainted fish [4–6].

The main thrust of ecotoxicology is to assess fates and impacts of pollutants that are inadvertently released into the environment, their bio-accumulation along food webs being related to the fact that the living organisms absorb the toxic substances at a rate greater than that at which these compounds are eliminated due to metabolic activities. Modern risk assessment procedures compare directly the concentrations of harmful substances in water and in the tissues of concern. It is already widely accepted nowadays that sub-lethal concentrations pose more serious threats for species, individuals and ecosystem and not necessarily the lethal dosage, formerly accepted in toxicological studies as the main threshold of concern [7]. In the European Union, any chemical with a wet mass bioconcentration factor $BCF_w > 100$ is considered to be potentially accumulation in consumers and is therefore considered as being deleterious for aquatic biota and food webs.

Heavy metals are found everywhere in the environment (water, air, soil) as results of human activities such as: transportation, industrial activities, agriculture, urbanization, etc. Marine and freshwater concentrate the greatest amount of heavy metals in the atmosphere and soil due to the water cycle that favors the transport of sediments and their disposal. For example, the concentration of heavy metals in a river increases several thousand times because of its tributaries that 'carry' different pollutants from diffuse or point-source pollution. In the aquatic environment there are many factors that influence heavy metal accumulation in living organisms, these factors acting differently, depending on the species and type of metal, for example: pH, various organic compounds, the humic substrate, complex particles, the presence or absence of other metals, anions, various ionic bonds, temperature, salinity, light intensity, the redox potential and dissolved oxygen concentrations [7].

The main anthropogenic pressures identified on the Romanian Black Sea coast are caused by the accelerated development of various social-economic activities like tourism and recreation, harbours and shipping activities, refining and petrochemical industries, construction sites, as well as by the municipal/industrial wastewater treatment plants that discharge insufficiently treated effluents.

The aim of this research was to study the accumulation of heavy metals from water and sediment into living tissues of relevant marine species from different trophic levels of a food web representative for shallow waters of the Romanian Black Sea Coast. These coastal ecosystems are directly threatened by a diverse array of pollutants, generated by the municipal wastewater treatment plant effluents and diffuse sources. The heavy metals concentrations analysed in this study (Cd, Pb, Cr, Ni, and Cu) were used to calculate the bioconcentration factors for a few key taxa like green algae: (*Ulva* spp. Linnaeus, *1753*); red algae: (*Ceramium* spp. Blume, 1827); molluscs: (*Mytilus galloprovincialis* Lamarck, 1819, *Rapana venosa* Valenciennes, 1846) and fish: (*Atherina boyeri* Risso, 1810; *Alosa pontica* Eichwald, 1838; *Sprattus sprattus* Lineaus, 1758, *Mullus barbatus* Linnaeus, 1758).

Thus, this study contributes to a better characterization of the Romanian Black Sea coast from an integrated point of view referring to the pollution with heavy metals at different compartment levels (water, sediment, biota) and makes possible comparisons with other studies in the Black Sea area.

Materials and methodology

Sampling sites

The Black Sea is an inland sea due to its geographical location having as neighbouring countries: Bulgaria, Georgia, Romania, Russia, Turkey and Ukraine. Its physical and chemical structure is determined by the hydrological balance, but also influenced by pollution and coastal degradation that affected the environmental state of the Black Sea by decreasing its biodiversity [8,9]. The human impacts upon the Black Sea basin caused changes in the physical, chemical and biological water quality parameters and accelerated its eutrophication (due to nitrogen and phosphorous compounds). The Danube River and the rest of its tributaries represent also important pollution sources [10,11]. Suspended solids, nutrients, heavy metals, detergents, hydrocarbons and organic micropollutants originating from municipal/industrial wastewater treatment plants and other major industrial operators represent important point sources of pollution for the Romanian coast of the Black Sea.

The latest studies on heavy metal impacts in the Black Sea were realised for the Turkish Black Sea coast: for water [8,12,13], sediments [13–15], biota: fishes [2,16,17] and molluscs [13,18]. This is the first study to evaluate the transfer factor between sediment and biota for the Romanian Black Sea coast.

Seven representative sampling sites, marked with S_1–S_7, were chosen during this survey (presented in Fig. 1). This sites were

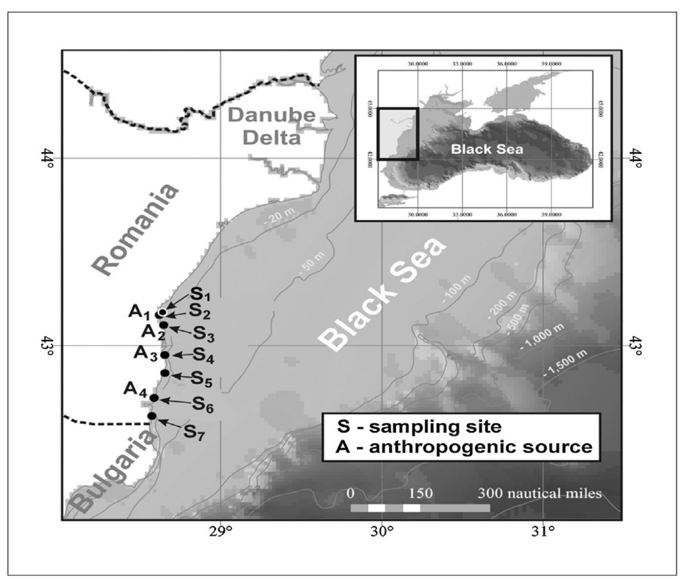

FIGURE 1

Map of the sampling sites.