CORRELATION PROFILE BETWEEN TRACE METALS IN SEDIMENT AND PHYSICOCHEMICAL PARAMETERS OF SEAWATER ON THE MONTENEGRIN COAST

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Abstract
Quality of the water was monitored by analyzing both physicochemical parameters in water (temperature, salinity, DO, pH and nutrient content) and trace metals (Cr, Cu, Pb, Ni, Fe, Mn, Zn and Hg) in sediment on the Montenegrin coast, during fall 2018. Another aim of the study was to find out whether any relationship existed between heavy metals concentration and physicochemical parameters by the calculation of correlation factors among them. Water and sediment samples were collected at 3 stations along the Montenegrin coast. Based on the obtained data we can conclude that significant amounts of trace metals are deposed in Montenegrin sediments and that there is a significant positive correlation among certain metals, as well as between some metals in sediment and physicochemical parameters of the water.

Keywords: Coastal waters, Sediments, Trace elements, Adriatic Sea

Introduction
Contamination of the natural environment with trace metals is a global problem. Trace elements from natural and anthropogenic sources continually enter the aquatic ecosystem where they pose a serious threat due to their toxicity, long-term stability and bioaccumulation [1]. Trace metals can be released from sediments into water above through natural or anthropogenic processes, causing potential danger to the ecosystem. Hydrographic medium conditions such as pH, oxidation state and redox potential [2] significantly affect metal solubility. The pH value of water [3] affects the metal toxicity in several ways, while the initial specificity and bioavailability of the metal may vary between the pH values of 4-8 [4]. In general, trace metal bioavailability and toxicity are dependent on temperature, dissolved oxygen concentration, salinity, conductivity and pH.

Material and Methods
The sediment samples were collected at three different sites along the Montenegrin coastline during the autumn of 2018 as it is shown in Figure 1. The sites Port of Kotor and Port of Tivat in the semi-enclosed Boka Kotorska Bay, as well as the site Port of Bar on the coastline of open sea, are situated in the proximity of different geochemical, hydrological and human impacts.

Fig. 1. Map of investigated area

Collected sediment samples were homogenized, frozen at -18 °C, freeze-dried at -40 °C for 48 h (CHRIST, Alpha 2-4 LD plus, Germany), ground to a fine powder and sieved through a less than 63 µm stainless steel mesh wire, for trace element analysis. The mineralized samples were analysed for Cr, Ni, Fe, Cu, Mn, Pb, Zn by flame-furnace atomic absorption spectrometer (Shimadzu AA 7000, F-AAS), while Hg content was measured following a CV-AAS procedure, by using Shimadzu Hydride System coupled to the atomic absorption spectrometer. The applied methods for the trace metal determination are specified in the Laboratory Procedure Book, IAEA (International Atomic Energy Agency), Marine Environment Laboratory, Monaco 2009. The basic hydrographic parameters were collected using the multiparameter probe and CT data loggers. Nutrient contents were measured by UV/VIS spectrophotometer (Analytik Jena Specord 250 Plus).

Results and Discussion
During sediment collection the depth waters had temperatures of 19.4-21.9°C, pH of 8.1-8.21, salinity of 28.8-38.4 PSU and DO concentrations of 6.36-7.01 mg/L.The nutrients had a maximum data of 0.72 µg/l NO_2^-, 3.69 µg/l NO_3^-, 0,43 µg/l PO_4^- and 0.95 µg/l NH_4^+. The maximum measured metal concentrations were 267 mg/kg Cr, 57.12 mg/kg Cu, 38130 mg/kg Fe, 742 mg/kg Mn, 172 mg/kg Ni, 58.8 mg/kg Pb, 183 mg/kg Zn and 4.52 mg/kg Hg. The metal distribution in sediments follows the order: Fe > Mn > Cr > Zn > Ni > Cu > Hg. Based on the data obtained we can see a correlation between the physicochemical parameters (pH and salinity) of water with metal concentrations. This is important for our study since pH and salinity are the vital factors in metal solubility and control metal speciation and thus their distribution within dissolved fractions [5]. The Cu, Fe and Hg concentrations in sediment were positively correlated with water pH ($r = 0.83$; $r = 0.89$, $r = 0.98$, $p < 0.05$). Salinity also influences the solubility of Mn and Zn ($r = 0.955$, $p < 0.05$ for Mn and $r = 0.808$, $p < 0.05$ for Zn). The present study shows that certain trace metals in sediments were significantly correlated. Very high positive correlations ($p < 0.05$) in the sediments were found for Fe with Cu, Ni with Cr, Cu and Fe, Pb with Cr, Cu, Ni, Hg with Cu and Hg with Fe.

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Trace metals in seawater can exist in a variety of physical and chemical forms. The simplest physical distinction is particulate versus dissolved forms. This is somewhat of an operational denition with 0.4 mm or 0.2 mm pore size lters generally providing this separation.Â Bruland et al. (1978b) reported the rst accurate zinc distribution in seawater and demon-strated its strong correlation with silicic acid. Subsequently, Bruland (1980), Bruland and Franks (1983), Martin et al. (1989, 1993), Morley et al. A total of 90 water and sediment samples were collected simultaneously in triplicate at 30 sampling stations. Selected metals were analyzed using ICP-MS, and the metalsâ€™ concentration varied among stations.Â Heavy metals are not only regarded as natural trace components of the aquatic environment but are also commonly known as environmental pollutants particularly receiving input from anthropogenic activities.Â Most of these studies were focused on the total metal content in sediments, organisms, plants, and fresh water bodies in order to have a better understanding on the ecotoxicological potential of heavy metals [19â€“21]. The relationship between environmental factors and the analyzed groups of parameters (MEs and TEs) in water was determined by principal component analysis (PCA) with multiple scaling. Two environmental variables were applied during the analysis. The first environmental variable is a type of water in which rivers and lakes were distinguished, while the other is the influence of hydrological characteristics in the river-lake ecosystem on tributaries, the runoff, and the lake. The PCA was preceded by detrended component analysis (DCA).Â Cluster analysis showed high variability in the content of TEs. Fig. 2. Dendrogram showing clustering of sampling sites on the basis of TE concentrations in water a) and bottom sediments b). 2332. Siepak M., et al. Fig. A correlation between the metal levels found in the mussel soft tissues Mussels with those found in sediments, for both 2005 and 2006, could be established, except for the levels of Zn South East Adriatic Sea observed. Montenegro Ã“ 2011 Elsevier Ltd. All rights reserved. 1. Introduction these mussels could be exposed to sub-lethal or even lethal levels of specific toxins.Â Collection of mussel and sediment samples and industrial effluents, as well as domestic and agricultural wastes, all of which contain various hazardous chemicals and can The mussel M. galloprovincialis and sediment samples were col- cause deleterious effects on aquatic organisms. metal source between lithogenic and naturally occurring. In this study we. used Fe to compute EF because it is the fourth major element in the earth's. crust and most often has no contamination concern. The Geoaccumulation. Index (Igeo) was calculated to determine metals in sediment of Montenegrin. coast. This expression was proposed by M?ller (1997) in order to calculate.Â Join ResearchGate to discover and stay up-to-date with the latest research from leading experts in Sediments and many other scientific topics. Join for free.