Ecotoxic Trace Metals in Waters of "Mljet" National Park - Croatia

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Abstract

Spatial and temporal distribution of five ecotoxic trace metals (Cd, Cu, Pb, Zn and Hg) in waters of the "Mljet" National park during two years period (2005 - 2006), was studied. Obtained concentrations of Cd, Cu, Pb and Zn are presented as dissolved and total fractions and mercury as total. Measurements of Cd, Cu, Pb and Zn concentration levels were performed by differential pulse anodic stripping voltammetry (DPASV), while total mercury by cold vapour atomic absorption spectrometry (CVAAS). Both methods enable measurements of extremely low trace metal concentrations ($< 10^{-8}$ mol L^{-1}) present in unpolluted waters of the Republic of Croatia.

Results suggest complex behaviour of different trace metal species investigated particularly in water columns of saline lakes "Veliko jezero" and "Malo jezero", two main water bodies in the NP "Mljet".

Introduction

Protected natural areas, particularly National parks, are very sensitive ecosystems because of their substantial uniqueness which should be preserved in their original form. Elevated trace metals concentration levels in such vulnerable systems could be an indicator for possible anthropogenic influence and potential risk in natural environment. Therefore, it is very important to assess actual ecotoxic trace metals concentration levels. Systematic survey (periodic, field/laboratory) is necessary to distinguish elevated trace metals concentrations naturally present in aquatic environment from the anthropogenic influence.

The "Mljet" National park was established in 1960 and represents the first institutionalized attempt to protect an original ecosystem in the Adriatic. Two saline lakes are a unique geological and oceanographic phenomenon of the worldwide importance. They originated approximately 10 000 years ago and, until the Christian era, they were freshwater lakes. Lakes of Mljet consist of the lake "Veliko jezero" covering an area of 1.45 km^2, with a maximum depth of 46 m, while lake "Malo jezero" has an area of 0.24 km^2 and a maximum depth of 29 m (Durbešić et al. 1995), indicating their isolated character and reduced mixing with the open water.

Trace metals are important elements in the biogeochemistry of natural systems. They occur naturally but are potential contaminants because human activities influence their levels in the aquatic environment. Many trace metals are required micronutrients for present organisms. At very low concentrations or availability, plants and animals may show nutrient deficiencies of certain trace metals (Simkiss and Taylor, 1989). Anthropogenic activities, such as mining, fossil fuel combustion, industrial processes, agriculture or tourism, have greatly altered the biogeochemical cycles of trace metals and enhanced their bioavailability (Garrels et al. 1975). At elevated concentrations or availability, certain trace metals may be toxic, and can have damaging effects on organisms (e.g. Cd, Cr, Cu, Hg, Ni, Pb, Se, etc.). As well as direct effects on the aquatic life one should also be aware that any possible contamination of the aquatic environment could possibly enter into the human food chain and have significant impact on human life.

Trace metals investigations have not been achieved in aquatorium of the "Mljet" NP until this research. In presented paper, spatial and temporal distribution of five ecotoxic trace metals (Cd, Cu, Pb, Zn and Hg) in the aquatic environment of the "Mljet" National park was presented.

Methods and Instrumentation

Water samples for determination of Cu, Cd, Pb and Zn were collected in pre-cleaned high density polyethylene bottles (HDPE) with a volume of 1 L and samples for Hg in pre-cleaned SIMAX Sklárny Kavalier borosilicate glass reagent bottles (Sázava, Czech Republic) with a volume of 1 L, all by scuba diving (Kniewald et al. 1987). Salinity was determined by the Atago refractometer S-10E (Tokyo, Japan), while pH and redox potential were determined by the Mettler Toledo MP 120 (Schwerzenbach, Switzerland). Water temperature was measured *in situ* with the alcohol thermometer.

Total Cu, Cd, Pb and Zn concentrations were measured in unfiltered samples while their dissolved fractions were measured in filtered samples (0.45 μm membrane acetate filters under nitrogen pressure). Prior to analysis, unfiltered samples for measuring Cu, Cd, Pb, Zn and Hg total concentrations and filtered samples for measuring Cu, Cd, Pb and Zn dissolved concentrations were acidified with extra clean nitric acid (Merck, Darmstadt, Germany) at pH < 2 and UV treated during 24 hours in order to digest organic matter (150 W Hg lamp).

Cu, Cd, Pb and Zn concentration measurements were performed on the ECO Chemie μAUTOLAB multimode potentiostat (Utrecht, The Netherlands) connected with a three-electrode system Metrohm 663 VA STAND (Herissau, Switzerland). Electrochemical method used (Branica, 1990; Bard and Faulkner, 2001) was differential pulse anodic stripping voltammetry (DPASV). Method detection limit in seawater samples was in the range of 1 do 10 ng/L, depending on metal. Total Hg was measured by cold vapour atomic absorption spectrometry (CVAAS) with detection limit 0.015 ng/L (Kwokal and Branica, 2000).

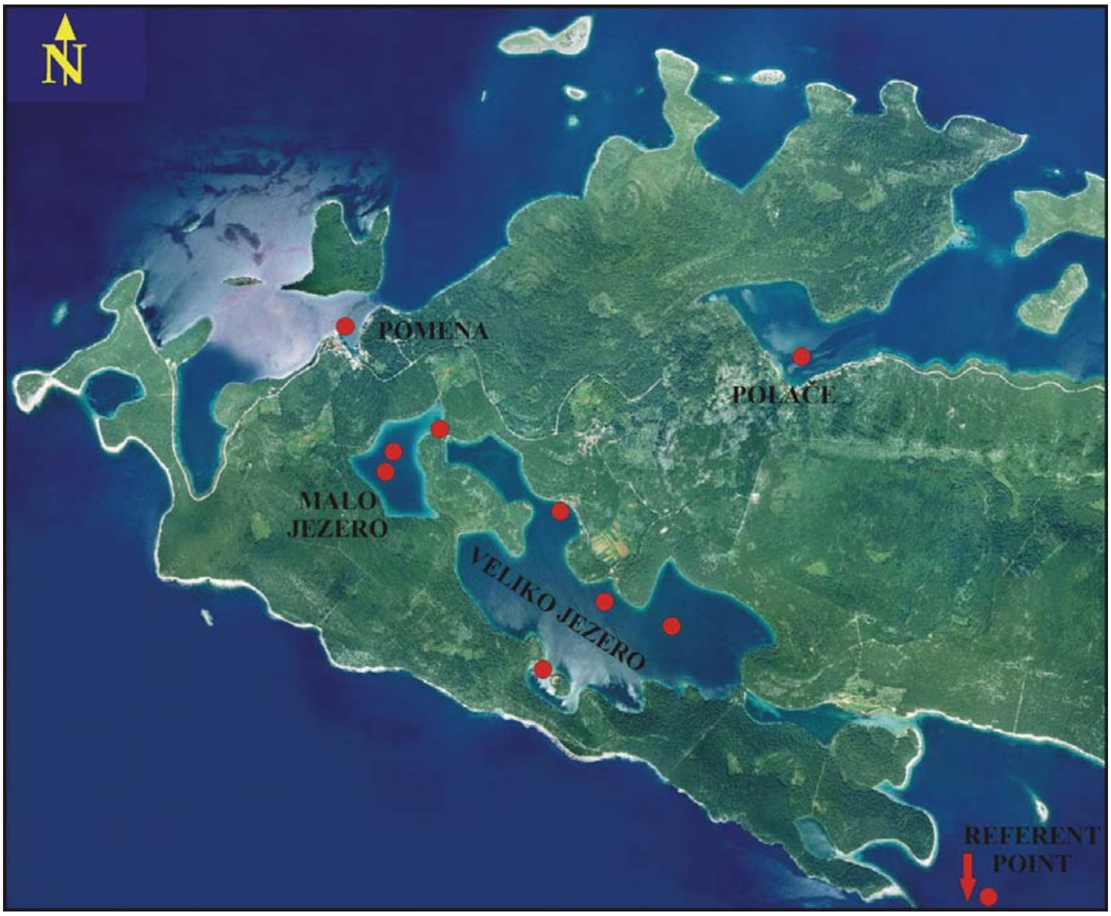

Fig. 1 Sampling locations in "Mljet" National Park

Sampling locations shown in figure 1 were determined by GPS instrument Garmin GPSMap 72 (Kansas City, USA) with an accuracy of ± 5 m, while sampling depths were determined by the dive computer Uwatec Aladin Pro (Henggart, Switzerland) with a depth accuracy of ± 5 cm. Referent sampling point is positioned at open sea, while two ports Polače and Pomena were also selected for better assessment and comparison of data.

Results and discussion

During 2005 and 2006, measurements show different behaviour of metallic species in water columns of the Mljet aquatorium. Generally, metal concentrations are higher in saline lakes comparing to the referent sampling point about kilometre south from the island and those found in two ports Polače and Pomena. This is due to the lakes isolated character and reduced mixing with open water. Anthropogenic influence is considered but it is not much probable because there is a lack of industrial and sophisticated agricultural activity, as well as mass tourism, although those should not be completely rejected from observation.

During mid July in 2005, highest metals concentrations in bottom water layer of both saline lakes in “Mljet” NP were detected. During March and June in 2006 highest concentrations, particularly Cu, Hg and Pb were detected in the middle layers of the water column. This behaviour is probably related with natural processes in the water column, such as enhanced precipitation of aragonite, calcium carbonate mineral present in both saline lakes, which is characteristic process for mentioned periods (Juračić et al. 1998; Sondi et al. 1995). One can assume that trace metals are adsorbed on the aragonite and migrate down through the water column.

During these two years, amounts of lead show significant difference between total and dissolved fractions. In both saline lakes, only about 50% of present Pb exists in dissolved fraction, implicating strong Pb affinity for sorption processes onto various particles of inorganic and organic origin dispersed in the water column. In other surface water samples (referent point, ports Polače and Pomena) difference is less significant, i.e. above 80% Pb is dissolved, so these waters contain less dispersed particles than water in two lakes.

Other trace metals (Cd, Cu and Zn) are mainly fractionated as dissolved species throughout all aquatorium, showing their poorer sorption ability than Pb. However, differences between total and dissolved fraction are pronounced in July of 2005, probably as a result of higher anthropogenic input from the tourism activity.

In 2005, Pb total concentrations in all samples exceed 100 ng/L in bottom water layers (nearly 700 ng/L in July) of both lakes. According to the Croatian National Regulative considering these Pb concentrations, waters in the Mljet National Park aquatorium are within class II (100 ng/L < total Pb < 2000 ng/L), where “*concentrations are not significantly above natural level*” (W.C.D. 1998). Hg total concentration levels show similar behaviour where total concentration in bottom layer of the Lake Malo jezero was 5.3 ng/L (July 2005) and in the bottom layer of the Veliko jezero was 7.2 ng/L (November 2005). Considering these total Hg concentration values, water is also in the class II: (5 ng/L < total Hg < 20 ng/L). In 2006, total Pb concentrations in all samples exceed 100 ng/L as well as in the middle and in the bottom layers of both lakes (class II). Total mercury concentrations in the Lake Malo jezero reached extreme values above 20 ng/L (March, 2006: 24.2 and 33.7 ng/L in the surface and the middle layer, respectively). Considering these total Hg concentrations, waters are in the class III (20 ng/L < total Hg < 100 ng/L), where: “*concentrations are below constant toxic level*”.

Achieved results undoubtedly confirm high vulnerability of the Mljet National Park aquatorium. Elevated Pb and Hg total concentrations in the water column of two saline lakes are above naturally present in unpolluted, open seawater (usually class I, “*no anthropogenic metal pollution*”) (W.C.D. 1998). However, these enhanced values are not result of anthropogenic input. Isolated character of the saline lakes and their reduced mixing with open waters favour trace metals accumulation caused by natural processes, such as sorption onto various inorganic and organic particles present in the water column. These processes extend retaining of trace metals in the water column.

Generally, before implementation of the Nature Protection Regulatives, it is very important to assess authentic conditions in the specific area. Regular monitoring on the field and in laboratory is necessary to observe changes in trace metals levels naturally present in the unpolluted aquatic environment.

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