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Marine lake as *in situ* laboratory for studies of organic matter influence on speciation and distribution of trace metals

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ABSTRACT

Karst marine lakes are unique marine systems, also recognized as *in situ* "laboratories" in which geochemical processes on a different scale compared to the open sea, can be observed. In this study, organic matter cycle and its impact on distribution of trace metals in the marine lake Mir, located on Dugi Otok Island, in the central part of the eastern Adriatic Sea, was investigated for the first time. Studied marine lake is small, isolated, shallow basin, with limited communication with the open sea. Intense spatial and seasonal variations of organic matter, dissolved and particulate (DOC, POC), and dissolved trace metals concentrations in the water column of the Lake are governed predominantly by natural processes. Enhanced oxygen consumption in the Lake during summer season, high DOC and POC concentrations and low redox potential result in occasional occurrence of anoxic conditions in the bottom layers with appearance of sulfur species. Speciation modeling showed that dissolved trace metals Cu, Pb and Zn, are mostly bound to organic matter, while Cd, Co and Ni are present predominantly as free ions and inorganic complexes. Trace metals removal from the water column and their retention in the sediment was found to depend on the nature of the relationship between specific metal and organic or inorganic phases, sulfides, Fe-oxyhydroxydes or biogenic calcite. The above is reflected in the composition of the sediments, which are, in addition to influence of karstic background and bathymetry of the basin, significantly affected by accumulation of detritus at the bottom of the Lake.

1. Introduction

Marine lakes represent a peculiarity of karstic coast. Formed by flooding of karst depression and hidden inland, they are characterized by poor water exchange with the sea, low tidal amplitudes, and temperature extremes, stratification of the water column and occurrences of hypoxia/anoxia in the bottom layer. All these features combined with their isolated character differentiate marine lakes in geochemical as well as biochemical terms in comparison to adjacent sea. Approximately 200 marine lakes are documented worldwide so far (Hamner et al., 1982; Burnett et al., 1989; Landing et al., 1991; Orem et al., 1991; Bates et al., 1993; Lyons et al., 1996; Hamner and Hamner, 1998; Cerrano et al., 2006; Colin, 2009 and references therein). Listed literature mainly deals with biological aspects of marine lakes, while comprehensive geochemical studies of such systems, especially on distribution of trace metals and organic matter, are scarce.

Among all the various pollutants, dangerous to fragile and isolated marine environments, heavy metals are the most toxic (Radix et al., 2000), persistent and abundant substances, prone to accumulation as well as resistant to biodegradation. In lacustrine sediments heavy metals can be of both natural as well as anthropogenic origin. Once introduced into the aquatic environment, metals are redistributed throughout the water column, deposited or accumulated in sediments and consumed by biota (Fichet et al., 1998). Compared to metals, organic matter has a more dynamic cycle due to seasonal changes, and is influenced by contribution via wet deposition and surrounding soil. Nevertheless, in small isolated waterbody, eg. marine lake, biogeochemical reactions affecting the specified metal and organic matter distribution take place on an entirely different scale compared to the sea. Accordingly, these and similar systems can serve as natural "laboratories", i.e. environments in which interactions between metal and organic matter can be studied under conditions almost like in a closed box model.

Specific conditions are required to form a marine lake and therefore they represent unique and fragile marine environments. Knowledge on the distribution of trace metals and organic matter in water column and sediment of such systems is prerequisite for better understanding of the ongoing biogeochemical processes ensuring their sustainability and protection. This paper describes geochemical processes that affect the distribution of trace

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elements and organic matter in closed marine lake (Lake Mir, Croatia). This is the first comprehensive biogeochemical study of Lake Mir and a starting point for a number of future studies.

2. Study area

Marine lake Mir is situated in the south-eastern part of the Dugi Otok Island, in the central part of the eastern Adriatic coast (43°53′12″N, 15°10′E), in a narrow area between Telašćica Bay and the open sea (Fig. 1). It was formed after the last ice age as flooded karst depression due to sea level rise. In 1998 Lake Mir with nearby Telašćica Bay was proclaimed Nature Park. Lake exhibits small water level changes throughout the year. Only in the south-eastern part of the lake, the sea tends to spill over into the lake during the storm. The shores of the lake are mostly low and rocky, while the lake bottom is rocky in shallow parts and covered with fine grain sediment in deeper. The deepest regions are covered with pellet mud, and during phytoplankton blooms these sediments are overlaid with aggregates (Žic et al., 2012).

3. Experimental

3.1. Sampling sites

Sampling locations include Lake Mir and Telašćica Bay (Fig. 1). Sediment samples were collected at 35 sites, including 33 surface sediments and two sediment cores, while at 11 of these sites surface and bottom waters (including one spring, M2) were also sampled. Soil samples were collected at 7 sites. Sediment and soil sampling coordinates are given in Supplement 1, while water sampling locations are indicated in Fig. 1. Sampling campaigns were conducted in the period from 2010–2013, including all four seasons; late winter (rainy season), spring, summer and beginning of the autumn. Sampling site coordinates were identified by GPS (GPS Map 76 CSx, Garmin Ltd, Kansas City, MO, USA) with an accuracy of ±5 m. Depth values were measured at all 35 sediment sampling locations using an Uwatec Aladin Teac 2 dive computer (Henggart, Switzerland), with a depth accuracy of ±5 cm.

3.2. Sampling and analytical techniques

3.2.1. Sediment and soil samples

Sediments were sampled by scuba diving using network sampling. Two sediment cores were sampled (L32 and L33). Each sediment core was divided into 2 cm slices (marked as L32/*x* and L33/*x*, where $x=1$ is the surface sediment slice). Soil samples were collected from the surface around the Lake. Sediment and soil samples were lyophilized, homogenized using an agate mill, and stored until digestion. Aliquots of selected sediment samples were stored separately, prior to lyophilization, and refrigerated before grain size and organic matter analysis.

3.2.1.1. Major and trace element analysis. All sediment and soil samples were analyzed for total concentration of 18 elements (Al, As, Ba, Ca, Cd, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, P, Pb, S and Zn). Selected set of sediment samples, ten from Lake Mir and one from Telašćica Bay, was further analyzed for additional parameters: sediment grain size distribution, carbonate content and total organic carbon (TOC). Selection was based on the results of the element data from all 35 locations, encompassing the entire surface of the lake and at the same time reflecting its heterogeneity.

Multielemental analysis of sediments and soils was performed using a Perkin-Elmer SCIEX ELAN 6100 ICP-MS (Inductively Coupled Plasma Mass Spectrometry) instrument. Phosphorus and

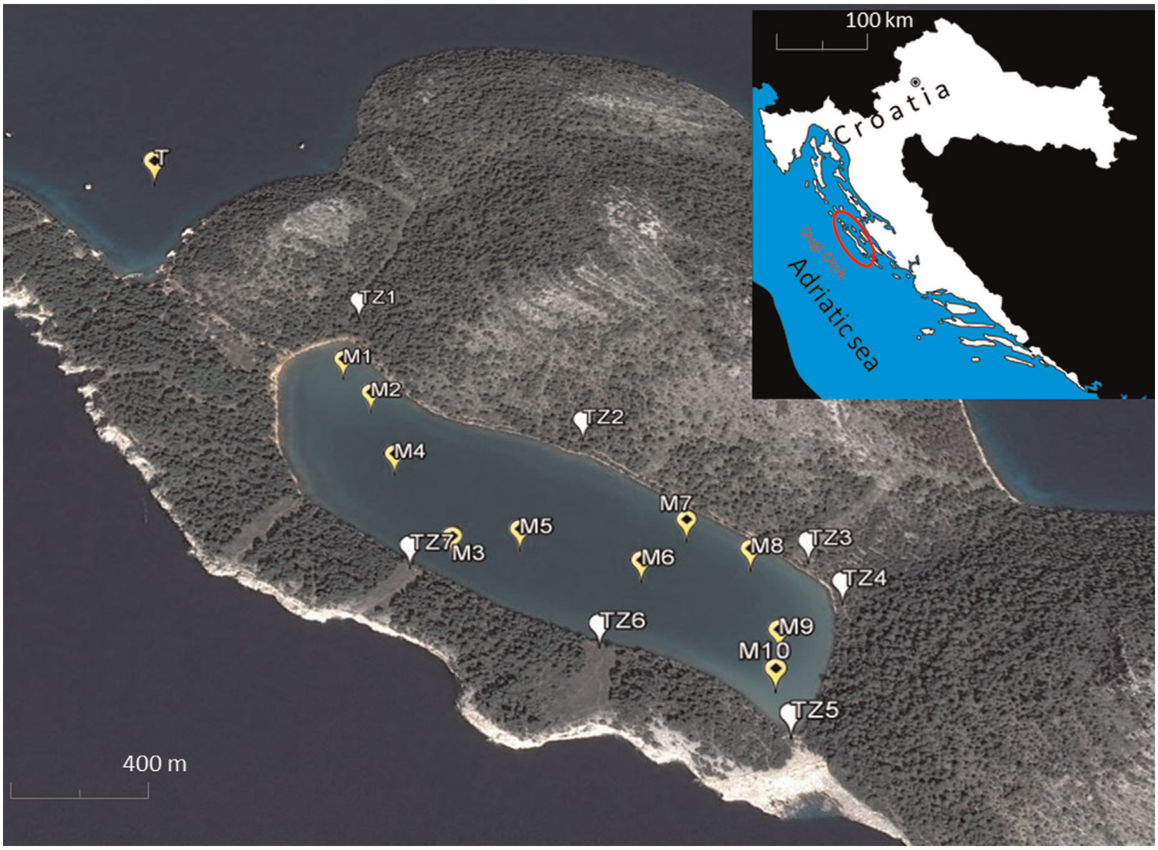

Fig. 1. Map of water sampling sites in Telašćica Nature Park.