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Natural causes of changes in marine environment: Mercury speciation and distribution in anchialine caves

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ABSTRACT

Mercury speciation and distribution were assessed, for the first time, from the water, sediment, rock, soil and air of anchialine caves. We evaluated the origin and distribution of four mercury species (total (THg), reactive (RHg), dissolved gaseous mercury (DGM) and monomethylmercury (MeHg)) in water from Bjejajka cave (Bjejajka) and Lenga Pit (Lenga) in the Croatian Adriatic Sea from 2006 to 2011.

Concentrations of all mercury species were elevated at both sites compared to adjacent seawater, which had concentration range of 0.5–2.4 ng L^{-1} for THg, 0.06–0.2 ng L^{-1} for RHg, 0.02–0.07 ng L^{-1} for DGM, and 0.01–0.02 ng L^{-1} for MeHg. In Bjejajka, the maximum THg concentration (350 ng L^{-1}) in the middle layer (3–7 m) of the 12 m deep stratified water column was up to 3 orders of magnitude greater than in adjacent seawater. During and after the rainy sampling periods in January 2009 and 2010, mixing of Bjejajka water column resulted in elevated concentrations, up to 3700 ng L^{-1} of THg (4 orders of magnitude higher compared to values in nearby seawater) in the bottom water layer. MeHg concentrations in the Bjejajka water column were also considerably elevated (0.7–6.3 ng L^{-1}) compared to the surrounding seawater (0.01–0.02 ng L^{-1}). The vertical distribution of MeHg concentrations followed that of THg, however the ratio of MeHg/THg above the Bjejajka halocline was drastically higher (up to 57%) compared to MeHg proportion (1–2 %) below the halocline, which was similar to that of surface seawater. In sediment of Bjejajka, THg concentrations were up to 3.3 mg kg^{-1}, considerably above concentrations in unpolluted Adriatic marine sediment (0.1–0.3 mg kg^{-1}). The highest THg amounts found in soil and air were inside and in close proximity to Bjejajka, while THg in rock ($\leq$0.01 mg kg^{-1}) were below reported values for unaltered carbonates.

Laboratory experiments indicate that bat guano was the major source of elevated mercury concentrations in the water column and sediment of Bjejajka. Concentrations of THg in bat guano were up to 0.45 mg kg^{-1}, above the range of THg concentrations found in unpolluted marine sediment. Seventy-two days after the addition of bat guano in solution, a 100-fold higher Hg concentration was observed, from 2.5 up to 252 ng L^{-1}. In Lenga bat guano was not spotted and THg water and sediment concentrations were drastically lower, mostly below 7 ng L^{-1} and 0.8 mg kg^{-1}, respectively.

1. Introduction

Anchialine environments, such as caves, pits, sinkholes and caverns, exist in many parts of the world. They have been recognized as significant aquatic environments for at least three decades (Iliffe et al., 1984). The importance of anchialine systems is due to their specific dual characteristics: highly stratified water column (estuarine like), with fresh and/or brackish water layers on the top of saline water, and connected with the open sea, usually through the karstificated carbonate rock. Usually, around the halocline is a pH minimum zone, and the increased acidity accelerates the dissolution of limestone often resulting in cave passages at this depth (Iliffe and Bishop, 2007). On the other hand, the anchialine environment features characteristics of the deep ocean (darkness, reduced water exchange, hypoxia/anoxia). Therefore, in anchialine systems, marine as well as terrestrial influences are frequently encountered. These intriguing features of the anchialine systems have motivated biological and ecological investigations worldwide (Iliffe et al., 1984; Pohlman et al., 1997; Humphreys, 1999; Kršinić, 2005; Bishop et al., 2012; Gottstein et al., 2012; Humphreys et al., 2012). However, anchialine ecosystems are still poorly understood aquatic

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environments. The absence of mercury studies in anchialine environments presents difficulties in comparing our data. Nevertheless, physico-chemical parameters, vicinity of the sea, the long residence time of water, and darkness reported from various anchialine systems worldwide (Iliffe et al., 1984; Pohlman et al., 1997; Humphreys, 1999; Beddows et al., 2007; Novosel et al.,, 2007) are comparable with the parameters discussed in this work. On the Croatian Adriatic coast, which is rich with karstic anchialine systems, caves in Mljet national park on the island of Mljet have been described several times during the last decade, mostly in ecological studies (Kršinić, 2005; Pavlinić et al., 2010). Recently, distribution and speciation of both dissolved and total trace metals (Cuculić et al., 2011) and iodine species and nutrients (Žic et al., 2008, 2011) were reported.

Anchialine caves have worldwide significance, such as very large and important karst aquifers in Texas and northern Mexico, Yucatan, and Lebanon (Beddows et al., 2007; Fleury et al., 2007). We may also consider anchialine caves a portal to subterranean estuaries. The term "subterranean estuary" was first introduced by Moore (1999) and has subsequently been adopted by the scientific community (Žic et al., 2008, 2011; Cuculić et al., 2011). Moreover, some data show that inputs from these systems may have significant influence on global oceans (Windom et al., 2006). Further investigations of other anchialine caves will provide additional information on the fundamental biogeochemical processes that govern trace mercury behavior. The reproducibility of results from these aquatic environments could make anchialine systems suitable natural laboratories for studying various biogeochemical processes in anchialine and other similarly stratified systems (Žic et al., 2008, 2011; Pohlman, 2011; Cuculić et al., 2011, 2012; Neisch et al., 2012).

Main sources of mercury input into the environment include natural ones, such as volcanic outgassing and evaporation from superficial soils, as well as anthropogenic, including fossil fuel combustion and waste incineration (Selin, 2009). Once introduced into the aquatic environment, Hg is redistributed throughout the water column, deposited and accumulated in sediments and biomagnified along the trophic chain (Fitzgerald et al., 1991; Long et al., 1996; Selin, 2009). MeHg as one of the most dangerous forms of mercury, is very efficiently concentrated through biological membranes (Heinz and Hoffman, 1998). Even in very low concentrations, MeHg have harmful effects upon the aquatic environment due to a high enrichment factor, efficient accumulation, as well as biomagnifying properties (Drevnick and Sandheinrich, 2003).

Although mercury is one of the most toxic elements, its distribution and speciation are unknown in anchialine environments so far. However, mercury biogeochemical processes in coastal regions have been extensively studied worldwide (Mason and Lawrence, 1999; Gårdfeldt et al., 2001; Kwokal et al., 2002; Heyes et al., 2006; Bratkič et al., 2013). Aquatic systems that could share some similarities with anchialine ones (caves) are coastal submarine groundwaters. Recently, studies reported groundwater discharge influence on mercury partitioning (Laurier et al., 2007), speciation and transport via submarine groundwater discharge and mercury dynamics in a coastal aquifer (Ganguli et al., 2012, 2014). Also, elevated total mercury concentrations in coastal groundwaters are detected, however, related processes are not clarified.

In this work, the distribution and speciation of mercury in the aquatic environment of anchialine caves were obtained for the first time. Caves described in this work are relatively small and isolated geological systems. However, our mercury and physico-chemical data reported here can be comparatively applied to the majority of anchialine caves worldwide.

2. Study area

All samples were collected on Mljet, an approximately 37 km long and 3 km wide island in the southwest Adriatic Sea (Fig. 1). The northernmost one third of the island was proclaimed as a national park in 1960, particularly for its heavily forested geography. The island geology is characterized by porous limestone and semi-porous dolomites with some flysch, an impervious, thin-layered sedimentary rock, as hydraulic barriers (Gušić et al., 1995). Bjejajka and Lenga are anchialine subterranean environments inside the national park. Both caves are connected hydraulically to the Adriatic Sea and are located about 100 m from the shore. Žic et al. (2008) reported that tidal amplitude in both caves was smaller (only 13 cm) compared to outside 17 cm. Tide in Bjejajka lagged the outside seawater level by 40 min and in Lenga appeared to be little or no phase shift. Both caves were formed in late Jurassic and early Cretaceous dolomites with limestone lenses.

Bjejajka (Fig. 2A) is a 22 m high and 40 m long cave, with a water depth of approximately 12 m and water volume of roughly 300 m^3 (Žic et al., 2008). The main pool, atop the narrow tunnel that extends into the karst rock, is about 4 m deep. A small colony of insectivorous bats (*Rhinolophus hipposideros*) seasonally inhabits Bjejajka (Pavlinić et al., 2010) and their droppings (guano) are evident in and around the shallow bottom, fringing the main pool. The bottom of the cave is mainly covered with clay (terra rossa) produced by the weathering of limestone and dolomite. Bjejajka has no noticeable anthropogenic influence, since it is located in a wooded area in the national park and is isolated and remote from human settlement.

The smaller Lenga (Fig. 2B) is a 22 m deep vertical well of which the upper half is dry, and it is connected with the atmosphere through a narrow opening (0.5 m). Lenga water volume is approximately 90 m^3 (Žic et al., 2008), 3 times less than that of Bjejajka. Lenga is surrounded by area that is used for local, small scale agricultural activities (vineyards, olive and fig trees), therefore somewhat anthropogenically influenced. The bottom of the pit is covered with parts of decayed terrestrial plants. Bats and guano have not been observed in Lenga.

3. Methods and instrumentation

Water samples for Hg determination were collected in pre-cleaned glass reagent bottles (Sázava, Czech Republic, 1 L) and

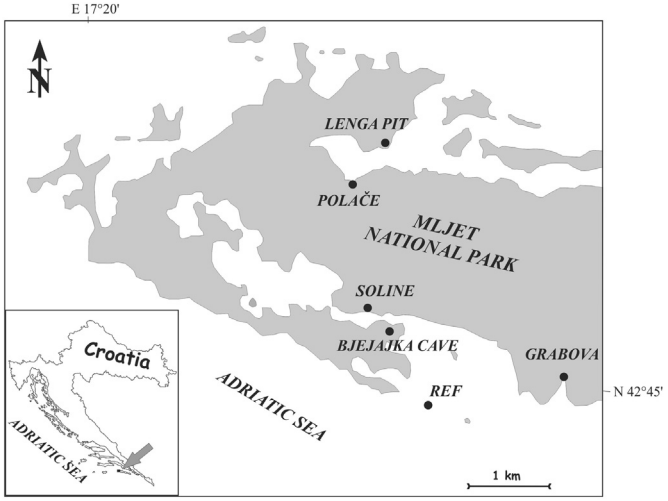

Fig. 1. Map of study area.