

Iodine and nutrient speciation in anchialine cave waters (Bjejjajka Cave, East Adriatic Coast)

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In oxic seawater dissolved iodine is principally consisted of iodate and iodide, at a total concentration of ~450 nM. Although iodate is thermodynamically favoured form of inorganic iodine, iodide concentrations may be high, as is the case in surface waters of temperate shelf seas. Both phytoplankton and bacteria are proposed to mediate in iodate reduction to iodide, but the results upon the extent of phytoplankton impact on the iodine system at natural iodine concentration levels are even contradictory, while reaction mechanisms remain largely unknown. Similarly, the opposite oxidation process of iodate formation is still not clear, but several recent findings in specific marine and lymnic environments, including the one in seven anchialine caves along the Adriatic coast, seem to support the hypothesis that oxidation is possibly related to bacterial activity during nitrification. In addition, bacterial respiration is considered to participate in iodate reduction at halocline.

The study of inorganic iodine speciation in anchialine caves waters was, however, only focused to iodate and iodide depth distributions, leaving significant uncertainty upon the total iodine concentration (that with organo-iodine included). Although organo-iodine is typically low in open ocean waters, in productive estuarine and marine environments it is found to be present in high concentration. To obtain information whether concentrations of a third iodine form are substantial enough so that might affect the inorganic iodine system, and whether there is a parallel between iodine and nutrient speciation (in particular that of nitrogen), an additional study of iodine speciation in the water column of Bjejjajka Cave was conducted in January and July 2009. Water samples were collected from various depths and were analyzed for iodate, iodide and total iodine. In addition, physico-chemical parameters (salinity, temperature, dissolved oxygen, pH and alkalinity) and nutrients (nitrate, nitrite, ammonium, phosphate and silicate) were measured at the same depths.

Bjejjajka Cave is an anchialine object situated on the island of Mljet (East Adriatic Coast), approximately 100 m from the nearest shore. The cave is 22 m high and 40 m long, with water depth of 12 m. Below the main pool which is ~4 m deep, a narrow tunnel extends into the karst rock. During both surveys water column was well stratified, with slight seasonal temperature variations obtained only in surface layers and pronounced, but rather diffuse salinity gradient below the well mixed surface layer. Due to organic matter degradation and lack of photosynthesis, hypoxia developed in deeper layers of the pool (~2.5 m in January and ~3.5 m in July) and maintained in deep water. While dissolved oxygen and pH profiles were similar, alkalinity increased linearly with decreasing salinity. Nutrient profiles were similar during both seasons, with concentrations well above those found in surrounding seawater in July. The

highest concentrations of nitrite and ammonium (up to 0.17 μM and 3.66 μM , respectively) were measured at the bottom of the main pool, reflecting both heterotrophic and autotrophic bacterial activity. Nitrate, phosphate and silicate concentrations were significantly higher at surface (up to 117 μM , 2.95 μM and 78.2 μM , respectively) than in deep water (~7 μM , ~0.25 μM and ~33 μM , respectively). While correlation between silicate and salinity was linear ($R^2=0.962$, $N=16$), hyperbolic-like relationship was obtained with nitrate and phosphate, but linear between them ($R^2=0.972$, $N=17$). Beside fresh-water source from soil leaching, an additional source of nitrate and phosphate could have also been bat droppings, while the source of silicate in deep water is not yet fully understood.

Unlike nutrients, total inorganic iodine concentrations linearly increased with salinity ($R^2=0.948$, $N=16$), attaining ~450 nM in bottom water of higher salinity ($S=35\text{‰}$), which is close to concentration found in surrounding seawater that feeds the cave. High iodate (mean=435 nM) and low iodide (mean=16 nM) concentrations in these samples contrast inorganic iodine speciation in Adriatic surface seawater, where the ratio between iodate and iodide is significantly lower (~4). During both surveys iodide concentration peaked at the bottom of the main pool, but the concentrations in July were about three times lower than in January (60 nM vs. 170 nM). These findings indicate that iodide oxidation to iodate probably occurs both within the karst matrix and the water column itself. These are the depths where heterotrophic bacteria might have contributed to iodate reduction, while autotrophic bacterial assemblages to iodide oxidation, as is the case with nitrogen speciation. Like total inorganic iodine, total iodine concentrations generally increase with salinity, but with some higher scatter ($R^2=0.851$, $N=16$). However, while regression of the data for total inorganic iodine against salinity gives an intercept (\pm std. error) of 8 (\pm 18) nM, with total iodine data the intercept is 212 (\pm 21) nM. It is only in near the bottom that total iodine concentrations were only about 5% higher than total inorganic iodine concentrations, as is the case in surrounding seawater. Thus, a third iodine form, which is probably organic in nature, appears to be a fresh-water derived species. Its high stability would explain conservative behaviour of total inorganic iodine in the waters of Bjejjajka Cave.