

# IODINE SPECIATION IN ANCHIHALINE CAVE-WATERS - THE FIRST EVER OBSERVATION OF IODIDE OXIDATION IN A MARINE SYSTEM?

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## Abstract

An exceptional combination of the estuarine- and deep-sea like speciations of dissolved inorganic iodine is found in waters of anchihaline cave Bjejjajka (Island Mljet, East Adriatic Coast). Low iodide concentrations below the halocline suggest that the processes of iodide oxidation, which commonly prevail in deep ocean waters, may also exist in these caves.

**Keywords:** *Chemical Speciation, Vertical Profile, Adriatic Sea.*

## Study area & methodology

Bjejjajka Cave is cut in late Jurassic and early Cretaceous dolomites with limestone lenses on the island of Mljet. It is one hundred meters from the shore in the Bjejjajka Bay, and is 22 m high and 40 m long, with water depth of 12 m. The level of water in the cave approximates that of the sea. It is not known whether the subterranean lake exchanges water with the sea through only porous karsts or larger passages. The waters were sampled in April and September 2006 by scuba diver. Temperature was determined *in situ* while salinity, pH and dissolved oxygen were measured immediately after sample collection. Iodide and iodate were determined directly by voltammetric methods.

## Results & discussion

The temperature of the cave water in April and September was similar; a gradual increase from 13°C at the surface to 14.5°C at the bottom in April and from 14.3°C to 15.1°C in September (Figure 1). A 3 m mixed surface-layer of lower salinity existed in both seasons. In the 9 m below this, salinity increased from 7-25 and 9-37 in April and September, respectively, suggesting lateral flow at depth. Dissolved oxygen and pH depth-profiles in September were similar, with approximately 81  $\mu\text{mol L}^{-1}$  and pH=7.23 at the surface, and 73  $\mu\text{mol L}^{-1}$  and pH=7.17 at the bottom and a slightly lower values of 67  $\mu\text{mol L}^{-1}$  and pH=6.76 at the halocline (4 m). Generally, iodide was less than 10  $\text{nmol L}^{-1}$  at all depths in both seasons while iodate followed a similar profile to salinity.

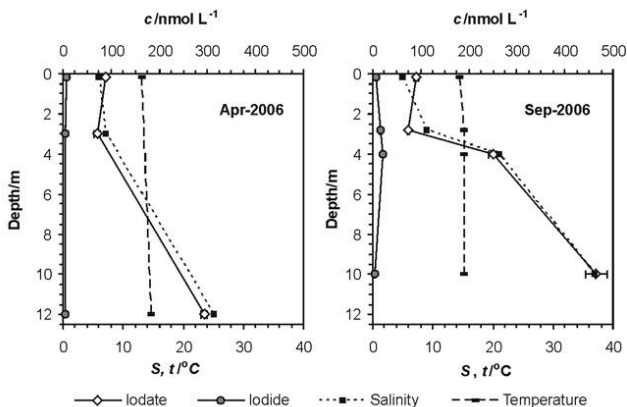


Fig. 1. Vertical profiles of temperature, salinity, iodate and iodide in Bjejjajka Cave.

In a combined plot of five anchihaline caves along the Adriatic shore, the iodate results suggest the mixing of two end-members; freshwater with low iodate and high salinity water with high iodate (Figure 2). Regression of the data for iodate against salinity (d.f. =17) gave a robust linear plot ( $r^2=0.957$ ) with gradient and intercept ( $\pm$  std. errors) of 10.2 ( $\pm$  0.5)  $\text{nmol L}^{-1}$  and 24 ( $\pm$  12)  $\text{nmol L}^{-1}$ , respectively. An intercept of zero is therefore within the 95% confidence limits. The upper end of this line tallies with the total inorganic iodine concentrations reported for the Adriatic (450  $\text{nmol L}^{-1}$ ) where, however, the iodate to iodide ratio is around 4 [1]. Meanwhile, the iodide concentration (mean=10  $\text{nmol L}^{-1}$ ) was essentially independent of salinity.

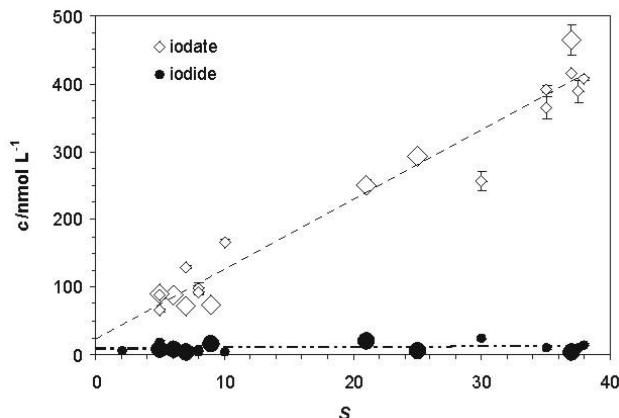


Fig. 2. Relationship between iodate and iodide concentrations and salinity in five anchihaline caves along the Adriatic Coast. Bigger symbols refer to Bjejjajka Cave.

The presence of high iodate, low iodide water in Bjejjajka Cave at 10 m in September is a very interesting observation, perhaps of far-reaching importance. The salinity of 37 together with the total iodine concentration of ( $469 \pm 23$ )  $\text{nmol L}^{-1}$  is consistent with the entry of coastal seawater into the base of the cave, as would be expected hydrologically. However, this can only be so if the high concentration of iodate in the cave-water also represents oxidation of the iodide in the seawater as it enters the system. No observations of the oxidation of iodide in the oceans are recorded; where it occurs, how quickly, and under what conditions [2]. Potentially then, this is the first observation of iodide oxidation in a marine system.

## References

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