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IODATE REDUCTION TO IODIDE UNDER OXIC AND HYPOXIC CONDITIONS DURING DE-STRATIFICATION OF THE CROATIAN ANCHIALINE POND ZMAJEVO OKO (DRAGON'S EYE)

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This study examines the impact of slow de-stratification on the inorganic iodine, sulphur and nutrient systems in the eutrophic anchialine pond Zmajevo oko (Rogoznica Lake). The observed changes in both the vertical distribution and the speciation of the investigated variables were pronounced. Although the redox conditions formed immediately after the de-stratification were oxic to hypoxic, iodate was reduced to iodide.

Key words: iodine, sulphur, nutrients, speciation, redox conditions, anchialine

INTRODUCTION

At a total concentration of about 0.45 μmol l^{-1}, iodine is the most abundant biophilic minor element in seawater (ELDERFIELD & TRUESDALE, 1980). In the oceans, the largest iodine reservoir on the earth and the principal source of terrestrial iodine, iodine mainly presents as its inorganic species; iodate (IO_3^-) and iodide (I^-). According to thermodynamics, iodate should predominate under oxic conditions, and iodide under anoxic ones. However, in surface oceans iodate and iodide co-exist, primarily due to the influence of biological processes. Meanwhile, in aquatic environments exposed to greater terrestrial influence or eutrophication, the organic iodine fraction can even predominate. Because of its biophilic nature iodine is involved in both inorganic and biologically mediated oxidation-reduction reactions. This is particularly pronounced in semi-isolated aquatic systems, such as anchialine environments, where processes that affect iodine speciation are found to be more intensive than those in the open oceans (ŽIC *et al.*, 2010, 2011).

The anchialine system investigated here is situated in the karstified carbonate rocks of the Croatian Adriatic coast. It was formed by the roof collapse of the primary cave system and is thereby completely open to the atmosphere, and consequently the system therein is dominated by photosynthesis. Accordingly, the concentrations of oxygen in the upper layers of the water column are maintained at near-saturation up to well-above saturation (up to 300%). The organic matter produced sinks to the bottom to establish anoxic and sulphidic conditions in the deep water. However, during autumn, de-stratification mixing between this highly reducing deep water with that in the upper layers produces intermediate redox

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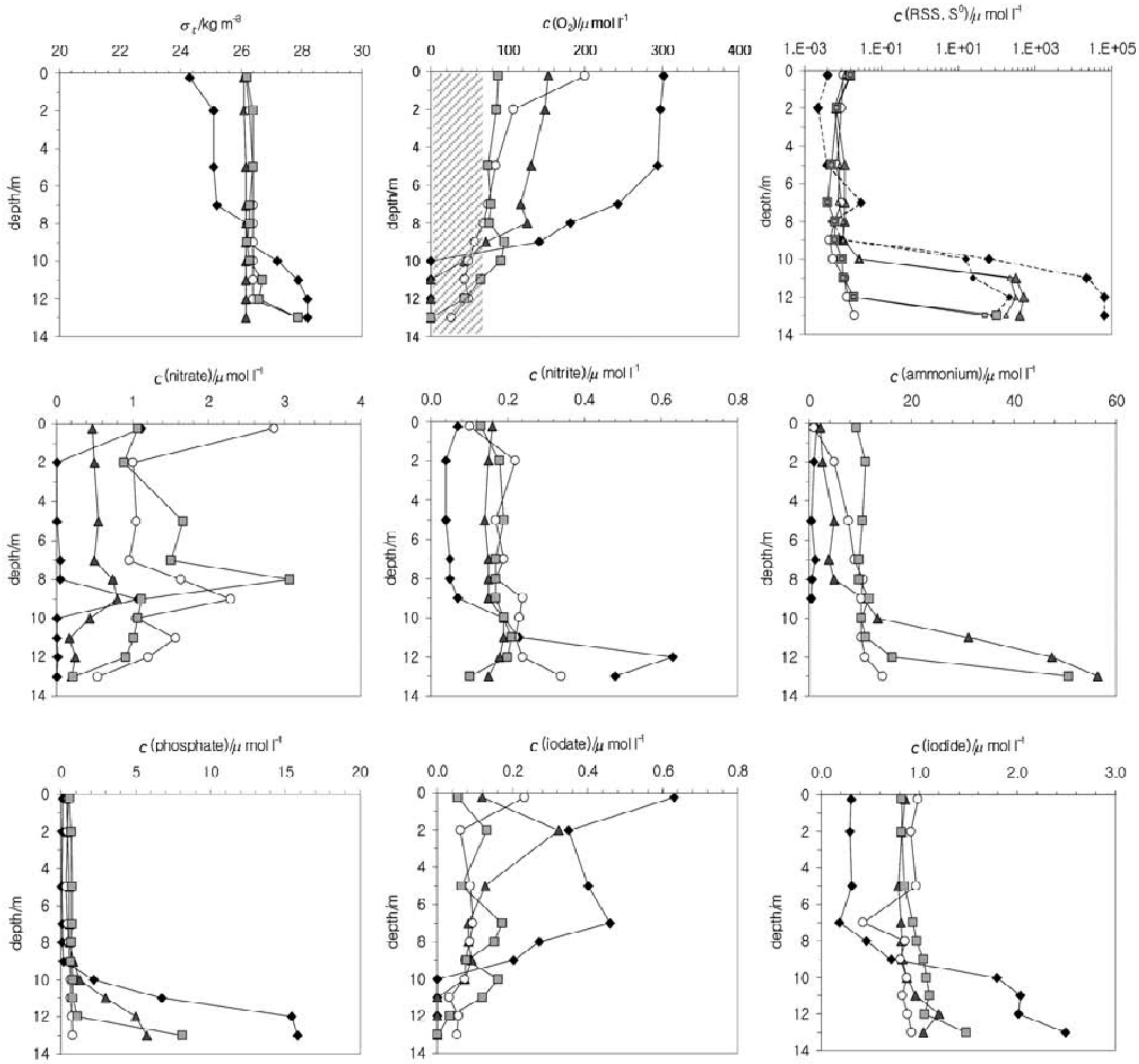

Fig. 1. Profiles of density, dissolved oxygen, reduced sulphur species and elemental sulphur, nitrate, nitrite, ammonium, phosphate, iodate and iodide in Zmajevo oko pond on Aug. 26th (black diamonds), Sep. 23rd (grey triangles), Sep. 26th (grey squares) and Sep. 29th (white circles). The shaded area on dissolved oxygen graph indicates hypoxic zone. The larger and the smaller symbols of the same shape on the sulphur speciation graph refer to RSS and elemental sulphur, respectively.

conditions. Therefore, de-stratification offers an opportunity to investigate the reactivity of the iodine system when it is exposed to a natural stress. Here, therefore, we present changes in inorganic iodine, sulphur and nutrient speciation before and during late-summer de-stratification of the anchialine pond Zmajevo oko.

MATERIALS AND METHODS

Depth profiles were taken from a small boat in the centre of the pond on August 26th and September 23rd, 26th and 29th 2003, using a 5 l Niskin sampler. Temperature was determined with a mercury in-glass thermometer immediately upon sample collection. Salinity was measured with a refractometer (Atago, Japan). Dissolved oxygen concentration was determined by the Winkler method (STRICKLAND & PARSONS, 1972). Iodate and iodide were determined by differential pulse voltammetry (HERRING & LISS, 1974) and cathodic stripping square wave voltammetry (LUTHER *et al.*, 1988), respectively. Reduced inorganic sulphur species, RSS, (*viz.* sulphide and elemental sulphur) were analysed by linear sweep voltammetry (LSV) (CIGLENEČKI *et al.*, 1996; CIGLENEČKI & ĆOSOVIĆ, 1997). The concentrations of nutrients (nitrate, nitrite, ammonium and phosphate) were measured by standard spectrometric methods (STRICKLAND & PARSONS, 1972).

RESULTS AND DISCUSSION

The profiles of Aug. 26th describe well the persistent structure of the water column during the stratified period (Fig. 1). The density gradient indicates that the water column was physically stable. High dissolved oxygen and low nutrient concentrations up to around 9 m suggest pronounced phytoplankton activity. As a result of settling of this organic material, and because the volume of water between 0 and 9 m represents almost 90% of the pond's volume, anoxic and sulphidic conditions developed in the 10% representing the deep water. The phosphate concentration profile is in accord with regeneration of the organic matter in the deep water and sediment. Although we have no ammonium results below 9 m, previous surveys confirmed up to 250 μmol l^{-1} of ammonium in deep water (CIGLENEČKI *et al.*, 2005). Iodine speciation was in accord with the redox conditions within the water column, so that iodate was more abundant than iodide in surface (oxic) layers, while in the anoxic layer it was essentially absent. The iodide profile is similar to that of phosphate and additionally suggests upwards diffusion of free iodide from the pond's sediment in the anoxic zone.

In September the water column lost hydrostatic stability (Fig. 1). The profiles indicate that the mixing between the deep water and that in the upper layers was not instantaneous, but slow. Thus, between Sep. 23rd and Sep. 26th dissolved oxygen concentration in the large volume of surface water (up to 8 m) decreased from about 150 μmol l^{-1} to about 90 μmol l^{-1}. Meanwhile, with the exception of the deepest sample, the redox conditions in deep water changed from anoxic and sulphidic to hypoxic and non-sulphidic. This pattern largely continued up to Sep. 29th although the near-surface water became more oxygenated. Ammonium and phosphorus profiles are comparable to those of RSS and support a slow mixing regime, while nitrogen speciation additionally suggests a pronounced activity of nitrifying bacteria and/or archaea arising from an influx of the ammonium nitrogen. When compared to the concentration profiles for other analytes in September, those for iodate and iodide were more uniform with depth. This is not surprising because the enrichment of total inorganic iodine in deep water relative to surface layers in August was almost two orders of magnitude lower than that of, for example, phosphate. As with dissolved oxygen, the mixing of surface waters with sulphide-rich anoxic deep-water also affected iodine speciation, so that on Sep. 23rd iodate was already largely reduced to iodide, and this continued to a lesser degree until the end of the survey. Overall, between Aug. 26th and Sep. 29th the iodate inventory for the pond decreased, while that of iodide increased by about 22 moles (75%) and 29 moles (65%), respectively. The results suggest that sulphide, the most powerful and abundant reducing agent in the system, could be responsible for iodate reduction to iodide even under oxic conditions. Therefore, this reinforces the finding that the reaction between sulphide and iodate precedes the corresponding reaction with oxygen (ZHANG & WHITFIELD, 1986).

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