

# Iodate and Iodide Distributions in the Waters of a Stratified Estuary

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Speciation and distribution of inorganic iodine in the highly stratified Krka estuary (east coast of the Adriatic Sea) were investigated in the period from December 2000 to April 2001. Conservative behavior of total inorganic iodine was confirmed during the investigated period, but significant temporal and longitudinal variations were also observed. Concentrations of iodate and iodide were less variable in the more saline layers ( $S \geq 10$ ) than in the upper brackish and interfacial layers, indicating lower dynamics and less pronounced influence of secondary processes on the inorganic iodine distribution. An increase in iodate and iodide concentrations toward the estuary mouth was determined in the upper layers. Seasonal variations in iodate and iodide distributions in the brackish layer were indicative of the important role of the freshwater phytoplankton and organic matter for the inorganic iodine cycle in the estuary.

## INTRODUCTION

The estuarine chemistry of iodine is very complex, and it has been widely investigated in numerous studies, which contributed useful information about the biophilic and redox sensitive nature of iodine.<sup>1–5</sup> In contrast to open oceans, estuaries are highly influenced by human activities *via* municipal wastewater discharges and spills, which may cause an increase in the concentration of nutritious salts, organic matter and other pollutants. Concentrations and relative abundance of iodate and iodide in estuaries vary significantly due to the influence of various factors, such as geomorphology and hydrology of the estuary, intensity of the primary production, the content and composition of dissolved and particulate organic matter, sediment composition, as well as human activities.<sup>6</sup>

Both conservative and non-conservative behaviors of iodate and iodide in the estuaries have been established. Non-conservativity of iodine in the water column can be attributed to the biological cycle of the phytoplankton and the formation of organic iodine in the reactions between highly reactive molecular iodine and hypiodite with or-

ganic compounds. Concentrations of organic iodine vary considerably between different estuaries but also within a single estuary. It can represent a significant proportion of the total iodine in some estuarine systems.<sup>4,7,8</sup> Depth profiles of organic iodine differ from those of iodate and iodide. The lowest concentrations of organic iodine were observed below the halocline, where the total iodine concentrations are similar to those detected in seawater. Somewhat higher values of dissolved iodine near the bottom are a result of the diffusion and re-mineralization processes. Reduced iodine forms (iodide and organically bound iodine) prevail in the estuaries that are affected by prolonged periods of oxygen deficiency.<sup>7,9,10</sup>

The objective of this work was to explain the processes that affect the concentrations and distribution of inorganic iodine in the Krka river estuary, which has specific hydrological, chemical and biological characteristics. It gave us the opportunity to study elemental speciation in two fundamentally different compartments, the upper fresh/brackish and the underlying marine layer, as well as in the narrow boundary layer between them.

### Scope of Study

The Krka River estuary is situated in the eastern part of the Adriatic coast. This karst river forms a 25 km long estuary that spreads from the Skradinski Buk waterfalls (43°49.3' N, 15°56.7' E) to the Šibenik Channel (43°43.3' N, 15°51.4' E) (Figure 1). The estuary is preceded by a series of waterfalls and moss-covered tufa barriers which retain sediment load from the upper region, the Visovac Lake. Within the estuary, both the input of suspended material (mainly via the Guduča Creek) and the sedimentation rate are low. Sedimentation material is mostly terrigenous in the upper part of the estuary, while in the lower part it mainly consists of the authigenic (biogenic) fraction.<sup>11</sup>

The depth gradually increases from 1 m below the waterfalls to 42 m in the Šibenik Channel. The main

source of freshwater is the Krka River, with the average input of  $55 \text{ m}^3 \text{ s}^{-1}$ , but significant monthly and seasonal variations have been observed (from  $5 \text{ m}^3 \text{ s}^{-1}$  to  $440 \text{ m}^3 \text{ s}^{-1}$ ). The estuary is highly stratified as a result of its sheltered position and low tidal movements (0.2–0.5 m).<sup>12</sup> The upper brackish current flows seaward, while the deeper seawater current has the opposite flow direction. The boundary layer is characterized by a steep halocline that varies both in thickness and depth in dependence on freshwater inflow and wind.

Variations in the exchange time of both freshwater and seawater depend on the season. For freshwater, the variations range from 20 days in winter to 80 days in summer, while for seawater from 50–100 days in winter up to 250 days in July and August.<sup>13</sup> As a result of the stable stratification of the estuary, a water temperature inversion was recorded during the winter. The tempera-

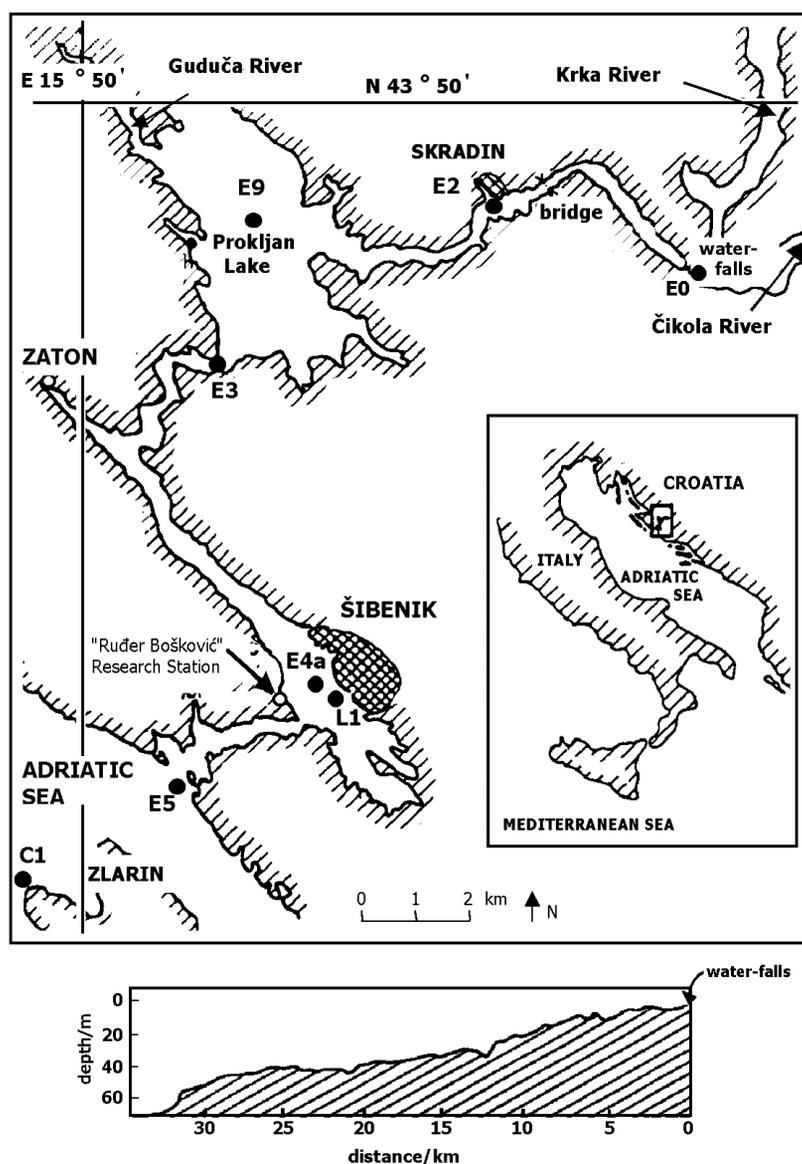


Figure 1. The Krka river estuary with locations of the sampling stations.

ture maximum around the halocline occurred from spring to autumn,<sup>14,15</sup> with the highest value of 34 °C recorded on August 01, 1998.<sup>16</sup>

## EXPERIMENTAL

Water samples were collected in the period from December 2000 and April 2001 at six estuarine stations (E2, E9, E3, E4a, L1, E5) and two referent stations for freshwater (E0) and seawater (C1) (Figure 1). Stations E0 and C1 represent two closest end-member locations where no mixing processes between the river water and seawater were observed.

At the estuarine stations E3, E4a and E5, samples were collected with 5 L Niskin samplers, while at stations E2, E9, L1 and C1 samples were taken by a scuba diver, facing the direction of the current.<sup>17</sup> Owing to good visibility and a veil-like appearance of the narrow intermediate layer, this sampling procedure enables collection of discrete samples around it. The temperature was determined *in situ* with an Hg-thermometer, the salinity with a refractometer (Atago, Japan) and pH with a manual pH-meter MP120 with an InLab 427 electrode (Mettler-Toledo AG) immediately after sample collection. Samples for the determination of iodine species were stored unfiltered in polypropylene bottles in dark at 4 °C until analyses, which were completed within two weeks. Voltammetric measurements were performed with a BAS-100A Electrochemical analyzer (Bioanalytical Systems, West Lafayette, Indiana, USA). An EA 290 HMDE electrode (Metrohm, Switzerland) combined with a Pt-counter electrode and an Ag/AgCl as a referent electrode were used. Iodate and iodide were determined directly by differential pulse voltammetry<sup>18</sup> and cathodic stripping square wave voltammetry,<sup>19</sup> respectively. Oxygen was removed from the samples by bubbling with nitrogen and by addition of sodium sulphite.<sup>20</sup> Necessary precautions were taken to avoid conversion of dissolved organic iodine to iodide.<sup>21</sup> Concentrations of iodate and iodide were determined by the standard addition method and the results are expressed as the arithmetic mean and the respective standard deviation of at least duplicate analyses. The precision

of the method for iodate determination was typically  $\pm 4\%$  at higher iodate concentrations and up to 15 % at concentrations below  $0.05 \mu\text{mol dm}^{-3}$ . The precision in iodide determination was typically below 6 % at iodide concentrations above  $0.01 \mu\text{mol dm}^{-3}$  and  $\pm 15\%$  at lower concentrations.

## RESULTS AND DISCUSSION

### *Sigma-t, Salinity, Temperature and pH*

During the investigated period, the stable vertical stratification at all estuarine sampling stations was characterized by a sharp density gradient in the interfacial layer, which divided the upper-brackish and the deeper-saline water. Due to the high salinity range along the depth profiles, temperature had only a minor influence on the hydrostatic stability of water layers, and it was only in December 2000 that isohaline conditions coincided with a slight temperature increase with depth ( $\Delta\sigma_t/\Delta z = -0.04 \text{ kg m}^{-3} \text{ cm}^{-1}$ ). Density gradients both in the brackish and saline layers were rather small (up to  $0.06 \text{ kg m}^{-3} \text{ cm}^{-1}$ ) when compared to the values obtained in the interfacial layer (up to  $2.21 \text{ kg m}^{-3} \text{ cm}^{-1}$ ).

The depth and longitudinal variations in salinity were in accord with the geomorphologic and hydrologic description of the Krka estuary. Salinity at the surface varied between 1.0 and 3.5 in the upper part of the estuary (stations E2 and E9), while the variations in the lower estuarine section (E3–E5) were more pronounced (between 2.3 and 10). Salinity of 38 was recorded in deeper layers. Lower salinity of the near-bottom layer was observed only in the most shallow part on December 1, 2000 ( $S = 32$ ). Within only a few days, however, the salinity at this station increased to 38, and the halocline was shifted toward the surface by almost 1 m (Figure 2). These data suggested that a high freshwater flow was compensated by a counter-flux of marine water.

The water temperature profiles showed a seasonal pattern. During winter and early spring, the temperatures

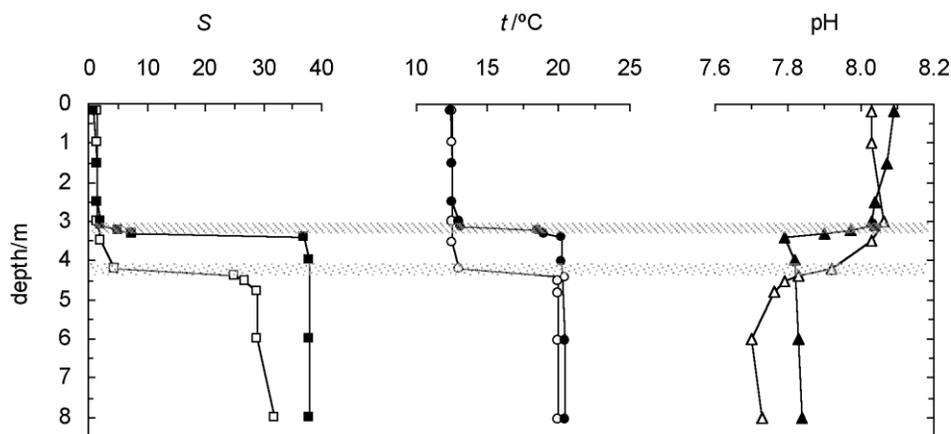


Figure 2. Salinity, temperature and pH depth profiles at station E2 obtained on December 1 (white filled symbols) and December 7 (black symbols) 2000.

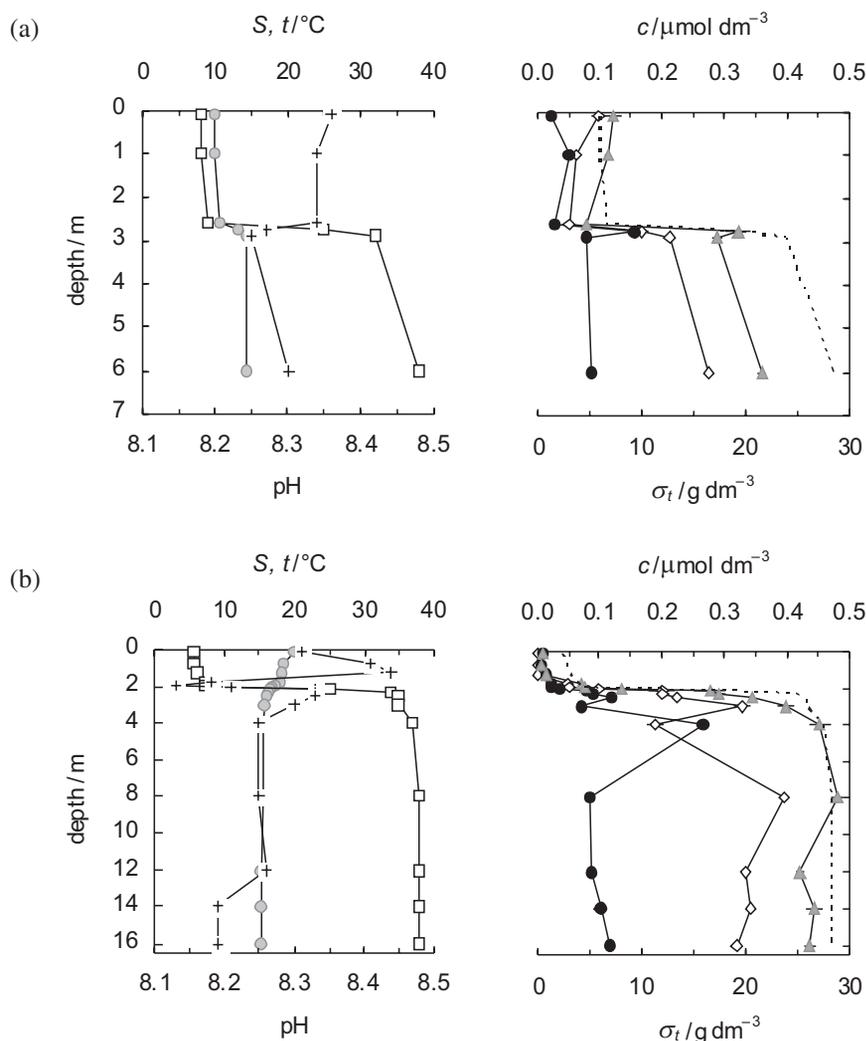


Figure 3. Depth profiles of salinity ( $\square$ ), temperature ( $\bullet$ ), pH (+), iodate ( $\diamond$ ), iodide ( $\bullet$ ), iodate+iodide ( $\blacktriangle$ ) and  $\sigma_t$  (---) at stations: a) E4a (February 15, 2001), b) L1 (April 30, 2001).

in the marine layer were always higher than those in the upper brackish layer, varying between  $\approx 20$  °C in December and  $\approx 15$  °C in February. An apparent diurnal variability of temperatures in the upper layers, caused by intensive solar irradiation, was registered by the end of the April. At the lower edge of the interfacial layer, within the salinity range between 25 and 38, a slight temperature maximum (up to 1.0 °C) was occasionally observed from December to April. According to the literature data, this maximum is most pronounced in the spring/summer season and appears as a result of intensive solar irradiation through the transparent brackish layer and slow mixing processes between the brackish and seawater.<sup>15</sup>

pH varied between 8.5 (in upper layers) and 8.1 (in saline water), with the exception of December 2000 when the pH range ranged between 8.1 and 7.7. The specific Z-shaped pH vertical profiles (as in Figure 3b) with higher values in the upper part of the steep halocline and lower values below it were especially pronounced in the spring season, indicating more intensive biological pro-

cesses around the intermediate layer. These pH variations could be caused by the increased photosynthetic activity,<sup>22</sup> with the maximum appearing as a result of the production phase, whereas the minimum reflects the respiration phase.

#### Iodate and Iodide

From the hydrological point of view, the physical and chemical properties of estuarine waters result from the interaction between the seaward flow of the Krka River freshwater and the opposite flow of marine water. It would therefore be appropriate to present iodate and iodide concentrations in both original waters first. At the riverine end, only iodide was detected in a low concentration ( $4.1 \pm 0.39$  nmol dm<sup>-3</sup>). As stated by Truesdale and Upstill-Goddard,<sup>23</sup> and Truesdale and Jones,<sup>24</sup> the distribution of iodine species within the estuaries, unlike that of nutrients, is primarily determined by the coastal end-member, since the iodine concentrations in river water as well in freshwater of anthropogenic source are far lower

than in seawater. Thus, more attention will be paid to the coastal end-member, where iodate, iodide and total inorganic iodine concentrations were in ranges from 0.27–0.34  $\mu\text{mol dm}^{-3}$ , 0.07–0.11  $\mu\text{mol dm}^{-3}$  and 0.35–0.45  $\mu\text{mol dm}^{-3}$ , respectively. Assuming higher salinity of these samples ( $S = 38$ ), the concentrations of total inorganic iodine are lower than those reported for ocean waters, where concentrations are around 0.45  $\mu\text{mol dm}^{-3}$ . However, both found concentrations of total inorganic iodine and the wide range of concentration at the reference coastal station are comparable to literature data for the Adriatic waters<sup>25,26</sup> and the Mediterranean high salinity waters (0.34–0.48  $\mu\text{mol dm}^{-3}$ ).<sup>8</sup> Depth profiles at station C1 indicate a slight enrichment of both iodate and iodide in the near-bottom area. These high iodide concentrations and low iodate to iodide mole ratios (between 3.0 and 4.0) are common for the euphotic zone, due to the biophilic nature of iodine.<sup>27</sup>

Within the estuarine area, according to these marked concentration differences between freshwater and seawater, wide concentration ranges of both iodate (<0.015–0.39  $\mu\text{mol dm}^{-3}$ ) and iodide (0.003–0.29  $\mu\text{mol dm}^{-3}$ ) were found.

*Depth Distributions.* – Iodate and iodide depth distributions at estuarine stations showed a similar pattern during the investigated period; low concentrations in the upper layer, a sharp concentration gradient at the freshwater/seawater interface and relatively high concentrations in the saline layer, indicating that dilution processes were the primary processes that affected iodate and iodide concentrations. Superimposed on this general pattern, the subsurface iodide concentration maximum (station E4a, Figure 3a) and multiple iodate and iodide peaks at the lower edge of the halocline (station L1, Figure 3b) were indicators of the specific conditions within the water

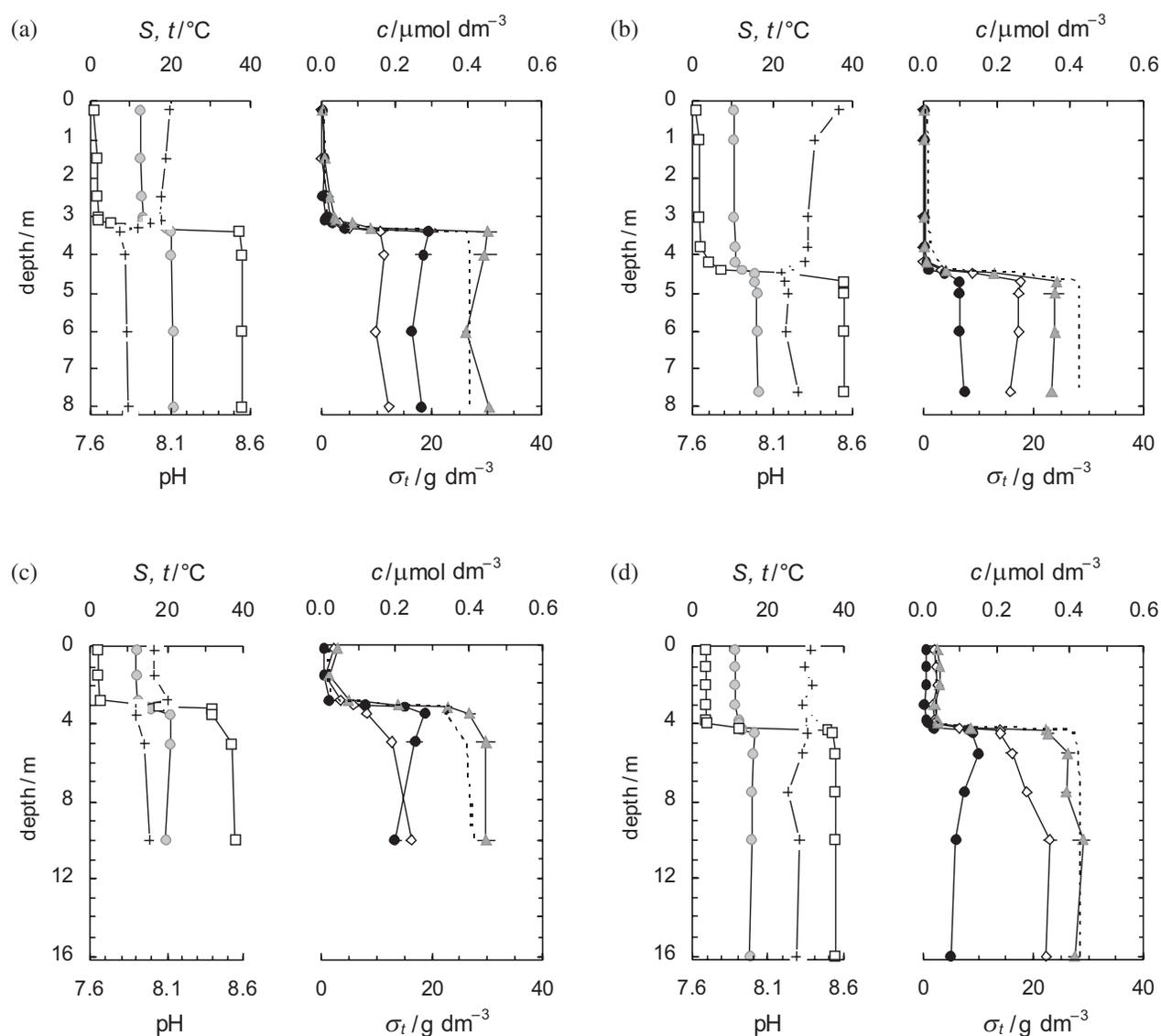


Figure 4. Depth distributions of salinity (□), temperature (●), pH (+), iodate (◇), iodide (●), iodate+iodide (▲) and  $\sigma_t$  (---) at station E2: a) 7 Dec. 2000 and b) 24 Mar. 2001 and at station E9: c) 8 Dec. 2000 and d) 25 Mar. 2001.

column in the Šibenik Bay and of high biogeochemical reactivity of iodine. According to the other studies conducted in the Krka estuary, the narrow interfacial layer between the low salinity brackish water and more saline marine water is enriched both in particulate and in dissolved organic matter,<sup>28–30</sup> phytoplankton,<sup>31–33</sup> as well as the bacterial population.<sup>34,35</sup> The main sources of dissolved organic matter are the degradation products of the freshwater phytoplankton. The upper and interfacial layers in the Šibenik Bay were found to be particularly environmentally disturbed due to additional nutrient input, so the enhanced phytoplankton activity and high primary production were confirmed in this lower part of the estuary. Assuming the biophilic nature of iodine and as its bioconcentration in some marine organisms has been confirmed, the peak concentration at the lower edge of the halocline (Figure 3a) may be explained by bacterial decomposition of the accumulated organic matter. Iodate and iodide depth profiles at station L1 (Figure 3b), situated in front of the wastewater outlet, reflect high anthropogenic influence on elemental speciation. These mirror-like profiles of iodate and iodide and a relatively uniform depth distribution of total inorganic iodine, which exclude the role of organic-iodine species, show how the untreated municipal wastewater discharges may induce dramatic changes in redox conditions within the water column.

Concentration maxima at the other estuarine stations were generally less pronounced. In contrast to other sampling periods, the concentration ratios between iodate and iodide below the halocline, at stations E2 and E9 in December 2000, were rather low (mainly below 1.0) (Figures 4a and 4c). More typical profiles at these stations are represented in Figures 4b and 4d. The hypoxic conditions that periodically occur in the Prokljan Lake and near the town of Skradin in autumn and winter<sup>14,36</sup> may explain the observed low iodate to iodide concentration ratio. Hypoxia occurs as a result of several factors; a marine phytoplankton bloom, stable stratification and a slow rate of water exchange. Hypoxia usually prevails until higher river flux is compensated by a counter-flux of seawater enriched in oxygen.<sup>36</sup> Relatively high temperatures below the halocline in December, low pH and re-establishment of the prevailing natural conditions in the deepest layers, which can be also obtained from the iodate and iodide depth distributions (Figure 4c), support this explanation.

Due to specific iodate to iodide concentration ratios in December, as mentioned above, two data groups were compiled for the linear regression analysis between iodine species and salinity. One group includes data from stations E2 and E9 in December 2000, and the other group includes the remaining sampling data. The difference between these two data groups is obvious in Figure 5. The results obtained indicate that both iodate and iodide

TABLE I. Linear regression parameters between iodine species and salinity. The units for both slopes and intercepts are nmol dm<sup>-3</sup>

	Slope ± std. err.	Intercept ± std. err.	r <sup>2</sup>	N
Dec. 2000				
Iodate	4.14 ± 0.31	6.48 ± 7.15	0.87	29
Iodide	7.15 ± 0.25	-1.14 ± 5.69	0.97	29
Iodate + iodide	11.29 ± 0.31	5.34 ± 7.01	0.98	29
Feb.–Apr. 2001				
Iodate	7.46 ± 0.23	-9.64 ± 5.85	0.92	101
Iodide	2.85 ± 0.16	0.59 ± 4.11	0.76	101
Iodate + iodide	10.31 ± 0.21	-9.05 ± 5.36	0.96	101

were linearly related to salinity during the entire period (Table 1). Although the correlation coefficients were high and the uncertainty of the slope low ( $P < 0.0001$ ), the lack of meaning of the intercept (negative values) and high uncertainty of the intercept (high standard errors) were caused by a large scattering of data points. This is partly due to temporal and longitudinal variations in iodine distributions included in these two composite groups. Better correlation was obtained when each sampling was analyzed separately, but still the intercept had generally no statistical significance. These results suggest that beside simple dilution, secondary processes affected iodine distribution and speciation, particularly the inter-conversion processes between iodate and iodide. Higher correlation coefficients for total inorganic iodine and similar slopes both for December and the period from February until April support the proposed inter-conversion mechanism. These data also indicate that only total inorganic iodine behaved conservatively during estuarine mixing, since the deviations from the hypothetical mixing line between the two end-members during the entire period were low only for total inorganic iodine (Figure 5). At higher salinities, iodate concentrations mainly drop below the mixing line, indicating its reduction within the estuarine area. At lower salinities, a scattering of data points indicated higher iodate involvement in the biogeochemical cycle. Contrary to iodate, the estuarine area was enriched in iodide and its concentrations were less variable at low salinities.

*Relationship between Iodate and Iodide and Seasonal Variations in Iodine Distribution.* – In iodine studies, particularly those that deal with natural aquatic systems where salinity changes might affect iodine concentrations, it has become common to rationalize iodine concentrations to salinity 35, so that changes in concentration profiles may be linked only to biogeochemical processes.<sup>37</sup> In this paper, the letter "r" in a subscript stands for the rationalized value of a substance, e.g., the rationalized concentration of a substance X is  $c_r(X) =$

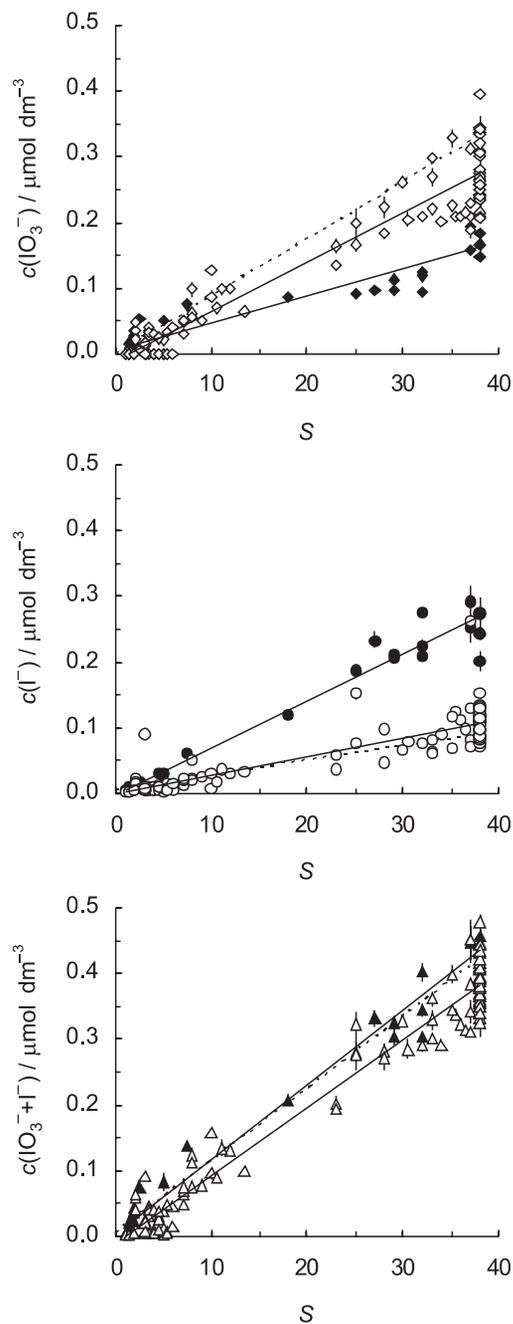


Figure 5. Relationship between concentrations of iodate ( $\diamond, \blacklozenge$ ), iodide ( $\circ, \bullet$ ) and total inorganic iodine ( $\triangle, \blacktriangle$ ), and salinity. Black symbols refer to December 2000 and white symbols to the period from February to April 2001. Solid lines indicate the linear regression best fit lines. Dotted lines indicate the mixing line between riverine and marine end-members.

$c(X) \cdot 35 \cdot S^{-1}$ . When rationalized, iodate and iodide concentrations show fewer variations at higher salinities, as well as a seasonal trend at lower salinities.

When a similar approach to iodate and iodide distributions in the Chesapeake Bay<sup>38</sup> is applied to the Krka estuary, at higher salinities ( $S \geq 10$ ) almost all data points in the relationship between rationalized iodate and iodide fall within the linear envelope, which represents the

hypothetical relationship between iodate and iodide based on the two end-member mixing model (Figure 6a). The intercepts refer to the lowest and the highest rationalized concentrations of total inorganic iodine at the coastal station C1, while the hypothetical slope is  $-1 \mu\text{mol dm}^{-3} / \mu\text{mol dm}^{-3}$  (as only inter-conversion processes between iodate and iodide are assumed). At lower salinities (Figure 6b), however, only a fraction of data points are within the hypothetical envelope and the scattering is more pronounced. The deviations during spring, when most of the sampling points fall below the hypothetical relationship, point to the removal of dissolved iodate and/or iodide, while during the late autumn/winter period both species were produced in the brackish surface layer. This seasonal trend in iodate and iodide distributions both at the upper estuarine section between stations E2 and E9 and the lower section between stations E3 and E5 is particularly obvious when rational-

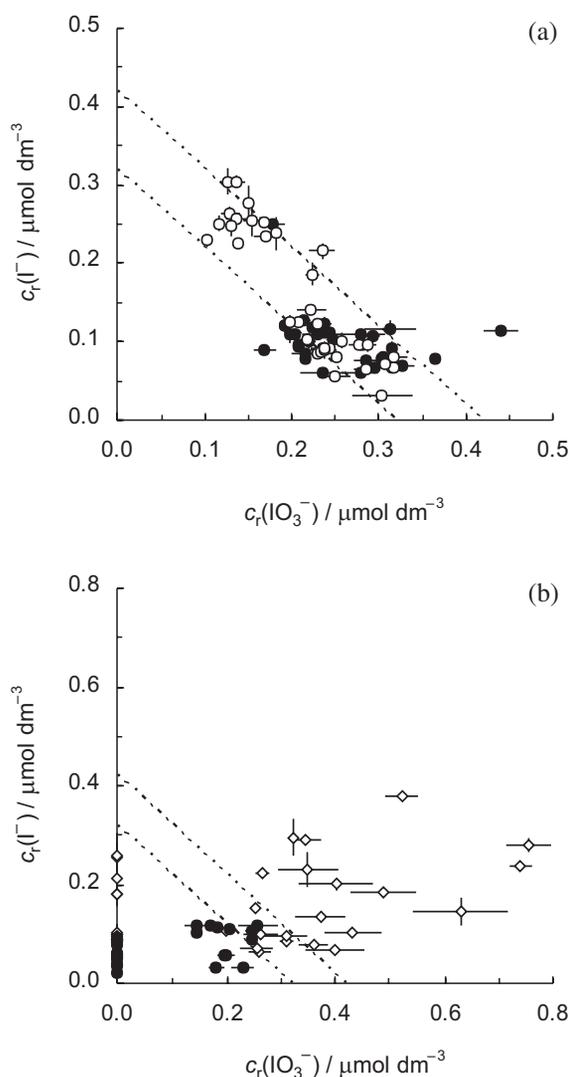


Figure 6. Relationship between rationalized concentrations ( $c_r$ ) of iodate and iodide: a) at higher salinities ( $S \geq 10$ ), and b) at lower salinities ( $S < 10$ ). White symbols refer to the late autumn/winter period, black symbols refer to the spring period.

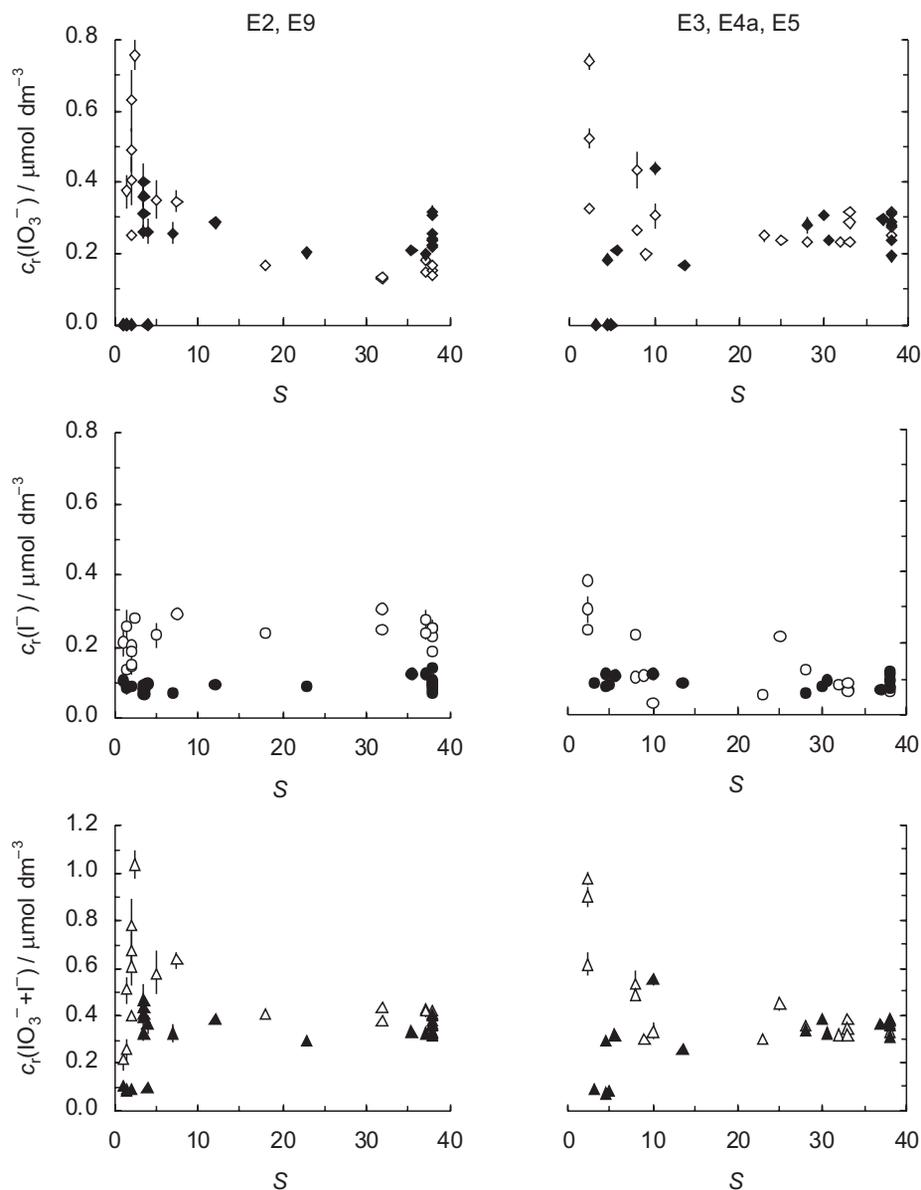


Figure 7. Relationship between rationalized concentrations ( $c_r$ ) of iodate ( $\diamond, \blacklozenge$ ), iodide ( $\circ, \bullet$ ) and total inorganic iodine ( $\triangle, \blacktriangle$ ), and salinity at stations E2/E9 (left side graphs) and E3/E4a/E5 (right side graphs). White symbols refer to the late autumn/winter period, black symbols refer to the spring period.

ized concentrations are plotted *versus* salinity (Figure 7) and the scattering of data points no more seems to be so randomly distributed at low salinity end. Unlike to graphs where concentration is plotted *versus* salinity (Figure 5), the relationship between rationalized concentration and salinity implies a hyperbolic form when the two end-member mixing model is applied, which bends up or down according to either the positive or negative intercept at zero salinity, respectively. If the intercept is equal to zero, the hyperbola does not bend in any direction, thus representing dilution processes.<sup>24</sup> Though the intercept can barely represent the concentration at zero salinity (like in this case where negative values and large standard errors of the intercept were found), temporal similarities in iodate and iodide distributions at various

stations cannot be neglected. During both the late autumn/winter and spring periods, iodate showed significantly higher reactivity than iodide at lower salinities, whereas variations in the more saline layer were less pronounced. Iodide concentrations, on the other hand, were tightly coupled along an almost horizontal straight line during spring, suggesting virtual absence of secondary processes that might affect iodide concentration and point to simple dilution. During winter, the concentrations were more variable, following the same upward trend as iodate in the upper layer in the lower estuarine section (E3–E5).

The role of the freshwater phytoplankton for iodate concentration thus seemed more important than that of the marine phytoplankton, since the obtained variations

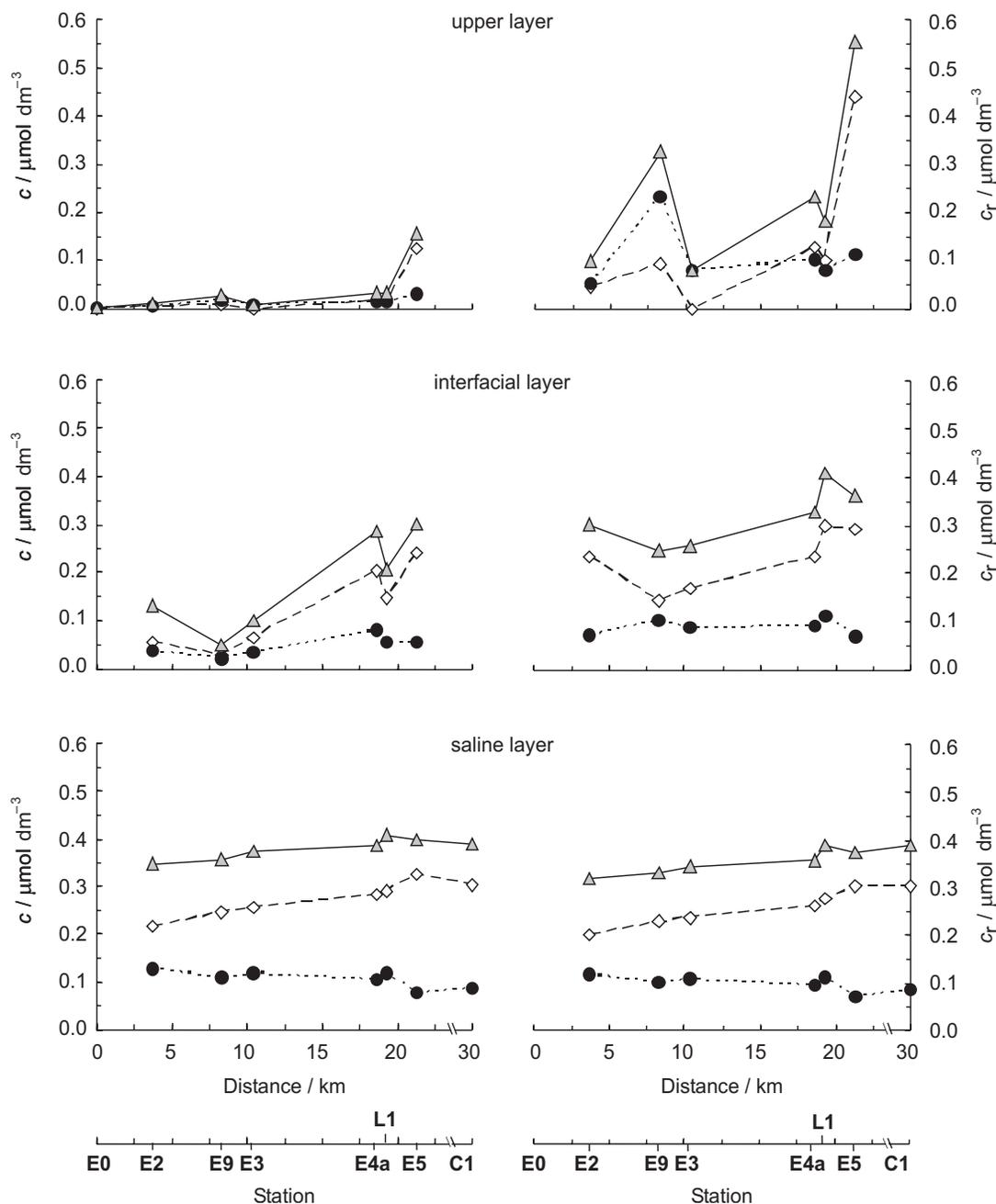


Figure 8. Longitudinal profiles of the average iodate ( $\diamond$ ), iodide ( $\bullet$ ) and iodate+iodide ( $\blacktriangle$ ) concentrations ( $c$  – left side graphs) and rationalized concentrations ( $c_r$  – right side graphs) in the brackish, interfacial and saline layers in the Krka estuary (April 2001).

were restricted to low salinities. In the freshwater/brackish layer, diatoms represent the most abundant phytoplankton group and the depletion of iodate during spring may reflect biological uptake when nitrate is depleted,<sup>39</sup> particularly as at this concentration level of iodate even reduced biological uptake may cause the observed differences. During winter, the phytoplankton biomass accumulates in the brackish layer, due to higher input of the Krka River nutritious salts. However, the phytoplankton activity is generally lower compared to that in the spring/summer period. Indicators of the possible role of living freshwater phytoplankton in iodate production were the

depth profiles of rationalized iodate concentrations and pH. While iodide concentration maxima were mainly recorded at the bottom of the interfacial layer, the iodate maxima were observed either at the surface or directly above the halocline. These iodate maxima agree well with pH maxima (which may indicate phytoplankton production) and were more pronounced during winter. Z-shaped distributions of rationalized iodate around the halocline were also observed during spring but these were far less pronounced. The role and importance of freshwater phytoplankton in the production of inorganic iodine need to be further investigated. Besides phytoplankton activity,

the processes including formation and degradation of organic iodine, dissimilatory iodate reduction as well as the photochemical processes in the surface layer could have also contributed to the observed variations in iodate and iodide distributions in the upper layer.<sup>4</sup>

*Longitudinal Distribution.* – Longitudinal profiles of iodate and iodide in three well separated water layers in the estuary (sections E0–C1) revealed that both speciation and distribution of inorganic iodine were not controlled only by the simple dilution but also by the secondary, biochemical processes (Figure 8). Brief attention will be paid first to the saline layer where longitudinal distributions showed fewer variations and a rather smooth pattern, due to less pronounced phytoplankton activity. Distributions in this saline layer indicated that beside iodate uptake/reduction and iodide production toward the head of the estuary, a slight removal of total inorganic iodine also occurred. The presence of the marine phytoplankton species capable of assimilating iodate and releasing dissolved iodine in the form of iodide,<sup>2,40,41</sup> such as the most abundant *Skeletonema Costatum* and *Chaetoceros* sp.,<sup>31</sup> has been confirmed in the Krka estuary. These results are consistent with our findings. Beside phytoplankton activity, the reduction of iodate at the boundary between anoxic sediment and oxic overlying water could have also contributed to the observed longitudinal variations in the more stagnant marine layer.<sup>42</sup> Anoxic conditions in the sediment profiles were determined at stations E2 and E9.<sup>43</sup>

Differences between the concentration and rationalized concentration scales were higher in the interfacial and brackish layers, but an increasing trend toward the estuarine mouth in the concentration of total inorganic iodine can be obtained on both scales (Figure 8). In addition to a specific distribution at the stations in the Šibenik harbor, an extremely high concentration of iodide ( $0.09 \mu\text{mol dm}^{-3}$ ) was detected in the water sample at a depth of 2.0 m at station E9 (April 2001). This unexpectedly high value above the halocline ( $S = 3.0$ ) might be connected with the marked brownish layer that was observed by a diver at this water depth. One day earlier, at station E2 situated upstream, the concentrations of both iodate and iodide were slightly enhanced at depths of 1.5 m and 2.0 m, and 2.0 m, respectively. It seems that such an unevenly formed layer of organic and/or inorganic origin is capable of accumulating a significant quantity of inorganic iodine. In the estuarine area situated downstream, which is affected by additional anthropogenic nutrient input (stations E4a, L1 and E5), the variations in iodate concentration were also high in the brackish layer. Upon presumption that the iodate uptake at station E3 was due to high freshwater phytoplankton activity, the production of inorganic iodine toward the estuarine mouth may reflect either an opposite process or the production of inorganic

iodine from organic matter. Results of the longitudinal spring distributions of chlorophyll-*a* and its breakdown products in the Krka estuary<sup>33</sup> (indicators of the physiological status of the phytoplankton biomass) support these explanations. Distribution of the most abundant degradation product (phaeophorbide-*a*) showed an increasing trend in the downstream direction and the highest concentration in the brackish layer at the estuarine transect from stations E4a to E5, where the chlorophyll-*a* concentrations were also higher. Allowing for the possibility that these longitudinal distributions in the brackish layer represent the typical pattern during spring, since iodide was virtually uninvolved in these processes, iodate was produced either from phytoplankton or from organic matter. Most of the recent studies report that dissolved organic iodine may be formed either from iodate or iodide via biotic or abiotic mechanisms, but that the main product of its decomposition would principally be iodide.<sup>3,4,7</sup> Contrary to these findings, our results show that not only was iodate produced in the upper layers at the outermost estuarine stations, but also that the production of iodate exceeded that of iodide. Though it is less likely that iodate was produced by bacterial or photochemical decomposition of the dissolved organic iodine, a contribution of sequential oxidation processes should be considered. Also, the production of iodate at the outermost station due to a specific phytoplankton assemblage at higher salinities, developed through additional nutrient input, cannot be rejected.

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## SAŽETAK

### Raspodjele jodata i jodida u vodama stratificiranog estuarija

Vesna Žic i Marko Branica

Raspodjele kemijskih vrsta anorganskog joda u visoko stratificiranom estuariju rijeke Krke (istočna obala Jadranskog mora) proučavane su u razdoblju od prosinca 2000. do travnja 2001. godine. Kroz promatrano razdoblje potvrđeno je konzervativno ponašanje ukupnog anorganskog joda, a uočene su i značajne vremenske i longitudinalne razlike u raspodjelama. U slanijim slojevima ( $S \geq 10$ ) koncentracije jodata i jodida su znatno manje varirale u usporedbi s onima u bočatom sloju i međusloju, što ukazuje na slabiju dinamiku i slabije izražen utjecaj sekundarnih procesa na raspodjelu anorganskog joda. U gornjim slojevima utvrđen je porast koncentracija jodata i jodida prema izlazu iz estuarija. Sezonske različitosti u raspodjelama jodata i jodida u bočatom sloju pokazatelj su važne uloge riječnog fitoplanktona i organske tvari za kruženje anorganskog joda u estuariju.