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Vesna Zic, Victor W. Truesdale, Cédric Garnier, Neven Cukrov. The distribution of iodine in the Croatian marine lake, Mir - The missing iodate. *Estuarine, Coastal and Shelf Science*, 2012, 115, pp.377-387. 10.1016/j.ecss.2012.07.026 . hal-01096854

HAL Id: hal-01096854

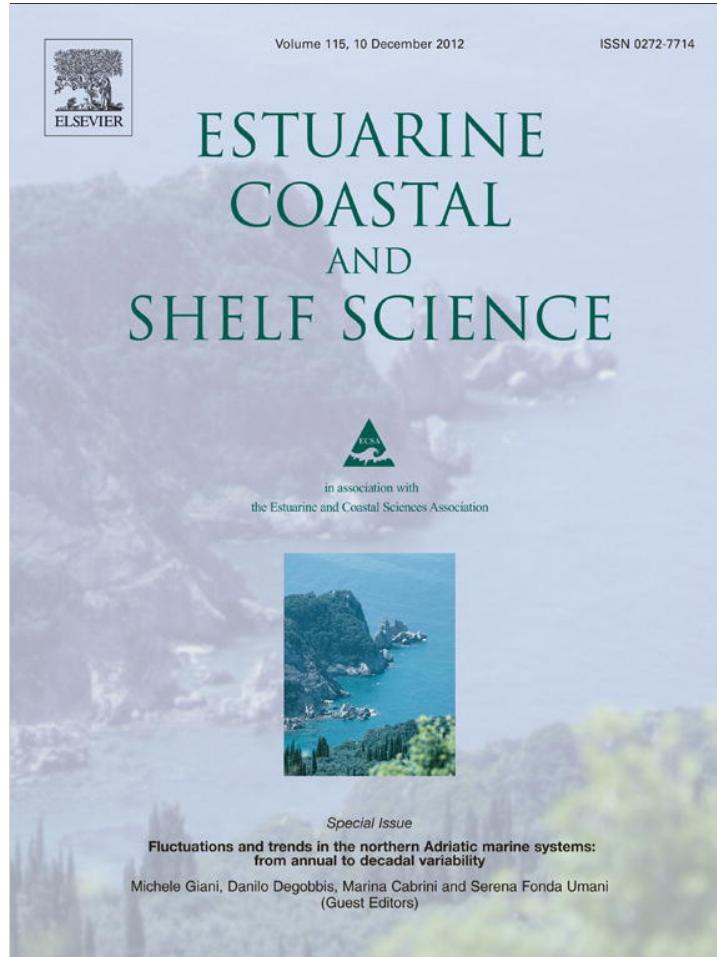
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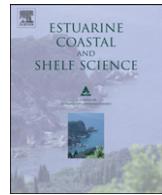
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## The distribution of iodine in the Croatian marine lake, Mir – The missing iodate

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## ARTICLE INFO

## Article history:

Received 16 January 2012

Accepted 27 July 2012

Available online 4 August 2012

## Keywords:

iodate  
iodide  
organic iodine  
nutrients  
marine lakes  
Croatia  
Dugi Otok  
Lake Mir

## ABSTRACT

The marine chemistry of iodine has been studied in the marine lake, Mir, regarded as a natural reactor situated in the karstified carbonate rocks of the Croatian Adriatic coast. The investigation covered the major variables: salinity, temperature, dissolved oxygen, pH and alkalinity, some nutrients, organic carbon, and iodide, iodate and organic-I. Lake Mir was found to be meso-trophic, with dynamic nutrient cycling of a magnitude usually associated with the temperate zone but within a Mediterranean climate. An essentially U-shaped pattern exists in the plot of nutrient concentration *versus* time for the June–November period studied. Together, the major variables and the nutrient chemistry confirm that Lake Mir is essentially isolated from the nearby (90 m) Adriatic seawater, and this also may explain the meso-trophic nature of the lake, with dry and wet deposition as the source of the extra nutrient. It is of note that iodate was essentially absent from Mir during the sampling period. This appears to be consistent with iodine's behaviour in the oceans in general, where iodate is reduced generally as a result of the presence of the biota. The chemistry of iodine in Lake Mir is consequently dominated by changes in iodide and organic-I concentrations, with the latter at higher concentrations than those found in seawater. Even so, the total iodine concentration in Mir is only about one-quarter of that in the adjacent Adriatic seawater, and again it is argued that this is probably a function of Lake Mir's isolation.

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## 1. Introduction

Dissolved iodine is generally present in seawater as iodate, iodide and organically bound iodine, at a total concentration of about 0.45  $\mu\text{mol l}^{-1}$  (Sugawara and Terada, 1957; Truesdale, 1975, 1994a; Elderfield and Truesdale, 1980; Nakayama et al., 1989; Wong, 1991; McTaggart et al., 1994; Campos et al., 1996). In the open, surface oxic oceans there is a zonal change from high proportions of iodate at the poles (Campos et al., 1999; Waite et al., 2006; Chance et al., 2010), to high proportions of iodide in the equatorial regions (Sugawara and Terada, 1957; Tsunogai and Henmi, 1971; Truesdale et al., 2000). A similar trend exists across the temperate continental shelf (Truesdale, 1978, 1994b; Wong and Zhang, 1992a; Wong, 1995; Truesdale and Jones, 2000; Truesdale and Upstill-Goddard, 2003). The zonal trend is consistent with the general oceanic circulation model (Broecker et al., 1982) where surface water sinks at high latitudes during winter, travels

southwards down the Atlantic, to join similar convective processing occurring around the Antarctic Continent. Eventually this water is released back to the surface flow in the Indian and Pacific Oceans. Accordingly, deep water in all the major ocean basins is high in iodate and low in iodide. Meanwhile, in anoxic systems, iodide is the predicted form of iodine (Wong and Brewer, 1977; Wong et al., 1985; Truesdale et al., 2001a; Waite et al., 2006).

Dissolved organic-I is mostly associated with inshore waters, since in open oceans it is a minor component and it represents only few percent of the total dissolved iodine pool (Truesdale, 1975). In near-shore environments, particularly estuarine waters, organic-I can sometimes exceed the sum of the inorganic fractions (Luther et al., 1991; Cook et al., 2000; Wong and Cheng, 2001a; Wong and Zhang, 2003; Schwehr and Santschi, 2003; Schwehr et al., 2005). The contribution of organic-I to total iodine generally increases with decreasing salinity, and is found to be associated with either higher productivity of these waters or greater input of terrestrial organic matter. The same pattern has been also confirmed in subterranean anchialine waters (Žic et al., 2011), which could well be regarded as subterranean (groundwater) estuaries (Moore, 1999; Humphreys, 2009). There, organic-I is derived from the porous carbonate bedrock. In humic-rich

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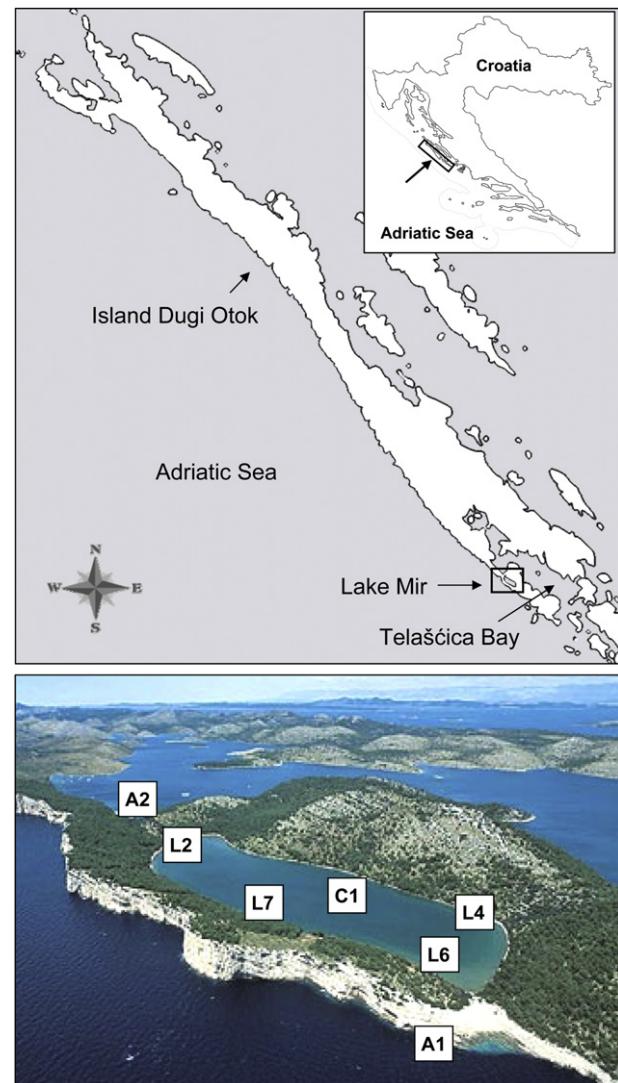
(Gilfedder et al., 2009) and oligotrophic (Gilfedder et al., 2010) limnic environments organic-I also predominates.

Iodine is generally thought of as a biophilic element although in seawater it is bio-intermediate. Thus, iodine is known to be absorbed by some macro-algae, e.g., *Laminaria digitata* (Shaw, 1959), concentrating at the extremely high  $3 \cdot 10^4$  times relative to its concentration in seawater. In microscopic algae the concentrations are much lower. However, a fairly abundant literature giving both the distribution of iodine and its interaction with these still leaves the precise mode of its oceanic cycling in doubt. In summary, uptake is small in comparison with reduction of dissolved iodate, I<sup>(+5)</sup>, to iodide, I<sup>(−1)</sup> (Sugawara and Terada, 1967; Tsunogai and Sase, 1969; Wong et al., 2002; Waite and Truesdale, 2003), and while iodate and iodide have been purported to be inter-converted by various species of these organisms, the culturing work (Sugawara and Terada, 1967; Tsunogai and Sase, 1969; Wong et al., 2002; Waite and Truesdale, 2003; Chance et al., 2007) does not agree with the field observations. To some, other microscopic organisms, e.g., non-photosynthetic bacteria, seem more likely to be involved, simply because the annual phytoplankton bloom in the temperate regions has not been linked definitively to iodate reduction (Truesdale, 1978, 1994a,b; Truesdale and Jones, 2000; Truesdale and Bailey, 2000, 2002; Truesdale et al., 2003a,b). Truesdale (1994a) re-assessed the evidence which originally suggested that algae were the likely agents of reduction (Elderfield and Truesdale, 1980).

The present study arose out of an iodine survey conducted on the marine lake, Mir in 2010. The lake was chosen as Žic and Branica (2006) and Žic et al. (2010) had shown that another, physically comparable anchialine system (Greek: αγκυλή – near the sea; Holthuis, 1973) in Croatia behaves as an isolated “reactor” in which various biogeochemical processes operate differently to those in open seas. Lake Mir is further of interest because, in spite its short distance from the surrounding Adriatic ( $\approx 90$  m), it displays up to four times a lower concentration of total iodine than does the nearby open seawater, with barely discernible iodate concentrations ( $\approx 0.02 \mu\text{mol l}^{-1}$ ). These preliminary results provoked the more intensive sampling of the lake over the summer and autumn 2011.

## 2. Study area

Lake Mir is a marine lake located at the eastern coast of the Adriatic Sea ( $43^{\circ}53'12''$  N,  $15^{\circ}10'$  E), at the south-eastern part of the island Dugi Otok in the Nature Park Telašćica (Fig. 1), formed by marine submersion of karst uvala (compound sinkholes). The lake is elongated,  $\approx(0.9–0.3)$  km, with a surface area of  $\approx 0.23 \text{ km}^2$  and a maximum depth of ca. 7 m. There is no obvious surface connection to the sea nor any known extensive sub-surface, tunnel-like, connection, so that seawater replenishment is restricted. Despite the fissures and cracks that are to be found in the rock at its northern and south-western part, communication with the surrounding Adriatic Sea is minimal since the lake's tidal range is only about 1 cm (Džaja, 2003), compared to the mean daily tidal range of 25 cm in the adjacent sea (Croatian Hydrographic Institute). The lake's low tidal range (less than 2 cm) was also confirmed during spring of 2012 with Sensus Ultra (ReefNet) data loggers (N. Cukrov, pers. comm.). The shores of the lake are rocky and the lake bottom in shallow areas (up to around 2 m) is rocky and/or sandy with gravels. At greater depths it becomes muddier, covered with clay or fine grey silt. The deepest regions are covered with pellet mud, and during phytoplankton blooms these sediments could be overlaid with formations of mucilaginous aggregates.



**Fig. 1.** The geography of the sampling locations. Lake Mir in relation to the Croatian coast (upper figure). The sampling positions on Lake Mir, and the two marine on the Adriatic coast (A1 and A2) (lower figure).

## 3. Sampling and analysis of waters

### 3.1. Sampling

Surface water samples from Lake Mir and the Adriatic Sea were collected in March 2010 (Fig. 1, Table 1) and between June and October 2011 at Stations L7 and A1 (Fig. 1), approximately twice per month. Depth profiles at the central lake station C1 (Fig. 1) were taken in June and September 2010 and July 2011 by a scuba diver progressively

**Table 1**

Salinity, alkalinity, iodate, iodide, total inorganic iodine and total iodine concentrations in surface samples at two marine (A1, A2) and four Lake Mir stations (L2, L4, L6, L7) in March 2010.

| Station | S    | A<br>(mmol l <sup>−1</sup> ) | c(IO <sub>3</sub> <sup>−</sup> )<br>(μmol l <sup>−1</sup> ) | c(I <sup>−</sup> )<br>(μmol l <sup>−1</sup> ) | c(TII)<br>(μmol l <sup>−1</sup> ) | c(TI)<br>(μmol l <sup>−1</sup> ) |
|---------|------|------------------------------|---|---|-----------------------------------|----------------------------------|
| A1      | 38.5 | 2.71                         | 0.340   | 0.080   | 0.420                             | 0.437                            |
| A2      | 38.0 | 2.86                         | 0.330   | 0.085   | 0.415                             | 0.417                            |
| L2      | 37.0 | 2.95                         | 0.024   | 0.052   | 0.076                             | 0.102                            |
| L4      | 37.0 | 3.03                         | 0.027   | 0.050   | 0.077                             | 0.104                            |
| L6      | 37.0 | 2.97                         | 0.022   | 0.050   | 0.072                             | 0.095                            |
| L7      | 37.0 | 2.98                         | 0.020   | 0.051   | 0.071                             | 0.093                            |

working deeper, so as to minimise disturbance. In September 2010 dense foam accumulated down-wind on the lake's surface, and the diver found mucilaginous aggregates at the bottom of the lake.

### 3.2. The major variables

Salinity, temperature and dissolved oxygen concentration depth profiles were determined *in situ* by a Hach Lange HQ40D Multi-meter. Salinity was calibrated by potassium chloride solution supplied by the manufacturer, while the oxygen meter used an automatic internal calibration, and was occasionally checked for a 100% of saturation. Immediately after collection the pH of samples was measured with an MP120-B (Mettler-Toledo AG) pH-Meter with an In Lab 427 electrode. The pH electrode was calibrated with standard pH 4 and 7 buffer solutions, and since no correction was made for ionic strength, the pH measurements are operational.

The salinity of surface samples was calculated from chlorinity, itself determined by a Mohr's titration (Millero, 2006), with a precision of  $\pm 0.5\%$ . Temperature was measured *in situ* with a mercury in glass thermometer, while pH was determined by pH 300 pH-Meter (Hanna Instruments). Alkalinity was determined according to ISO 9963/1:1995(E), by titration with  $0.100 \text{ mol l}^{-1}$  hydrochloric acid solution using Bromocresol Green-Methyl Red indicator. The relative standard deviation (Coefficient of variation) on replicate samples was less than  $\pm 1\%$ .

### 3.3. The iodine speciation

The concentrations of iodate, iodide and total iodine in unfiltered samples were measured by voltammetry, using a PAR 384B Electrochemical Analyser in conjunction with PAR 303A static mercury drop electrode (SMDE), with an Ag/AgCl (sat. NaCl) reference electrode and a platinum wire as a counter electrode. Iodate and iodide were determined directly by differential pulse voltammetry (Herring and Liss, 1974) and cathodic stripping square wave voltammetry (Luther et al., 1988), respectively. Total iodine (TI) was determined indirectly as iodate after oxidation of reduced iodine species by UV-irradiation (24 h, 150-W mercury lamp; Hanau, Germany) in the presence of hydrogen peroxide. This was followed by treatment with hypochlorite to destroy any trace of peroxide as well as to re-oxidise iodine species of lower oxidation state than iodate that might have formed during irradiation (Truesdale, 1975; Butler and Smith, 1980; Stipaničev and Branica, 1996; Wong and Cheng, 1998). To facilitate the removal of dissolved oxygen, as well as to destroy the excess of hypochlorite, sodium sulfite was also added to the samples (Wong and Zhang, 1992b). Peak currents were determined from the baseline-corrected voltammograms, with either the baseline being constructed using a spline function or by second-derivative mode implemented in a home-written software package, ECDSOFT (Omanović and Branica, 1998; Pižeta et al., 1999; Omanović, 2006).

Calibration was by the standard addition method and linear regression analysis was used to calculate the concentration in the original sample. This offered a high level of analytical quality control as any deterioration of the methods was detectable early, either in poor replication of the calibrations or poor overall reproducibility. Detection limits in iodate and iodide analyses were around  $0.015 \mu\text{mol l}^{-1}$  and  $0.001 \mu\text{mol l}^{-1}$ , respectively. The overall precision was evaluated from a larger set of duplicate measurements, as described by Currie and Svehla (1994), and expressed as a relative standard deviation, it was typically within  $\pm 2\%$  for iodate,  $\pm 4\%$  for iodide and  $\pm 5\%$  for total iodine analyses. The concentration of organic iodine was calculated as the difference between total iodine (TI) and total inorganic iodine (TII; iodate + iodide) concentration,

so that precision was about  $\pm 10\%$ . Iodine samples were stored in the dark at  $4^\circ\text{C}$  for no more than a week before analysis.

### 3.4. Nutrient analysis

The concentrations of nutrients were measured on Perkin Elmer Lambda 25 UV/Vis spectrometer. Due to the higher concentration of organic matter in lake samples, the spectral curves were corrected for the background absorbance either by omission of a key reagent specified by the method or by application of second-derivative spectroscopy.

Nitrate + nitrite, nitrite and ammonium were measured according to Zhang and Fischer (2006), Griess-Ilosvay method (Strickland and Parsons, 1968) and Bower and Holm-Hansen (1980), with method detection limits of about  $0.5 \mu\text{mol l}^{-1}$ ,  $0.03 \mu\text{mol l}^{-1}$  and  $0.4 \mu\text{mol l}^{-1}$ , respectively, and the overall precision  $\pm 10\%$ .

Orthophosphate and total phosphorus concentrations were analysed according to ISO 6878:1998(E). The method is based on formation of phosphomolybdate complex, which is subsequently reduced with ascorbic acid to form a strongly coloured blue molybdenum complex, the absorbance of which is measured spectrometrically at about 880 nm. For total phosphorus determination, prior to orthophosphate ions analyses, samples were digested with sulfuric acid and nitric acid, the reagents that are more effective in the presence of large quantities of organic matter than peroxodisulfate oxidation. Detection limits in orthophosphate and total phosphorus analyses were  $0.04 \mu\text{mol l}^{-1}$  and  $0.15 \mu\text{mol l}^{-1}$ , respectively, while precision was typically better than  $\pm 10\%$ . Samples were analysed within 48 h.

### 3.5. Dissolved and particulate organic carbon

To determine the total and dissolved organic carbon content, an aliquot was filtered on 25-mm glass filters (GFF, Whatman) using an all-glass filtering system (Wheaton) under vacuum. All the glass equipment (filter, tubes, filtering system) was calcined at  $450^\circ\text{C}$  for 4 h prior to use. The resulting dissolved fraction was stored in a 24-ml glass tube equipped with a teflon/silicone septum (Wheaton), and poisoned with  $50 \mu\text{l}$  of  $1 \text{ mol l}^{-1}$   $\text{NaN}_3$  (Aldrich), and stored in the dark at  $4^\circ\text{C}$  until analysis. Filters were dried to constant weight at  $60^\circ\text{C}$ , and then exposed to HCl fumes for 4 h to remove all the inorganic carbon (Lorrain et al., 2003). The dissolved organic carbon (DOC) concentrations were determined using a Shimadzu TOC-VCSH analyser, using the high-temperature ( $680^\circ\text{C}$ ) catalytic oxidation method with IR detection of  $\text{CO}_2$  (Benner and Strom, 1993), calibrated using potassium hydrogen phthalate (Fisher Scientific, Analytical Reagent grade) (Louis et al., 2009). The particulate organic carbon (POC) concentration on the filters was determined using the same equipment, via the Shimadzu SSM-5000 module which uses catalytic oxidation at  $950^\circ\text{C}$ , and is calibrated using glucose (Fisher Scientific, Analytical Reagent grade). The sum of the DOC and the POC yielded the total organic carbon (TOC) content to an accuracy of 10%. Precision was typically better than  $\pm 5\%$ .

## 4. Results

### 4.1. The preliminary survey

The preliminary survey in March 2010 showed that spatially, the major constituents of Mir Lake surface water were fairly constant, and close to that of Adriatic water (Table 1). Thus, salinity and alkalinity in shore samples from positions L2, L4, L6 and L7 (Fig. 1) were  $37.0 (\pm 0.3)$  and  $2.98 (\pm 0.03) \text{ mmol l}^{-1}$ , respectively, which

corresponds well with values of 38.0 ( $\pm 0.3$ ) and 2.79 ( $\pm 0.11$ ) mmol l<sup>-1</sup>, respectively, in the Adriatic seawater at A1 and A2. Meanwhile, the concentration of TII of 0.074 ( $\pm 0.003$ ) µmol l<sup>-1</sup> in lake water was about 20% of that in seawater. This difference in concentration was greater for iodate than for iodide as the iodate concentration was only 8% of the seawater value, while that of iodide was 62% of the seawater value. The organic-I concentration in the lake (TI–TII) was slightly higher in the lake than in the sea.

#### 4.2. Depth profiles at station C1

##### 4.2.1. Major constituents

In June and September 2010 the depth profiles for the major constituents (salinity, temperature, dissolved oxygen, alkalinity, and pH) confirmed the consensus (e.g., Carić et al., 2010) that Lake Mir is well mixed (Fig. 2). In July 2011 this also appears to have been the case up to around 5 m, but the deeper water may be stratified. Given the lower temperature and salinity of the bottom water this appears to have been caused by a lack of mixing during the summer, with warming and evaporation of near surface water. This corresponds with a period of stable meteorology, lacking rain and strong winds. Alkalinity and pH measurements, where made, comply with this interpretation. The depth profile of dissolved oxygen in July 2011 indicates that most of the water column was oxic. Hypoxic conditions were representative only in the deepest layer.

##### 4.2.2. Nutrients

Although the differences in distribution are only minor, over the period from June to September 2010 nitrate and nitrite concentrations decreased, and that of ammonium increased (Fig. 2). This appears to agree with a system in which nitrate is taken up in the spring bloom, but ammonium is the form to which nitrogen is predominantly regenerated, particularly later in the year. The profiles in July 2011 additionally confirm this seasonal pattern in the upper half of the water column. Meanwhile, and in accordance with the vertical profiles for the major constituents, regeneration of nutrients from settling algae and a possible diffusion of ammonium out of the lake sediment predominates in the bottom waters.

##### 4.2.3. Organic carbon and suspended solids in July 2011

The profiles of particulate and dissolved-organic carbon (Fig. 2), as well as of suspended solids were relatively uniform with depth, with the mean values ( $\pm$ s.d.) of 0.13 ( $\pm 0.01$ ), 0.31 ( $\pm 0.01$ ) mmol l<sup>-1</sup>, and 9.3 ( $\pm 0.8$ ) mg l<sup>-1</sup>, respectively. Meanwhile, the seawater sample from marine station A1 on the same day had POC and DOC concentrations of only 0.01 mmol l<sup>-1</sup> and 0.09 mmol l<sup>-1</sup>, respectively, while the concentration of suspended solids was 3.9 mg l<sup>-1</sup>.

##### 4.2.4. Iodine species

The most notable feature of the iodine distributions is that at all three samplings (Fig. 2), the iodate concentration in Lake Mir water was below the detection limit for the method. Meanwhile, between sampling occasions there is much variation in the shapes of the profiles for organic iodine while, in comparison, that for iodide is more uniform. Altogether, this imposes changes upon the shape of the profile for TI.

Over the top 5 m, the iodide concentration depth-profile is essentially vertical, but with considerable variation between sampling occasions. For June and September 2010, and July 2011 the iodide concentrations are about 0.11, 0.03 and 0.06 µmol l<sup>-1</sup>, respectively. Tentatively then, there may be a seasonal pattern whereby iodide concentrations decrease from spring to summer. The small increase in iodide at the bottom in July 2011 may correspond with the similar trend in ammonium, except that an

identical increase was evident in June 2010 without any corresponding change in the major constituents or ammonium. Accordingly, only a tentative deduction can be made here.

The vertical profiles of total iodine take on three different shapes over the period sampled, with the average concentration of 0.19 µmol l<sup>-1</sup> in June 2010 and 0.12 µmol l<sup>-1</sup> in September 2010 and July 2011. Meanwhile, the average organic-I concentrations were similar in June and September 2010 (0.08 µmol l<sup>-1</sup>) and ca. 30% lower in July 2011 (0.05 µmol l<sup>-1</sup>). Since the profiles for iodide were essentially vertical, except at depth in July 2011, the organic-I profiles mostly follow those of total iodine. Accordingly, in June 2010 organic-I concentration was higher in the top 3 m of the water column, while in September 2010 concentrations were higher in deeper layers. The profile in July 2011 was rather uniform with depth (Fig. 2) and, because total organic carbon displays the same feature, the mean ratio ( $\pm$ s.d.) between organic-I and TOC was within a narrow range of  $(1.2 \pm 0.2) \cdot 10^{-4}$ , the mole ratio which is consistent for *in-situ* formed organic matter. Within this setting, the shape of organic-I profile in September 2010 will be consistent with settling and accumulation of organic matter in deeper layers, which is also supported by diver observations of mucilaginous aggregates on the lake bottom. Additionally though, a strong south-east wind in September 2010 caused intensive foam production at the lake surface, and because the foam is found to be greatly enriched in organic-I (Truesdale et al., 2012), its production could have also affected organic-I distribution in the surface layers. In particular, the bubbles introduced by waves have the ability to effectively scavenge surfactant organic matter from the bulk water. Although wave action also mixes the surface layer, the net effect will be an increase in the amount of organic matter at the surface. Monahan (2001) describes this as, 'organic memory'.

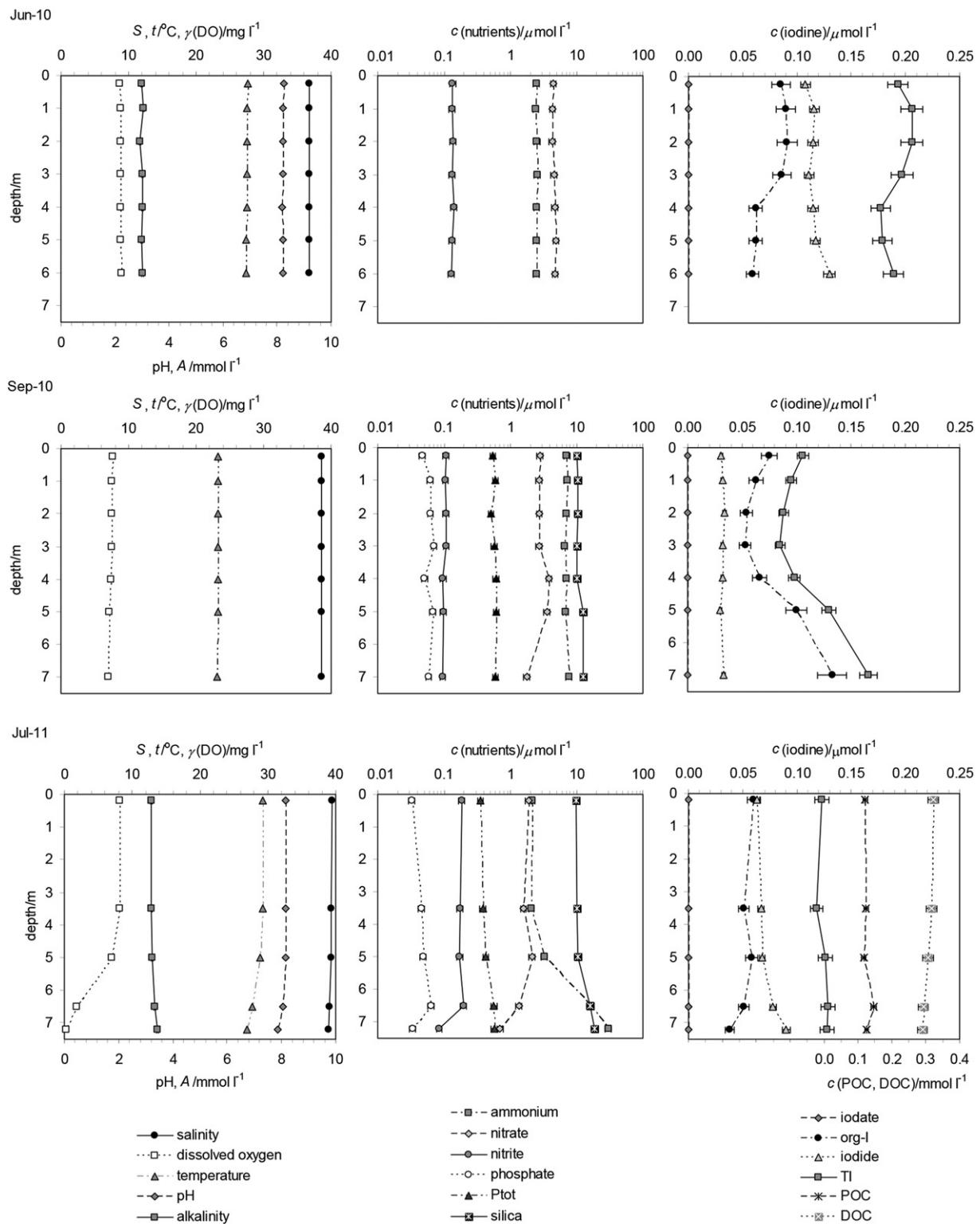
#### 4.3. The 2011 time series investigation, twinned for open seawater and Lake Mir

##### 4.3.1. The general variables

Although there was very little salinity variation at the seawater station A1 ( $38.5 \pm 0.6$ ), at the Mir station L7 salinity was slightly lower (37.2) in early June, increasing steadily to 41.7 in October, at a steady rate ( $\pm$ s.e.) of 0.034 ( $\pm 0.003$ ) d<sup>-1</sup> (Fig. 3); in accordance with the low amount of precipitation (150 mm), and hence net evaporation experienced between June and October (Station Velike Sestrice; Croatian Meteorological and Hydrological Service). The coefficient of determination ( $r^2$ ) for regression of salinity against time in seawater and in Mir were 0.406 (7 df) and 0.946 (10 df), respectively. The temperature for Lake Mir surface water was about 2 °C higher than that of the seawater. Similarly, a *t*-test ( $p = 0.05$ ) showed that the alkalinity of Lake Mir water was significantly higher than that of seawater by an average of about 0.4 mmol l<sup>-1</sup>. Meanwhile, the pH of the open seawater was generally higher than in Lake Mir surface water; essentially it increased from 8.2 to 8.4 between June and October while the pH in lake water fluctuated more closely around a mean of 8.2, with the higher values between mid-July and October.

##### 4.3.2. The nutrient concentrations

The total-P concentration of Lake Mir surface water was ca. 3 times greater than in the surface water of the open sea (Fig. 3). The phosphate concentration of the seawater was almost undetectable until the latter part of the year. Nevertheless, in Lake Mir concentrations of phosphate of about 0.1 µmol l<sup>-1</sup> were present for much of the year, with a noticeable decrease in late July. The concentrations of ammonium, nitrite and nitrate were all very much higher and more dynamic in Lake Mir than in the open sea, generally



**Fig. 2.** Profiles of main physico-chemical parameters (salinity, temperature, dissolved oxygen, pH and alkalinity), nutrients (ammonium, nitrate, nitrite, phosphate, total phosphorus and silica), and iodine species (iodate, iodide, organic-I and total iodine) at central lake station (C1) in June and September 2010 and July 2011. On iodine graph for July 2011 particulate and dissolved organic carbon concentrations are also presented. Please note the log scale on nutrient profiles.

providing a U-shaped curve between June and October. The precise position of the minima for the curves does not appear to be identical. Up to August the concentration of silica in the lake surface water was about 2–10 times higher than in seawater, showing a notable maximum in July, while in the period that followed the concentrations and the patterns were more comparable (Fig. 3).

#### 4.3.3. The variation of iodine species at the seawater sampling point

The investigations of iodine in Adriatic seawater were primarily intended as a baseline or reference point for the Lake Mir study. However, as they are also of interest within the context of marine iodine chemistry they are firstly described in detail. The constancy of total iodine concentrations indicates that no appreciable gain or

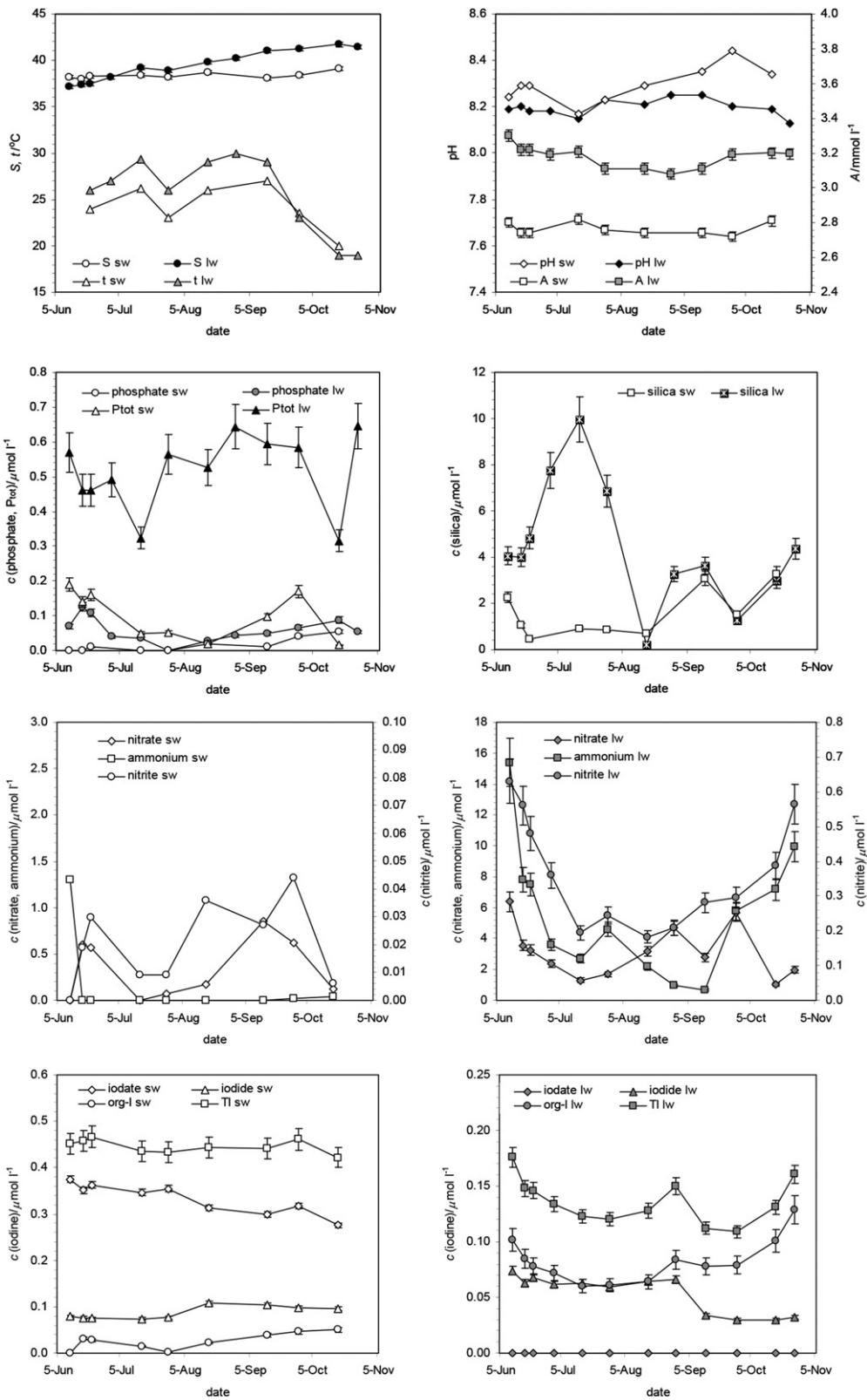
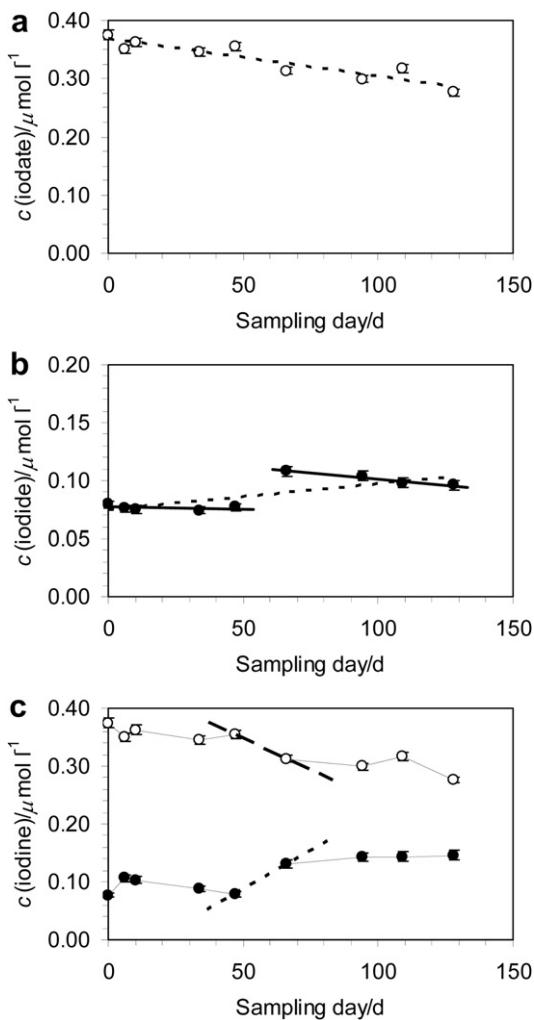


Fig. 3. The variation with time between June and November 2011 of the concentration of several species at sampling stations A1 (seawater, sw) and L7 (lake water, lw).

loss of iodine occurred over the investigated period. Meanwhile, iodate concentration decreased uniformly during the 130 days of investigation at a rate of  $0.7 (\pm 0.1) \text{ nmol l}^{-1} \text{ d}^{-1}$  (Fig. 4a). This was a robust result, as linear regression gave a coefficient of

determination ( $r^2$ ) of 0.86 which is significant at  $p = 0.01$  using the Pearson correlation. In contrast, the iodide results are better taken as two trends: a more or less constant iodide concentration of  $0.077 \mu\text{mol l}^{-1}$  over the first half of the period, followed by



**Fig. 4.** Variation in the concentration of iodine species in Adriatic seawater. (a) Iodate; the dotted line is the linear regression line for the points. (b) Iodide; dotted line, as previously. Black lines are separate regressions for the 5 and 4 points, respectively. (c) Mirror-like images of iodate (white circles) and iodide + organic-I (black circles). The slopes (long-dashed for iodate and dotted for iodide + organic-I) are described within the text.

a steadily decreasing concentration rate of  $0.2 (\pm 0.03) \text{ nmol l}^{-1} \text{ d}^{-1}$  (Fig. 4b). The profile of organic-I (Fig. 3) suggests that after an initial decrease, it increased from about mid-summer until autumn. The organic-I results should be viewed with somewhat greater caution, since organic-I contributes only up to around 10% to TI. A subtraction of large numbers (organic-I = TI – iodate – iodide) introduces higher uncertainty here.

An alternative view of the iodine system, which is also supported by iodine profiles on Fig. 3, is given by Fig. 4c, where the change in reduced iodine (iodide + organic-I) coincides with one in iodate. This de-couples the iodate concentration decrease over the sampling period into two distinct shorter periods, and since the reproducibility of the iodate measurements was  $\pm 2\%$ , the change in the shape of the iodate profile is sufficiently reliable to support this view. Similarly, the profile of the combined reduced iodine species (iodide + organic-I) is also free of higher uncertainty, since reduced iodine is calculated as a difference between TI and iodate. A mid-period shift in the concentration of iodate, with a gradient of  $-2.2 \text{ nmol l}^{-1} \text{ d}^{-1}$  is comparable to that of reduced iodine of  $2.7 \text{ nmol l}^{-1} \text{ d}^{-1}$ . The results tentatively suggest a seasonal pattern in iodine distribution, where iodate appears to be reduced at the

expense of iodide and organic-I. However, given that the survey covered only the surface samples over the four-month period, it would be premature to give greater weight to this, even though it is potentially important an observation.

#### 4.3.4. Iodine species in Lake Mir

The most notable result is the essential absence of iodate from the surface water of Lake Mir, as compared to that in open seawater where iodate concentration decreased steadily from  $0.38 \mu\text{mol l}^{-1}$  in June to  $0.28 \mu\text{mol l}^{-1}$  by the middle of October (Fig. 3). Meanwhile, the iodide concentration at both locations was very similar for about the first four months whence, in contrast to the slight increase in the open sea, in Lake Mir it decreased by about twice as much. Total iodine displayed a U-shaped curve in Lake Mir, similar to that of nitrogen species, while it remained essentially constant in the sea. These latter results for total iodine and iodide thereby imposed a U-shape upon the time-series graph for organic-I concentration in Lake Mir.

Although the lake is apparently well-isolated from the surrounding Adriatic, there appears to be a notable correlation between dissolved organic-I in the lake and in seawater. This was confirmed by a plot of the concentration of organic-I in the open seawater against that in Lake Mir water (Fig. 5a) which, provided the first point of the time-series was omitted, gave an  $r^2$  of 0.721 and a statistically significant Pearson correlation coefficient at  $p = 0.01 (df = 6)$ . However, introducing the first point of the time series negates the correlation completely. The observed temporal similarity in organic-I, together with comparable organic-I/TOC mole ratios for the lake water and the Adriatic surface water in July 2011 ( $1.2 \cdot 10^{-4}$  and  $1.5 \cdot 10^{-4}$ , respectively) suggest that the (micro)biological processes, which are most likely involved, were similar at both locations.

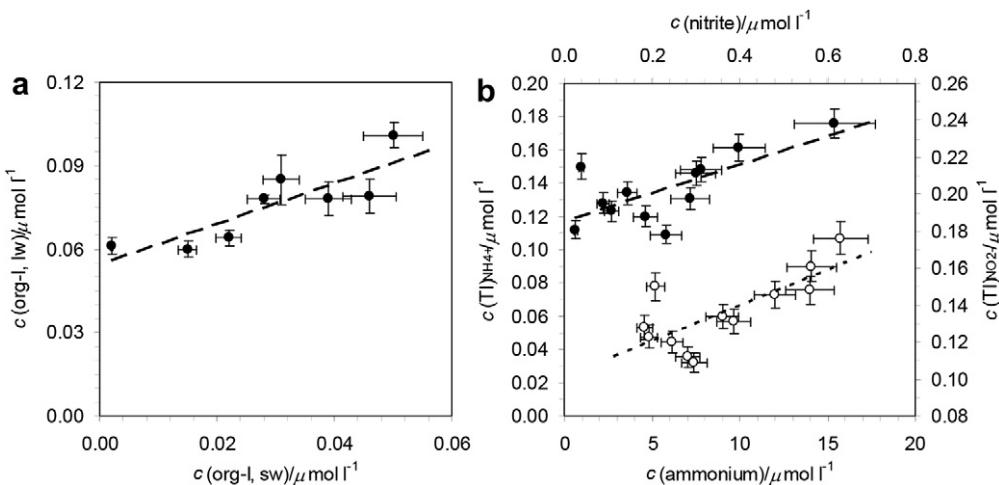
Fig. 5 also suggested that for Lake Mir, total reduced iodine (iodide + organic-I) correlates well with each of the reduced nitrogen compounds (Fig. 5b), as all of these graphs are U-shaped. The separate regression of total iodine concentration upon those of ammonium and nitrite yielded  $r^2$  of 0.51 and 0.56, respectively, for the same 12 points and give statistically significant Pearson correlation coefficients at  $p = 0.01 (df = 10)$ , suggesting that the processes involved in nutrient dynamics also affect the iodine system. In contrast, the regression of TI against that of nitrate yielded  $r^2 = 0.113$  and a statistically non-significant correlation.

## 5. Discussion

The marine lake, Mir, is an unusual natural environment in which various biogeochemical processes manifest themselves differently from those in the adjacent, open sea due to the specific geomorphology and hydrology of the lake isolating it from the sea. Concentration changes within the lake are not obscured by the rapid advection in of seawater. The isolation eliminates the inevitable problem of vertical advection between surface and deeper waters in open, marine systems. Overall, these conditions impose an overall reduced inventory (concentration) for iodine in the lake. The iodine system is additionally more simplified, since it is represented only by chemically reduced species, viz. iodide and organically bound iodine. These findings indicate that Lake Mir serves as a valuable outdoor laboratory for iodine studies.

### 5.1. The isolation of Lake Mir

If the  $\approx 90 \text{ m}$  of land separating Lake Mir from the Adriatic Sea were pervious to seawater the chemistry of Mir would have been identical to that of the sea. In fact, while an overall similarity in salinity, temperature, alkalinity and pH suggests a common origin



**Fig. 5.** The co-variation between various species in Lake Mir water and seawater. (a) Organic iodine in lake water versus organic iodine in seawater. (b) Total iodine versus ammonium (black circles), and nitrite (white circles) in the surface of the Lake Mir between June and November 2011. The best fit linear regression lines are shown.

for the two, the consistency of the differences between the two water bodies points to a sustained isolation of Mir water as shown by the saw-tooth shape of the salinity plot for seawater. This salinity change in the lake water from 42 to 37 would require about 600 mm of rain, assuming an average lake depth of 4 m and an area of 0.23 km<sup>2</sup>. This is comparable to the area's actual rainfall of 600–700 mm yr<sup>-1</sup> (Džaja, 2003). However, as the rainfall and evaporation effectively occur in separate seasons, this imposes the saw-toothed shape upon the salinity *versus* time graph; this both supports and is supported by the longer data series of Carić et al. (2010). Even though these same processes also occur in seawater, a comparable rise in the salinity of the seawater will be damped because the surface seawater will be mixed with deeper water, a feature not likely in Mir because of its isolation. This is supported by the more stable, ≈ 2 °C colder temperature of the Adriatic seawater; the smaller body of water is able to heat up more quickly. This is also reflected in the differences in the alkalinity and the pH between Mir and the sea although these are not necessarily as easy to explain as those for salinity and temperature. Alkalinity and pH are both involved in the carbonate system, which is affected by both photosynthesis and respiration and even, perhaps, calcite precipitation/dissolution within the Lake. The precise reasons for the differences are less relevant here but it is important that subtle differences occur, as these point to the isolation of Mir water.

In contrast to the subtle changes made against the large concentrations of the major variables of seawater, mentioned above, the low concentrations of the nutrients in Mir are markedly enriched relative to those in seawater. For example, the results show that at times ammonium-N and nitrate-N concentrations in Mir were 15 and 6 times greater, respectively, than those found in the seawater. Similarly, org-P seems to have been 3–6 times more concentrated. Even so, these differences still support the isolation thesis for Mir. Moreover, since the runoff is low (Džaja, 2003), as shown here from the subtle annual salinity variations, the atmospheric (wet plus dry) deposition is considered to be the most important source of nutrients to the Lake. Between 2006 and 2010, the average annual nitrate and ammonium supply *via* atmospheric deposition at Zadar, the station closest to the Lake Mir, was 0.8 ( $\pm 0.3$ ) g m<sup>-2</sup> (Statistical Yearbooks of the Republic of Croatia, [http://www.dzs.hr/hrv/publication/stat\\_year.htm](http://www.dzs.hr/hrv/publication/stat_year.htm)). Such a flux would be sufficiently high to increase the inorganic nitrogen concentration in the entire water column by about 14 ( $\pm 6$ ) μmol l<sup>-1</sup> yr<sup>-1</sup>, in approximately equal proportions of nitrate and ammonium.

This, for example, accords with the global atmospheric loading rates of total N of up to 3 g m<sup>-2</sup> yr<sup>-1</sup> (Shaw et al., 1989). Given the almost persistent phosphorus limitation in Lake Mir water (Carić et al., 2010 and Fig. 3 in this study), it appears that the atmospheric phosphorus deposition in this area is well below that required for a Redfield N:P ratio of 16:1, as observed in some other lake environments (Jassby et al., 1994). Overall then, the annual nutrient condition in Mir water reflects the balance between the atmospheric nutrient input, a highly restricted water exchange with the surrounding Adriatic, and the biological cycling within the lake.

##### 5.2. The reduced total-iodine inventory in the lake

At about 0.14 μmol l<sup>-1</sup>, the total iodine concentration in Mir is only about one-third of the equivalent concentration of that in seawater. Thus, the iodine results provide one-third, independent strand of evidence to support the isolation thesis for Mir. In this case, however, instead of representing a process of enrichment, they represent a loss although the processes responsible for the nutrient enrichment may still be responsible for the iodine depletion. Thus, unlike the N-nutrients, atmospheric iodine deposition is typically less than 0.01 μmol l<sup>-1</sup> (Truesdale and Jones, 1996; Baker et al., 2001; Gilfedder et al., 2008a,b). Accordingly, when a simple calculation is made for the Mir area based upon dry- and wet-deposition iodine fluxes of up to 9.2 μmol m<sup>-2</sup> yr<sup>-1</sup> for a coastal site (Baker et al., 2001), the annual flux from the atmosphere is only sufficiently high to increase the inorganic iodine concentration in the water column by ≈ 0.002 μmol l<sup>-1</sup>. Even if allowance is made for an organically bound iodine, which is ubiquitous in both rainwater and aerosol (see: Saiz-Lopez et al., 2012 for a detailed review), the flux still appears to be too low to affect the water column. Indeed, the accompanying study of foams formed on the surface of Lake Mir (Truesdale et al., 2012) suggests that the lake acts rather as a source of atmospheric iodine. In particular, natural foams from Lake Mir are enriched in organic-I up to 630 times relative to the surface water in the lake, and it is argued that organic-I is enriched in the lake micro-layer, becoming available as a supply-flux of iodine to the marine aerosol.

The iodine profiles (Figs. 2 and 3) are consistent with the iodine system being markedly affected by biological cycling (starting with phytoplankton, and ending in regeneration). This is supported by the organic-I/TOC mole ratio of  $(1.2 \pm 0.2) \cdot 10^{-4}$  in the lake water

(Sec. 4.2.4), which is close to the literature value of  $(1.0\text{--}1.6) \cdot 10^{-4}$  for I/C assimilation ratios in seston in the Pacific Ocean (Elderfield and Truesdale, 1980) and coastal Antarctic Ocean (Chance et al., 2010). The ratio is also comparable to  $\text{TI}_{\text{diss}}/\text{DOC}$  ratio of  $2.7 (\pm 0.5) \cdot 10^{-4}$  for the water column of a humic-rich freshwater lake (Mummelsee) (Gilfedder et al., 2009), where sediment-core iodine supports efficient biological uptake. Therefore, although the water column of Lake Mir seems to be well mixed during most of the year, it can be reasonably presumed that at least some of the iodine would be ultimately deposited into the sediment, since the contribution of POC to TOC is high (Sec. 4.2.3), and the surface sediments of Lake Mir seem to be in contact with well-oxygenated water during most of the year. Thus, Price and Calvert (1973) demonstrated that, relative to anoxic sediments, oxic ones are enriched in iodine. Therefore, the iodide flux from the lake sediment would only be pronounced during short periods of eventual anoxia in the near bottom layer (Gilfedder et al., 2009; Chapman and Truesdale, 2011).

The lack of anoxic conditions within the water column of the Lake Mir, together with a more restricted water exchange and lower terrestrial influence, also explains the large difference in the iodine budget between the Lake Mir and the nearby anchialine pond, Rogoznica Lake (Croatian: Zmajevi oko – Dragon's Eye). There, anoxic and sulfidic conditions in the sediment and bottom water promote iodine remobilisation during early diagenesis, and iodide diffuses from the lake sediment (Žic and Branica, 2006). Additionally, given that the amount of suspended solids in Lake Mir is also high, another pathway of iodine burial into the sediment may involve sorption of inorganic constituents onto solid-phases (e.g., Neal and Truesdale, 1976; Ullman and Aller, 1985). Against this background, although restricted, the water exchange between the Lake Mir and the surrounding Adriatic probably prevents this aquatic environment from becoming eutrophic, yet helps maintain the depletion in iodine. Therefore, over a prolonged period a quasi-steady state could be attained, with the overall reduced-iodine inventory in the lake.

### 5.3. A context for Mir iodine chemistry based upon the distributions of the nutrients

Our nutrient results show that Lake Mir is meso-trophic, rather than oligotrophic, as is the surrounding Adriatic Sea. Thus, the maximum ammonium, nitrate, phosphate and silicate concentrations in Mir are about 16, 6, 0.15, and  $10 \mu\text{mol l}^{-1}$ , respectively, and these are often more typical of nutrient concentrations normally found in the temperate-zone coastal waters in winter, prior to the spring algal bloom (e.g., Ewins and Spencer, 1967). The influence of biology upon the distribution of nutrients in Lake Mir has been described by Čalić et al. (2007) and Carić et al. (2010), who give much information about the particular species of phytoplankton. From this it seems that nutrient cycling in Lake Mir follows a conventional pattern involving a net reaction between uptake and regeneration by micro-organisms.

It is concluded that Lake Mir presents a marine environment similar to a temperate zone coastal water, but without the complication of winter advection from deeper water. In this respect it ought to display the nutrient cycling properties associated with temperate waters to an enhanced degree. By the same argument, advection of iodate-rich deeper water into temperate surface waters has the capacity to mask iodate reduction. This argument would seem to explain the apparent absence of iodate in Lake Mir. The term, 'absence' is an operational expression, defined by our inability to determine iodate concentrations lower than  $\approx 0.015 \mu\text{mol l}^{-1}$ . Therefore, against the overall reduced iodine inventory in the lake water, a small amount may represent as much as 10–15% of the

iodine inventory, which is not insubstantial. It is, nevertheless, quite clear that the system promotes iodate reduction and/or uptake. The literature about this topic provides numerous possible explanations such as bacterial action during decomposition (Truesdale, 1994a; Truesdale and Bailey, 2002); dissimilatory iodate reduction by bacteria (Amachi et al., 2007); phytoplankton uptake and iodate reduction (Moisan et al., 1994; Wong et al., 2002; Chance et al., 2007); abiotic factors when the iodine system is exposed to reducing conditions (Zhang and Whitfield, 1986; Bluhm et al., 2010). None of these possible pathways is preferred at the moment, since all might well affect iodine speciation simultaneously.

The lack of iodate in Mir water could also support the hypothesis that iodide oxidation to iodate possibly runs in parallel with nitrification (Truesdale et al., 2001b), as supported by observations in several anchialine water bodies along the Croatian coastline (Žic et al., 2008, 2010, 2011). The inorganic nitrogen speciation over this study supports this as nitrate-nitrogen seems to be largely chemically depressed relative to ammonium and to organic-N. This is deduced from the foam study where natural foams and laboratory-foams generated from the Lake Mir surface water were also enriched in organic-N (Truesdale et al., 2012). A possible exception might be in the late winter period (Carić et al., 2010), when low iodate concentrations were detected in the lake. However, closer inspection of the nitrate and ammonium profiles and that of salinity presented by Carić et al. (2010) suggests that it is far more likely that the late-winter increase in concentration of both species can be ascribed to atmospheric input and not *in-situ* nitrification. Within this context, the system differs markedly from several aquatic environments where iodate formation can be linked to regenerated nitrate (Žic et al., 2008, 2010; Gilfedder et al., 2009). The lack of stratification in the Lake Mir and the fragility of a consortium of the ammonium and nitrite oxidising bacteria and/or archaea (Ward, 2008) may inhibit nitrification. Therefore, the data provide direct evidence that the iodine system in Lake Mir is relatively similar to the nutrient pattern of up-take and regeneration of the nutrients, with its prevalence toward reduced species.

In addition, in this system rich in organic matter, photochemical processes might ultimately contribute to an inter-conversion between the reduced iodine species within the water column (Truesdale et al., 1995; Spokes and Liss, 1996; Wong and Cheng, 2001b).

## 6. Conclusions

Lake Mir provides a meso-trophic marine environment separated from the coastal, Adriatic Sea by about 90 m of karstified carbonate rock. The additional nutrients available to Mir seem likely to arise from both wet and dry atmospheric precipitation. The more intensive nutrient cycling in Mir compared to the open seawater is accompanied by a more intensive iodine chemistry such that iodate is essentially absent, and iodide much reduced in concentration. Conversely, however, an organic-I component is more prevalent than in the open sea, amounting up to 80% of the total iodine. The reduced iodine inventory in the lake supports the isolation thesis for Mir.

Although the measurements made at the open sea station were intended as a reference set for Lake Mir, they showed a steady decrease in iodate concentration over the 130 days of study between June and October. It is too early to ascribe these changes to *in situ* iodate reduction because it is possible that water has flowed past the sampling point. As always with iodine, advective effects can give a false impression of a seasonal chemical reduction. Despite this, the effect warrants further investigation especially as so few temporal effects of iodine have been studied.

## Acknowledgement

We would like to thank the expert associate, Ms. Milena Ramov and other personnel from Nature Park Telašćica for generous help in sampling. The financial support of the Ministry of Science, Education and Sports of the Republic of Croatia, under Project 098-0982934-2720, "Interactions of trace metals in aquatic environment", is gratefully acknowledged. We thank the Croatian Meteorological and Hydrological Service for meteorological data. We also thank two anonymous reviewers for their valuable comments.

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