



## The role of highly stratified nutrient-rich small estuaries as a source of dissolved inorganic nitrogen to coastal seawater, the Qishon (SE Mediterranean) case

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### ABSTRACT

We studied the role of small, highly stratified, sulfate and nutrient enriched estuaries, as a source or sink of inorganic nitrogen species, using the Qishon estuary at the Mediterranean coast of Israel, as a case study. Measurements of nutrient concentrations,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate + nitrite,  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  were performed during 2008–2009 along the upper-fresh and lower-saline water masses, as well as sediment porewater depth-profiles. Such estuaries are characterized by relatively low removal flux of  $\text{NO}_3^-$  (via sedimentary denitrification) and enhanced ( $\times 3$ ) upward flux of  $\text{NH}_4^+$  (via sulfate reduction), attributed to the penetration of seawater of low  $\text{NO}_3^-$  and high dissolved oxygen and sulfate concentrations. The role of such small estuaries in releasing dissolved inorganic nitrogen, especially in sensitive oligotrophic areas as the Levantine basin and in the long-term, as a result of enhanced seawater penetration due to the expected sea level rise, has important environmental policy implications.

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### 1. Introduction

Several coastal areas in the SE Mediterranean are characterized by relatively small stream estuaries with low base flows, high loads of anthropogenic nitrogen from point and diffusive sources and high population densities. Due to the shortage of freshwater in such regions (which is expected to be exacerbated in the future), large portions of the flow in the stream estuaries contain sewage or industrial effluents, which are being treated at different levels. The levels of pollution at the river estuaries along the Mediterranean coast of Israel are monitored and reported by the national marine environmental monitoring program (Herut et al., 2011). In several cases, as along the Mediterranean coast of Israel, the bottom bathymetry of the lower parts of the coastal streams lies below sea level, which enables the penetration of seawater and the formation of highly stratified estuaries up to a few kilometers inland (Herut and Kress, 1997). Despite the abundance of such small, stratified estuaries, their role in regulating the delivery of dissolved inorganic nitrogen (DIN), including nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ) and ammonium ( $\text{NH}_4^+$ ) to the coastal area, especially in sensitive oligotrophic areas such as the Levantine basin, has not yet been thoroughly assessed.

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Streams and estuaries have the ability to remove permanently  $\text{NO}_3^-$ , primarily by denitrification under sub-oxic/anoxic conditions. A statistical analysis of the parameters controlling denitrification rates in 49 streams in the USA (Mulolland et al., 2009) showed that the rates of denitrification decreased in response to the increase in ecosystem respiration rates and the specific decrease in discharge (discharge to riverine width ratio). In addition, it was found that an increase in  $\text{NO}_3^-$  concentrations decreased denitrification rates down to a threshold at which they were no longer limited by  $\text{NO}_3^-$  concentrations. The sediment denitrification rates may also be associated with the  $\text{NO}_3^-$  concentrations in the overlying water, as was shown in the Great Ouse River in England, whose maximal denitrification rate was no higher than  $500 \mu\text{M}$   $\text{NO}_3^-$  (Trimmer et al., 1998). Denitrification rates are lower in estuaries than in streams (Piña-Ochoa and Álvarez-Cobelas, 2006), probably due to a lower sediment area to water mass ratio (Alexander et al., 2000). Estuaries are often considered as reducing sites for  $\text{NO}_3^-$  (Cornwell et al., 1999; Brion et al., 2004; Burgin et al., 2007), yet this is not always the case. A recent study on the Elbe estuary in Germany has shown that compared to historical data, anthropogenic dredging activities had significantly reduced the capacity of the estuaries to remove  $\text{NO}_3^-$  and to serve as a sink for nitrogen (Dähnke et al., 2008).

Stable isotopes in DIN species were used in a number of studies to observe their production and removal processes. These studies relied on the fact that most microbial processes preferentially consume  $^{14}\text{N}$  or  $^{16}\text{O}$  isotopes of DIN, leading to enrichment of the

remaining  $\text{NO}_3^-$  pool, with  $\text{NO}_2^-$  oxidation being an exception (Casciotti, 2009). The nitrogen isotopic enrichment factor ( $\epsilon$ ), expressing the kinetic fractionation factor of light  $^{14}\text{N}$  due to enzymatic processes, ranges between 0‰ and 20‰ (Granger et al., 2004) and 5‰ and 25‰ (Casciotti, 2009) for  $\text{NO}_3^-$  assimilation and denitrification, respectively. Similar proportions of  $^{18}\text{O}$  and  $^{15}\text{N}$  enrichment were observed during assimilation (Granger et al., 2004) and denitrification (Granger et al., 2008) in laboratory cultures. Deviations from the 1:1 ratio during denitrification were attributed to additional recycling, e.g., Sigman et al. (2005). In addition, during nitrification, hence the two-step process of  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$  (via hydroxylamine,  $\text{NH}_2\text{OH}$ ) and  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$ , the DIN pool is extensively fractionated. The produced  $\text{NO}_2^-$  is  $^{15}\text{N}$  depleted, with  $\epsilon$  values of 14–38‰ (Casciotti et al., 2003) and imprinted in  $\text{NO}_3^-$  after further oxidation. The  $\delta^{18}\text{O}$  of the produced  $\text{NO}_3^-$  depends on the incorporation of O atoms from  $\text{H}_2\text{O}$  and atmospheric  $\text{O}_2$ . According to Anderson and Hooper (1983) during  $\text{NH}_4^+$  oxidation one O atom is incorporated from  $\text{H}_2\text{O}$  and additional O atom from  $\text{O}_2$ , while during  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$ , the O atom originates from water. The resulted isotopic effect is further altered by enzymatically catalyzed O exchange between  $\text{H}_2\text{O}$  and  $\text{NO}_2^-$  and by several kinetic fractionation effects of  $\text{O}_2$  and  $\text{H}_2\text{O}$  incorporation into  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$ , and the oxidation of  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$ . Casciotti et al. (2010) have found that the rate of  $\text{H}_2\text{O}$ – $\text{NO}_2^-$  oxygen isotope exchange was 1–25% for four species of ammonia-oxidizing bacteria.

While most studies on DIN in rivers and estuaries have focused on mid- to large-scales, the role of small, highly stratified, estuaries as a sink or source of DIN is yet to be fully understood. The aim of this study was to use the estuary of the Qishon stream on the Mediterranean coast of Israel as a case study for assessing such processes. The lower Qishon system is characterized by a highly stratified water column, low base flows (summer and winter base flow discharges vary between  $0.02$  and  $0.2 \text{ m}^3 \text{ s}^{-1}$  and between  $0.2$  and  $0.6 \text{ m}^3 \text{ s}^{-1}$ , respectively, Vachtman et al., 2012), high DIN loads (mostly anthropogenic) and elevated  $\text{SO}_4^{2-}$  concentrations (seawater origin), which enhance the potential of nutrients released by the decomposition of organic matter under anaerobic conditions (sulfur bacterial reduction). We used the isotopic composition of  $\text{NO}_3^-$  ( $^{15}\text{N}$  and  $^{18}\text{O}$  of  $\text{NO}_3^-$ ), the concentration of nutrients and major ions, the  $\delta^{13}\text{C}$  of the dissolved inorganic carbon (DIC) and  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  in this estuarine system for this assessment. We believe that the knowledge generated by the study will contribute to better environmental policies, which would take into consideration the anthropogenic loads of nitrogen and their implications on stream water quality and DIN export. Moreover, global warming and the consequent sea level rise are expected to enhance seawater penetration inland and hence the impact of such estuarine systems on the marine coastal environment, especially at sensitive sites like the oligotrophic SE Mediterranean.

## 2. Materials and methods

### 2.1. Study area

The flow regime of the coastal streams in Israel is characterized by a low summer base and increased winter base flows, with a few annual floods. The Qishon stream drainage basin occupies  $1100 \text{ km}^2$ , with intensive agricultural activity taking place within the basin. The 7-km long Qishon estuary (Fig. 1) is characterized by the penetration of seawater, thereby producing a highly stratified water column. Along the estuary, there are two industrial plants producing fertilizers, an oil refinery, a sewage treatment plant and additional smaller industries. Five estuarine sampling stations, designated Qishon Harbor (QH), Carmelit (C), Fishing

Harbor (FH), Julius Bridge (JB) and Histadrut Bridge (HB), located along the lower 3 km (from river mouth upstream, Fig. 1) and additional upstream sampling station, Jalame (J), located 14 km south-east of the stream mouth, were visited between December 2007 and May 2009. The sampling stations are located along a salinity gradient of 21–39 ppt, which were exposed between 2007 and 2009 to an estimated total nitrogen load (as  $\text{N-NO}_3^-$ , the major DIN form) of 240 tons per year.

In the past high loads of anthropogenic heavy metals (Herut and Kress, 1997; Herut et al., 1999), nutrients (Kress and Herut, 1998) and organic matter (Cohen et al., 1993) were introduced to the Qishon estuary mainly by industrial effluents. However, since 2002, a dramatic decrease in heavy metals (approximately 2 orders of magnitude) and organic matter has been recorded, probably due to the introduction of treatment facilities at the industrial sites (Herut et al., 2011). In recent years, the concentrations of heavy metal and organic compounds in the water column (Herut et al., 2011) have been below the ecological water quality criteria (Buchman, 2008). Nevertheless, some heavy metal concentrations in the sediments indicate low potential (ERL concentration levels) for inducing toxic effects in marine organisms (ERL (Effects Range Low), ERM (Effect Range Medium); Long et al., 1995; Buchman, 2008). All heavy metal concentrations were below ERM but their maximal concentrations ( $\text{ug gr}^{-1}$  sediment dry wt.) of Hg (0.3), Cd (3.5), Cu (79), Zn (288), Ni (48) and Cr (92) exceeded ERL levels (Herut et al., 2011).

### 2.2. Sampling

Potential  $\text{NO}_3^-$  sources (end-members) were sampled for their isotopic composition; these sources included the Qishon upstream, effluents of the industrial plants, East Mediterranean seawater (10 km offshore), and a composite rainwater sample of most (30) rain events collected between October 2007 and September 2008. Estuarine samples were collected in five campaigns in December 2007, March 2008, October 2008, February 2008 and May 2009, thereby representing seasonal variability. At each sampling station, measurements of water column profiles of salinity, dissolved oxygen (DO), temperature, turbidity and pH were taken. The water samples were collected in Niskin bottles from 20 cm below surface and 20 cm above streambed (2.5–10 m water depth), representing surface and bottom water masses.

To account for DIN turnover in the sediment, two estuarine 20 cm-long sediment cores were collected during early spring and fall seasons (March 2008, October 2008) using a gravity corer and 50 cm-long Perspex liners. The sediment cores were treated in the laboratory within a few hours after collection. Cores were sliced under anaerobic conditions into 1–2 cm slices, which were transferred into argon-flushed 50-ml tubes. Porewater samples were extracted by centrifugation at 4000 rpm and filtered ( $0.45 \mu\text{m}$ ). Subsamples for analyses of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  of  $\text{NO}_3^- + \text{NO}_2^-$  were kept frozen. Subsamples for  $\delta^{13}\text{C}$  DIC analyses were poisoned (with  $\text{HgCl}_2$ ) to prevent biological activity. These samples as well as samples for analysis of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  and of major ions were kept at  $4^\circ\text{C}$  until analysis.

### 2.3. Analytical methods

Salinity, DO, temperature and pH were measured in the field with a Multiparameter Sonde (YSI 6600) instrument. Major ions ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{Sr}^{2+}$ ) were analyzed with an inductive coupled plasma-atomic emission spectrophotometer (ICP-AES, Perkin-Elmer), with a precision of <2%. Concentration of the nutrients ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$ ) were measured by standard spectrophotometric methods (Spectrophotometer, Skalar SANplus), with a detection limit below  $0.1 \mu\text{M}$ . Measurements (in duplicate)

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