The benthic regeneration of N and P in the Great Brak estuary, South Africa

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ABSTRACT

The Great Brak is a temporarily open/closed estuary (TOCE) located on the south coast of South Africa. The construction of the Wolwedans Dam in 1989 reduced baseflow to the estuary by 56%, decreasing the intensity of flushing events and causing the mouth to breach less often. The aim of this study was to investigate the flux of inorganic nutrients (NH_4^+, TOxN [NO_3^- + NO_2^-], SRP) as well as total N and P across the sediment–water interface in the estuary. There have been very few studies on nutrient cycling and benthic pelagic coupling in South African estuaries. This study showed that the sediment had a net efflux of NH_4^+, SRP, TN and TP while TOxN was taken up or converted to other forms of N. The estuary acted as a source of N and P during both summer and winter. If the estuary remains closed for a prolonged period (12 months), with an increased organic load present on the benthos, the associated rates of efflux of N and P would increase. In order to reduce the organic load to the system better flushing methods or, more importantly, an increase in base flow, is needed to reduce residence times of water in the estuary.

Keywords: water quality, nutrient cycling, benthic-pelagic coupling, estuary

INTRODUCTION

The Great Brak Estuary is a temporarily open/closed estuary (TOCE) meaning that the mouth is often separated from the sea by the formation of a sand bar. These types of estuaries are commonly found along the South African coast and constitute about 70% of the estuaries in the country (Whitfield, 1992). Since TOCEs generally have a relatively small catchment (less than 500 km^2) (Whitfield, 1992) they are greatly influenced by hydrodynamics, water circulation patterns and anthropogenic activities that impact on the water quality of inflowing river water (Human and Adams, 2011). Estuaries are the confluence of land and sea, where the freshwater from rivers mixes with oceanic water to form highly productive systems. Land- and ocean-derived materials are processed in different compartments within an estuary, such as the water column and shallow light-limited subtidal and intertidal sediments (Magalhaes et al., 2002). The transformation of these materials is dependent on several parameters, i.e., the rate of external input, and the recycling and removal efficiency by biological, chemical and/or physical processes, as well as the residence times of the estuary (Seitzinger, 1990; Balls, 1994; Sakamaki et al., 2006). Continued modification of coastal environments, in particular the rise in inorganic and organic nutrient loading, has led to large-scale eutrophication of many estuaries around the world (Jickells, 1998). The exchange of nutrients between the sediment and water interface (benthic pelagic coupling) of intertidal and subtidal areas of estuaries is capable of playing two important, but opposing, roles (Magalhaes et al., 2002). It has been found that regenerated nutrients that are fluxed into the water column are able to supply most of the N and P required for phytoplankton primary production (Rizzo, 1990; Cowan et al., 1996).

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In contrast large amounts of inorganic nutrients have been removed from the overlying water column by bacterial mats (Teague et al., 1988; Ogilvie et al., 1997). Since nutrient loads, which would otherwise be discharged into coastal waters, are taken up by primary producers and removed from the water column, primary producers act as a biological control over coastal eutrophication. Because the processes of removal and production occur simultaneously, the net direction of nutrient flux will depend on which is the dominant process (Magalhaes et al., 2002).

Nixon (1981) and Kemp et al. (1992) state that high rates of primary production can occur in shallow estuaries as a result of effective recycling and retention within benthic and pelagic processes. The release of regenerated nutrients (N and P), in particular remineralized phytodetritus, from the sediments to the water column in shallow water systems, results in these nutrients subsequently being utilized by the primary producers (Jensen et al., 1990; Koho et al., 2008). Ultimately the inorganic N form that becomes available to primary producers depends on the type of bacteria present as well as the state of oxygenation. Under anoxic conditions NO_3^- is reduced to gaseous N_2 (denitrification) by heterotrophic bacteria in the sediment and leads to a loss of N through the water column resulting in a loss of bioavailable nitrogen from the estuary (Jorgensen and Sorensen, 1988; Herbert et al., 1999). Alternatively, processes such as dissimilatory nitrate reduction to ammonium (DNRA) and ammonia oxidation (Anammox) also occur under anoxic conditions and result in a bioavailable form of N released to the estuary (Matheson et al., 2002; Brandes et al., 2007; Prescott et al., 2008). Nitrifying bacteria, present in the sediment, under oxic conditions (nitrification) convert NH_4^+ to NO_2^- to NO_3^-, which can subsequently be released to the water column. Similarly, the flux of phosphate from the sediment is also affected by oxygen levels as well as soil redox potential; the release of PO_4^{3-} (or SRP) occurs under hypoxic or anoxic conditions (Koop et al., 1990; Slomp, 2012).

Benthic pelagic coupling is influenced by three factors, namely, the depth of the water column, temperature and

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mixing events. It is believed that benthic pelagic coupling may be more pronounced in shallow water systems than in deeper coastal regions since a larger fraction of phytodetritus is able to reach the bottom sediment (Hargrave, 1973; Nixon, 1981) which can then be remineralized into a more available form for primary producers (Oviatt et al., 1986, Jensen et al., 1990). Taljaard et al. (2009) believed that in-situ regeneration of inorganic nutrients through biochemical processes (e.g. remineralization) in South African TOCEs is not a significant source of inorganic nutrients to the water column; however, they also stated that further studies were warranted to confirm their findings. When water column temperatures increase, the rate of remineralization increases and results in more NH_4^+ being released from the sediment, that in turn can support higher rates of primary production (Vouve et al., 2000). However, it has also been noted that the contribution of N from the sediment to phytoplankton demand may be less important than other sources of N during periods of high primary production (Hopkinson, 1987). Mixing events may disturb benthic pelagic coupling by re-suspension of either surface sediment particles or nutrient-rich pore water (Porter et al., 2010), which can result in a shift from net heterotrophy to net autotrophy in the water column in just a few days, following a mixing event (Lawrence et al., 2004). Remineralized N from sediments is frequently in inorganic form and as a result is readily taken up by primary producers (Boynton et al., 1995). The aim of this paper is to investigate the flux of inorganic nutrients (NH_4^+, TOxN [NO_3^- + NO_2^-], SRP) as well as total N and P across the sediment-water interface in the estuary. There have been very few studies related to nutrient cycling and benthic pelagic coupling in South African systems, consisting of one published article by Howard-Williams and Allanson (1981), two unpublished PhD theses (Switzer, 2003; Goeck, 2005) and one specialist study by Taljaard et al. (2008), of which only the latter considered a TOCE.

STUDY SITE

The Great Brak Estuary (34°03′23″ S; 22°14′18″ E) is located on the south coast of South Africa approximately 420 km east of Cape Town (Fig. 1). It is 6.2 km long, and drains a forested, semi-arid catchment area of 192 km^2. The Wolwedans Dam, with a capacity of 23 x 10^6 m^3, is located 3 km upstream of the estuary (DWA, 2009), essentially starving the estuary of freshwater. The catchment generally receives equal amounts of rain throughout the year with peaks in spring and autumn. The area is subjected to occasional flooding as well as droughts, further decreasing the availability of freshwater to the estuary. The mean annual run-off varies from as little as 4.3 x 10^6 m^3 to as much as 44.5 x 10^6 m^3 (DWA, 2009). The estuary has a high-tide areal cover of 0.6 km^2 and a tidal prism of 0.3 x 10^6 m^3. The mouth of the estuary is bounded by a low rocky headland on the east and a sand spit on the west (DWA, 2009). Directly inland of the mouth is the lagoon basin that houses a permanent residential island about 400 x 250 m in size (DWA, 2009). The lower estuary is relatively shallow (0.5 to 1.2 m deep) while the middle and upper estuary depth ranges between 2 and 5 m, with some deeper areas in scouring zones near the rocky cliffs and bridges (DWA, 2009). The mouth of the estuary closes when high waves coincide with periods of low river inflow. The estuary is artificially breached at 2 m mean sea level (MSL) in order to prevent the low-lying properties on the island from flooding.

MATERIALS AND METHODS

Benthic flux chambers provide a simple method of investigating nutrient flux in situ. It has been demonstrated in estuarine benthic studies that nutrient concentrations in the overlying water are proportional to the nutrient fluxes occurring at the sediments (Dollar et al., 1991; An and Joye, 2001; Switzer, 2003). In this study, two periods in 2012 were selected for benthic chamber deployment, one during the summer and the other in the winter. The chambers were deployed at Sites 1 to 3 (Fig. 1) in the lower reaches of the estuary. The summer deployment period represents long daylight hours and high water temperatures and the winter deployment period is representative of low water temperatures and short daylight hours. In summer chambers were deployed at Site 1 and the winter deployment occurred at Sites 2 and 3 (Fig. 1).

Sunrise in summer was at 06:07:51 and sunset was at 18:25:09; sampling in summer started at 15:20 in the afternoon. Sunrise in winter was at 06:52:23 and sunset was at 17:34:23; sampling started at 7:00. Evening hours are indicated on Figs 3–14 as shaded areas. The chambers were composed of an acrylic material (Fig. 1). A total of two light- and two dark-chamber experiments were deployed to determine the flux of nutrients across the sediment-water column interface. The chambers were placed at an average depth of 15 cm into the sediment and covered an area of 0.15 m^2. When submerged the chambers were at a depth of 0.5 m. The total volume of a chamber was approximately 40 ℓ and the chamber contained a volume of 37 ℓ of water when deployed. Samples were collected by syringe through nylon tubing inserted into the chambers and were replaced by ambient water enclosed in a submerged collapsible plastic bag attached to the outer wall of the chambers. In order to mimic stirring, water was sucked into a 50 mℓ syringe and pushed back into the chambers 10 times before a sample was taken. Care was taken not to disturb the sediment. The sampling tube was kept bubble-free before drawing each sample. Sampling started immediately after deployment of the chamber, i.e., at Time 0. Chambers were deployed for 24 h and sampled every 1 h for TN, TP, NH_4^+, TOxN and SRP in summer. Based on the summer results that showed either a steady increase or decrease over the incubation period, a decision was taken to draw samples every 3 h during the winter sampling session. Benthic flux was calculated as follows (Dollar et al., 1991):

$$F\,(\text{flux}) = V\,(Ct - Co) / (A \times T)$$

Where: V = volume (ℓ) of water inside the benthic chamber over the sediment at initial deployment, Co and Ct = the concentrations (µM) of nutrient before and after time T (h), and A = area (m^2) of sediment enclosed in chamber. As per convention, negative flux denotes flux from overlying water to sediment and positive flux (efflux) denotes flux from sediment to overlying water.

The collected water samples were filtered through 0.47 µm syringe filters and frozen. Filtered samples for ammonium (NH_4^+) and soluble reactive phosphorus (SRP) were analysed using standard spectrophotometric methods (Parsons et al., 1984). The detection of total oxidized nitrogen (TOxN) (NO_3^- + NO_2^-) was done according to the reduced copper cadmium method as described by Bate and Heelas (1975). Unfiltered water samples were collected for the simultaneous detection of total nitrogen (TN) and phosphorus (TP) and were analysed using the persulphate digestion as described by Grasshoff et al. (1983). Here, TN and TP include both the dissolved and organic fractions.

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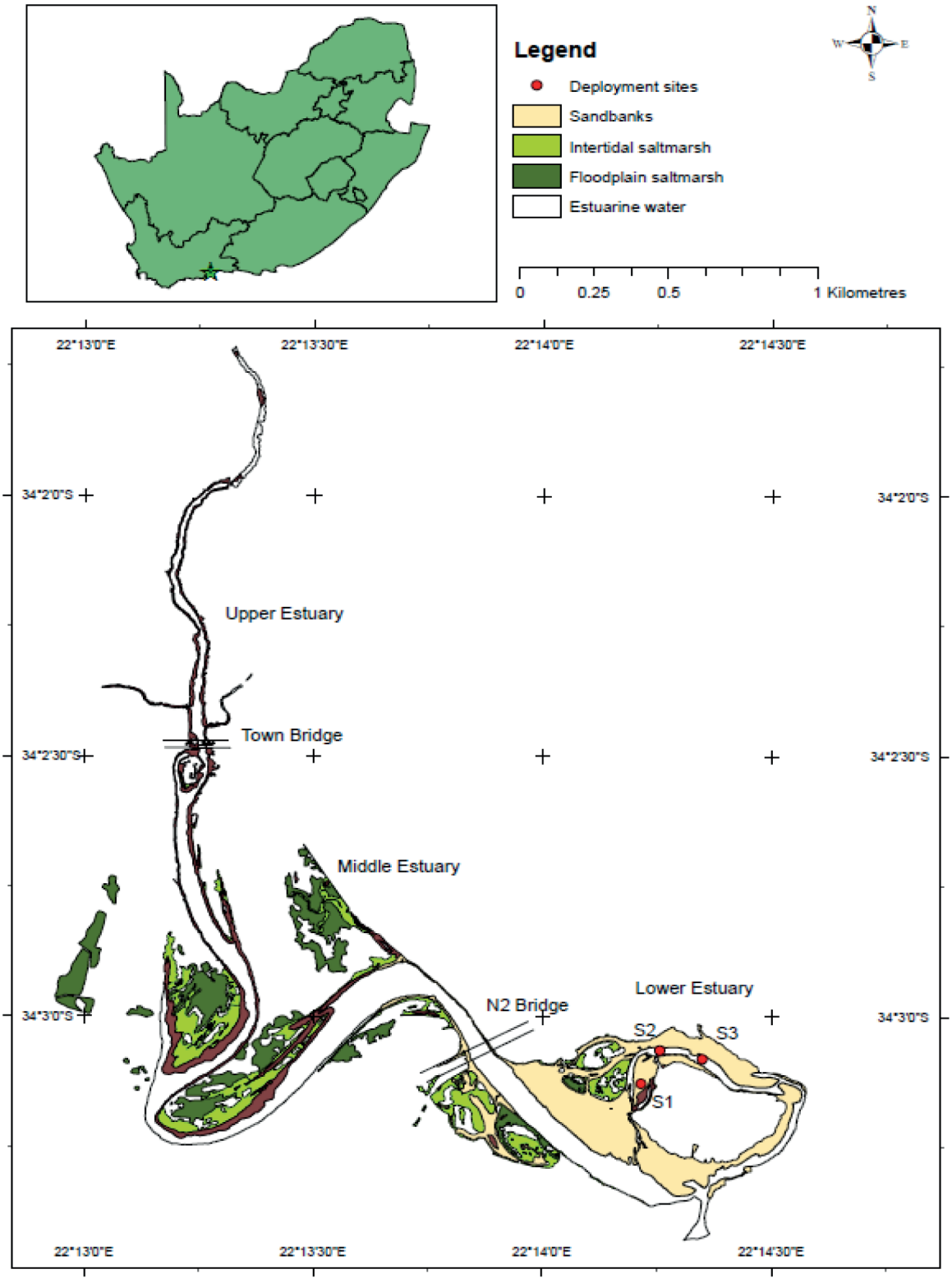

Figure 1

Sampling sites in the Great Brak Estuary, located on the south coast of South Africa

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Figure 2
Light and dark benthic chambers deployed at the Great Brak Estuary

RESULTS

The temperature for all incubations during the summer deployment (March 2012) ranged between 25 and 30°C (Fig. 3 A) and was significantly higher ($U = 1.00$, $p < 0.05$) than the temperature during the winter deployment (June 2012) which ranged between 12 and 15°C (Fig. 3B). Dissolved oxygen during summer decreased steadily over the 25-h cycle for all incubations except Light 2 (Fig. 4A), which had a slight increase in dissolved oxygen during the light period, probably due to autotrophic O_2 production resulting in nutrient uptake. A similar decreasing dissolved oxygen concentration pattern over time was observed for the incubations in winter (Fig. 4B). However, the averaged dissolved oxygen concentration in July was significantly higher than that of March ($U = 300.5$, $p < 0.05$).

The TN concentration in both the light and dark chambers during summer increased slightly over the 25-h period. The concentration in the dark increased from 50 to 65 µM while that in the light increased from 50 to 60 µM (Fig. 5). In winter the concentration in the light increased from 60 to 80 µM (Fig. 6) and the concentration in the dark increased from 50 to 80 µM. Thus, the average efflux of TN (2.30 mmol·m^{-2}·d^{-1})

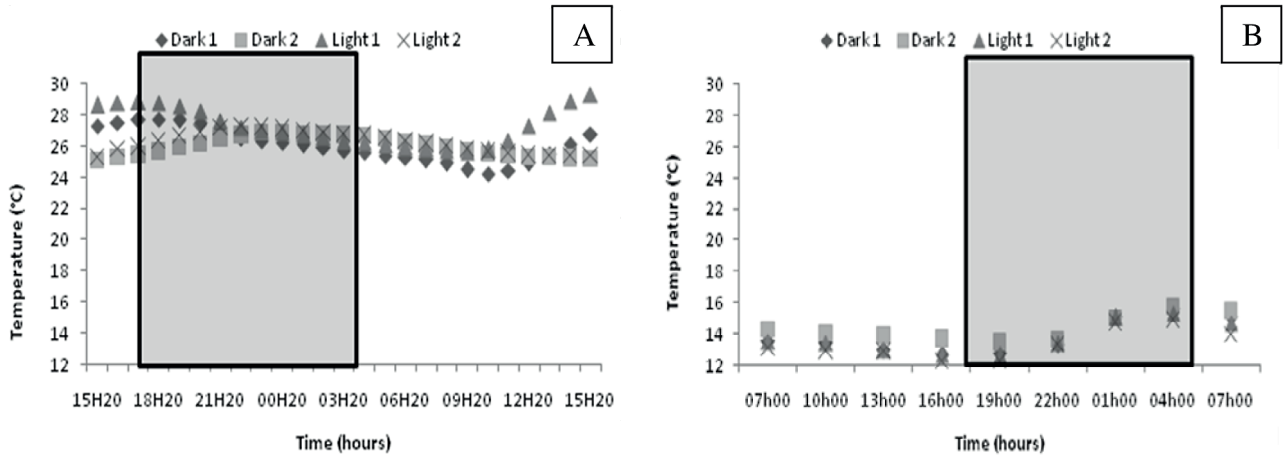

Figure 3
Temperature during incubation time in (A) summer (March 2012) and (B) winter (July 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

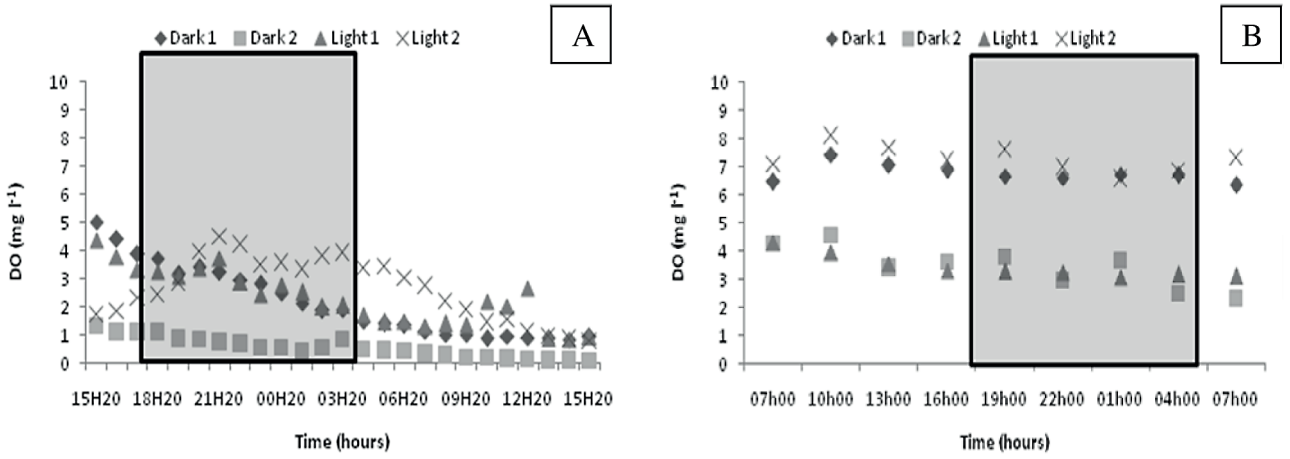

Figure 4
Dissolved oxygen concentration during incubation time for (A) summer (March 2012) and (B) winter (July 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

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during winter was significantly higher than summer (1.51 mmol·m^{-2}·d^{-1}) (U = 6174, p < 0.05) (Table 1).

During summer, the TP in Light 2 and Dark 2 was significantly higher than in Light 1 and Dark 1 (H = 101.09, n = 250, p < 0.05) (Fig. 7). There were no significant differences in the TP concentration during winter (F = 2.76, d.f. = 3, p > 0.05) (Fig. 8). The average efflux of TP (Table 2) from the benthos in summer (0.12 mmol·m^{-2}·d^{-1}) was significantly higher than the efflux in winter (0.05 mmol·m^{-2}·d^{-1}) (U = 2 509, p < 0.05).

The average NH_4^+ concentration in both dark incubations during summer was significantly higher than the light incubations (F = 20.10, d.f. = 3, p < 0.05), with concentrations in Dark 1 and Dark 2 increasing from 1 to 12 µM and 1.2 to 7 µM, respectively, while that of Light 1 and Light 2 increased from 1 to 4 µM and 1.5 to 3 µM, respectively (Fig. 9). During winter the average NH_4^+ concentration in Dark 1 increased from 4 to 7 µM and was significantly lower in concentration than Dark 2, which increased from 4 to 11 µM (H = 17.17,

TABLE 1
Total efflux of TN from the benthos of light and dark chambers

	Summer (March 2012) F (mmol·m^{-2}·d^{-1})	Winter (July 2012) F (mmol·m^{-2}·d^{-1})
Light 1	1.20	1.45
Light 2	0.92	2.78
Dark 1	1.69	2.03
Dark 2	2.24	2.95
Average	1.51	2.30

TABLE 2
Total efflux of TP from the benthos of light and dark chambers

	Summer (March 2012) F (mmol·m^{-2}·d^{-1})	Winter (July 2012) F (mmol·m^{-2}·d^{-1})
Light 1	0.06	0.03
Light 2	0.22	0.01
Dark 1	0.10	0.03
Dark 2	0.10	0.14
Average	0.12	0.05

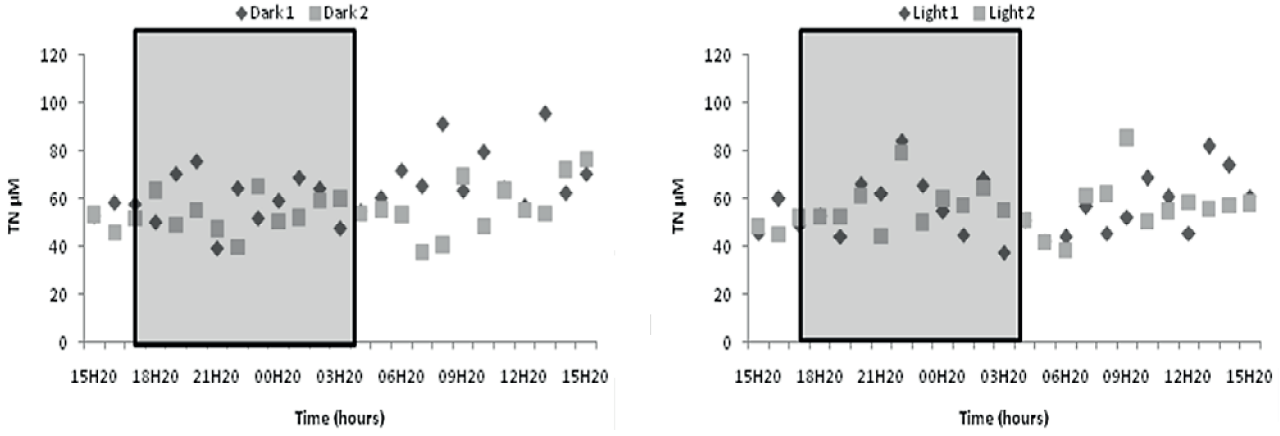

Figure 5

Change in concentration of TN over a 25-h cycle in summer (March 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

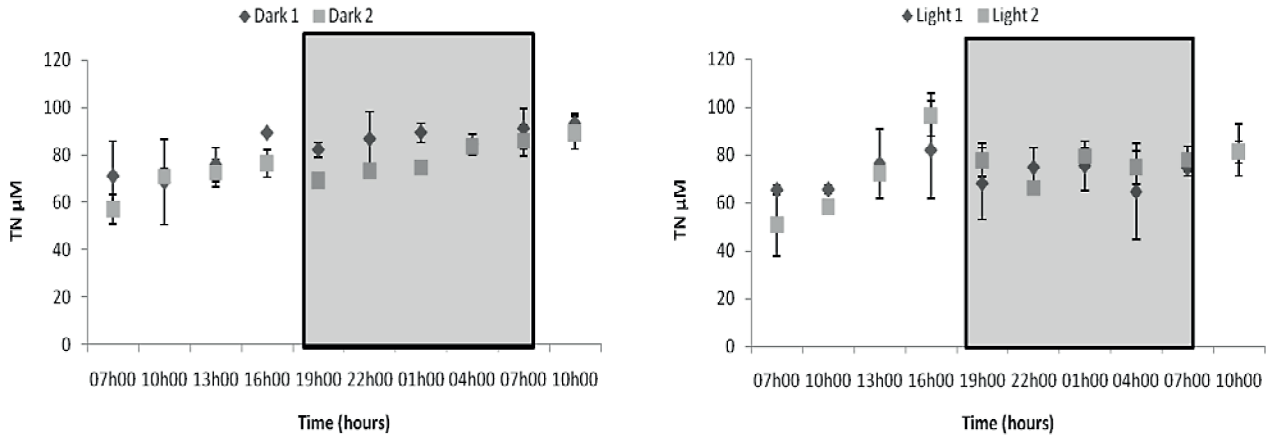

Figure 6

Change in concentration of TN over a 27-h cycle in winter (July 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

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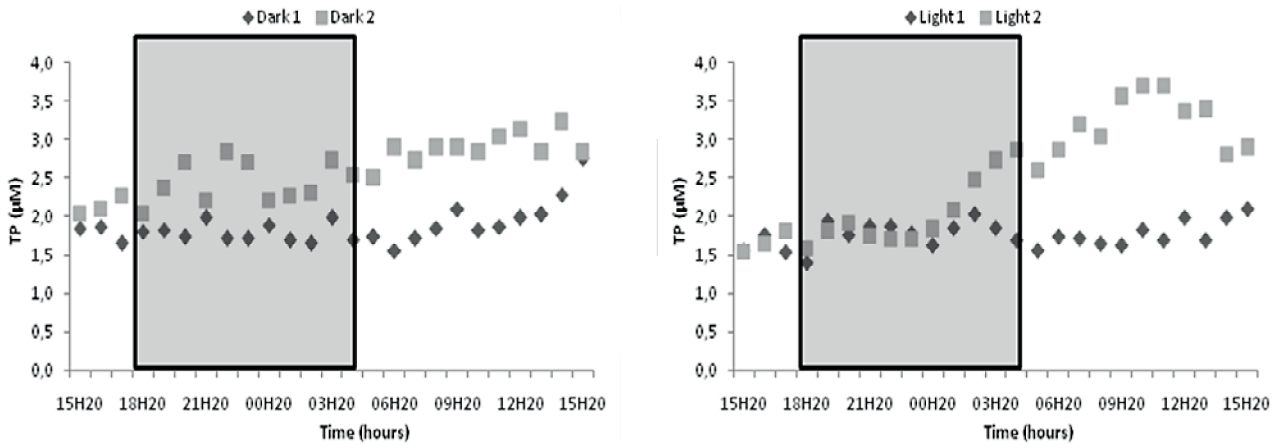

Figure 7

Change in concentration of TP over 25-h cycle in summer (March 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

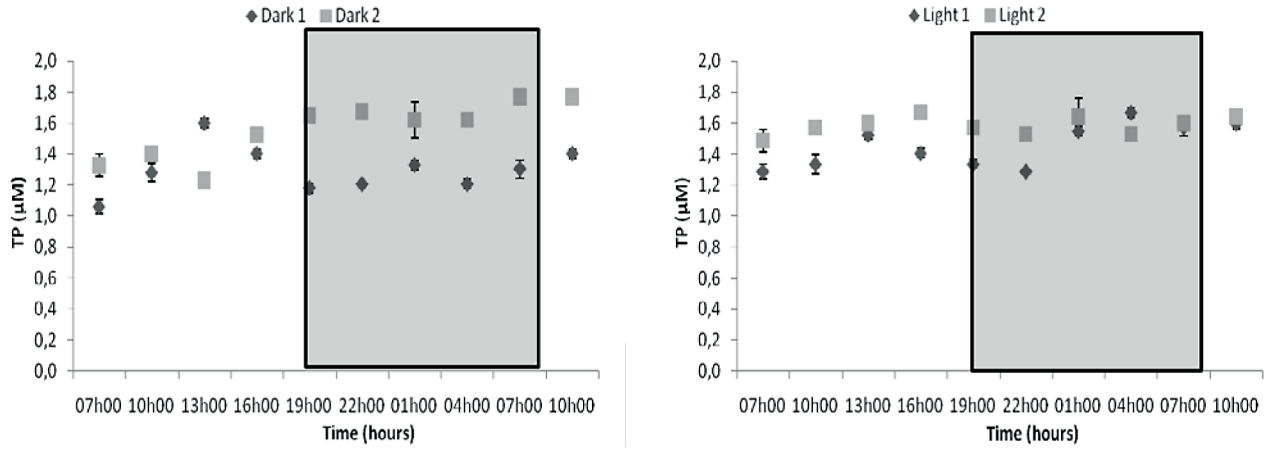

Figure 8

Change in concentration of TP over 27-h cycle in winter (July 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

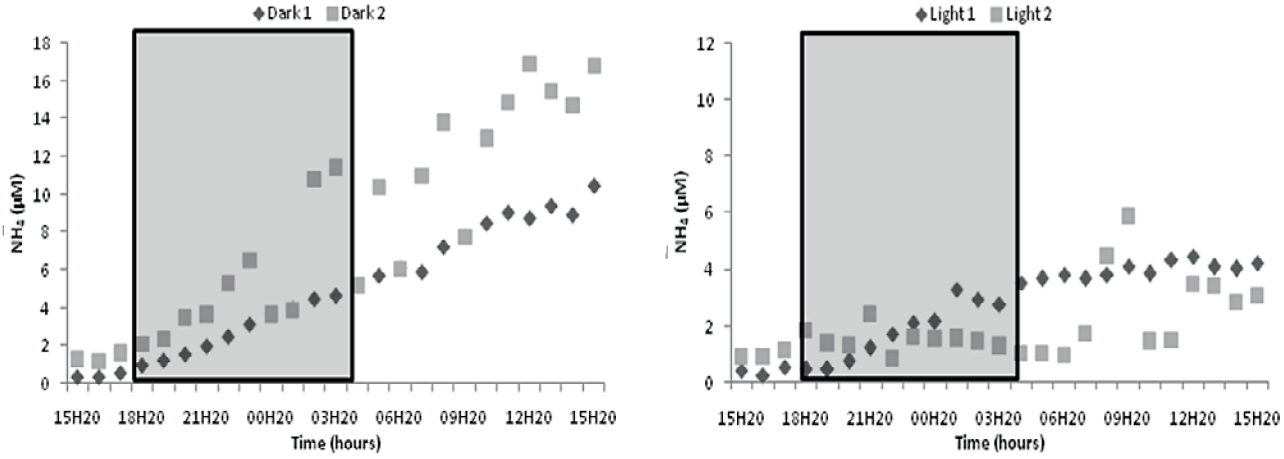

Figure 9

Change in concentration of NH_4^+ over a 25-h cycle in summer (March 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

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$n = 120$, $p < 0.05$) (Fig. 10). The average NH_4^+ concentration in Dark 2 was also significantly higher than in Light 2, the latter increasing from 3 to 6 µM ($H = 17.17$, $n = 120$, $p < 0.05$) (Fig. 10). The average efflux of NH_4^+ was always from the benthos into the water column in both the summer and winter deployments. Although the average efflux of NH_4^+ from the benthos was slightly higher in summer (0.61 mmol·m^{-2}·d^{-1}) compared with winter (0.50 mmol·m^{-2}·d^{-1}) (Table 3), there was no significant difference ($U = 5.00$, $p > 0.05$) between the two periods.

The concentration of TOxN during summer in both dark chambers decreased from 6 to 4 µM and in both light chambers decreased from 8 to 3 µM (Fig. 11). Similarly, in winter the TOxN in both dark and light chambers decreased over the incubation period (Fig. 12), from ~10 to 5 µM. In all instances there was a negative average flux of TOxN (Table 4) indicating a decrease in the TOxN over the incubation period, averaging 0.24 mmol·m^{-2}·d^{-1} during summer and 0.09 mmol·m^{-2}·d^{-1} during winter. However, no significant difference was found between the two periods ($U = 4$, $p > 0.05$). The direction of flux may be an indication of denitrification, and/or phytoplankton uptake.

During the summer deployment, the average SRP concentration in Light 2 was significant higher ($H = 41.38$, $n = 250$, $p < 0.05$)

TABLE 3
Total efflux of NH_4^+ from the benthos of light and dark chambers

	Summer (March 2012) F (mmol·m^{-2}·d^{-1})	Winter (July 2012) F (mmol·m^{-2}·d^{-1})
Light 1	0.40	0.31
Light 2	0.35	0.27
Dark 1	1.00	0.93
Dark 2	0.70	0.48
Average	0.61	0.50

TABLE 4
Total negative flux of TOxN in light and dark chambers

	Summer (March 2012) F (mmol·m^{-2}·d^{-1})	Winter (July 2012) F (mmol·m^{-2}·d^{-1})
Light 1	−0.05	0.02
Light 2	−0.16	−0.10
Dark 1	−0.55	−0.03
Dark 2	−0.19	−0.27
Average	−0.24	−0.09

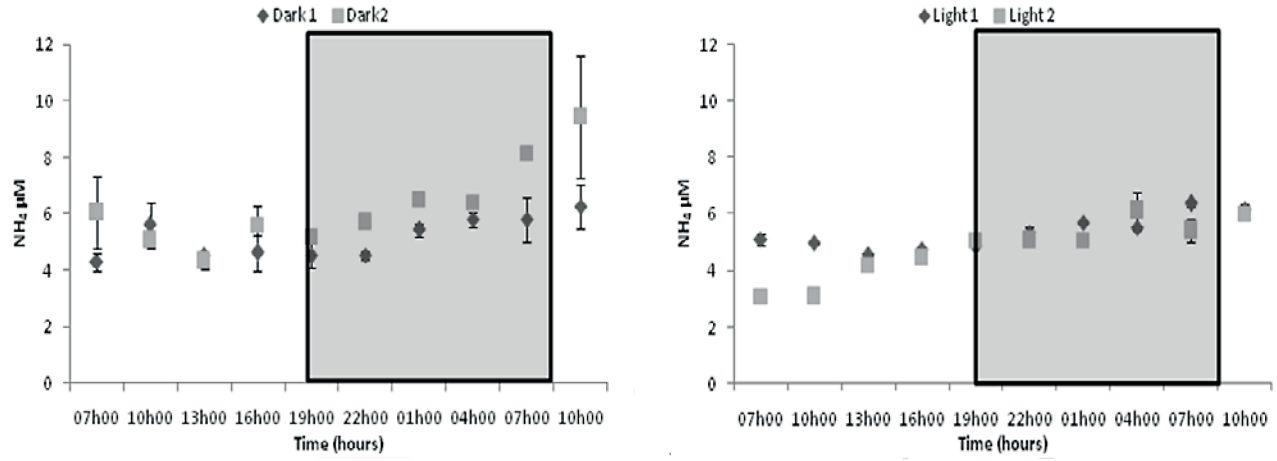

Figure 10
Change in concentration of NH_4^+ over a 27-h cycle in winter (July 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

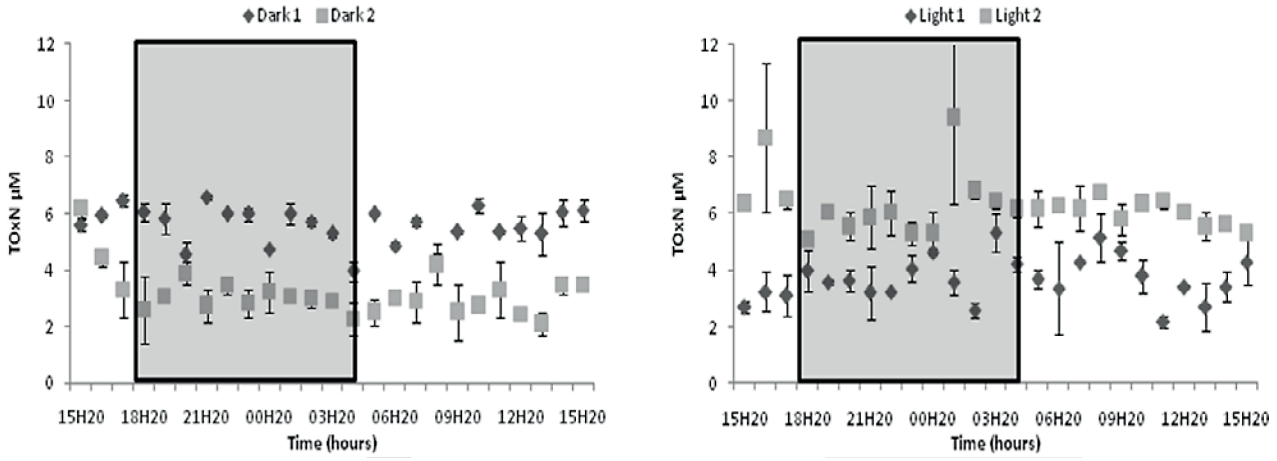

Figure 11
Change in concentration of TOxN over a 25-h cycle in summer (March 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

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than in Light 1 and both Dark 1 and 2 (Fig. 13). In winter Dark 2 had a SRP concentration range from 0.40 to 0.45 µM which was significantly higher ($H = 68.43$, $n = 120$, $p < 0.05$) than Dark 1 (0.23 to 0.37 µM) (Fig. 14). Similarly, the SRP concentration in Light 2 was significantly higher than in Light 1. Both dark incubations also had significantly higher SRP concentrations than both light incubations ($H = 68.43$, $n = 120$, $p < 0.05$) (Fig. 14). The average efflux of SRP in summer was 0.043 mmol·m^{-2}·d^{-1} and was significantly higher ($T = -4.47$, d.f. = 3, $p < 0.05$) than the average efflux of 0.010 mmol·m^{-2}·d^{-1} in winter (Table 5).

The benthic microalgae present within the chambers generally had a Chl *a* concentration of less than 35 mg·m^{-2}. There was an increase in benthic Chl *a* concentration in the both summer and winter in the light chambers after deployment. The benthic Chl *a* remained relatively stable in the dark chambers.

During summer the phytoplankton chl *a* concentration was generally below 4 µg·ℓ$^{-1}$ in the light and less than 1 µg·ℓ$^{-1}$ in the dark. During winter the Chl *a* concentration remained relatively stable for all chambers, except Light 1 where there was a decrease after deployment.

TABLE 5
Total efflux of SRP from the benthos of light and dark chambers

	Summer (March 2012) F (mmol·m^{-2}·d^{-1})	Winter (July 2012) F (mmol·m^{-2}·d^{-1})
Light 1	0.031	0.011
Light 2	0.064	0.008
Dark 1	0.043	0.013
Dark 2	0.036	0.005
Average	0.043	0.010

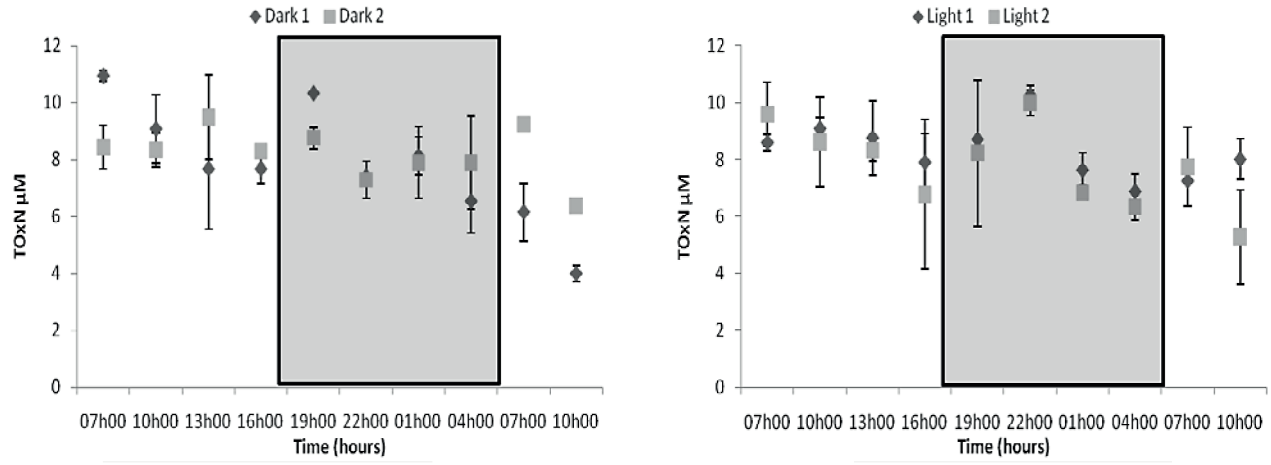

Figure 12

Change in concentration of TOxN over 27-h cycle in winter (July 2012). The shaded area represents the evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

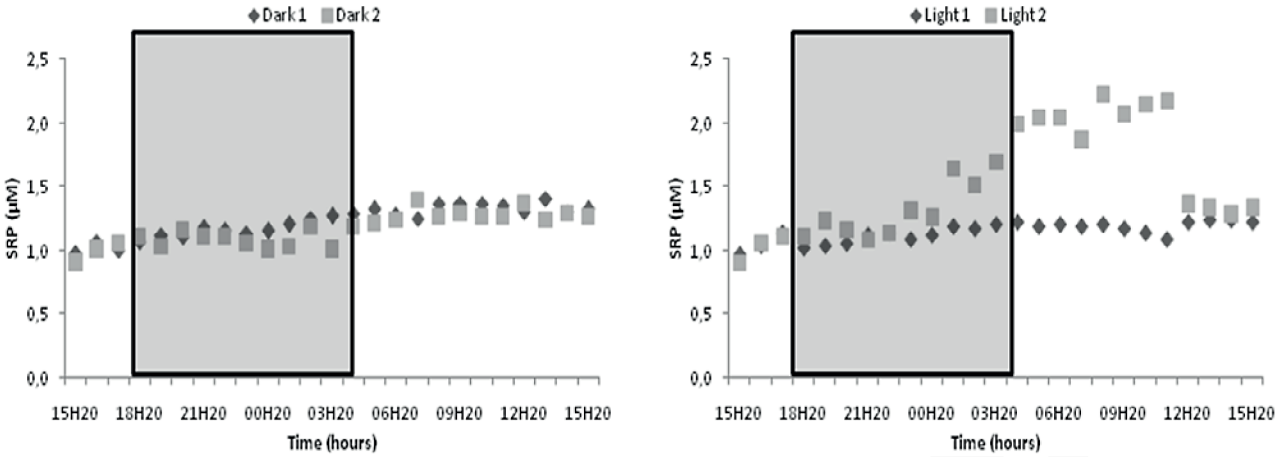

Figure 13

Change in concentration of SRP over 25-h cycle in summer (March 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations).

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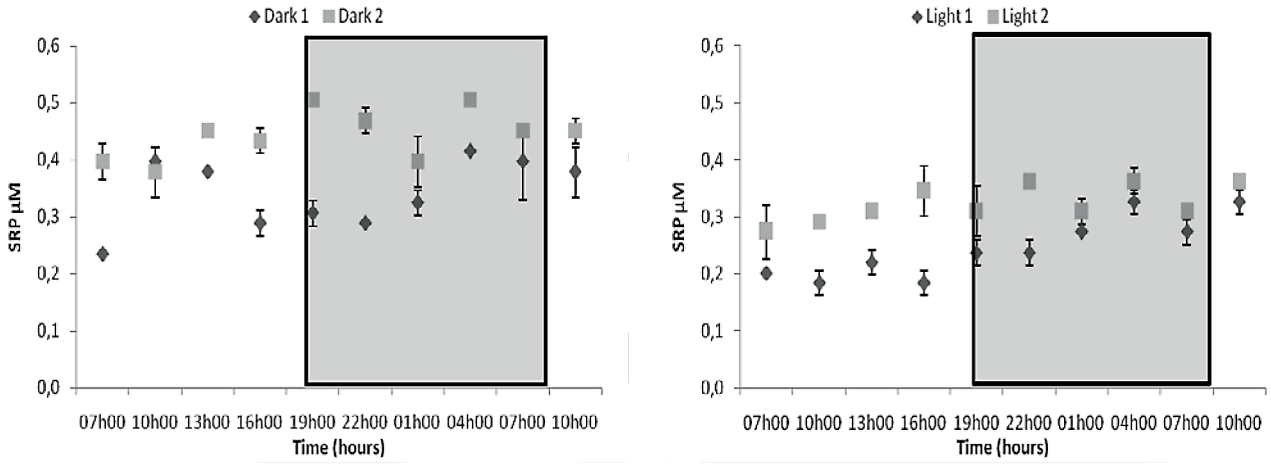

Figure 14

Change in concentration of SRP over 27-h cycle in winter (July 2012). The shaded area represents evening hours. (Dark 1 and 2 are dark incubations and Light 1 and 2 are light incubations)

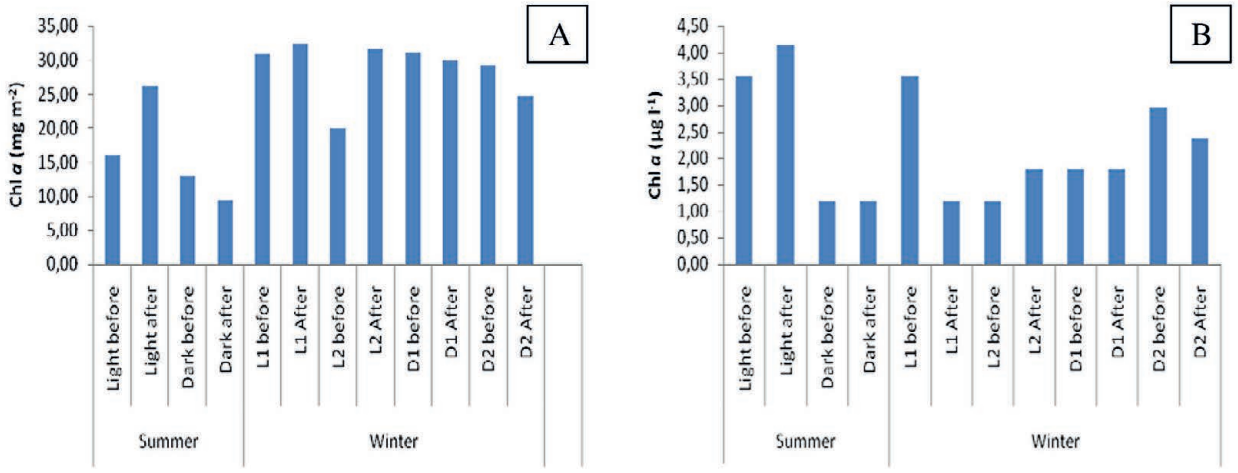

Figure 15

(A) The benthic microalgae and (B) phytoplankton Chl a concentrations during summer and winter before and after deployment

DISCUSSION

The objective of this study was to quantify the exchange of inorganic nutrients and TN and TP across the sediment-water interface to determine nutrient regeneration during the closed mouth state. Temperature in the chambers increased during the day and decreased during the night, during both the summer and winter deployments, although the average temperature in summer was significantly warmer than in winter. This was also found in the East Kleinemonde Estuary by Taljaard et al. (2008), who stated that these findings illustrated that temperature in the estuary water column is largely a function of atmospheric temperature. Except for one light chamber in summer (March 2012) showing an increase in dissolved oxygen concentration during daylight hours, dissolved oxygen concentrations in all chambers during both the summer and winter deployments steadily decreased over the incubation period. This pattern has also been observed by Nicholson et al. (1996). They did a series of deployments (each deployment consisted of 3 light and 3 dark chambers) and found that in 18 out of 24 deployments there was no difference between dark and light chamber oxygen fluxes, all decreasing over the incubation period. While six of the chambers showed evidence of oxygen production during daylight hours due to microphytobenthos or phytoplankton biomass, there was always a net oxygen decrease over the 24-h cycle. Similar findings were discussed by Sundby et al. (1986) in Gullmarsfjorden, Revsbech et al. (1988) in Aarhus Bay, and by Pratihary et al. (2009) in the Mandovi Estuary in India. Berelson et al. (1998) stated that there was no tendency for oxygen uptake rates to decrease during daylight hours of incubation in their studies.

Total oxidized nitrogen (TOxN) concentrations in the water column decreased over the incubation period in both summer and winter. The decreasing TOxN trend (negative flux) observed in both periods was due to uptake from the water column (phytoplankton and benthic microalgae), and processes such as denitrification, which converts NO_3^- to nitrogen gas N_2, as well as the dissimilatory nitrate reduction to ammonium (DNRA), whereby NO_3^- is transformed directly into ammonium by microbes present in highly reduced sediment (Herbert et al., 1999; Brandes et al., 2007; Prescott et al., 2008). Pratihary et al. (2009) found a negative TOxN flux that decreased over the 24-h cycle in most of the periods sampled and attributed this to a combination of low nitrification rates and the benthos acting as

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a sink for NO_3^-. The results from this study displayed an increasing NH_4^+ efflux in all chambers during both summer and winter, which suggests that the benthos of the Great Brak Estuary was acting as a source of NH_4^+. Under conditions of anoxia, dissimilatory nitrate reduction to ammonium potentially competes with denitrification for oxidized inorganic nitrogen (NO_3^- or NO_2^-) (Thornton et al., 2007; Spooner and Maher, 2009), and generally rates of denitrification decrease with increasing organic carbon loads (Heggie et al., 1999). A consequence of DNRA is that it produces nitrogen in a bioavailable form through the reduction of oxidized inorganic nitrogen to NH_4^+, which may be directly assimilated by microorganisms and plants (Thornton et al., 2007). However, the increases in NH_4^+ are due to remineralized organic matter present in the sediment. Other authors (Pedersen et al., 1999; Spooner and Maher, 2009) have reported similar increases in NH_4^+ efflux with a simultaneous decrease in NO_3^- flux (negative flux), which they attributed to a lack of oxygen penetration into the sediment.

Although the results showed no significant difference in the efflux of NH_4^+ during both periods, other studies have indicated that seasonal temperatures do influence fluxes. For example Takayangi and Yamada (1999), Jahnke et al. (2005) and De Vittor et al. (2012) indicated that NH_4^+ efflux from the sediment increased to sustain a summer maximum and dropped off sharply as bottom water began to cool. The higher NH_4^+ efflux was related to the low oxygen concentration which, coupled with a rise in temperature, led to an increased remineralization of organic matter.

The average SRP efflux from the benthos to the water column in summer was 0.043 $mmol \cdot m^{-2} \cdot d^{-1}$ and 0.010 $mmol \cdot m^{-2} \cdot d^{-1}$ in winter. These effluxes are relatively low when compared to those found by Pratihary et al. (2009), where the efflux ranged from 0.12 $mmol \cdot m^{-2} \cdot d^{-1}$ in winter to 0.24 $mmol \cdot m^{-2} \cdot d^{-1}$ in summer. The lower rates of SRP effluxes from the benthos to the water column could be occurring because the SRP may be forming complexes with the bottom sediments thereby retaining most of the SRP in a bound form. Heggie et al. (1999) observed that the sediments in Australian intermittently open closed lagoons (ICOLLS), similar to South African TOCEs, retain P by the formation of iron hydroxide complexes (similar complexes are formed with aluminium) in the oxic zones. Upon depletion of oxygen in the chambers in the Great Brak, there was an increase in the efflux of SRP. This was expected because under depleted oxygen conditions the hydrous iron oxides become reduced and SRP is released leading to higher concentrations of SRP in the water column (Spooner and Maher, 2009). Although the SRP efflux was low, there was consistent efflux of SRP during both deployment periods, following a similar trend to that of NH_4^+. Results indicate that the efflux of SRP was more pronounced during summer than in winter. This is mainly linked to the difference in temperature since higher temperatures will result in a greater release of SRP during the decomposition of organic matter (i.e. anoxia occurs). Remineralization varies significantly with season and is a response to changing bottom temperatures and organic matter inputs (De Vittor et al., 2012).

A large component of the TN and TP in the chambers is composed of organic N and P. This is evident from the low inorganic N and P concentrations found during the incubation period. The TN and TP are composed of both the inorganic and organic fraction, so it stands to reason that an increase in either component would lead to an increase in the TN and TP. There was only a slight increase in TN and TP within the chambers over the deployment periods. This efflux of TN and TP was due to an efflux of inorganic nutrients, NH_4^+ and SRP, during the incubation period. The availability of organic N and P serves as a regular source for the processes of DNRA and remineralization to NH_4^+ and SRP. The sources of DON and DOP to the benthos of shallow water systems are primarily derived from the benthic and pelagic primary producers (Pedersen et al., 1999). The major primary producers in the water column of the Great Brak Estuary were *C. glomerata, Z. capensis* and *R. cirrhosa*. Evidence of DON release from the benthos can be inferred from the studies of Enoksson (1993) and Pedersen et al. (1999). These experiments showed that after the addition of diatom cells and *Z. marina* leaves, respectively, to the sediment, DON was released after the first few days of incubation. They suggested that the released DON was due to leaching of plant and algal storage compounds after autolysis, as well as hydrolysis and mineralization. The supply of organically rich detritus to the sediment coupled with low dissolved oxygen within the bottom water during prolonged closed mouth conditions acts as a source of inorganic and dissolved organic N and P to the water column.

Another important biological component that may have influenced the fluxes in the chambers, is the effect of macrofaunal species. Observations during 24-h sampling of the chambers in the Greak Brak indicate that there are numerous fish, shrimp and crustaceans within the surrounding shallow waters of the estuary as well. There have been no such studies conducted in TOCEs that link the benthic nutrient flux to different faunal groups in the overlying water column in South African estuaries. Studies from other parts of the world (Vetter and Hoppkinson, 1985; Hansen and Kristensen, 1998; Kristensen and Hansen, 1999; Lillebo et al., 1999; Lavrentyev et al., 2000; Webb and Eyre, 2004) have found that macrofauna enhance benthic reactivity and increase the efficiency of both inorganic nutrients and oxygen consumption between the water column and benthos. *Trypaea australiensis* Dana (formally *Callianassa australiensis*) increased benthic oxygen demand by 80% and approximately 15% was used for respiration by the shrimp while the remainder was used for oxidation reactions and microbial respiration (Webb and Eyre, 2004). Macrofaunal activities were found to increase dissolved oxygen consumption due to the enhancement of oxidation reactions like sulphide and pyrite oxidation, nitrification and increased respiration by macrofuana and microbial communities (Kristensen et al., 1991; Pelegri et al., 1994; Paterson and Thorne, 1995). Within the Great Brak Estuary the dominant macrofauna *Upogebia africana* Ortmann and *Callianassa kraussi* Stebbing are found distributed on the intertidal sand and mudflats. At the sites where chambers were deployed they have been reported to be in densities of 41 and 20 $ind \cdot m^{-2}$, respectively (Wooldridge 2008). Although the contribution of macrofauna to nutrient cycling did not form part of the scope of this research, they clearly have an important role to play since they are able to enhance the efflux of nutrients out of the sediments.

CONCLUSION

Temporarily open/closed estuaries are characterized by low river inflow, weak flushing and long residence times resulting in prolonged mouth closure (Whitfield 1992, Taljaard et al., 2009b). These characteristics make TOCEs vulnerable to nutrient enrichment and a build-up of organic matter (Newton and Mudge, 2005; Human and Adams, 2011). Studies on ICOLLS showed that sediments were the most important sources and sinks of N and

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P to the water column and could potentially contribute as much as 3-4 times the catchment discharges (Smith et al., 2001; Palmer et al., 2002; Spooner and Maher, 2009). In the case of the Great Brak, respiration from the organisms in the benthos (benthic respiration) seems to be the major metabolic process occurring during the incubation period with a net flux of oxygen toward the benthos. This study showed that the sediment had a net efflux of NH_4^+, SRP, TN and TP and acted as a source of N and P during both study periods. Organic matter, introduced either via the catchment or internally from the pelagic and benthic primary producers, ensures a sufficient organic load to fuel growth. This ensures that there is always N and P available for the macrophytes present within the estuary. This is especially so under prolonged closed mouth conditions. The build-up of organic matter in the Great Brak Estuary has been exacerbated by reduction in flushing since the construction of a large dam further upstream. There has also been a significant reduction in base flow that would have flushed the estuary regularly. While water from the dam is made available to breach the mouth, it is often not sufficient to flush the estuary. This causes an accumulation of both sediment and organic matter within the estuary until the system gets flushed by a major flood. If the estuary remains closed for a prolonged period (12 months), with an increased organic load present on the benthos, the associated rates of effluxes of N and P would increase. In order to reduce the organic load to the system better flushing methods or, more importantly, an increase in base flow, is needed to reduce residence times of water in the estuary.

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