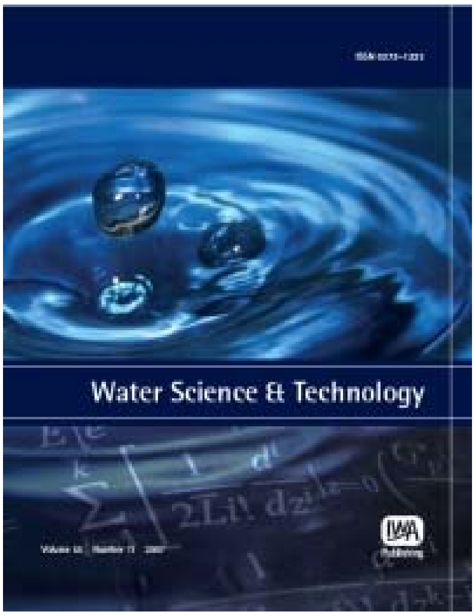
Water Science & Technology

Benthic nutrient fluxes and sediment oxygen consumption in a full-scale facultative pond in Patagonia, Argentina

M. Faleschini and J. L. Esteves

ABSTRACT

The study of benthic metabolism is an interesting tool to understand the process that occurs in bottom water at wastewater stabilization ponds. Here, rates of benthic oxygen consumption and nutrient exchange across the water–sludge interface were measured *in situ* using a benthic chamber. The research was carried out during autumn, winter, and summer at a municipal facultative stabilization pond working in a temperate region (Puerto Madryn city, Argentina). Both a site near the raw wastewater inlet (Inlet station) and a site near the outlet (Outlet station) were sampled. Important seasonal and spatial patterns were identified as being related to benthic fluxes. Ammonium release ranged from undetectable (autumn/summer – Inlet station) to $+30.7$ kg-NH_4^+ ha^{-1} d^{-1} (autumn – Outlet station), denitrification ranged from undetectable (winter – in both sites) to -4.0 kg-NO_3^- ha^{-1} d^{-1} (autumn – Outlet station), and oxygen consumption ranged from 0.07 kg-O_2 ha^{-1} d^{-1} (autumn/summer – Outlet station) to 0.84 kg-O_2 ha^{-1} d^{-1} (autumn – Inlet station). During the warmer months, the mineralization of organic matter from the bottom pond acts as a source of nutrients, which seem to support the important development of phytoplankton and nitrification activity recorded in the surface water. Bottom processes could be related to the advanced degree and efficiency of the treatment, the temperature, and probably the strong and frequent wind present in the region.

Key words | ammonium release, benthic metabolism, denitrification, municipal facultative pond, temperate region

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INTRODUCTION

The importance of benthic metabolism related to organic matter mineralization and oxygen consumption has been a topic widely studied in natural environments because it has an important role in the nutrient concentration in surface waters and, thus, in their productivity. Sediments in shallow coastal waters are known to be important sites for the accumulation of organic matter and the subsequent mineralization and recycling of nutrients (Bonanni *et al.* 1992).

The magnitude of nutrient exchange between sediment and water column are controlled by factors such as redox potential, dissolved oxygen, supply and quality of organic matter, temperature, porosity, bioturbation, and surface sediment resuspension episodes (Pratihary 2008).

The direct measuring techniques that are frequently utilized to study the nutrient and oxygen fluxes into the sediment–water interface could be *in situ* or *ex situ*. The former use a benthic chamber (Torres *et al.* 2009), whereas the latter technique incubates sediments in the laboratory under controlled conditions (Cook *et al.* 2004).

The intensity and magnitude of the processes that occur in the bottom water seem to be more notable in wastewater facultative ponds than in natural environments because of the mostly organic matter, nutrient, and bacterial concentrations in addition to important phytoplankton development. Previous studies of the surface sludge of stabilization ponds have yielded values of organic matter higher than 60% of the dry weight (Ayres *et al.* 1993; Faleschini & Esteves 2011).

In particular, the nitrogen dynamics in facultative stabilization pond studies is one of the most controversial subjects

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involved in determining which are the major processes involved in their removal. Most of the studies on stabilization pond performance have been made on the basis of nitrogen concentrations measured in the treated water. However, an important number of the processes involved in the nitrogen cycle and with consequences in the surface water quality are, in part, the result of a process that occurs in the bottom water layer and in the sludge, as follows: (1) organic nitrogen and phosphorus degradation; (2) denitrification – the nitrate produced in the aerobic surface layer could (because of mixing processes) achieve the anaerobic layer and be denitrified with the consequent release of N_2; (3) also, this layer is responsible for other anaerobic metabolic processes where gaseous compounds (CH_4, H_2S, CO_2) that leave the pond are obtained.

Despite the relevance of the sludge in the treatment of wastewater by means of stabilization ponds, few studies have analyzed the sludge, maybe because of the difficulty of sample collection in full-scale treatment plants. Some studies have measured the nutrient release from the sediments: Lumbers & Andoh (1987) and Bryant & Bauer (1987). Zimmo *et al*. (2004) incubated sediments from a facultative pond in the laboratory to measure the nitrification and denitrification rates.

The purposes of the present study were to study the nutrients and dissolved oxygen fluxes in the sludge–water interface from the full-scale facultative pond of Puerto Madryn city. As we know, it is the first report using a benthic chamber in this kind of environment.

METHODS

Study site and sampling

Fieldwork was conducted in a primary facultative pond that is part of the wastewater treatment system of Puerto Madryn city, which has been working since 2001. This pond has a surface area of 25 ha and an average depth of 1.5 m, and receives raw wastewater from 90,000 inhabitants, with a mean flow of approximately 15,000 m^3/day. Climatic characteristics of the study site and details of the pond performance have been described in Faleschini *et al*. (2012).

In order to achieve the objectives, there were three sampling sessions (autumn 2009, winter 2009, and summer 2010) in two sampling sites in the facultative pond: a site near the raw wastewater inlet (Inlet station) and a site near the outlet (Outlet station) (Figure 1).

Nutrients and dissolved oxygen fluxes in the sludge–water interface

In situ benthic mineralization rates and dissolved oxygen demand were estimated using opaque benthic chambers. Special care was taken at the time of placing the chamber, submerging it slowly from the boat with the aid of a wire, taking advantage of the shallowness, and minimizing disturbance of the bottom. The experiments were carried out in the morning (between 9 am and 1 pm), and, due to the complexity of the maneuver, a single incubation was performed in each season and each site.

The chamber system isolated a known water volume (9.7 liters) and a known sediment–water interface area (0.09 m^2) (Esteves *et al*. 1986). A magnetic bar, driven by electric motor, ensures complete mixing of the water within the system and maintains flow over a modified YSI-58 polarographic oxygen and temperature probe (Yellow Springs Instrumental Co.) (Figure 2). The chamber was connected to the surface by a 2 mm internal diameter silicone tube, which allowed the withdrawal of water samples by syringe every 30 min approximately, collecting 15 mL for rinsing and 30 mL as the sample. Dissolved oxygen and temperature were monitored in real time at intervals of 10 min. The experiment time duration was approximately 3 h. Samples were stored, refrigerated in the dark, until their arrival at the laboratory. Water samples were filtered (Whatman GF/C) and frozen for analysis of NH_4^+, NO_3^-, and PO_4^{3-} concentrations, according to the techniques described in APHA (1980).

Equation (1) was used for flux calculations. As a convention, positive values mean flux from the sludge to water and negative values mean flows from the water to the sludge. Because we do not have previous records of the use of a benthic chamber in this kind of environment, the incubations were made for a maximum period of 3 h. However, for the calculation we used the time span in which the concentration presented a linear behavior.

$$F = \frac{(C_t - C_0) * \mathrm{V}}{T * \mathrm{A}} \tag{1}$$

where:

F is the flux in the sediment–water interface (mg X compound $m^{-2}\,h^{-1}$)
C_t is compound X concentration at final time (mg/L)
C_0 is compound X concentration at initial time (mg/L)
V is the chamber volume (liter)
T is the experimentation time (h)
A is the chamber surface area (m^2).

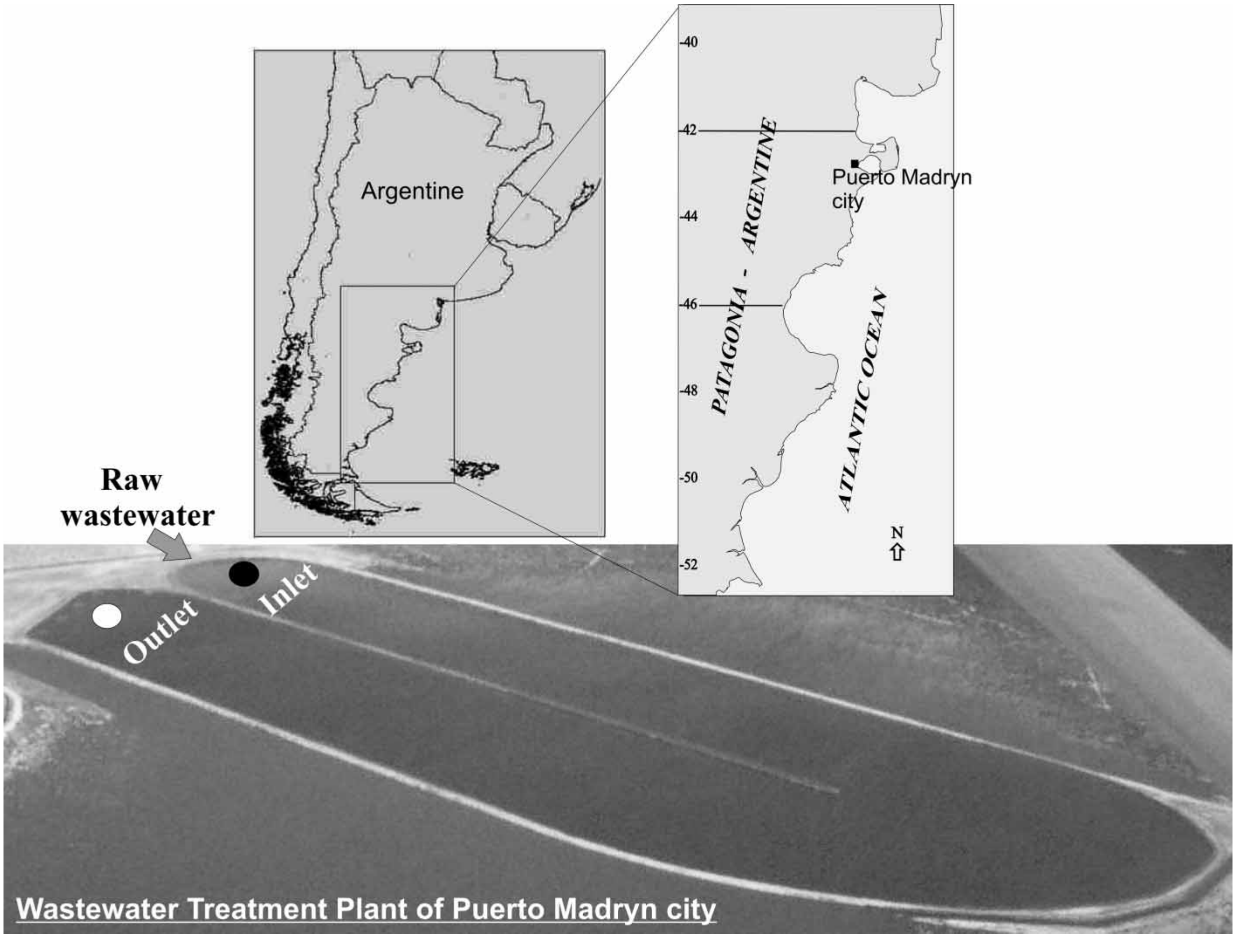

Figure 1 | Sampling point distribution into the facultative pond at Puerto Madryn city.

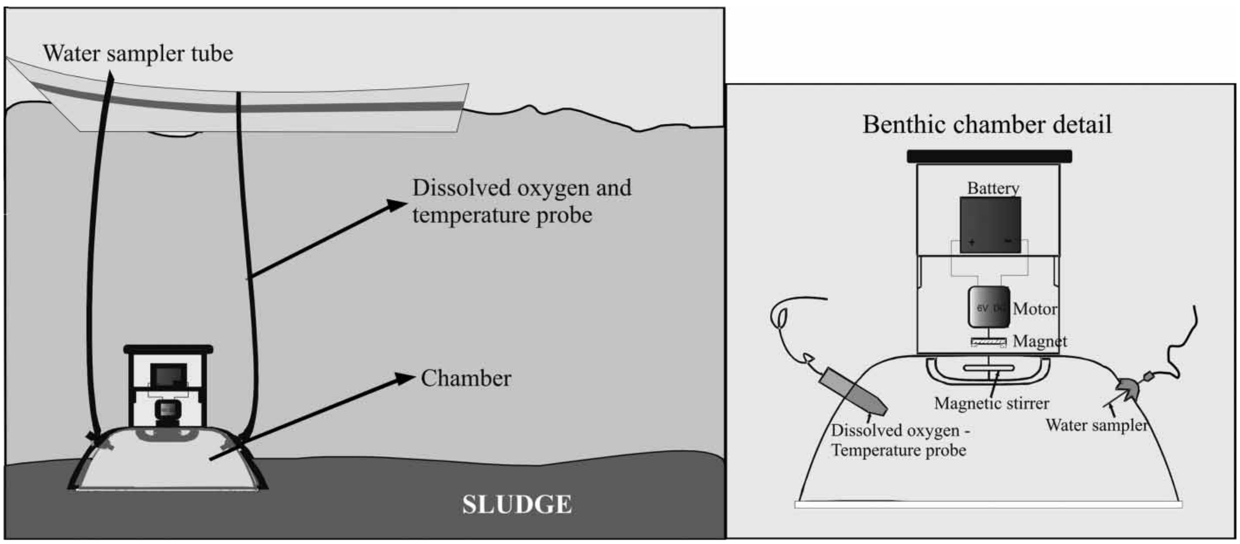

Figure 2 | Equipment used to study the sludge–water exchanges of nutrients and dissolved oxygen.

RESULTS AND DISCUSSION

Ammonium and phosphate fluxes

The ammonification process showed different behaviors between sampling sites. At the Inlet station, a significant flux from the sediment to the water was observed only during winter ($+32.4$ mg-NH_4^+ m^{-2} h^{-1}), whereas in the other seasons the process could be described as negligible. Conversely, the bottom pond at the Outlet station showed important NH_4^+ positive fluxes during summer and autumn, with a greater magnitude than that recorded at the Inlet station. Mass fluxes of $+128.1$ mg-NH_4^+ m^{-2} h^{-1} (autumn) and $+108.2$ mg-NH_4^+ m^{-2} h^{-1} (summer) were obtained, with a maximum difference in concentration during the span time of $+130$ mg-NH_4^+/L. In winter, the Outlet station had a mass flux of $+15.8$ mg-NH_4^+ m^{-2} h^{-1}, less than that of the Inlet station, reflecting the importance of temperature in the degradation metabolism process (Figure 3).

In all cases in which fluxes were detected, these were positive, reflecting the active mechanisms of ammonification and organic phosphorus degradation processes in the bottom pond. Considering the warmer months and extrapolating the chamber results, the sludge from the Outlet region released to the water column between 25.9 and 30.7 kg-NH_4^+ per hectare per day represents an equal flux (summer) and even 25% greater flux (autumn) than the ammonium load per day per hectare entering the pond from the raw wastewater. These benthic fluxes seem to support the fast phytoplankton uptake and the greater nitrification activity recorded during the warm months, reflected in values in

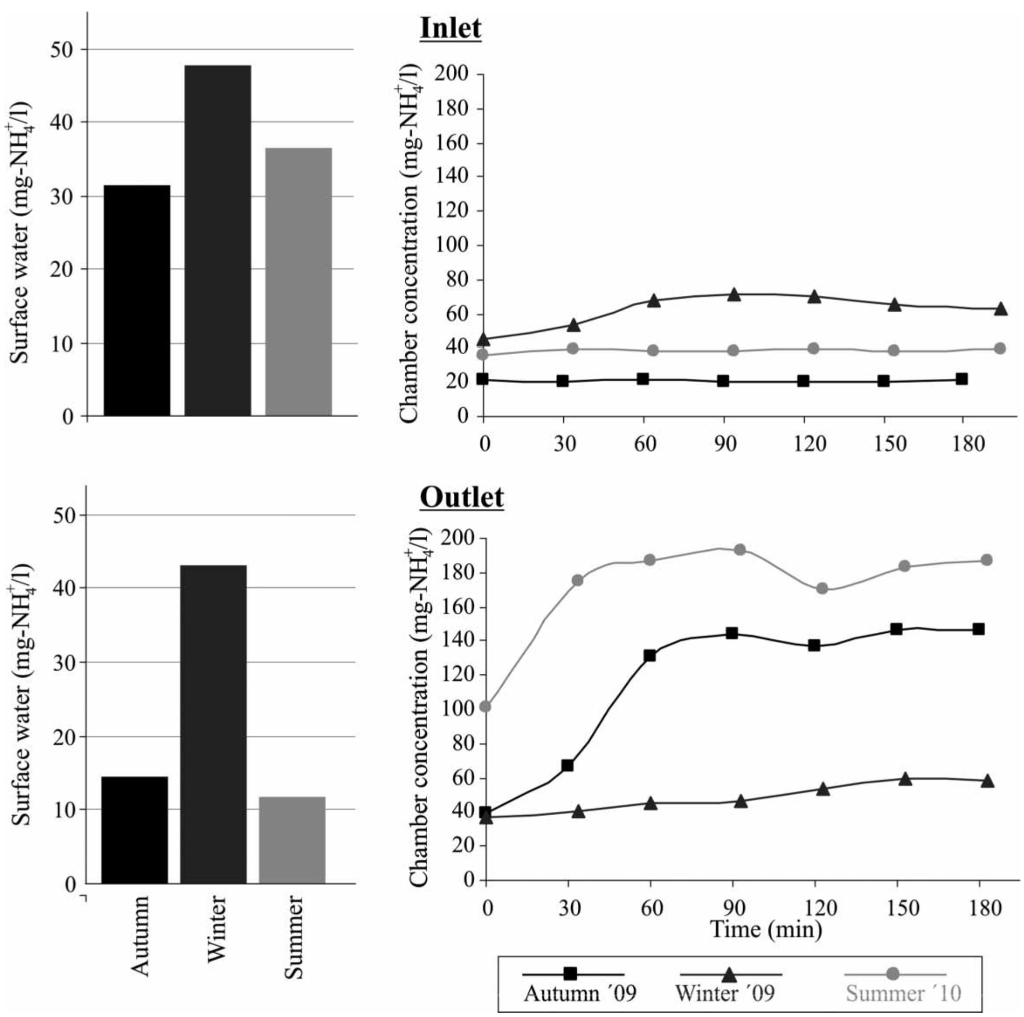

Figure 3 | NH_4^+ evolution in the surface water and inside the benthic chamber.

the surface water of more than 2,000 μg/L of chlorophyll-*a*, NO_3^- concentration between 1 and 6 mg/L and NH_4^+ concentration not exceeding 15 mg/L.

Our results for NH_4^+ fluxes described a clearly seasonal pattern in the algal sludge behavior in a stabilization pond working in a temperate climate, finding a storage period during cold months and experiencing a thermal overturn during warm months, when the algal sludge was digested faster and ammonium demand from the column water was at a maximum.

Phosphate behavior inside the chamber was similar to that of ammonium: at the Inlet station, the highest mass flux was detected in winter (+1.90 mg-PO_4^{3-} m^{-2} h^{-1}) while at the Outlet station, the higher mass fluxes were recorded in the warmer months (+19.3 mg-PO_4^{3-} m^{-2} h^{-1} in autumn and +4.6 mg-PO_4^{3-} m^{-2} h^{-1} in summer).

Nitrate flux

NO_3^- behavior in benthic chamber experiments has been used to study the denitrification rate in many natural environments, reflecting a decrease in their concentration during the incubation period (Tomaszek & Czerwieniec 2003; Naqvi *et al.* 2006).

Seasonal and spatial patterns were observed for NO_3^- concentration in the surface water: minimum concentration at the Inlet station during winter and summer (<0.02 mg/L) and maximum at the Outlet station during summer (6.09 mg/L), being 440 times more concentrated in summer and 4 times more concentrated in autumn than at the Inlet station. It is important to state that a fraction of the nitrate present at the Inlet station could be attributed to the nitrate carried by raw wastewater ($NO_3^- = 0.04 \pm 0.02$ mg/L in Faleschini *et al.* (2012)).

Inside the chamber, an initial NO_3^- increase and then a fast decrease were observed at both sites during autumn. The increase could be associated with nitrate release from the porewater and/or nitrification process (autumn was the only season in which a temperature of up to 10 °C was coincident with dissolved oxygen of up to 2.5 mg/L at t_0 inside the chamber). As a consequence, the net balance was an increase in nitrate concentration at the start of the experiment and thus nitrate consumption was recorded (starting when the dissolved oxygen was lower than 0.5 mg/L).

During the periods of decrease, these fluxes were calculated: −2.4 mg-NO_3^- m^{-2} day^{-1} (Inlet – autumn), −16.8 mg-NO_3^- m^{-2} day^{-1} (Outlet – autumn), −0.3 mg-NO_3^- m^{-2} day^{-1} (Inlet – summer), and −7.4 mg-NO_3^- m^{-2} day^{-1} (Outlet – summer) (Figure 4). These negative fluxes reflect the NO_3^- transformation to molecular nitrogen by the denitrification process. We can discard the possibility of assimilatory NO_3^- reduction to NH_4^+ because of the elevated ammonium concentration inside the chamber (even up to 35.3 mg/L), which should inhibit this metabolic route (Jørgensen 1989). During winter, the NO_3^- concentrations inside the chamber in both sites were so low that the fluxes were negligible.

The rates calculated represent the minimum denitrification that could be occurring in the bottom pond. Indeed, the nitrate concentrations that were encompassed in the chamber at t_0 were very low in comparison with their concentration in the surface water (the Outlet in summer had a surface concentration of 6.09 mg/L, whereas the concentration at t_0 inside the benthic chamber was 0.1 mg/L). Because the chamber experiments were made during calm weather conditions, the stratification in the water column was maximal. Perhaps this could underestimate the 'true' denitrification rate in the pond, because the frequently strong winds present in Puerto Madryn would act to provide NO_3^- to the lower layer, favoring the denitrification process.

The denitrification values obtained here were lower compared with those of Zimmo *et al.* (2004), who reported denitrification values in sediment incubations from stabilization ponds between 160 and 560 mg-N m^{-2} d^{-1}. An important difference with our study is that in Zimmo *et al.*'s (2004) study, the incubations were made adding KNO_3, so at the start of the experiment the initial concentration was approximately 5–7 mg-NO_3^-/L.

Dissolved oxygen flux and temperature

In the surface water, the Inlet station presented dissolved oxygen values up to 3 mg/L in autumn and winter. These elevated concentrations for raw wastewater could be related to a turbulent aeration of raw wastewater on its way to the sewer system (about 10 km). When the chamber was placed, part of the surface water column with an important oxygen content was dragged to the bottom, reflected in a high concentration at t_0. The O_2 present initially was quickly consumed (in 90 min the concentrations were less than 0.5 mg/L), independent of the initial concentration. In all cases, the measured mass fluxes were negative, indicating an O_2 consumption of −3.5 mg-O_2 m^{-2} h^{-1} (autumn), −3.0 mg-O_2 m^{-2} h^{-1} (winter), and −0.8 mg-O_2 m^{-2} h^{-1} (summer).

The Outlet, during summer and autumn, presented very low dissolved oxygen concentrations in the surface water

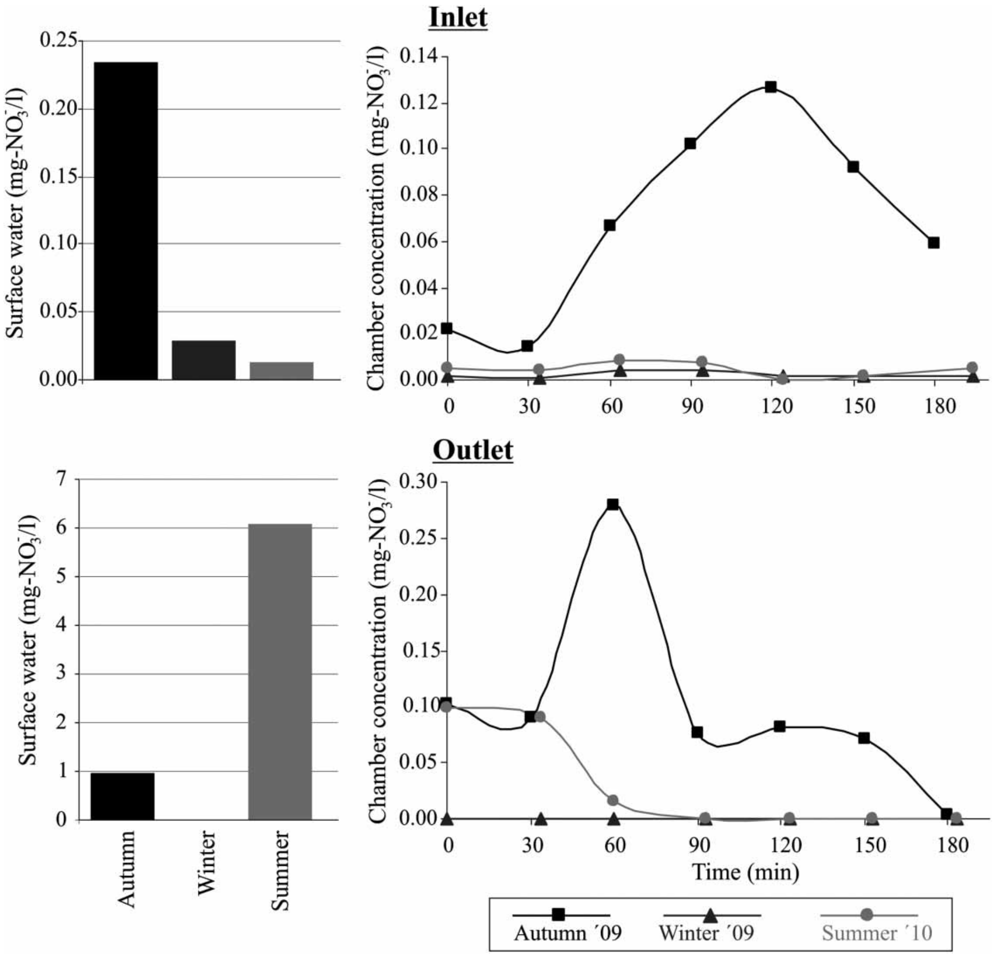

Figure 4 | NO_3^- evolution in the surface water and inside the benthic chamber.

(<2 mg/L) and at t_0 inside the chamber. Therefore, the fluxes were lower than those in the Inlet station: -0.3 mg-$O_2\,m^{-2}\,h^{-1}$ (autumn) and -0.4 mg-$O_2\,m^{-2}\,h^{-1}$ (summer). This could be explained by the organic overload described in this pond (Faleschini *et al.* 2012); thus, in the warm seasons, the oxygen consumption for aerobic metabolism was greater than the oxygen produced by the phytoplankton plus that incorporated by superficial aeration. Only in winter was the dissolved oxygen concentration in the surface water and inside the chamber significant (4.6 and 4.4 mg/L, respectively), followed by a fast consumption reflected in a mass flux of -2.3 mg-$O_2\,m^{-2}\,h^{-1}$ (Figure 5).

In parallel with oxygen measurement, temperature variation was recorded inside the chamber: in the Inlet station, the higher temperatures of the raw wastewater were notable as a result of the exothermic organic matter degradation during transport. The average temperature of raw liquid was 17.9 °C and all samples were higher by at least 2 °C than in the Outlet (the highest range occurred in winter: 4.7 °C). With regard to the season, the temperature range in the surface water was: 13.7–17.0 °C (autumn), 6.2–10.5 °C (winter), and 20.5–24.5 °C (summer). In all ranges, the lowest value corresponded to the Outlet station and the largest to the Inlet station.

CONCLUSIONS

The important degradation of organic matter recorded at the bottom pond represents a substantial source of nutrients to the water column in the facultative pond in Puerto Madryn. The highest NH_4^+ and PO_4^{3-} fluxes were recorded at the Outlet station and during the warmer months. Nutrient fluxes from the bottom pond seem to support the greater phytoplankton development and nitrification activity that were recorded in the surface water during the warmer months. The Inlet station recorded greater NH_4^+ and PO_4^{3-} fluxes than the Outlet station only during winter, but in all

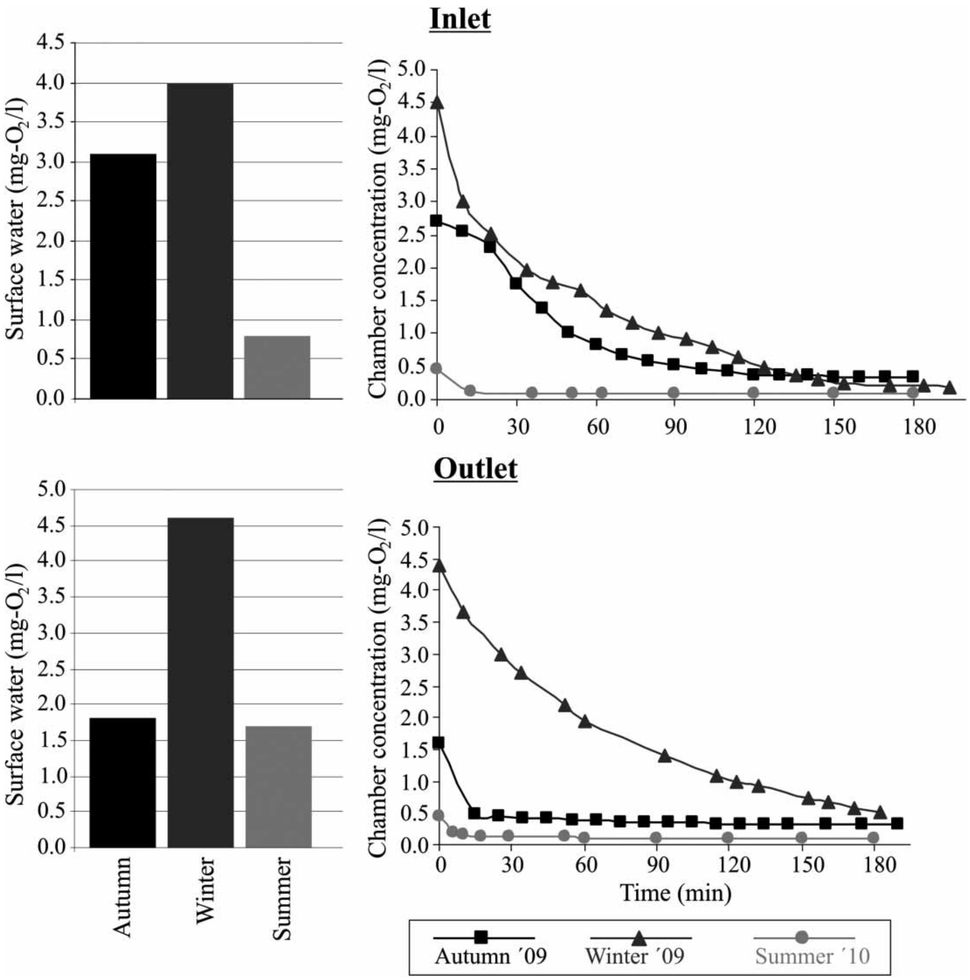

Figure 5 | O_2 evolution in the surface water and inside the benthic chamber.

cases these fluxes were seven times lower than those in the warmer months.

In the surface water, the presence of nitrate was clearly seasonal and spatial; the higher concentrations were found in the warmer months and at the Outlet station. As a result, the highest denitrification rates under these conditions were achieved. The denitrification rate reached a maximum value during autumn at the Outlet station. A significant NO_3^- gradient concentration between the surface and bottom water was observed. This highlights the importance of the denitrification process.

Temperature and dissolved oxygen were clearly higher at the Inlet than at the Outlet station, caused by the raw wastewater entry with elevated temperature and dissolved oxygen, results of the exothermic process and turbulence during transport. In all cases, the oxygen inside the chamber was quickly consumed, reaching a concentration less than 0.5 mg-O_2/L at the end of all experiments.

Processes occurring in the bottom water and the sludge of stabilization ponds are linked with the upper water column and have an impact on its quality. The bottom processes could be related to the advanced degree and efficiency of the treatment, the temperature, and probably the wind.

The study of the sludge–water interface exchange represents an interesting tool to increase the understanding of organic matter degradation and nitrogen dynamics in wastewater stabilization ponds.

REFERENCES

APHA 1980 *Standard Methods for the Examination of Water and Wastewater*, 15th edn. American Public Health Association, Washington, DC.

Ayres, R. M., Lee, D. L., Mara, D. D. & Silva, S. A. 1993 The accumulation, distribution and viability of human parasitic nematode eggs in the sludge of a primary facultative waste stabilization pond. *T. Roy. Soc. Trop. Med. H.* **87** (3), 256–258.

Bonanni, P., Caprioli, R., Ghiara, E., Mignuzzi, C., Orlandi, C., Paganin, G. & Monti, A. 1992 Sediment and interstitial water chemistry of the Orbetello lagoon (Grosseto, Italy); nutrient diffusion across the sediment-water interface. *Hydrobiologia* **235–236** (1), 553–568.

Bryant, C. W. & Bauer, E. C. 1987 A simulation of benthal stabilization. *Water Sci. Technol.* **19** (12), 161–167.

Cook, P. L. M., Revill, A. T., Butler, E. C. V. & Eyre, B. D. 2004 Carbon and nitrogen cycling on intertidal mudflats of a temperate Australian estuary. II. Nitrogen cycling. *Mar. Ecol.-Prog. Ser.* **280**, 39–54.

Esteves, J. L., Bonin, P., Blanc, F., Mille, G. & Bertrand, J. C. 1986 Reduction du nitrate dans les sediments marins comparaison des activites mesurees *in vitro* et *in situ*. *Deuxième Colloque International de Bactèriologie marine, Actes de Colloques* **3**, 319–324.

Faleschini, M. & Esteves, J. L. 2011 Characterization and degradation process of sludge profiles inside a facultative pond (Patagonia, Argentina). *Water Sci. Technol.* **64** (11), 2239–2245.

Faleschini, M., Esteves, J. L. & Camargo-Valero, M. A. 2012 The effects of hydraulic and organic loadings on the performance of a full-scale facultative pond in a temperate climate region (Argentine Patagonia). *Water Air Soil Pollut.* **223** (5), 2483–2493.

Jørgensen, K. S. 1989 Annual pattern of denitrification and nitrate ammonification in estuarine sediment. *Appl. Environ. Microbiol.* **55** (7), 1841–1847.

Lumbers, J. P. & Andoh, R. Y. G. 1987 The identification of the benthic feed-back in facultative ponds. *Water Sci. Technol.* **19** (12), 177–182.

Naqvi, S. W. A., Naik, H., Pratihary, A., Souza, W. D., Narvekar, P. V., Jayakumar, D. A., Devol, A. H., Yoshinari, T. & Sainto, T. 2006 Coastal versus open-ocean denitrification in the Arabian sea. *Biogeosciences* **3**, 621–633.

Pratihary, A. K. 2008 Benthix exchange of biogenic elements in the estuarine and nearshore waters of western India. PhD Thesis, Mangalore University-National Institute of Oceanography, Goa, India, p. 176.

Tomaszek, J. A. & Czerwieniec, E. 2003 Denitrification and oxygen consumption in bottom sediments: factors influencing rates of the processes. *Hydrobiologia* **504** (1–3), 59–65.

Torres, A. I., Gil, M. N., Amín, O. A. & Esteves, J. L. 2009 Environmental characterization of a eutrophicated semi-enclosed system: nutrient budget (Encerrada Bay, Tierra del Fuego Island, Patagonia, Argentina). *Water Air Soil Pollut.* **204** (1–4), 259–270.

Zimmo, O. R., van der Steen, N. P. & Gijzen, H. J. 2004 Quantification of nitrification and denitrification rates in algae and duckweed based wastewater treatment system. *Environ. Technol.* **25** (3), 273–282.

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