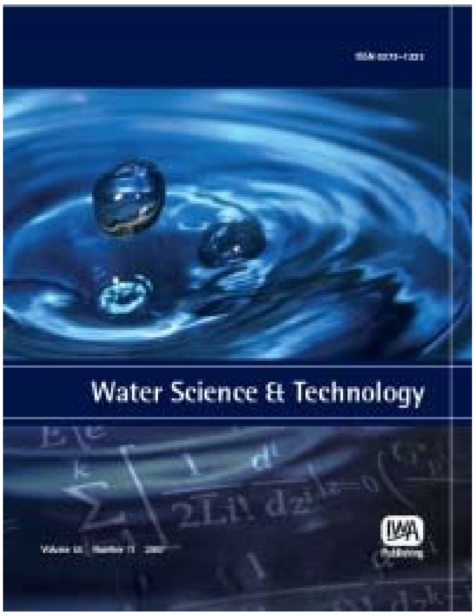
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Characterization and degradation process of sludge profiles inside a facultative pond (Patagonia, Argentina)

M. Faleschini and J. L. Esteves

ABSTRACT

To investigate the characteristics and degradation process in sludge profile, three sampling sessions were made in three different places inside the primary facultative pond of Puerto Madryn city, which was located in a region with a temperate climate in coastal Patagonia (Argentina). The sludge showed an extremely negative redox potential (between −441 and −282 mV) and elevated water content and organic matter concentration, ranging from 83.3 to 97.1% for porosity and from 22.5 to 64.4% for organic matter. The surface layer at the Outlet station during the summer showed the greatest concentration of pigments, reaching a maximum value of 10.6 mg/g for chlorophyll-*a* and 40.9 mg/g for phaeophytin, and a fast diminution with sediment depth. The important concentration of pigment in the surface layer, coincident with phytoplankton bloom in the water column, could support the importance of nitrogen removal via uptake and organic sedimentation in the water column. In warm months the degradation rate was clear, as reflected in a decrease in sediment layer, and even part of the clay bottom was captured inside an 8 cm core sample, registering extremely low concentrations of pigments, carbohydrates, proteins and lipids. The season and the degree of treatment have an influence on sludge characteristics and the organic matter degradation process.

Key words | degradation process, facultative pond, organic matter, Patagonia, sludge characterization

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INTRODUCTION

Stabilization ponds represent a widespread option for wastewater treatment with various associated benefits such as high efficiencies of organic matter and pathogenic organism removal; lower implementation and operation cost than conventional technology; and flexibility, simplicity and independence of electrical energy. In this sense, this treatment system is a feasible alternative in developing countries. A significant number of publications that discuss the performance of this treatment system has focussed on the process taking place in the water column (Abis & Mara 2003; Rockne & Brezonik 2006; Camargo Valero & Mara 2010; among others), but information about the processes that occur in the sludge of stabilization ponds is scarce. A huge majority of sludge studies has focused on the health aspects related to sedimentation of egg parasite, bacteria and/or heavy metal concentrations (Ayres *et al.* 1993; Saqqar & Pescod 1995; Nelson *et al.* 2004; Alonso *et al.* 2006) and the pattern of sludge accumulation (Papadopoulos *et al.* 2003; Abis & Mara 2005). Few studies have characterized the sludge based on inorganic or organic matter (Lumbers & Andoh 1987; Nelson & Jiménez 2000).

The anaerobic water layer and sediments in facultative stabilization ponds present an environmental complexity not found in other systems (including anaerobic or aerobic wastewater ponds and natural sites with high impact from pollution). They receive settled materials present in raw wastewater with high biodegradable organic material and organisms, such as bacteria, virus and parasite eggs and algae growing *in site*. The bottom water and sediment result is completely anoxic conditions, with the possibility that the nitrate produced in the aerobic layer reaches this section and then leaves the system by denitrification. Also, the bottom pond plays an important role in organic material degradation by anaerobic metabolism and production and/or consumption of inorganic compounds. In comparing rates of degradation in aerobic

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environments of the main components of organic matter, it was found that the carbohydrates were used more quickly, followed by proteins and lipids (Harvey *et al.* 1995).

In natural sites, chlorophyll-*a* and phaeopigment concentrations in the sediment are usually used as an indicator of the phytoplankton sedimentation process. Chlorophyll-*a* is the pigment found in the greatest quantity in phytoplankton and is used as an indicator of phytoplankton biomass in the water column, whereas phaeopigments (mainly phaeophytin), are a product of chlorophyll degradation, and are an indicator of phytoplankton decomposition (King & Repeta 1994). Previous studies have shown that chlorophyll-*a* is degraded more rapidly and completely under aerobic than anoxic conditions (Sun *et al.* 1993).

The aim of this study was to characterize physically, chemically and biologically the sludge profile from a facultative pond, taking into account the degree of treatment and the seasons, and its link with the degradation process.

METHODS

Study site and sampling

This work was carried out in Puerto Madryn city, located in the Patagonia region, Argentina (42°46′ S–065°02′ W). The city is in a semi-arid zone with a temperate-cold climate and an important water deficit. The weather conditions clearly determined three air temperature intervals throughout the year, with average figures of 7.7 °C in winter, 14.0 °C in spring and autumn and 19.9 °C in summer. The sewage treatment system under study consists of a primary facultative pond in a U-shape (25 ha surface and 1.5 m depth) and two maturation ponds connected in series. The system has been in operation since 2001 and during the study period received 15,000 m^3/day of raw sewage from approximately 90,000 inhabitants, resulting in a mean theoretical hydraulic retention time of 25 days. The surface organic loading was 69.8 kg DBO_5/ha·day and the length/width ratio of the first half pond is 4.90; as a consequence an overloading was detected in the inlet region, and even in winter this situation affected the entire pond (Faleschini *et al.* submitted).

Three sampling sessions were made (Autumn '09 – Winter '09 – Summer '10), in three sampling sites inside the facultative pond: near the raw wastewater Inlet (**Inlet**), in the half-way stage (**Intermediate**) and near the Outlet (**Outlet**) (Figure 1).

Sediment characterization

Sediment samples were collected with a cylindrical acrylic core with an internal diameter of 4.5 cm and a length of 30 cm. To obtain the sediment samples we ensured that the core has penetrated into the compacted clay layer (bentonite) at the pond bottom, which helped in the sediment collection because this layer produced a plug that sealed the bottom of the core (Nelson *et al.* 2004). From each site, three replicates of different places were taken. Approximately 10 cm of sediment with 200 ml of overlying water was collected. The samples were kept in a dark icebox on the way back to the laboratory. Then, the overlying water was siphoned off from the cores with Teflon tubing and each corer was carefully sliced into four fractions of 2 cm each (0–2 2–4, 4–6 and 6–8 cm). The same layer of each replicate was combined into a composite sample.

The following measurements, in triplicate, were conducted in each sample: redox potential (Altronix TPA-1) – porosity by drying the sediment at 120 °C until reaching constant weight and organic matter by ignition loss at 500 °C for 8 h (APHA 1980) – chlorophyll-*a* and phaeophytin by acetone extraction and fluorometer analysis (Lorenzen & Jeffrey 1980) – carbohydrates by sulfuric acid and phenol method (Dubois *et al.* 1956 modified by Gerchacov & Hatcher 1972) – proteins by Folin–Ciocalteu method (Lowry *et al.* 1951) – lipids by chloroform–methanol method (Bligh & Dyer 1959). The concentrations have been determined as milligrams of the compound 'X' per gram of dry sediment and expressed hereafter as miligrams per gram (mg/g), except for porosity and organic matter, which are expressed as percentage (wet sediment for porosity and dry sediment for organic matter).

RESULTS AND DISCUSSION

Redox potential

The sediments, as expected, have extremely negative values: Inlet ranged from −392 to −282 mV, Intermediate from −392 to −332 mV and Outlet from −441 to −328 mV. The seasonal pattern was clear: less reduced sediments were found during winter, intermediate values were found in

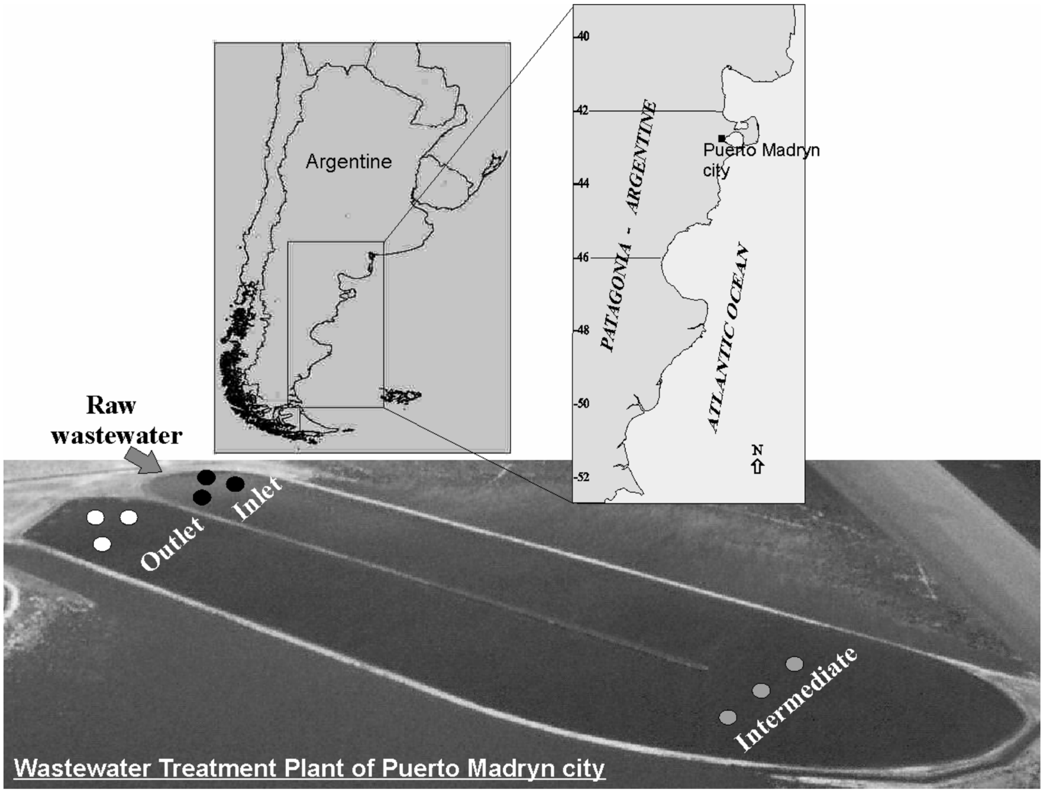

Figure 1 | Sampling points distribution into the facultative pond at Puerto Madryn city.

the autumn and the most reduced values were registered during summer.

Porosity and organic matter

In general, the porosity was higher than 90% and with a tendency to decrease with the increasing sediment depth (older layer has a greater compaction) coinciding with that reported by Carré & Baron (1987). More than 90% of the samples presented organic matter values higher than 40%, with a maximum of 64.4% and minimum of 22.5% (in winter) coincident with minimum porosity. A gentle decrease in the organic matter with depth was observed, except during winter in the Outlet where the decrease was abrupt as of 4 cm depth. There was a strong correlation between porosity and organic matter ($r = 0.89$; $p < 0.001$). Sediments from other primary facultative ponds have reported porosity values between 93.2 and 98.5% and organic matter between 46.3 and 66.1% (Ayres *et al.* 1993). The Outlet during winter (fractions 4–6 and 6–8) showed the minimum porosity and organic matter (83.3–85.0% and 22.5–24.0%, respectively).

Chlorophyll-*a* and phaeophytin

Faleschini *et al.* (submitted) reported the following in the Outlet surface water of this facultative pond: maximum values of chlorophyll-*a* and phaeophytin during summer (3.2 and 4.7 mg/l, respectively) and minimum values during winter (0.01 and 0.02 mg/l, respectively).

In the sludge, the highest chlorophyll-*a* concentration was observed for Outlet station in surface fraction during summer (10.6 mg/g). A sharp tendency to decrease with the sediment depth was observed, indicating a recent surface sedimentation and that the biodegradation process remains active. The lowest values (<0.1 mg/g) were registered at Inlet station, 4–6 layer (in summer); at Intermediate station, surface layer (in winter) and 4–6 cm layer (in summer) and at Outlet station, deepest layer (in summer) (Figure 2). In general, the surface section showed the higher concentrations, which is predictable because it receives the recent settled material, this being more noted during summer in the Outlet station, which reflects the bigger primary productivity during the warm months and their consequent sedimentation. The surface layer could include live

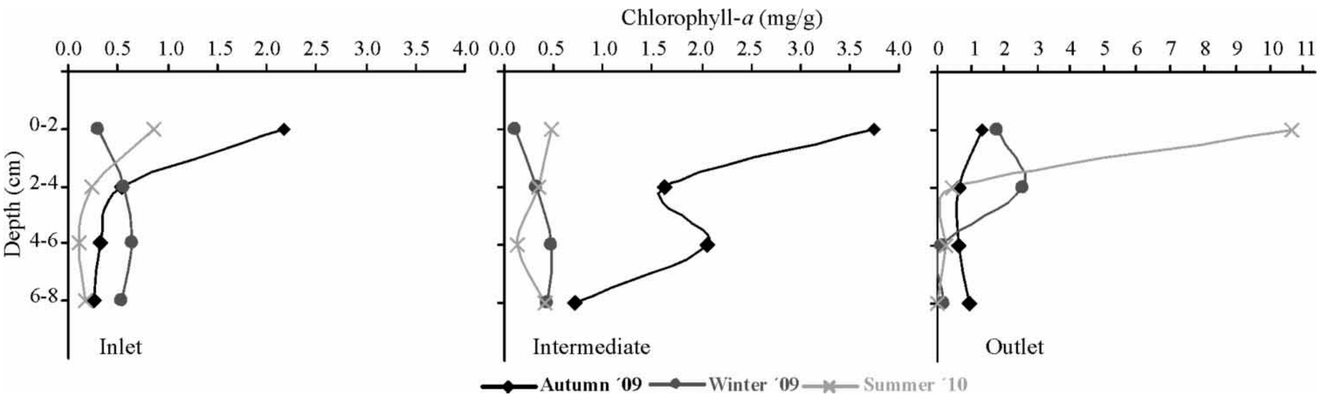

Figure 2 | Distribution of chlorophyll-*a* inside the sludge.

phytoplankton, whereas the chlorophyll-*a* present in the deeper layers should correspond to dead cells not yet degraded.

Phaeophytin presented extensive high values in the surface layer: Inlet during autumn (6.6 mg/g); Intermediate during autumn (8.4 mg/g); and Outlet during summer (40.9 mg/g). Nevertheless, at Inlet and Intermediate stations a tendency to accumulate with sediment depth starting from the fraction 2–4 cm was observed; whereas the Outlet presented an opposite behaviour, being more noted during autumn and summer, because of the high concentrations in the surface layer (see Figure 3).

Although quantifying the organic nitrogen sedimentation rate was not a specific aim in our study, the elevated pigment concentration registered in the sediment and mainly in the surface layer, is a finding that could support the papers that claim that organic nitrogen sedimentation via biological uptake is an important mechanism for nitrogen removal in stabilization ponds (Ferrara & Avci 1982; Santos & Oliveira 1987; Camargo Valero *et al.* 2010). This was observed more clearly during the warm season, coincident with highest ammonium removal in the water surface (Faleschini *et al.* submitted).

Carbohydrates

Carbohydrates presented different behavior between sites. In the surface fraction at the Inlet station, low dispersion was registered, with values between 25.1 and 38.7 mg/g. Both winter and summer presented an increase in the first three fractions and then decreased to values between 30.1 and 34.8 mg/g. An opposite picture was observed in autumn in the first three fractions, but with a similar concentration in the deepest fraction than in the other seasons. The Intermediate station showed a decrease in the first three fractions and then increased in the 6–8 cm layer. In the Outlet station during summer, the fraction 0–4 cm had a maximum concentration on the order of 50 mg/g and then decreased to reach the smallest value (1.9 mg/g). A greater dispersion was observed in the Outlet station in the surface

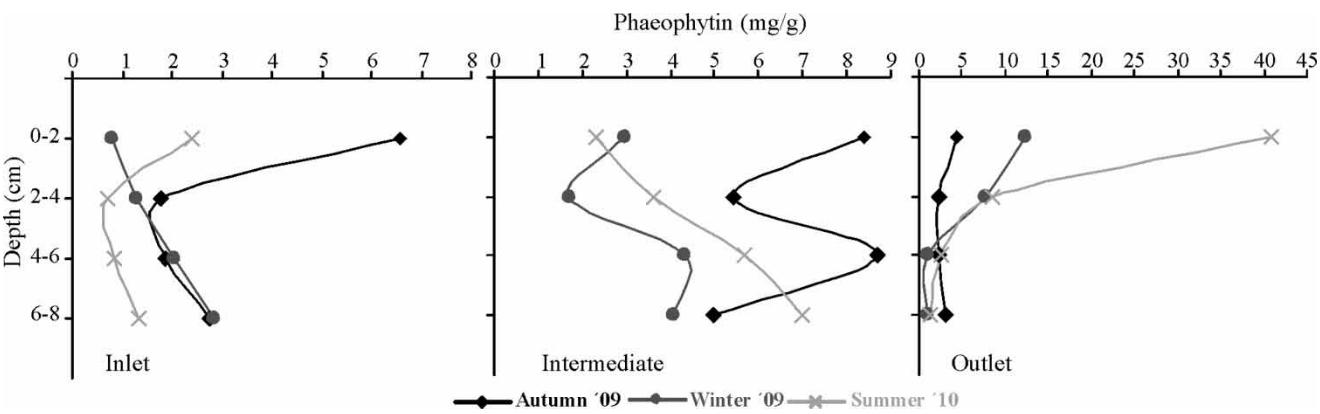

Figure 3 | Distribution of phaeophytin inside the sludge.

layer, with a maximum concentration in summer (54.2 mg/g) and a minimum in autumn (7.6 mg/g) (Figure 4). The Inlet did not provide a marked pattern, possibly due to a mixture in the origin of the material settled, between the purely sewage contribution and the algal material. Whereas, in the Intermediate and Outlet stations, the recent sedimentation was reflected in the surface layer being of greater importance in summer, then winter and autumn (probably the latter would be reflecting a greater degradation rate in autumn than deposition compared with winter).

Proteins

Proteins showed an irregular behavior, with concentrations between 3 and 9 mg/g in most samples, lacking a clear pattern with sediment depth and during treatment evolution. Similar to that observed for carbohydrates, the Outlet station showed a sharp decrease from 8.6 mg/g in 4 cm deep sediment to 0.5 mg/g at the deepest fraction during summer, and in the other seasons a constancy in function of depth was registered (Figure 5). A possible explanation for the irregular behavior in the first two stations of the system could be, as for carbohydrates, the strong and continuous influence from the sewage material settled, not reaching the time for the establishment of a vertical pattern. In the Outlet, only in the summer was a concentration decline registered depending on the sediment depth.

Lipids

Lipids represented an important percentage of the total dry weight of sediment (between 8 and 13%) and of the total organic matter (between 13.5 and 34.7%). Maximum values were obtained at the Inlet station in fraction 0–2 cm independent of season, but during autumn and summer a sharp decrease with the sediment depth was registered. The origin of an important fraction of lipids observed in the Inlet station could be associated with material present in the raw wastewater whereas in the Outlet station an important proportion corresponding to phytoplankton is likely. During summer, the Outlet station presented a similar pattern of carbohydrates and proteins: a marked decrease

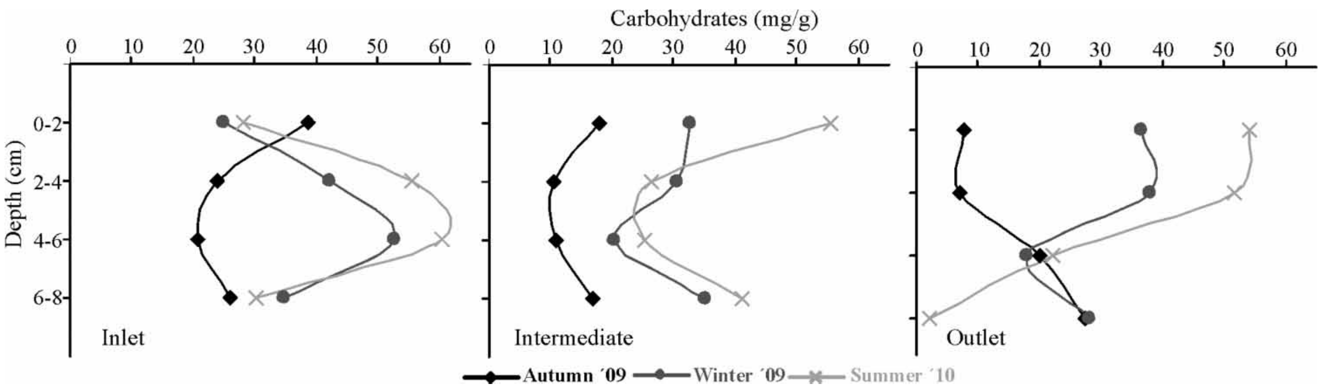

Figure 4 | Carbohydrate concentration in sediment profiles.

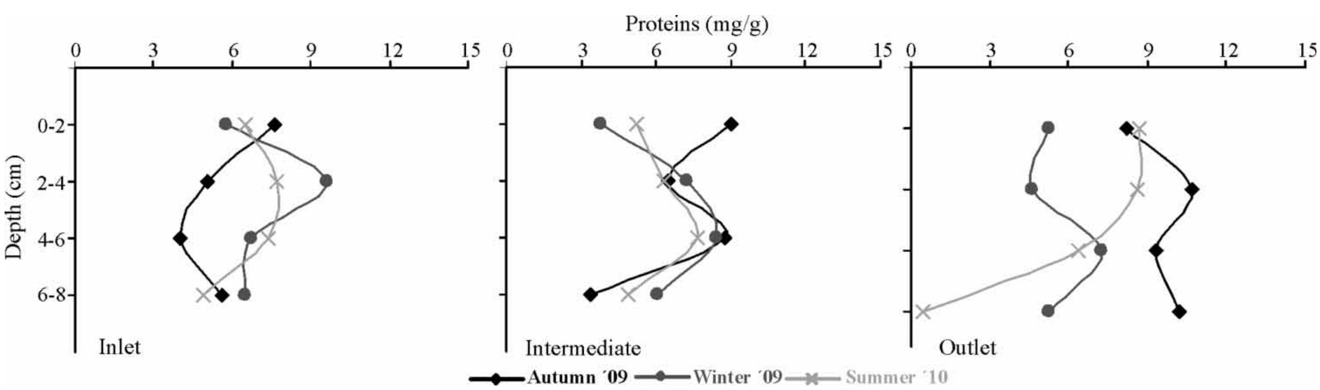

Figure 5 | Protein concentration in sediment profiles.

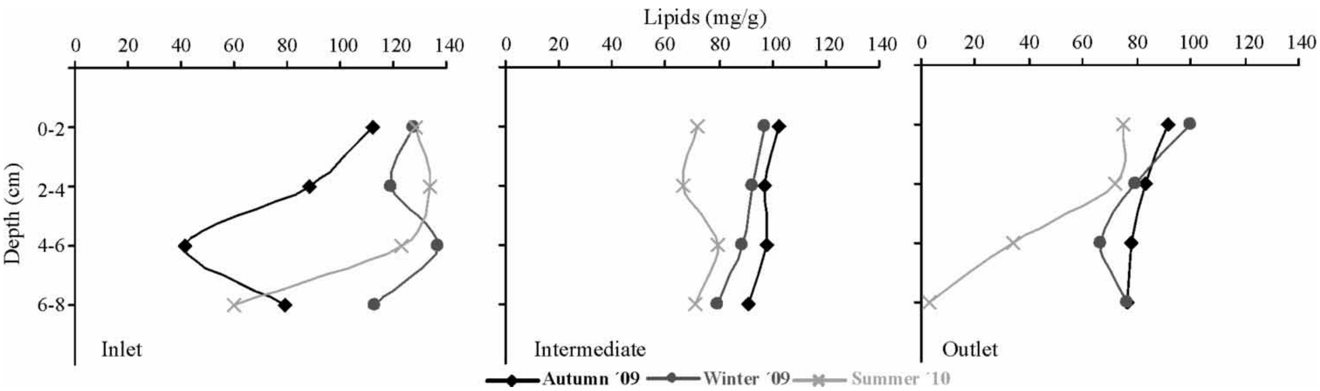

Figure 6 | Lipid concentration in sediment profiles.

from 4 cm deep, reaching a value of 3.0 mg/g at fraction 6–8 cm (Figure 6).

CONCLUSIONS

The sludge analysis allowed us to discern differences along the facultative pond (Inlet, Intermediate and Outlet stations), in depth of sediment (0–8 cm profiles, fractional every 2 cm) and between seasons (autumn, winter and summer).

The sludge from the pond showed a negative redox potential reflecting a reduced environment and elevated water content and organic matter. The composition of organic matter revealed differences between sampling stations. The Inlet station had the lowest content of pigment concentration, with the majority corresponding to dead cells, so a considerable proportion of the organic content at this site could reflect sedimentation of sewage origin. The Outlet station presented the most elevated concentration of phytoplankton settled (either degraded or in the process of degradation) in the surface layer and during summer, reflecting important and recent phytoplankton sedimentation. In this season, the degradation rate was faster than sedimentation and, as a consequence in the deepest fraction, low concentrations of pigments, carbohydrates, proteins and lipids were registered. The elevated pigment concentration and the seasonal-spatial pattern could support the theory that organic nitrogen sedimentation via biological uptake is an important mechanism for nitrogen removal in stabilization ponds. The season (influencing phytoplankton dynamics and bacterial metabolism) and the degree of treatment had an influence on the sludge characteristics and organic matter degradation process. A deeper knowledge of the process taking place in the sludge will be helpful to understand the results that generally are obtained in the water column of stabilization ponds.

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