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Innovative microcosm experiments for the evaluation of the regeneration rates of nutrients in sediments of a hypersaline lagoon

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ABSTRACT

The aim of this study was to evaluate the regeneration of nutrients from the sediments to the water column in varying salinities, with an innovative experiment that closely simulates real environment. *In vitro* experiments were carried out simulating six scenarios with two sediment types (low carbonate and high carbonate). Local water and sediments were added to microcosms where circulation was forced. Results showed nitrogen release from low carbonate sediment in the lagoon, mixed and seawater (1.69, 4.68 and 7.36 μmol m^{-2} day^{-1}, respectively). Phosphate diffusive fluxes were positive in lagoon water and low carbonate sediment (2.24 μmol m^{-2} day^{-1}), negative with mixed water (−0.30 μmol m^{-2} day^{-1}) and seawater (−0.51 μmol m^{-2} day^{-1}). A phosphate release surge was observed in the low-carbonate sediment with overlying mixed water and seawater that, in the natural environment, may boost primary production.

1. Introduction

During the last century, most coastal areas have been strongly impacted by increased anthropogenic activities and the consequent release of contaminants and nutrients. Although these releases have been significantly reduced during the last few decades, due to better regulation, contaminants have accumulated in the sediment over time (Rigaud et al., 2013). Several studies have shown that this accumulation has caused sediment to become a source of nutrients and contaminants in the water column, with the potential to alter the quality of the aquatic environment and threaten organisms (Cunha and Wasserman, 2003; Joshi et al., 2015; Rigaud et al., 2013; Ruttenberg, 2014).

Araruama Lagoon, in Rio de Janeiro, Brazil, is a perennial hypersaline system, strongly affected by the semi-arid climate of the region (de Souza and Azevedo, 2020). In these types of systems, geochemical, physical and biological specificities control the environment's responses to contaminants. Salinity can affect communities of benthic organisms (including bacteria) and the properties of sediment grains that form in areas of mixed salinity, as well as other physicochemical properties (Wilson and DePaul, 2017). The development of living organisms in this kind of environment is impaired by excessive osmotic pressure, high temperatures and low oxygen availability, and only organisms that have specific adaptive mechanisms are able to survive (Lamptey and Armah, 2008). This strong environmental pressure can lead to trophic processes that are controlled by physical and chemical factors, even though biological effects are minimal (Breaux et al., 2019).

The continuous enrichment of coastal environments with organic matter, whether allochthones (originating in the drainage basin and transported by rivers to the lagoon, where it settles and is preserved in the sediment) or autochthonous (produced in the lagoon itself), can cause a very complex phenomenon known as eutrophication (Nienhuis, 1992; Ulloa et al., 2017). Anthropogenic inputs of nutrients may also lead to excessive eutrophication, especially where the seawater exchange is restricted, such as in coastal lagoons. In Brazil, and in other tropical and subtropical regions with humid climates, most suffocated and restricted coastal lagoons are rich in organic material (Knoppers and Kjerfve, 1999; Lopez-Monroy et al., 2017). The biogeochemical characteristics of these environments are different from other bodies of water due to the limited exchange of water with the ocean and the constant anthropogenic impacts (Bertucci et al., 2016), which contribute

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to greater sediment accumulation and eutrophication (Lenzi et al., 2003; Souza et al., 2003). This phenomenon promotes changes in the biological and chemical conditions of a body of water and consequently leads to a decrease in the water quality.

In recent decades, the population of the municipalities bordering the Araruama Lagoon has grown considerably (IBGE, 2010). This growth has resulted in a greater contribution of domestic and industrial effluents, as well as inputs from agricultural activities, with the increased use of fertilizers. Thus, the lagoon has become a sewage receiving body, a consequence of the uncontrolled impacts of its surroundings. Given this scenario, and because of characteristics such as low renewal rate and the presence of hypersaline waters, Araruama Lagoon is now highly susceptible to the effects of eutrophication.

An oft-proposed solution to minimize the effects of pollution in coastal lagoons is the construction of artificial channels between the lagoon and the sea, increasing the water exchange rate and diluting the contamination. However, contact between the sediment and water with a low concentration of contaminants can cause an intensification of the regeneration and diffusion of nutrients, due to the increased gradient (Joshi et al., 2015).

In Araruama lagoon, the intensification of phosphate release from the sediments is particularly important, because the system is limited for this element. In a recent study, Silva (2019) applied the SEDEX procedure (sequential extraction) to 16 sediment samples and identified that most of the phosphate is associated to autigenic and biogenic apatite ($Ca_5(PO_4)_3$), indicating that biologic and chemical processes are controlling the retention of phosphate in the sediments. It is expected that modifications in the chemistry of the water (for instance, reduction in the overlying water concentrations of Ca^{+2}) would improve apatite dissolution (Atlas, 1975; Spagnoli and Bergamini, 1997). Furthermore, oxi-redox potential of the sediment was reported to influence apatite dissolution/precipitation (Yuan et al., 2019). However, none of these dynamics study was carried out in hypersaline environments. Dissolution of apatite, iron complex and organic phosphates is just a first step for diffusion, which depends on a favorable gradient.

According to Kjerfve et al. (1996), dredging a second ocean channel to Araruama Lagoon is likely to accelerate the decrease of lagoon salinity; however, the water exchange rate would not be significant. This channel was modeled by Garcia-Silva and Rosman (2016), who indicated possible changes and observed a significant decrease in salinity. The dredging of the original channel might also decrease salinity, depending on the depth and hydraulic area attained (Carvalho, 2018). At the same time, the reduction of salinity would eliminate the apparent buffering capacity provided by the hypersaline environment, and could thus potentially decrease the water quality. In any case, the stock of nutrients in the sediment is related with the impact of the increased opening of connections with the sea.

The diffusion of regenerated nutrients that promotes lagoon eutrophication, to the overlying water is controlled by the rates at which sedimentary organic matter is degraded. These rates, along with transport processes and other chemical and biological processes, produce the vertical concentration gradients observed in the water/sediment interface (Klump and Martens, 1981). The study of the kinetics of these gradients in varying physical and chemical conditions (salinity, pH, Eh, temperature, *etc.*) may allow a better comprehension of the factors that hinder or promote release of nutrients to the water column. In the present study, we apply innovative *in vitro* experiments that simulate real environment with varying physical and chemical scenarios where the kinetics of nutrients from sediment to water column and *vice-versa* was evaluated.

2. Materials and methods

2.1. Study area

Araruama Lagoon, in the state of Rio de Janeiro, Brazil, is a hypersaline coastal lagoon located between latitudes 22°50′–22°57′S and longitudes 42°00′–42°30′W (Fig. 1). Its surface area is 210 km^2 (including the sea connection channel) and it is considered to be one of the largest perennial hypersaline coastal lagoons in the world (Kjerfve et al., 1996). The hypersalinity of the lagoon is the result of semi-arid climatic conditions, a small drainage basin, a negative water balance and a choked entrance channel.

There is only a single long narrow connection, the Itajuru Channel, with a stable inlet, between the lagoon and the ocean. This channel is 7 km long, with a maximum depth of 4 m, near the entrance to the ocean, but with an average depth of 2 m. The lagoon has a length of 40 km and a maximum width of 13 km, with an average depth of 3 m. There is a predominance of extensive shallow areas, between 1 and 2 m, with larger depths in the region of Massambaba Cove (Kjerfve et al., 1996). The physiography of the lagoon consists of several elliptical cells of various sizes, separated by spits of sand and submerged dunes (Kjerfve et al., 1996). The sandy spits are located along the south shore, and protrude into the lagoon from the sandbanks of Massambaba and Cabo Frio. Alves (2006) observed that the generation and propagation of wind-waves in Araruama Lagoon influence the formation of these sandy spits, a process of redistribution and transport of sediments. The lagoon has carbonate sedimentation with extensive shell deposits dominated by the bivalve *Anomalocardia brasiliana* (da Silva et al., 2005).

The lagoon is bordered by the municipalities of Saquarema, Araruama, Iguaba Grande, São Pedro da Aldeia, Cabo Frio and Arraial do Cabo. The lagoon is also affected by the municipalities of Rio Bonito, Casimiro de Abreu, and by Silva Jardim, which contain part of the headwaters of the São João River basin, tributary to Juturnaíba Reservoir, which has supplied drinking water to the entire region for the last 50 years.

2.2. Design of the microcosm experiments

The microcosm experimental setting is innovative and was developed to reproduce as closely as possible real conditions, and to allow the controlled modification of the physical and chemical conditions. The system was designed with two compartments that continuously exchange water, maintaining redox potential and oxygenation always elevated, as in the natural environment (Fig. 2).

The first compartment (reservoir 1) is a glass container of 50 × 50 × 20 cm (length × width × height) where the sediment was disposed. The second compartment (reservoir 2) is smaller (15 × 20 × 20 cm - L × W × H), where a small-flow aquarium pump was placed (45 L h^{-1}) allowing exchange of water between both compartments. The recycling of the water occurs naturally *via* pumping (to the sediment compartment) or hydrostatic pressure, back to the pump compartment (Fig. 2).

The flow could be maintained for several months, as long as the pump continues to function. The volume of water in reservoir 1 was about 25 L (50 × 50 × 10 cm), the pump flow was maintained around 48 L h^{-1} and the 100% exchange time was 29 min.

Seawater, lagoon water and sediments sampling was done according to description of the item "sampling". A 5-cm-thick sediment layer was laid on the bottom of reservoir 1 and the microcosm was filled with water to the level of 15 cm. Ten microcosms were prepared with the different characteristics, as described in Table 1. After installation of the experimental equipment, a natural stratification of the redox potential (redoxicline) was developed in the sediment. This layer structure of the sediment remained until the end of the experiment, demonstrat-

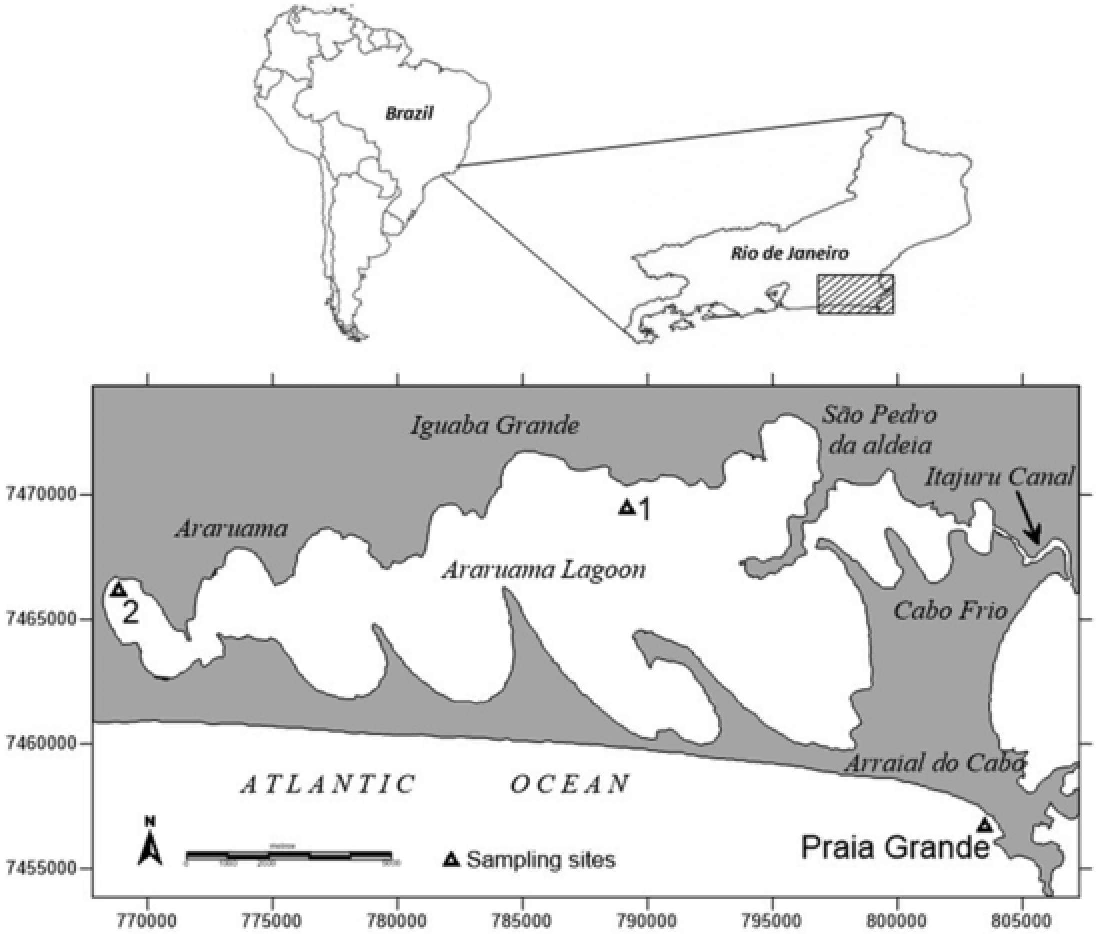

Fig. 1. The Eastern coast of the state of Rio de Janeiro, Brazil, showing the location of the Araruama Lagoon and the stations where water and sediment samples were collected.

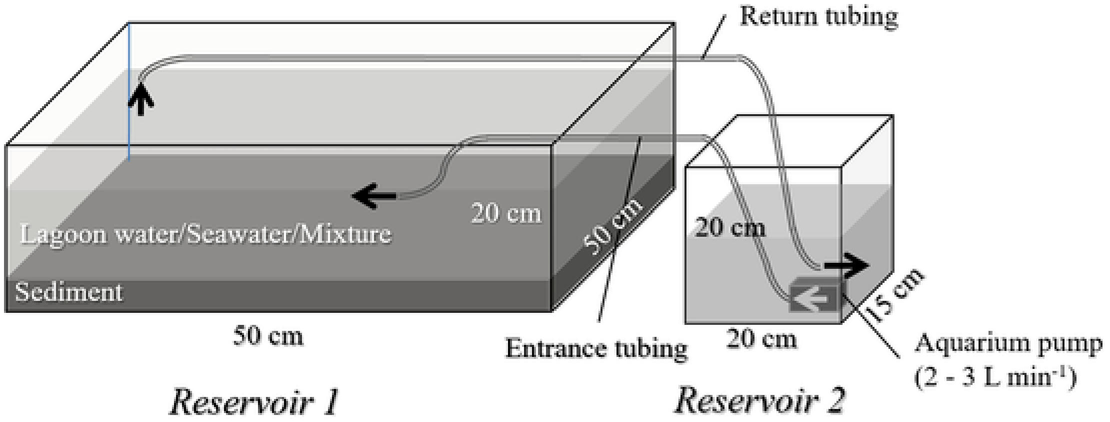

Fig. 2. Reservoir system for the *in vitro* experiments.

ing that there was no significant disruption in the system and it did not develop anoxia in the water column.

2.3. Sampling

The experiments were carried out with sediments collected from station 1 (23K – E = 789,159; N = 7,469,271), which was shown to be poor in carbonates, and from station 2 (23K – E = 768,842; N = 7,466,166), which was highly carbonatic; and with lagoon water from the same station 1 and marine water collected from Praia Grande, Arraial do Cabo (23K – E = 804305E; N = 7,456,467) (Fig. 1). The weight of sediment and volume of water to be placed in each microcosm were carefully measured. Sediment samples were collected with consecutive launches of a Van Veen grab sampler, at stations 1 and 2 (depths of 5 m and 0.9 m, respectively), until the required volume was reached. About 60 kg of sediment samples were collected in each of the two stations (1 and 2; Fig. 1), then packed in plastic bags for transportation to the laboratory in a cooler at 4 °C. The mass of sediment in each microcosm ranged from 11 to 14 kg and the volume of water was about 25 L.

Approximately 140 L of seawater were sampled in Praia Grande, in the municipality of Arraial do Cabo, out of the reach of the plume of

Table 1
Physical and chemical characteristics of each experiment.

Microcosm	Scenario	Sediment from station	Type of water	Weight sed (kg)	Pump flow (mL s^{-1})
1	1	1	Lagoon	13.3	18.18
2	2	2	Lagoon	13.9	11.72
3		2	Lagoon	11.3	10.41
4	3	2	Mixture	12.26	11.36
5	4	2	Sea	11.5	18.65
6		2	Sea	13.16	13.22
7	5	1	Mixture	12.4	9.69
8		1	Mixture	10.9	12.3
9	6	1	Sea	13.2	11.54
10		1	Sea	12.8	16.86

water from the Itajuru Channel (Fig. 1). It is important to mention that, at the time of the sampling, the water was not too cold, denoting the absence of any strong upwelling phenomenon, which would bring high phosphorus concentrations. A lagoon water sample (approximately 120 L) was collected at station 1, near Iguaba Grande (Fig. 1). Both seawater and lagoon water were collected with 20-L polypropylene bottles decontaminated with HCl 5%. The mixtures were obtained by filling bottles with 10 L of each type of water, thoroughly mixed.

The sampling, preparation and beginning of the microcosm experiments occurred on only one day, January 11, 2016, and sampling in the microcosm began the next day. Starting values were measured in the sediments and in the water before the microcosms were prepared. The parameters pH, Eh, dissolved oxygen, temperature, chlorophyll α and phaeopigments (by fluorimetry) were measured daily in the morning and afternoon. Water samples were collected within each tank, on January 12 (morning), January 13 and 14 (morning and afternoon), January 15 (morning), January 18 (morning), January 21 (morning), February 3 (afternoon) and February 17 (morning). The laboratory where the microcosm experiments were conducted was maintained in gloom throughout, since light could develop primary production, affecting the diffusion rates of nutrients. For this reason, the chlorophyll α and the phaeopigments were monitored continuously.

The parameters pH, Eh, dissolved oxygen, temperature, chlorophyll *a* and phaeopigments were measured on the same days and times as the water sample collections, and graphs were constructed to monitor their evolution. For the verification of pH and Eh, a Hanna HI8424 portable meter was used, with specific electrodes for each parameter. Dissolved oxygen and temperature were measured with a Mettler-Toledo Seven2Go Pro oximeter. Chlorophyll *a* and phaeopigments were monitored with an AquaFluor™ Turner Designs spectrofluorimeter.

2.4. Analytical procedures

The concentrations of dissolved nutrients ammonium (NH_4^+-N), nitrite (NO_2^--N) and phosphate (PO_4^{3-}-P), and total carbon and total phosphorus, were determined in accordance with the methodologies described by Grasshoff et al. (1983) and Strickland and Parsons (1972). Nitrate (NO_3^--N) was determined by the method of reagent resorcinol, due to the salinity of the samples (Zhang and Fischer, 2006).

Dissolved inorganic nitrogen (DIN) and phosphate (PO_4^{3-}-P) flows through the sediment-column water interface were calculated according to the following equation (Hargrave and Connolly, 1978):

$$F = \frac{V\,(Co - Ct)}{A} \times \frac{10^4}{T}$$

where:

F = mass unit flow (mmol m^{-2} day^{-1});
V = volume of incubated water on the sediment (L);
Co and Ct = concentrations of the dissolved inorganic constituents, before and after time t;
A = enclosed sediment area (cm^2);
T = incubation duration (h).

Factor 10^4 converts the incubated area from cm^2 to m^2. The transfer of dissolved compounds from the sediment to the overlying water column results in an increase in the concentration of these compounds throughout incubation.

3. Results and discussion

Both sediments showed a sandy granulometry (100.0% for sediment 1 and 99.6% for sediment 2), but there was a clear distinction in the concentrations of calcium carbonates (24.4% and 66.7% for sediments from stations 1 and 2 respectively). Organic carbon concentrations were 1.84% in sediment from station 1 and 4.69% in sediment from station 2. Seawater presented a salinity of 34.27; the water of Araruama Lagoon (Station 1) presented a salinity of 59.95; and the proportionated mixture of both resulted in a salinity of 47.11. Other parameters were measured at the beginning and the end of the experiments (as shown in Table 2).

It was possible to observe that, in all experiments, after 38 days there was an increase in the parameters temperature, salinity, electrical conductivity and total dissolved solids, which is probably due to a slight evaporation of the water during the experiments. The pH decreased, except in experiments 5, 6 and 10 (seawater), where a slight increase was recorded. pH oscillations are expected to be associated with release of organic acids from the sediment, oxidation and primary production and the presence of bases (Stumm and Morgan, 1981). The increase in salinity (electrolytes) observed throughout all the experiments should promote increase in pH, due to increase in bases concentration. In contrast, release of organic acids from the sediments, reduction in primary production (the experiments were carried out in gloom) and oxidation reduce pH. The results indicate that in most experiments

Table 2
Physical-chemical parameters temperature, salinity, conductivity, total dissolved solids and pH at the beginning (T_0) and at the end (T_{end}) of the experiments (after 38 days).

Microcosm	Sediment	Water	T (°C)		Salinity		C (mS cm^{-1})		TDS (g/L)		pH	
			T_0	T_{end}	T_0	T_{end}	T_0	T_{end}	T_0	T_{end}	T_0	T_{end}
1	1	Lagoon	26.8	28.8	59.95	60.9	82.76	87.2	55.17	56.05	8.52	7.89
2	2	Lagoon	26.4	28.8	59.95	70.88	82.76	97.64	55.17	63.65	8.52	7.96
3	2	Lagoon	26.9	29.2	59.95	66.88	82.76	93.74	55.17	60.61	8.52	8.09
4	2	Mixture	26.4	29.2	47.11	54.56	66.71	78.16	44.57	50.9	8.2	7.95
5	2	Sea	26.6	29.4	34.27	43.5	50.65	64.12	33.97	41.79	7.88	8.14
6	2	Sea	26.3	29.5	34.27	43.63	50.65	64.2	33.97	41.9	7.88	7.99
7	1	Mixture	27.1	29.7	47.11	54.11	66.71	78.34	44.57	50.56	8.2	7.82
8	1	Mixture	26.9	29.8	47.11	53.8	66.71	77.24	44.57	50.3	8.2	7.88
9	1	Sea	27.4	29.9	34.27	42.04	50.65	62.08	33.97	40.56	7.88	7.76
10	1	Sea	27.3	30	34.27	41.17	50.65	60.5	33.97	39.81	7.88	8.05

reduction of pH prevails over increase in pH. A more detailed discussion was presented farther.

The results of the microcosm experiments are presented as graphs, showing the evolution of the concentrations with time of the experiments (Figs. 3–9). The physical and chemical parameters pH and dissolved oxygen were measured with the aim of following variations due to the design of the experiment, so their graphs were presented as Supplementary materials (S.M.) 1 and 2, respectively. Chlorophyll α and phaeopigments were measured in order to follow up any oscillation in primary production, that would upset the evaluation of rates of nutrient regeneration. Furthermore, the phaeopigments were measured to assess the occurrence of decomposition of primary producers during senescence or final death. Their graphs were also presented as Supplementary materials 4 and 5.

In all scenarios, for both sediments, the pH drops systematically to values around 7.8 (S.M. 1), which can be attributed to buffering potential from the contact with the sediment that releases organic acids or retains electrolytes as the pH changes. It was possible to verify that the contact with the sediment promoted a significant modification in the water column. It is interesting to note that there was no distinct behavior for the different waters used in the microcosms (seawater, lagoon or mixture). No significant variations were observed between replicates, showing that the results are reliable. The small variations observed between the replicates can be attributed to slight differences between sed-

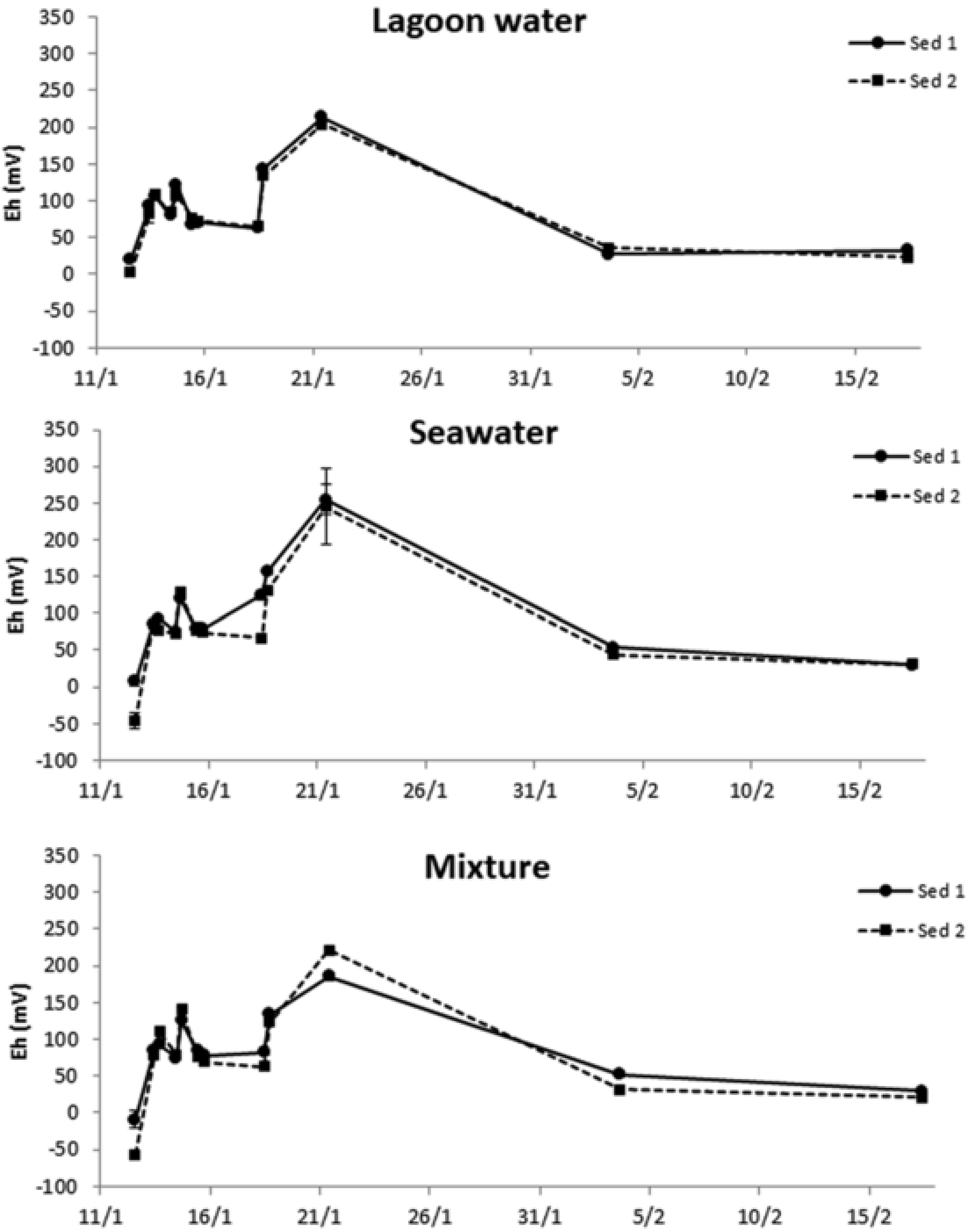

Fig. 3. Evolution of the redox potential (Eh) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

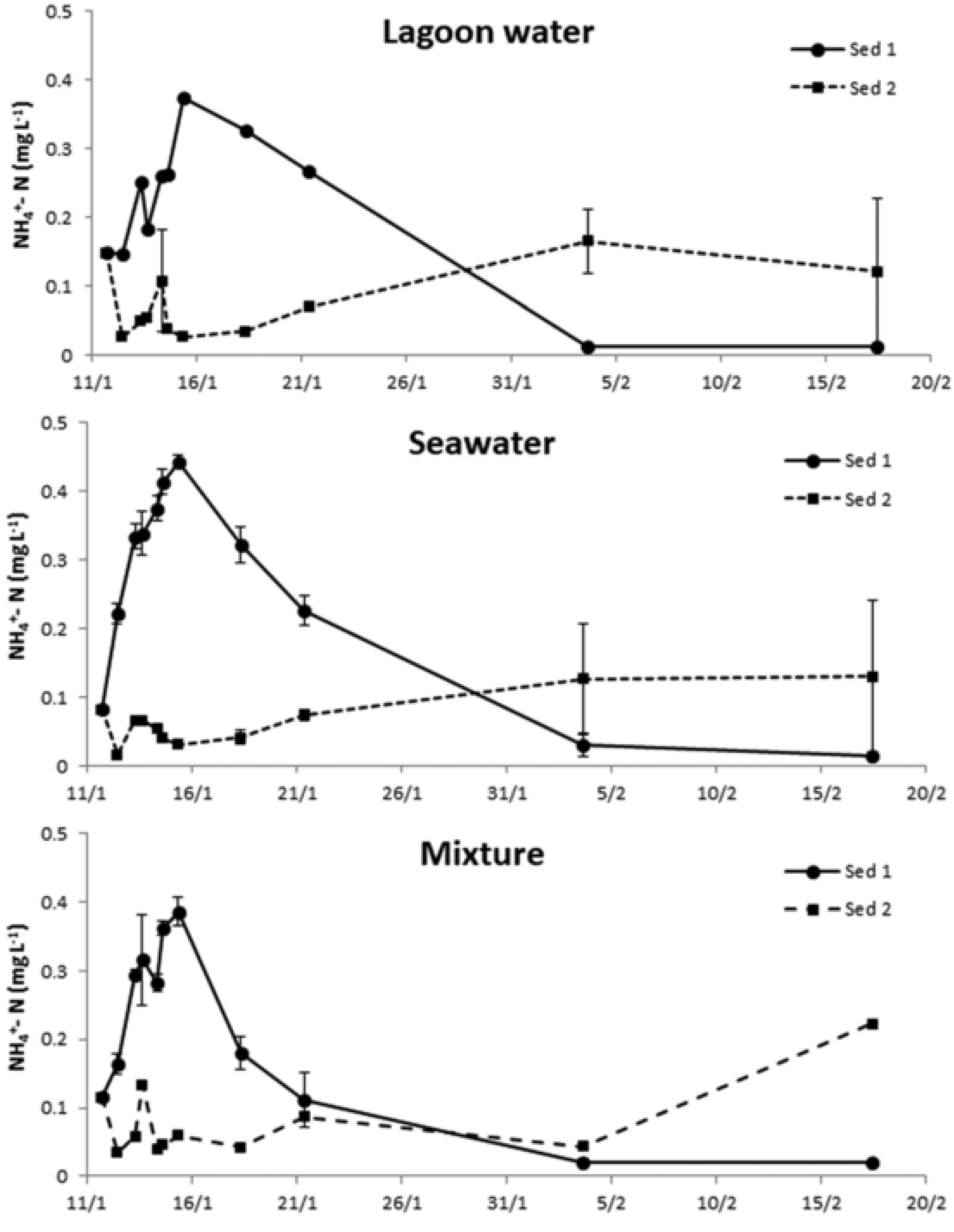

Fig. 4. Evolution of the dissolved ammonium (NH_4^+-N) (mg L^{-1}) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

iment mass and water flows in each microcosm. Despite these differences, both maintained the same trend of sudden fall and oscillations in the first week of the trial.

The temperature ranged from 24.4 to 30.5 °C. This parameter was measured as a standard procedure, but its interpretation is hampered by the fact that the experiment was performed *in vitro* in an uncontrolled ambient temperature. No large fluctuations in dissolved oxygen occurred in the water for over a month (S.M. 3). The design of the microcosms successfully avoided any anoxia, or excessive oxygenation. This demonstrates that the microcosms, by their size and aeration rate, reproduce well the behavior of the natural oxygenated system (Moreira-Turcq, 2000). Changes in oxygen levels in the bottom water have consequences for the early diagenetic pathways and the efficiency of reoxidation of reduced metabolites, and for the nature, direction and magnitude of sediment-water exchange flows (Middelburg and Levin, 2009).

Chlorophyll α and phaeopigments fluorescence measurement is a qualitative measure (Gostev and Fadeev, 2011). As the goal was simply to evaluate whether the darkness of the microcosms was suppressing primary production, a quantitative measure was not necessary. The microcosm experiments were developed in gloom conditions, and consequently the concentrations of chlorophyll α fall systematically to values close to zero (S.M. 3 and 4). Thus, the results show the absence of primary production, which could modify the concentrations of nutrients in the water, masking transferences between sediments and water.

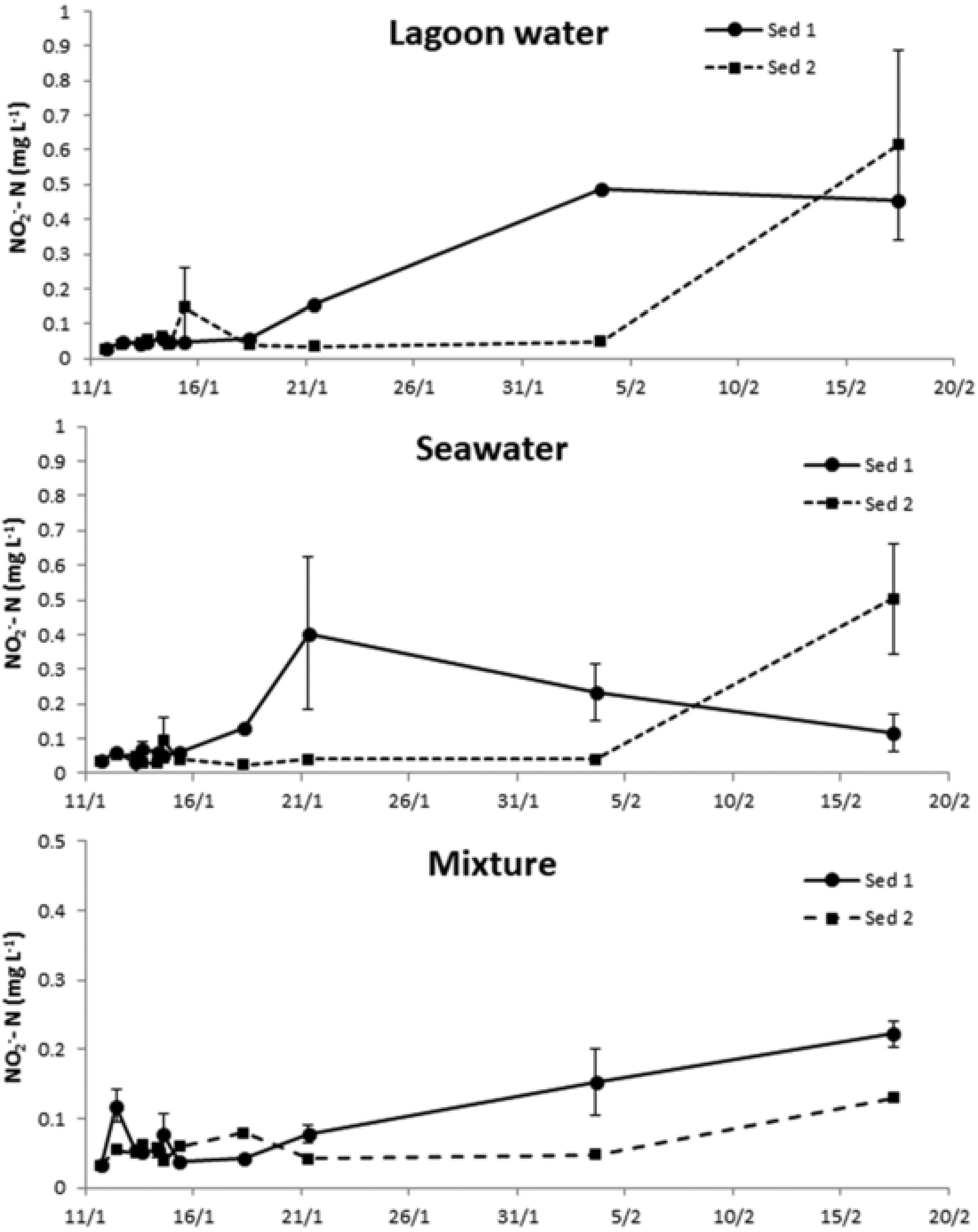

Fig. 5. Evolution of the dissolved nitrite (NO_2^--N) (mg L^{-1}) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

Regarding the concentration of phaeopigments, the fall is not clear at the beginning of the microcosm experiments, which is probably due to the decay of chlorophyll α (Bianchi et al., 2002). However, as the experiment unfolds, the concentrations fall quickly. It is possible that the intense mortality of phytoplankton, especially in microcosms with lagoon water, contributed to some of the nutrient concentrations observed in the water during the study. Apparently, in some instances, sediment from station 2 seems to release aging phytoplankton pigments in the beginning of the experiments. After a certain period, these aged cells seem to be deposited in the sediment. Therefore, in all experiments, the concentrations at the end are below the initial values. In any case, nutrient consumption in the water column can be discarded.

At the beginning of the experiments, the Eh values were low, possibly due to the shock of the contact between the water (oxidized) and the anoxic sediment (Fig. 3). Moreover, the turbulence that occurred in the assembly of the experiment should contribute to reduced values of Eh in the water (Joshi et al., 2015). As the experiment evolves, the circulation of water and its oxygenation promote oxidation. The increase in Eh reflects remineralization (of organic matter) by the respiration (Joshi et al., 2015), that is, the oxidation of organic matter consuming DO. The nutrients, which are in dissolved inorganic forms, tend to increase as well as Eh, since they are released into the water column, as organic matter is degraded. From the second week, the experiment seemed to return to a certain equilibrium, where the Eh attained values

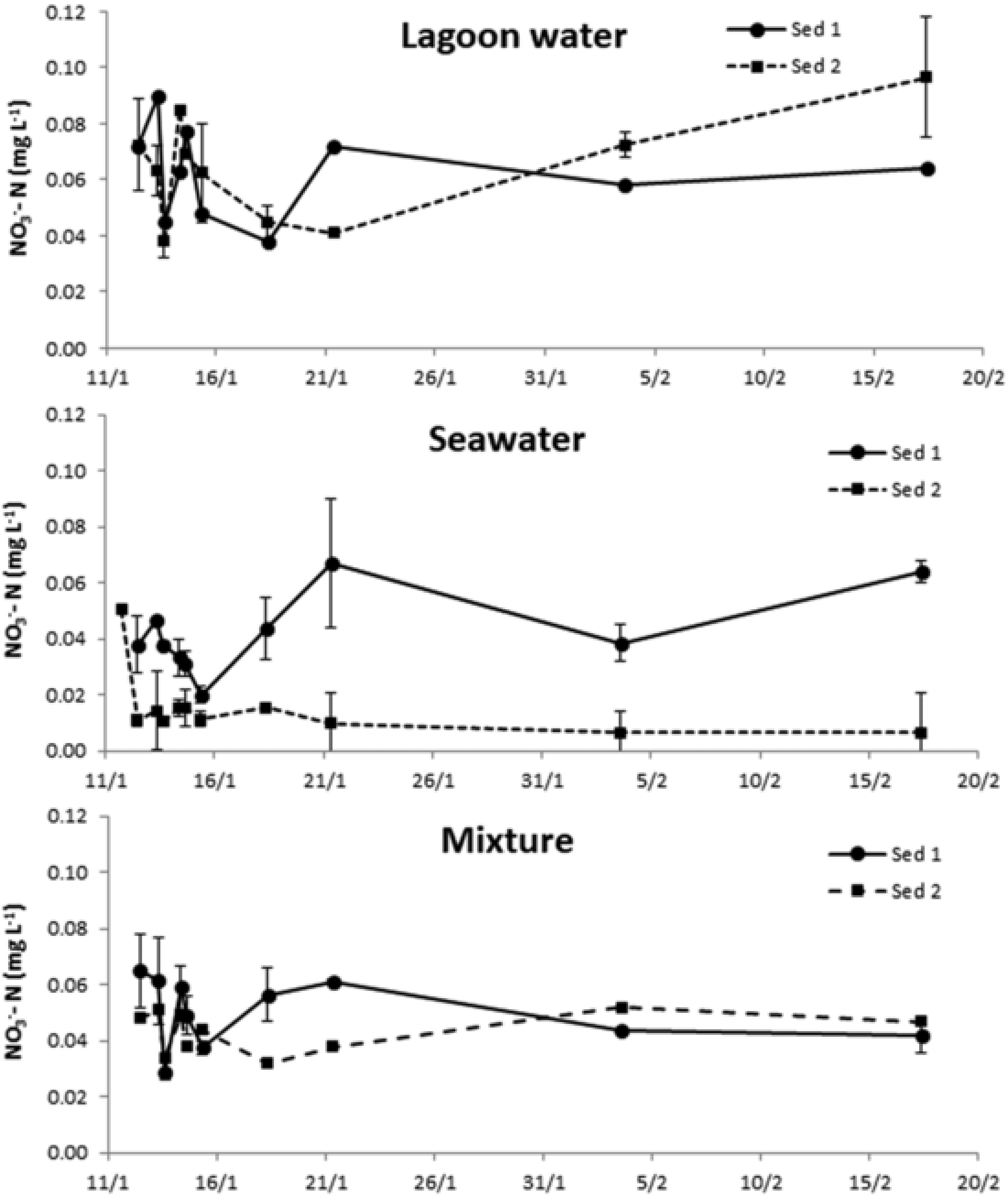

Fig. 6. Evolution of the dissolved nitrate (NO_3^--N) (mg L^{-1}) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

close to slightly oxidizing, remaining there until the end of the experiment.

In Fig. 3, the similarity of the curves is noteworthy, in sediment 1 and sediment 2. The type of water applied in the microcosm also has no influence on the behavior of the Eh. Although not measured, a redoxicline seems to be formed within the sediment, as indicated by change in colors with depth (see graphical abstract).

During the process of regeneration, an intense ammonium transfer from sediment into the water column was expected, at the beginning of the experiment. Metzger et al. (2019) showed that this release may be intense, mainly in macrotidal environments (Bourgneuf Bay, Loire estuary, France). This intense release can be observed in Fig. 4 for the microcosm experiments in all scenarios with sediment 1, characterized by a sandy granulometry.

After the release of ammonium to the water column, the concentrations did not remain high because there should be oxidation due to the water recycling in the system. It is observed in Fig. 4 that much of the ammonium is converted to nitrite, but as the experiments evolved, a moderate conversion to nitrite and nitrate can be observed (Figs. 5 and 6). Most of the nitrogen released from the sediment remains in the system as nitrite until the end of the microcosm experiments. Studies by Knoppers et al. (1996) in the Araruama Lagoon suggest that the sediment accumulates ammonium from sewage effluents disposal, which is released back to the water column. This pattern is in agreement with other studies in the same lagoon (Mello, 2007; Silva, 2014; Souza, 1993).

Experiments carried out with sediment 2 showed minor releases of ammonium that remained until the end of the experiment. The same tendency for nitrite and nitrate increase was observed, which may indi-

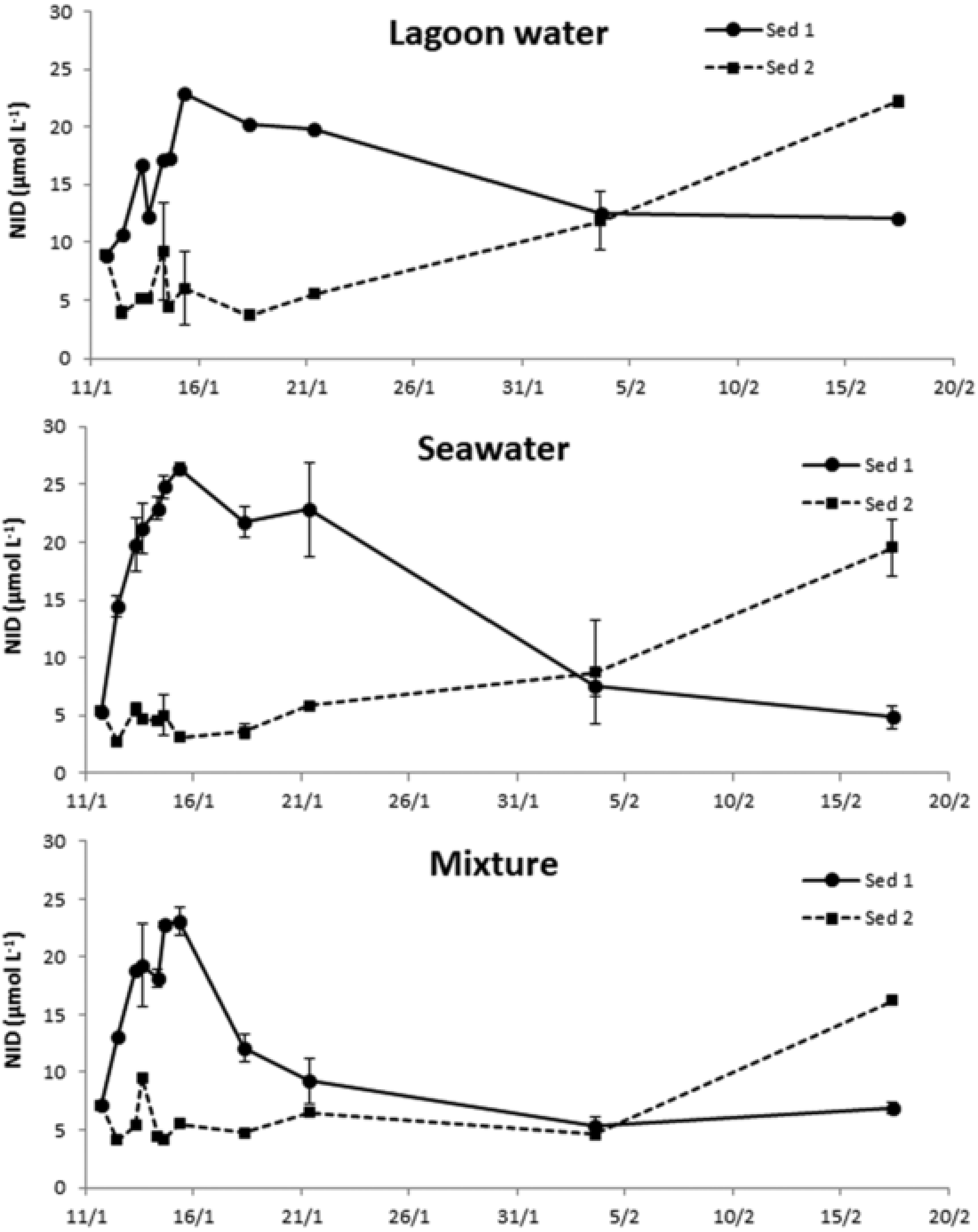

Fig. 7. Evolution of dissolved inorganic nitrogen concentration (DIN) (μmol L^{-1}) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

cate small release of nitrogen forms to the water column in the conditions of the experiment. The higher release of nitrogen inorganic forms in sediment 2 when compared to sediment 1 suggests a greater amount of accumulated organic matter in sediment 2, which can be associated with the percentages of total organic carbon found in sediment samples 1 and 2 (1.84% and 4.69%, respectively). Therefore it can be proposed that regions where sediments are richer in organic matter may constitute sources of nutrients for the water column, The remineralization of nutrients from organic matter has been examined, constituting a complex biogeochemical process where the role of biological respiration may be relevant (Ferguson et al., 2004; Trimmer et al., 2000). The details of this process could not be evaluated in the present study, but the experiment setting we proposed may provide opportunities for future research.

The concentrations of nitrite (Fig. 5) varied significantly, especially by the end of the experiment, when there should probably be regeneration from sediments and conversions from ammonium into nitrite altogether. Nitrite is an intermediate form between nitrate and ammonium and its concentrations are typically lower in the environment (Lopez-Monroy et al., 2017). Unexpectedly over the one month of experiments, it was not possible to observe any intense conversions from nitrite into nitrate (Fig. 6), indicating that the process of oxidation was not relevant, or that it simply takes more time (more than a month) for the system to achieve oxi-reduction balance.

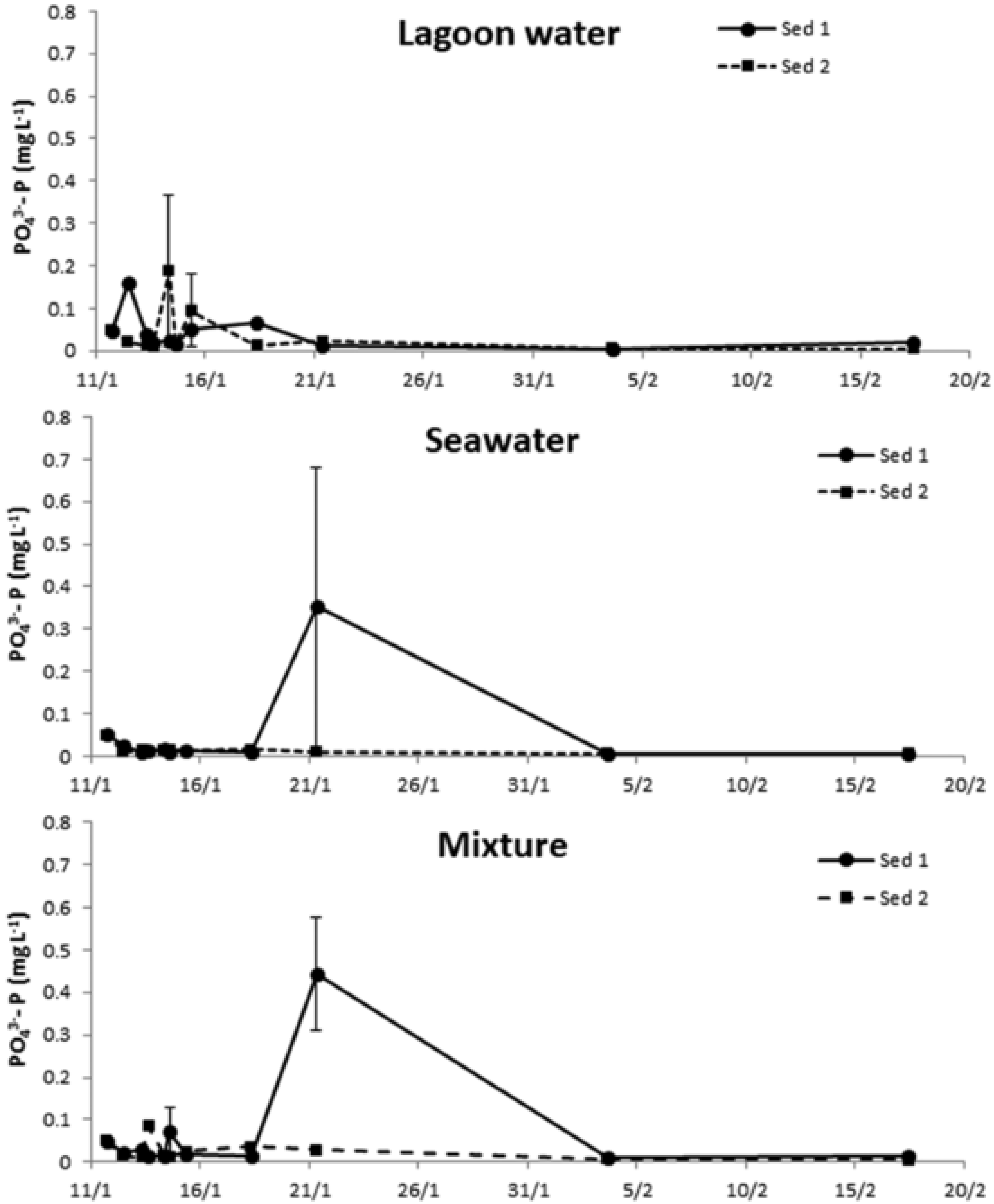

Fig. 8. Evolution of the dissolved phosphate (PO_4^{3-}-P) (mg L^{-1}) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

Due to conversions from one species into another, the assessment of nutrient regeneration is difficult, but it can be more clearly evaluated as the sum of the forms of molar nitrogen is considered. Graphs with the molar sum of concentrations (μmol L^{-1}) of the species of nitrogen were built to better evaluate its regeneration (Fig. 7). It is possible to see that the different forms of nitrogen in the water do not increase significantly in the microcosms with sediment 1. However, regeneration is consistent in the case of all microcosms containing sediment 2, mainly in the final days of the experiment, which can be attributed to remineralization of organic matter that present higher concentrations. Intense organic matter remineralization was shown to be a relevant process in oxygen rich environments. Wang et al. (2018) studied oxygen consumption in the water column of two Mexican lagoons and although nitrogen sources are allochthonous, remineralization of organic matter was intense. The recirculation in the microcosms promoted intense oxygenation, therefore increasing nitrogen release in the organic matter richer sediment microcosms (sediment 2).

Strong phosphate regeneration did not occur, at least not during the period of the microcosm experiments (Fig. 8). The higher release of phosphate observed in experiments with mixed water and seawater in sediment 1 may be related to the diffusion of available phosphate in the interstitial water, due to the gradient between sediment and water (Monbet et al., 2007; Stiller and Nissenbaum, 1999). However, the dissolved phosphate settled back to the sediment probably due to the oxidizing conditions of the water column that may have promoted reactions with iron oxi-hydroxides (Ruttenberg, 2014). It is necessary to underscore that the experiments were carried out in gloom conditions, and therefore there was little or no primary production, so that in the mo-

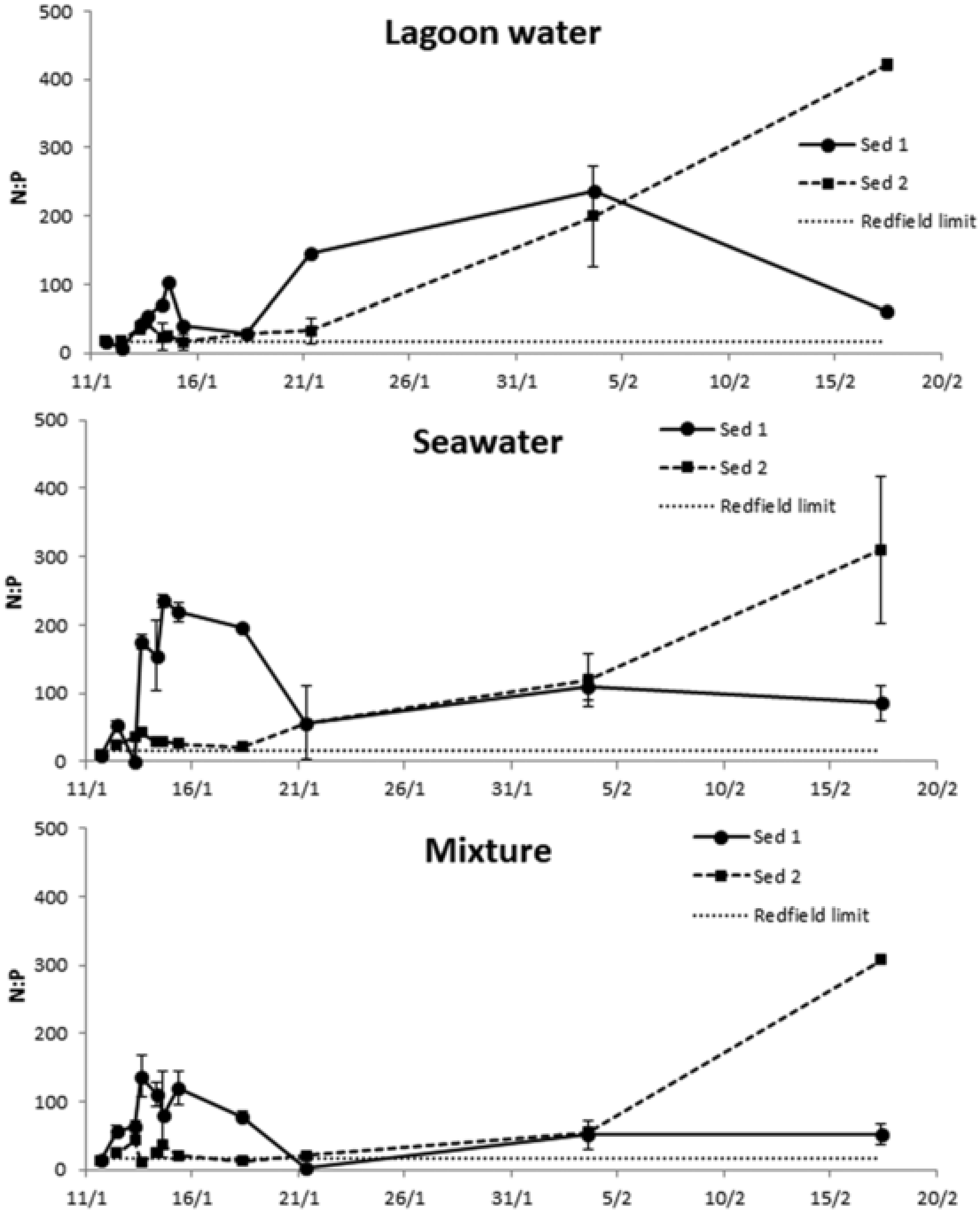

Fig. 9. Evolution of molar ratio between the dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) in the water, during the regeneration microcosm experiments. The error bars show differences between two experiments with the same conditions.

ments of strong release of phosphorus, there was no consumption. In the natural environment, this release would generate a strong primary production (phosphate is a limiting element in Araruama Lagoon; Souza et al., 2003), associated with moments of reduced wind incidence that may stratify the redox potential in the water column, inducing fluxes from the sediment to the water column and further primary production. The scenario with the mixture of waters and sediment 1 presents a significant emission to the water column.

It is interesting to note that the presence of an oxidizing layer at the sediment-water interface observed in this study may prevent or hinder the flow of phosphate to the water column. This observation was also verified by Baumgarten and Niencheski (2010) when studying the sedimentary column as a reservoir and nutrient source in estuarine coves from Patos Lagoon, South Brazil. The results indicate that aside from a few release events that are reverted by settling, the phosphate concentrations remain low. It is important to observe the molar ratios of nitrogen-phosphorus to verify whether this precipitation of phosphate induces its limitation in the system.

The results of the report DIN:DIP (Fig. 9) indicate that phosphate is a strongly limiting element in the system, with mean values frequently well above the Redfield ratio. The highest ratio was above 400 (lagoon water and sediment 2). In a study carried out in the same lagoon, values of 178 in spring and 34 in autumn were found (Knoppers et al., 1996).

As for total phosphorus (TP) concentrations in the sediments in experiments with mixed water (microcosm 7 and 8) and seawater (micro-

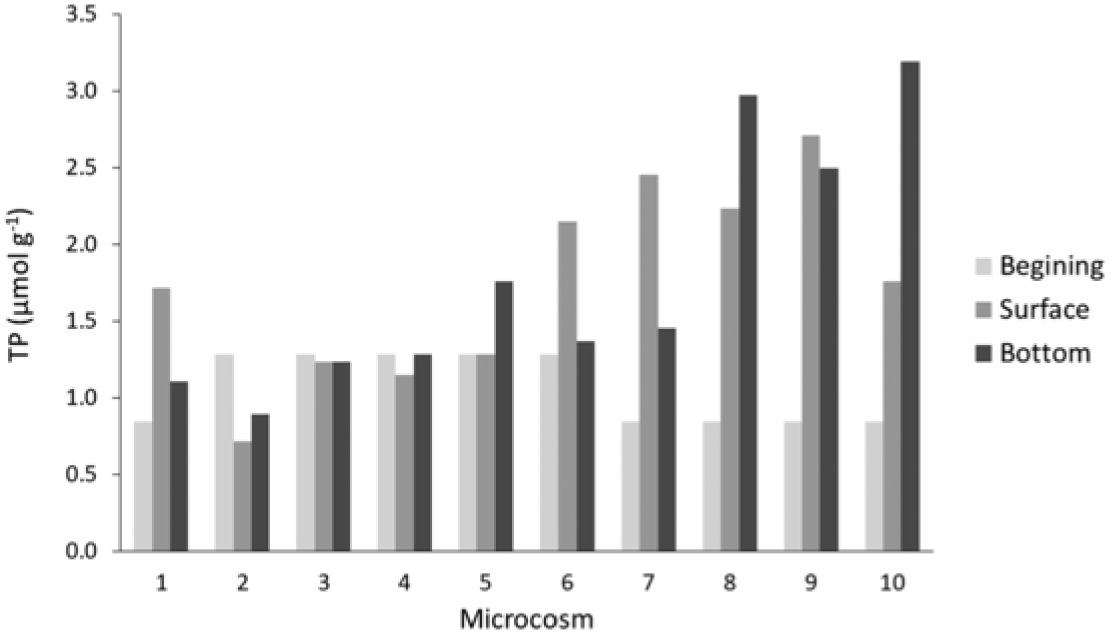

Fig. 10. Total phosphorus concentration (TP) (μmol g^{-1}) at the beginning and end of the *in vitro* regeneration experiments.

cosm 9 and 10) with sediment 1, the observed values were significantly higher at the end of the experiment (Fig. 10), demonstrating a retention of phosphorus. Zhang and Huang (2011), in a study on phosphate sorption in sediments in Florida Bay, concluded, after simulating different salinity gradients (from 2 to 72), that phosphate adsorption on the sediment surface increases as salinity decreases. One of the hypotheses for this process is that phosphate can precipitate with other minerals such as iron oxi-hydroxide and calcium. When reacting with calcium, for example, calcium phosphate, a species of *neoformed* apatite amorphous mineral, is formed (López and Morguí, 1992). This apatite remains stable and precipitated in the sediment. According to Silva (2019), a sequential extraction procedure in sediments from Araruama Lagoon showed that the phosphorus fraction linked to autigenic apatite was the one that presented the highest concentrations and it seems to be the most important mechanism of phosphorus fixation in sediments.

The values of the diffusive flows of dissolved inorganic nitrogen (DIN) and phosphate (PO_4^{3-}-P) of the samples revealed that, during the experiment period, nutrients were released and taken in. The DIN showed positive mean values in the simulated scenarios with sediment 1 and water from the lagoon, mixed water and seawater (1.69, 4.68 and 7.36 μmol m^{-2} day^{-1}, respectively). Negative values were recorded in the experiments with sediment 2 in contact with lagoon water, mixed water and seawater (−3.66, −3.44 and −1.70 μmol m^{-2} day^{-1}, respectively) (Fig. 11).

The mean value of phosphate diffusive flows (PO_4^{3-}-P) was positive in the scenario with sediment 1 and lagoon water (2.24 μmol m^{-2} day^{-1}), and negative with mixed water (−0.30 μmol m^{-2} day^{-1}) and seawater (−0.51 μmol m^{-2} day^{-1}). In the experiments with sediment 2 in contact with lagoon water, mixed water and seawater, the flows were all negative (means of −0.78, −1.08 and −1.70 μmol m^{-2} day^{-1}, respectively) (Fig. 12).

In experiments with sediment 2 the general trend was negative flows for both DIN and PO_4^{3-}-P, while for sediment 1, both were positive. The different concentrations of carbonate (24.4 and 66.7 for sediments 1 and 2 respectively) may have intensified phosphorus sequestration in sediment 2. Carbonatic sediments are rich in Fe but poor in P (Zhang et al., 2004) and can increase phosphate adsorption capacity to carbonates, forming insoluble compounds that precipitate in the sediment (de Jonge and Villerius, 1989).

4. Conclusions

The results of the microcosm showed that the system is able to reproduce environmental conditions for the assessment of environmental processes and exchanges between sediment and water. The experiments did not demonstrate any high or sudden regeneration of nutrients within the period of 38 days. On the other hand, they were released into the water column and precipitated back into the sediments over time. The conditions of the experiment seem to have promoted oxidation from ammonium to nitrite, but very little to nitrate (it may be that more time is necessary). When considering the molar sum of nitrogen-dissolved forms (DIN), a regeneration process can be perceived.

Except in the experiments where there were sudden releases of phosphate to the water column, concentrations remained low. In the natural environment, these sudden releases may promote intense primary production, because phosphate is a limiting element. However, higher concentrations of total phosphorus in the sediment were observed at the end of the evaluated period, indicating that there is retention of this element in the sediment, possibly due to the different salinity gradients and the Eh of the microcosms.

It is concluded that the dynamics of nutrients in sediments of the hypersaline lagoon of Araruama is affected by the reduction of salinity and by redox potential, which may severely affect primary production and the eutrophication process. The results confirmed that physicochemical changes in the Araruama Lagoon cause alterations in the sediment that influence the patterns of nutrient distribution at the sediment-water interface. It is possible that the hypersaline and carbonate environment, together with iron oxi-hydroxides are favorable to phosphorus sequestration. It can be inferred, based on these *in vitro* experiments that changes in nutrients' mobility in the sediment-water interface of the Araruama Lagoon may occur in the case of reduction of salinity, resulting from the opening of new channels of connection with the sea, or from freshwater transposition from the Juturnaíba Reservoir.

A possible remediation process for the system is the application of high specific surface materials in the sediment that would be able to adsorb nutrients and hinder eutrophication in the water column. For instance, nets coated with 2D photothermal materials (Xie et al., 2020a; Xie et al., 2020b), or zeolites can be tested in the same experimental set.

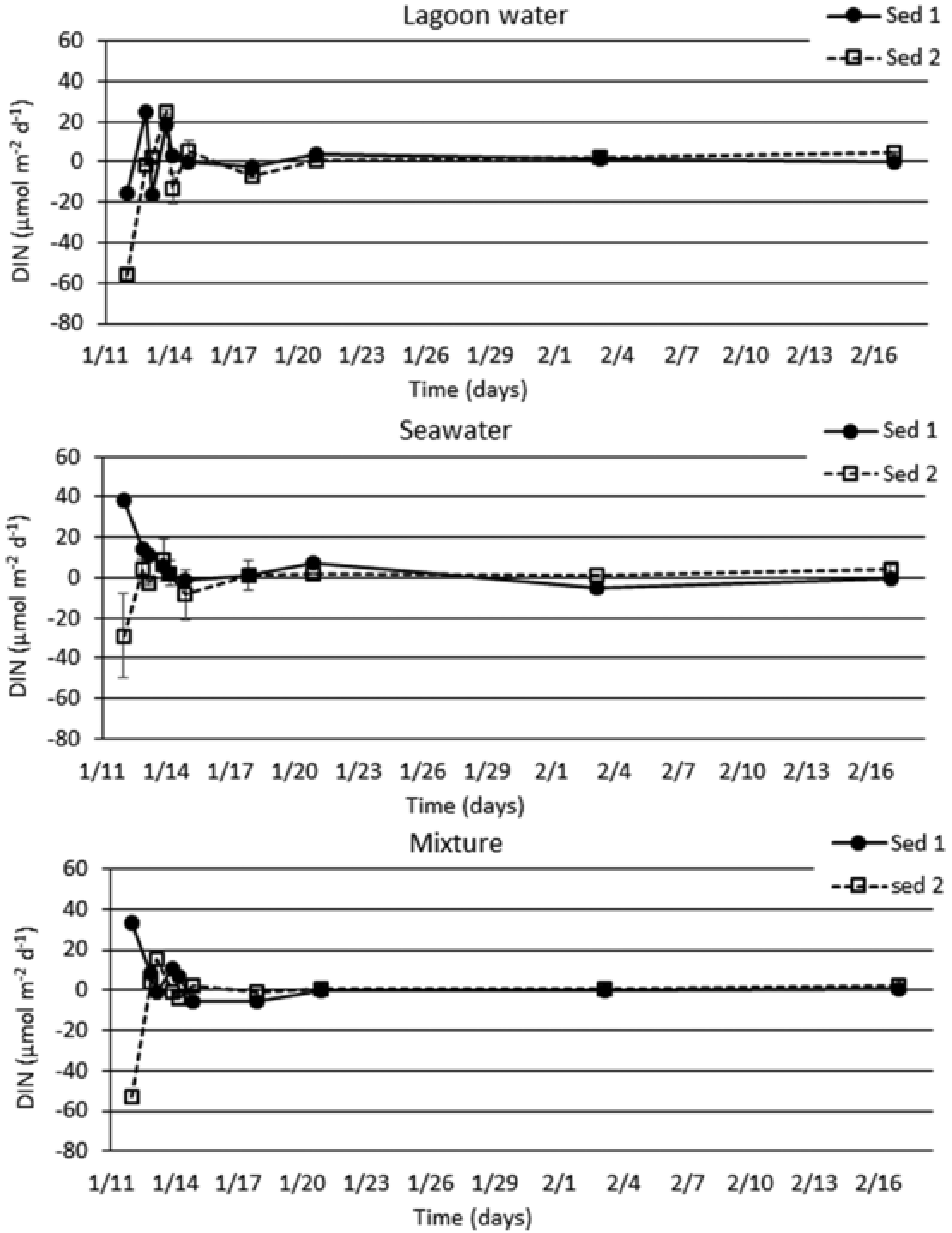

Fig. 11. Diffusive flows of dissolved inorganic nitrogen (DIN) (μmol m^{-2} day^{-1}) at the sediment-water interface during the *in vitro* regeneration experiments. The error bars show differences between two experiments with the same conditions.

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Availability of data and material

The authors declare that data of the present research is available for verification under request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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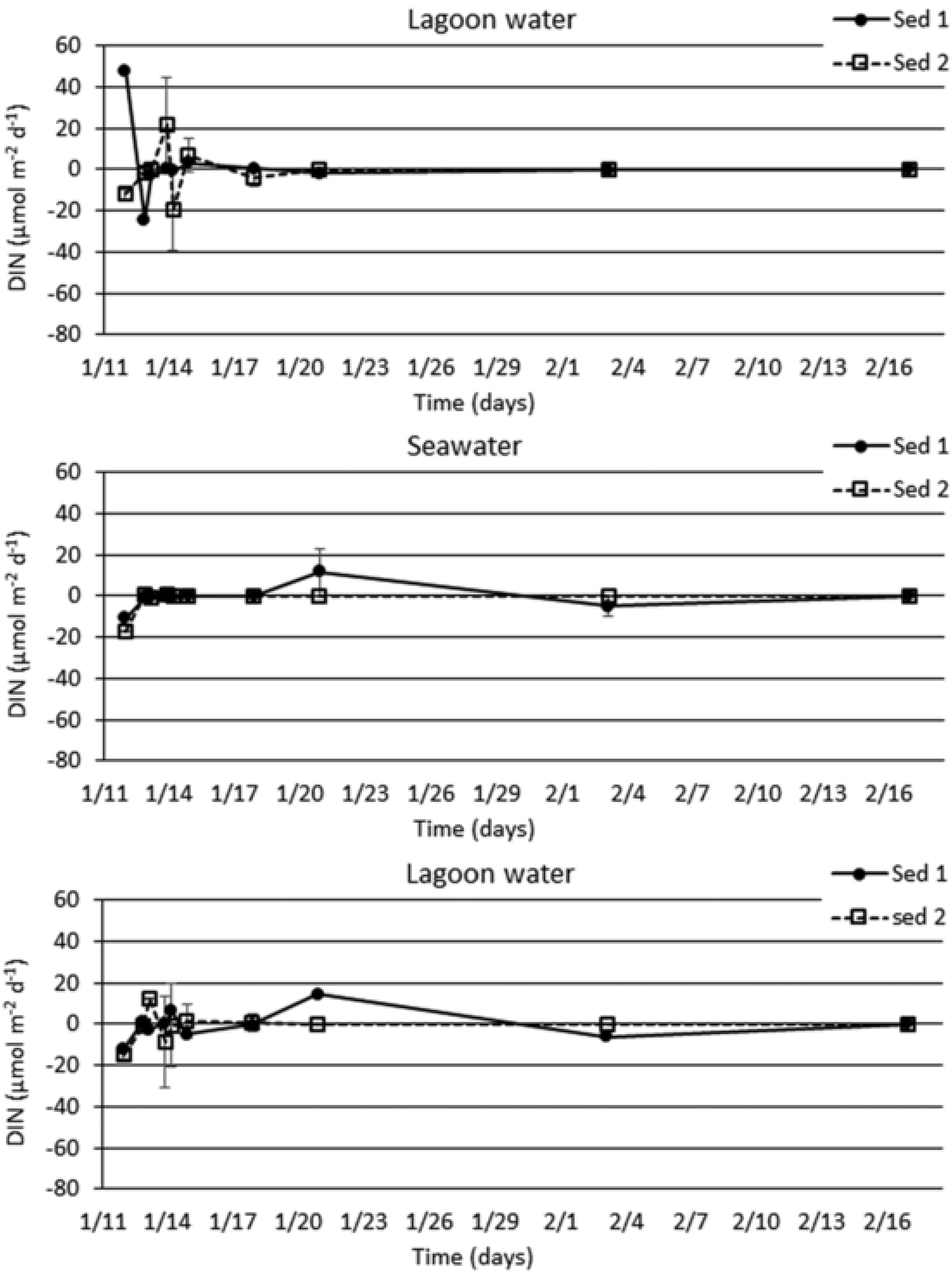

Fig. 12. Diffusive flows of phosphate (PO_4^{3-}-P) (µmol m^{-2} day^{-1}) at the sediment-water interface during the *in vitro* regeneration experiments. The error bars show differences between two experiments with the same conditions.

cosm experiments were conducted, and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for granting a scholarship to TCSMG (grant #001). JCW is grateful to CNPq for a research fellowship (grant #302741/2017-8).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2021.112252.

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