UNIVERSIDADE FEDERAL DO RIO GRANDE DO NORTE
CENTRO DE TECNOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA SANITÁRIA

JÉSSICA PAPERA DE OLIVEIRA

LIBERAÇÃO DE FÓSFORO PELO SEDIMENTO NA PRESENÇA DE OXIGÊNIO EM UM LAGO RASO TROPICAL

Natal - RN
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Orientadora: Profª Drª Vanessa Becker

Coorientadora: Drª Fabiana Araújo

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Summary

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Apresentação

Este trabalho tem como proposta avaliar a degradação da qualidade da água de uma lagoa do nordeste brasileiro, a qual é utilizada para abastecimento humano. Esta vem sofrendo crescente eutrofização nos últimos anos. O processo de eutrofização tem como um de seus principais resultados o crescimento exacerbado de populações de cianobactérias. Essas florações de algas trazem consequências negativas para a qualidade da água, associadas ao aumento da turbidez, redução das concentrações de oxigênio dissolvido, aumento na mortandade de peixes e, além disso, algumas espécies são potenciais produtoras de toxinas. A deterioração da qualidade da água na lagoa, associada as florações de cianobactérias dificultam o tratamento da água.

A eutrofização é um processo que ocorre naturalmente ao longo de décadas, no entanto, ele pode ser acelerado devido à influência da ação antrópica. Atividades humanas no entorno de corpos d'água tais como agricultura, pecuária e despejo de águas residuárias, aumentam o aporte externo de nutrientes, principalmente nitrogênio e fósforo, acelerando o processo de eutrofização. Geralmente, o aporte de fósforo é fator determinante na eutrofização, visto que ele é, frequentemente, limitante para o crescimento da produção primária. Além disso, controlar o fósforo é mais simples do que controlar o nitrogênio, uma vez que este pode ser obtido inclusive sendo fixado da atmosfera. Sendo assim, é aconselhável que as medidas para controle da eutrofização em ambientes de água doce possuam foco no ciclo do fósforo.

O fósforo proveniente de fontes externas, tanto pontuais quanto difusas, não fica apenas na coluna d'água, ele é depositado no sedimento, o qual, de acordo suas características e as condições ambientais, possui capacidade de acumulação de fósforo. Porém, o sedimento não age apenas como sumidouro de fósforo, ele pode devolver parte do que foi acumulado através do processo chamado de fertilização interna. O fósforo fica

acumulado no sedimento em diversas formas classificadas de acordo com o tipo de composto no qual ele se encontra. Sendo assim, não é todo o fósforo no sedimento que pode facilmente retornar à coluna d'água, algumas dessas formas são mais móveis que outras. Portanto, a liberação de fósforo pelo sedimento depende das formas de fósforo presentes nele, bem como das condições do ambiente na interface água-sedimento. Dos fatores que influenciam os mecanismos de liberação e retenção de fósforo, pode-se destacar temperatura, pH, oxigênio dissolvido, organismos e ressuspensão.

Constantemente, a concentração de oxigênio dissolvido próximo ao sedimento é tratada como o fator mais importante para a fertilização interna. Isso porque condições anóxicas favorecem a liberação de fósforo ligado à ferro. Nosso objeto de estudo é uma lagoa inserida em região urbana, cuja água é utilizada para abastecimento humano. Ela possui boas condições de mistura, ou seja, toda a coluna d'água possui oxigênio dissolvido, mas que, ainda assim está se tornando cada vez mais eutrofizada. Portanto, é importante investigar a contribuição da ciclagem interna de P para a degradação da qualidade da água do sistema, visando auxiliar na busca de soluções de manejo adequadas para o sistema.

Diante disso, neste trabalho, analisamos as formas de fósforo presentes no sedimento da lagoa, e verificamos o potencial de liberação de fósforo pelo sedimento.

LIBERAÇÃO DE FÓSFORO PELO SEDIMENTO NA PRESENÇA DE OXIGÊNIO EM UM LAGO RASO TROPICAL

O fósforo (P) possui um papel importante na eutrofização de ambientes de água doce e as fontes externas são consideradas uma das principais causas do enriquecimento dos corpos d'água por P. Para controlar a eutrofização, é necessário que o aporte externo seja reduzido, porém, P acumulado no sedimento pode retornar para a coluna d'água, através do processo de fertilização interna. No sedimento, nem todas as formas de P são móveis, e sua liberação depende de diversos fatores, tais como temperatura, oxigênio dissolvido, organismos, pH, e ressuspensão. A liberação de P em condições de anoxia é amplamente discutida, mas, o oxigênio não é o único fator que pode influeniar na liberaçãode P. Neste estudo, nós avaliamos a contribuição potencial da fertilização interna para a eutrofização da Lagoa de Extremoz, a qual é um ambiente raso com coluna d'água misturada, que vem sendo gradualmente eutrofizado. A qualidade da água desse sistema é relevante, visto que ela é utilizada para abastecimento humano. Para avaliar o processo de fertilização interna, nós realizamos um experimento utilizando sedimento da lagoa com água da lago, e sedimento com água deionizada, em condições semelhantes às da interface água-sedimento durante 40 dias. Além disso, quantificamos as frações de P no sedimento da lagoa em diferentes profundidades, bem como no sedimento do experimento inicial e final. A principal fração do sedimento foi P orgânico refratário, e a maior parte do P móvel está ligada a óxidos de Fe e Al. Menos da metade do fósforo presente no sedimento da lagoa é considerada móvel. Durante o experimento, a temperatura variou em até 3,2°C, fazendo o sedimento da Lagoa de Extremoz liberar P para a água, apesar da presença de oxigênio. No final do experimento, quase todo o fósforo presente na água sobre o sedimento foi orgânico (P-Org). Nos tratamentos com água da lagoa filtrada, P-Org representou 99,5% do P total. E, nos tratamentos com água deionizada, P-Org representou 93,6% do P total . A maior parte do

fluxo de P para a água, após o aumento a temperatura, também foi composta por P orgânico. Também detectamos um aumento em formas orgânicas de P ao final do experimento. O aumento da temperatura, seguido das mudanças nas concentrações de fósforo na água, principalmente o P-Org, sugerem que os efeitos da temperatura e do metabolismo dos microorganismos controlam o fluxo do P na presença de oxigênio.

Palavras-chave: Lagoa de Extremoz, lagoa costeira, Fracionamento, Sedimento, Aeróbio, Temperatura.

SEDIMENT PHOSPHORUS RELEASE IN A TROPICAL SHALLOW LAKE UNDER THE PRESENCE OF OXYGEN

Phosphorus (P) is a key nutrient in the eutrophication of freshwater and external nutrient sources are considered one of the main causes of P enrichment. To try and control eutrophication, external loading can be reduced. However, P accumulated in the sediment can be cycled back into the water, due to the process of internal loading. Not every form of P in the sediment is likely to be released into the water column, and its release from sediment is influenced by several factors, such as temperature, dissolved oxygen concentration, organisms, pH, and sediment resuspension. P release under anoxic conditions is largely discussed, but oxygen is not the only factor affecting P release. In this study, we evaluate the potential contribution of internal P loading to the eutrophication of Lake Extremoz, which is a well mixed shallow system that has been suffering increasing eutrophication. The quality of its water is relevant as it is used for human consumption. To evaluate internal loading, we have carried out an experiment utilising sediment with lake water, and sediment with deionised water, under conditions similar to the sediment-water interface over a 40-day period. We have also analysed P forms in the sediment per depth range, and before and after the experiment. The main P fraction in the sediment was refractory organic P, and the main mobile fraction was P bound to Fe and Al oxides. Less than half of the P in the sediment is in mobile P forms. During the experiment, temperature varied up to 3.2°C, what led to P release from sediment into the water column, regardless of the aerobic conditions. By the end of the experiment, the majority of the P in the water overlying the sediment was organic (P-Org). In the units that had lake water, P-Org represented 99.5% of the total P. And, in the units that had deionised water, P-Org represented 93.6% of total P. Most of the P flux into the water after the increase in temperature was composed by organic phosphorus. We also saw an increase in organic P forms in the sediment of the experiment. The increase in the temperature, followed by the changes in phosphorus concentrations in the water, mainly P-

Org, suggest that the effects of temperature and microorganisms' metabolism control P flux in the presence of oxygen.

Key-words: Lake Extremoz, Coastal Lake, Fractionation, Sediment, Oxic, Temperature

1. Introduction

Phosphorus (P) is considered a key nutrient in the eutrophication of inland freshwater (Carpenter, 2008) as it usually is a limiting factor for primary production. Increased P availability can lead to an enhanced primary productivity and nuisance algae blooms (Heisler et al., 2008). Known consequences of P enrichment and dense algae blooms include increased turbidity, bottom water hypoxia, and fish kills. Therefore, controlling P must be the focus when dealing with freshwater eutrophication (Schindler, 2012).

External nutrient sources are considered the main cause of eutrophication, thus the first measure to mitigate it is to control external P loading (Jeppesen et al., 2007). Sources of allochthonous P can be point, e.g. disposal of human sewage, and non-point such as rearing livestock and synthetic fertilisers. This means that whole catchment measures are necessary to control the nutrient input. However, in many cases, this is not enough to achieve the desired restoration of the environment as legacy P keeps being released into the water column. A consequence of this internal nutrient loading is the perpetuation of the eutrophic state of the system (Jeppesen et al., 2005; Søndergaard et al., 2013, 2001; Spears et al., 2012).

Not every form of P in the sediment is likely to be released into the water column (Wang et al., 2013). P in the sediment is divided into fractions according to what compounds it is bound to. Following the sequential P fractionation proposed by Paludan and Jensen(1995), P forms include interstitial water and loosely sorbed P (P-Water), redox sensitive P bound to iron (Fe) compounds (P-BD), P bound to aluminium (Al) hydroxides (P-NaOH), calcium (Ca) bound P (P-HCl), humic bound P (Humic-P) and refractory P. Of these fractions, the mobile pool is considered to

comprise the sum of the inorganic parts of P-Water and P-BD, and the organic parts of P-Water, P-BD and P-NaOH. While the inorganic parts of P-NaOH, P-HCl, Humic-P and Refractory-P are considered to be the non mobile pool (Jensen et al., 2015).

P release from sediment is influenced by several factors, such as temperature, dissolved oxygen concentration, organisms, pH, and sediment resuspension (Søndergaard et al., 2003). These factors affect each P form differently. For instance, anoxic conditions near the sediment cause Fe reduction, what results in the release of the P-BD fraction (Zhu et al., 2012), thus oxygen depletion is often seen as a main enabler of internal loading. Whereas, presence of oxygen is associated with P retention (Olszewska et al., 2017), so much that hypolimnion oxygenation is regarded as a lake restoration method (Beutel and Horne, 1999; Singleton and Little, 2006). However, in oxygenated environments P can still be released through processes other than the classic Fe reduction release mechanism, such as mineralization of organic matter, bioturbation and pH or temperature induced solubilisation (Søndergaard et al., 2001).

Temperature is another important factor for internal loading, as higher temperatures can increase P compounds solubility (Jensen and Andersen, 1992), as well as affect the biota in both water and sediment, which is involved in the P cycling through immobilization of inorganic P and mineralization of organic matter. The pH can influence P release as well. For instance, low pH values are related to the release of calcium bound P, whereas high pH values induce the release of P-NaOH (Jin et al., 2006).

Finally, P release is a complex process, and its understanding is not restricted to the release mechanisms related to oxygen. In the present study, we evaluate the potential contribution of P release from the sediment of a eutrophic shallow lake.

2. Material and methods

2.1 Study Area

Lake Extremoz (05°42'76"S; 35°17'69"O) is a natural tropical lake in the Doce river catchment, in the Northeast region of Brazil. According to Köppen's classification, the climate of the region is tropical with dry summer As (Alvares et al., 2014). Its maximum storage capacity is 11 million m^3 (SEMARH, 2015), and an average depth of 4m (Pinto and Becker, 2014), and a maximum depth of 7m (unpublished data). This lake's main use is human supply, providing water for 60% to 80% of the population of the north region of Natal, Brazil (Araújo et al., 2000), hence the relevance of the quality of its water. It's near an urban area and industries. There is also agriculture, rearing livestock and leisure activities in its surroundings. It has been described as having a lack of seasonality, and well mixed water column (Pinto and Becker, 2014).

Its average TP concentration between Oct/2017-May/2018 was 30.9 $\mu g.L^{-1}$, , and the average chlorophyll-a concentration was 30.4 $\mu g.L^{-1}$ (Moreira, 2018). According to the classification proposed by Salas and Martino (1991), the total phosphorus is within the mesotrophic range, while the chlorophyll-a classifies it as eutrophic.

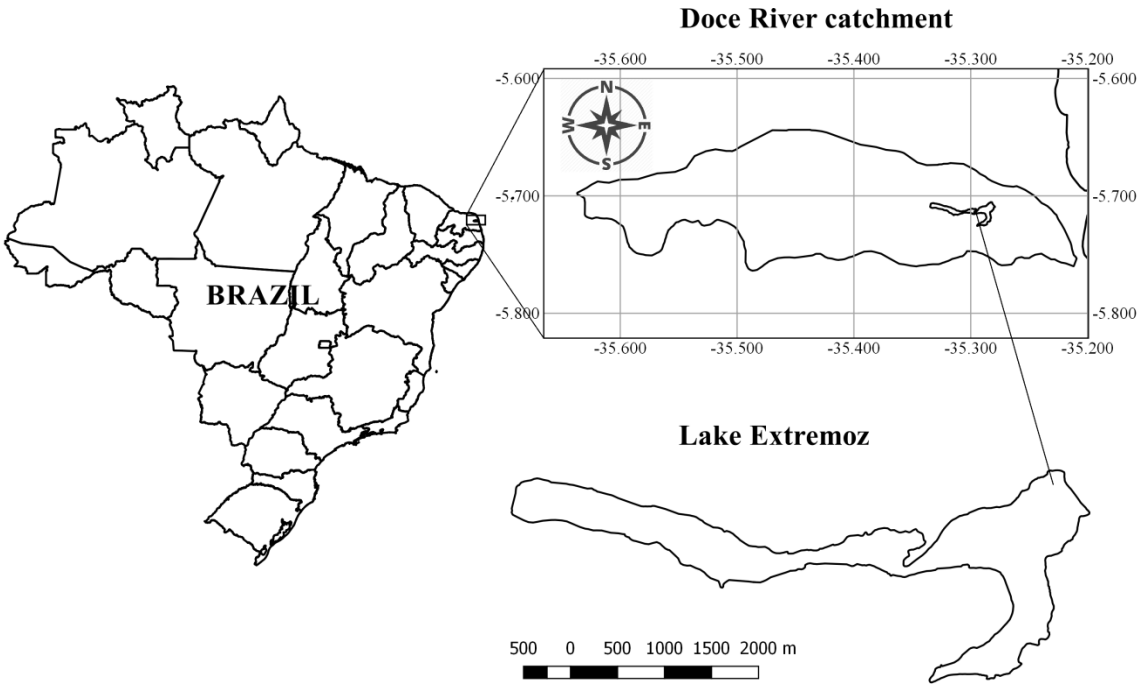

Fig. 1 Location of the Lake Extremoz in the northeast of Brazil.

2.2 Water and sediment sampling

We sampled the water near the bottom, with aid of a Van Dorn sampler, aiming to better approximate the conditions near the sediment for the phosphorus release experiment. We placed the water in polyethylene gallons for transport to laboratory

We collected sediment in the lake using a Kajac corer. First, we collected a core and sliced it *in situ* into 2 cm slices, 0-2 cm, 2-4cm, 4-6 cm, 6-8 cm, 8-10 cm. They were stored separately in transparent polyethylene containers.Then we collected several samples of the most superficial 10 cm of the sediment. They were stored together in a polyethylene container, for that sediment was to be used in the phosphorus release experiment. All the containers with sediment were placed in a thermally insulated box for transport to laboratory. The sampling took place in August 2018.

2.3 Phosphorus fractions in the sediment

We extracted the different fractions of phosphorus in sediment following the method described by Cavalcante et al. (2018). For all fractions, we measured the concentration of soluble reactive phosphorus (SRP) (Murphy and Riley, 1962), and total phosphorus (TP) concentration (Valderrama, 1981) when applicable. We performed the fractionation of the sediment profile by depth in triplicates.

In the total phosphorus analyses in all the supernatants of the fractionation, we registered the absorbance 2 minutes after the addition of the reagent, as we noticed the peak of absorbance occurred at this time, for theses specific samples.

We calculated the mobile P pool in the sediment, considered to be composed by the fractions with higher potential to contribute to the internal loading. As shown in Fig. 2, the mobile P pool comprises the SRP of P-Water and P-BD fractions, and the organic part of P-Water, P-BD and P-NaOH (de Vicente et al., 2008; Jensen et al., 2015; Reitzel et al., 2005).

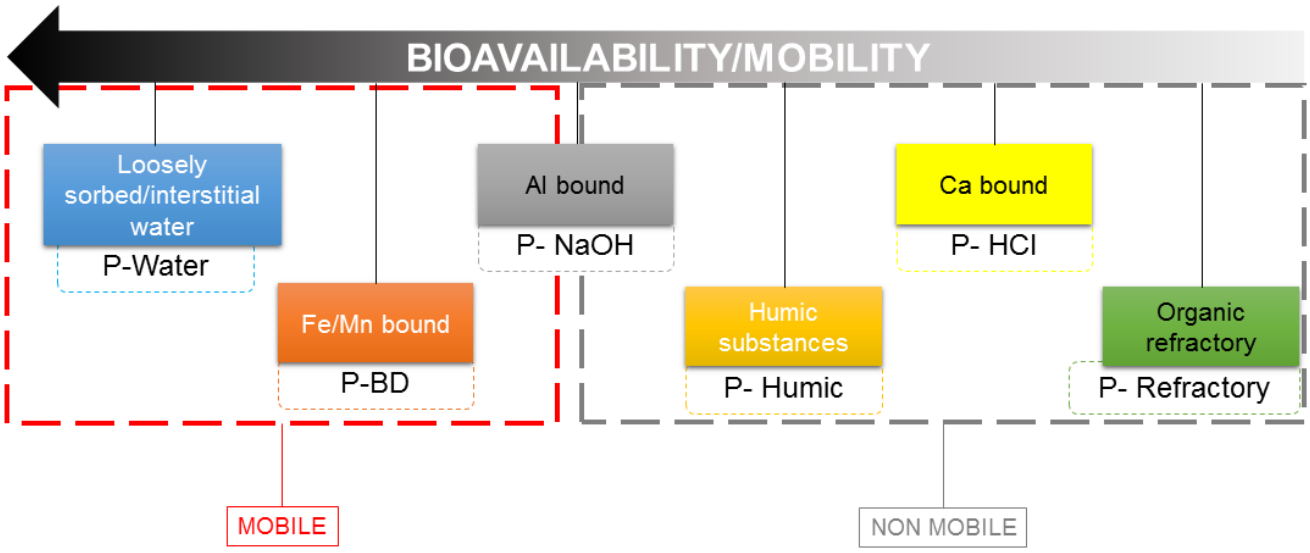

Fig. 2. Scheme representing P forms from most mobile to least mobile (left to right), showing the division of the mobile and non mobile pools.

2.4 Phosphorus release experiment

Temperature and DO near the bottom of the lake were measured *in situ*. Once in the laboratory, we established initial parameters of the water collected from the lake measuring pH, TP and SRP. We filtered the water through a 1.2 µm membrane. We also measured TP and SRP concentrations in the laboratory's deionized water.

The experiment was set up as shown in Fig. 3 using eight beakers with 1L capacity each. All of them received 200g of homogenised wet lake sediment, only from the most superficial 10 cm. Four out of the eight beakers were filled with 800 mL of filtered water from the lake (NAT) while the other four were filled with 800 mL of deionized water (DEI). We covered the beakers with tin foil to keep a dark environment, closer to the condition of the water-sediment interface and placed them in a room with no control of temperature. The distribution of the beakers was random to avoid environment bias.

After adding sediment and water to the beakers, they were left to settle down for 24h to start counting the day 1 of the experiment, which lasted until day 40. We sampled 60 mL of water from each beaker on the days 1, 5, 10, 15, 21, 26, 33 and 40 of the experiment, and measured the TP and SRP concentrations. The concentrations of organic P (P-Org) were calculated by subtracting SRP from TP. On each sampling day, the volume of water that was removed from the NAT units

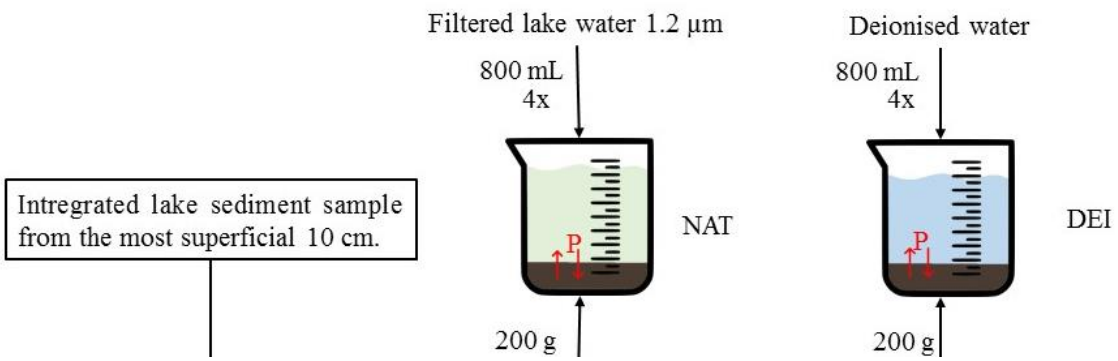

Fig. 3. Phosphorus release experiment scheme. NAT are the units which received filtered water from the lake, and DEI are the units which received deionised water.

was replaced with filtered lake water, and, in the DEI units, it was replaced with deionized water. The replacement water was kept under the same conditions as the experiment units.

We calculated the P flux [$\mu g.m^{-2}.d^{-1}$] between water and sediment according to the following equation:

$$f_{t_{0-i}} = \frac{(C_i - C_0).V}{(t_i - t_0).A}$$

The equation takes into account P concentration in the water at the beginning (C_0) and at the end (C_i) of each time interval ($\mu g.L^{-1}$), the volume of water overlying the sediment (L), the time interval (t_i-t_0) (d), and the approximate area of sediment in contact with the water (m^2). We calculated the fluxes of SRP, TP and P-Org.

Based on the behaviour of the P concentrations throughout the experiment, we have calculated the fluxes of two intervals, from day 0 to day 21 and from day 21 to day 40.

Regarding the sediment, we considered that the P fractions content in the homogenised sample of several 10 cm cores is equal the average of the content by depth. Therefore, we used the average values of each fraction of all depths as the initial fractionation of the experiment.

We monitored pH, DO and temperature of the water in all of the units on the sampling days.

To analyse the difference between P contents in the sediment, P fractions and P mobile pools in different samples we used Welch's t-tests.

3. Results and discussion

3.1 Sediment profile - Phosphorus fractions in the lake

The sediment of Lake Extremoz is mostly composed by Refractory P, which is the largest fraction of P in all layers (Fig. 4). When we analysed the sediment composition by depth, it presented a decrease in the total amount of P from the most superficial layer, until the 4-6 cm depth range (Fig. 4a). But, in the range 6-8 cm the total amount of P was almost twice the value of the most superficial layer, mostly due to the larger amount of refractory P. The deepest layer had the second highest amount of P.

The higher total amount of P in deeper layers is an indication that a rather large P contribution to the sediment occurred in the past. This contribution could have happened due to an event of high external input, or as a consequence of the lake being more oligo/mesotrophic in the past, which gives it better conditions to act as a P sink.

The largest mobile fraction of Lake Extremoz's sediment is iron bound P (Fig. 4). This fraction is redox sensitive, thus expected to be released under anoxic conditions (Smolders et al., 2006). The lake is characterized by a well mixed water column (Pinto and Becker, 2014) and, currently, does not present anoxic conditions at the bottom. Despite the oxygenated sediment-water interface, Lake Extremoz is, gradually, getting more enriched with nutrients, and one of the main consequences of eutrophication is oxygen depletion (Smith and Schindler, 2009). Therefore, in the future, the lake can have the iron reducing conditions that favour the release of the P-BD fraction into the water column, further aggravating its eutrophic state.

Regarding the relative mobility of the P present in the sediment of the lake, the depth with the larger percentage of P in the mobile pool is 0-2 cm, in which 48.44% is considered mobile (Fig. 4b). Also, the relative contribution of the mobile P pool decreased with increasing depth. Most superficial layers have a larger amount of potentially mobile P, because they are still going through

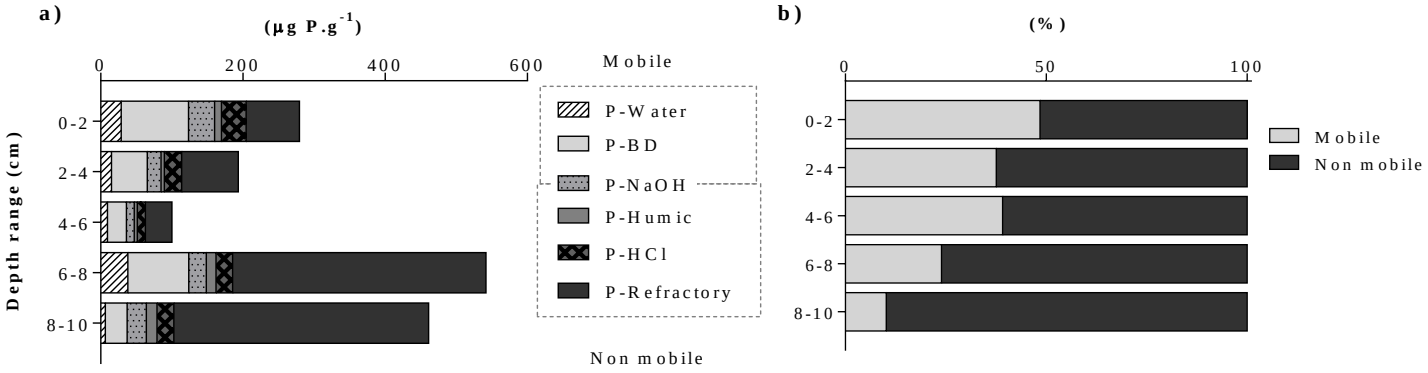

Fig. 4. Content of P forms in the sediment profile (a) and the relative content of mobile and non mobile pools (b).

processes of release/retention and diagenetic transformations, tending to be more recalcitrant with time as they are buried (Rydin et al., 2011; Xu et al., 2013).

3.2 P release experiment

The temperature varied up to 3.2°C throughout the experiment. It started with averages of 25.8°C for NAT and 25.0°C for DEI on day 1, and increased sharply between the days 15 and 26, reaching values up to 28.2°C (Fig. 5a). The increase in temperature of the water is compatible with the increase in the temperature of the air during the experiment. On the day 0 of the experiment, the average air temperature was 24.3°C, and on day 40 it was 27.2°C (INMET, 2018). The water in both NAT and DEI units remained oxygenated during the whole of the experiment, with DO

concentrations above 4 $mg.L^{-1}$ (Fig. 5b). In the NAT units, pH was near neutral at the start and that did not change over time (Fig. 5c).

In the DEI units, pH started neutral and decreased around day 15, reaching values near 5 by the end of the experiment (Fig. 5c). A possible explanation is that, due to the lack of light and decomposition of organic matter there was a net respiration in the DEI units. These processes have CO_2 as a product, which induces the formation of carbonic acid in the water (Talling, 2014). Deionised water is expected to have alkalinity nearly null, not being able to buffer the effects of the carbonic acid on its pH, hence the acidification, while Lake Extremoz has an average alkalinity of 47.85 $mg.L^{-1}$ $CaCO_3$ (average value between April/2017 and March/2018) (Medeiros, 2019), giving it a better capacity to resist a decrease in pH. This change, however, did not seem to have influenced the P release. For instance, a low pH environment is expected to increase release of P-HCl (Li et al., 2015), yet, there was neither significant change in said P fraction in the DEI units, nor higher concentrations or P fluxes in DEI with relation to NAT.

With respect to the SRP concentrations, NAT and DEI followed a similar pattern. After the settling period, on day 1, SRP concentrations in both NAT and DEI units had increased, reaching their highest concentrations with averages of 22.8 $\mu g.L^{-1}$ and 8.3 $\mu g.L^{-1}$, respectively (Fig. 6a). Regarding TP, NAT had a concentration of 76.0 $\mu g.L^{-1}$ and DEI had 0.0 $\mu g.L^{-1}$ at the beginning of the experiment (Fig. 6b). Past the settling period, the TP concentration in DEI had a sharp increase to an average of 49.3 $\mu g.L^{-1}$ (Fig. 5b). The concentrations of P-Org during the experiment followed the same pattern as the TP (Fig. 6), although, for NAT, there was not an increase after the settling period.

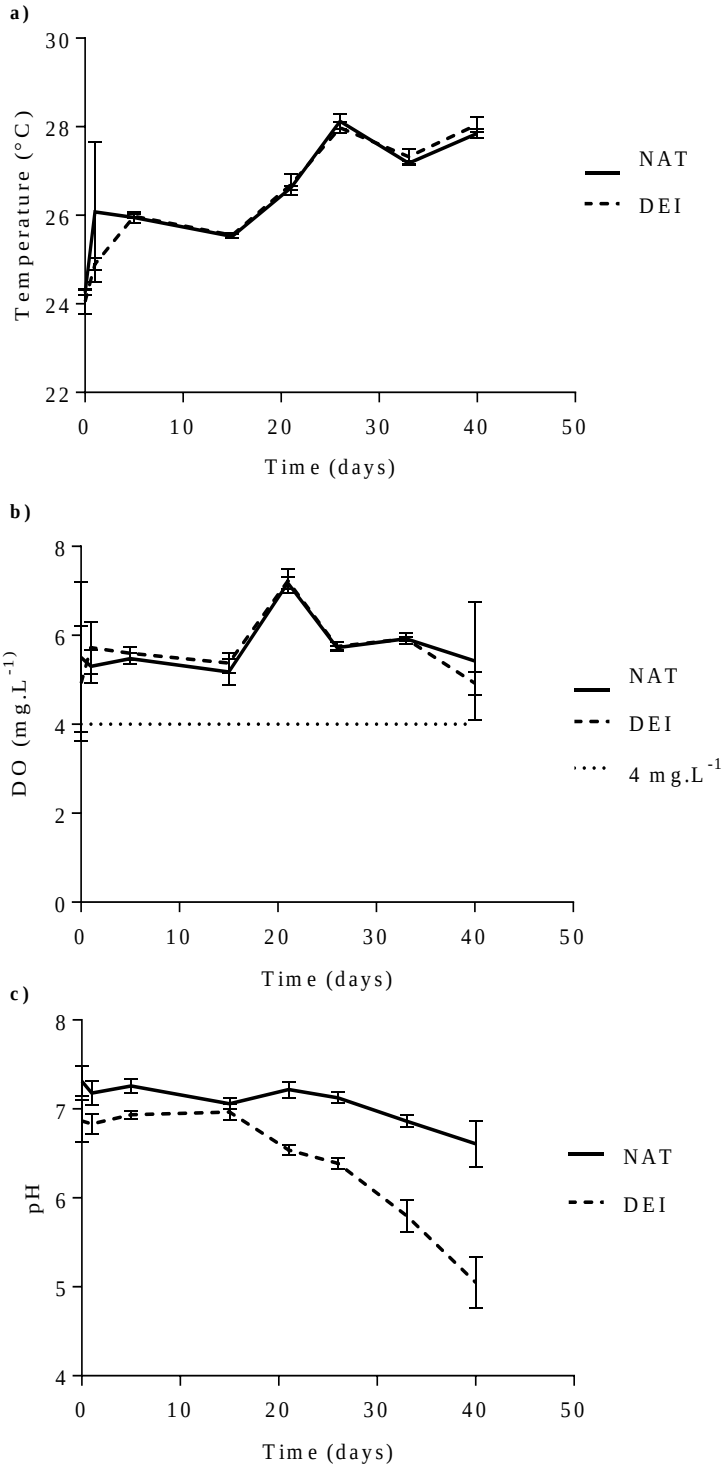

Fig. 5. Monitored data throughout the experiment, including temperature (a), dissolved oxygen (b) and pH (c).

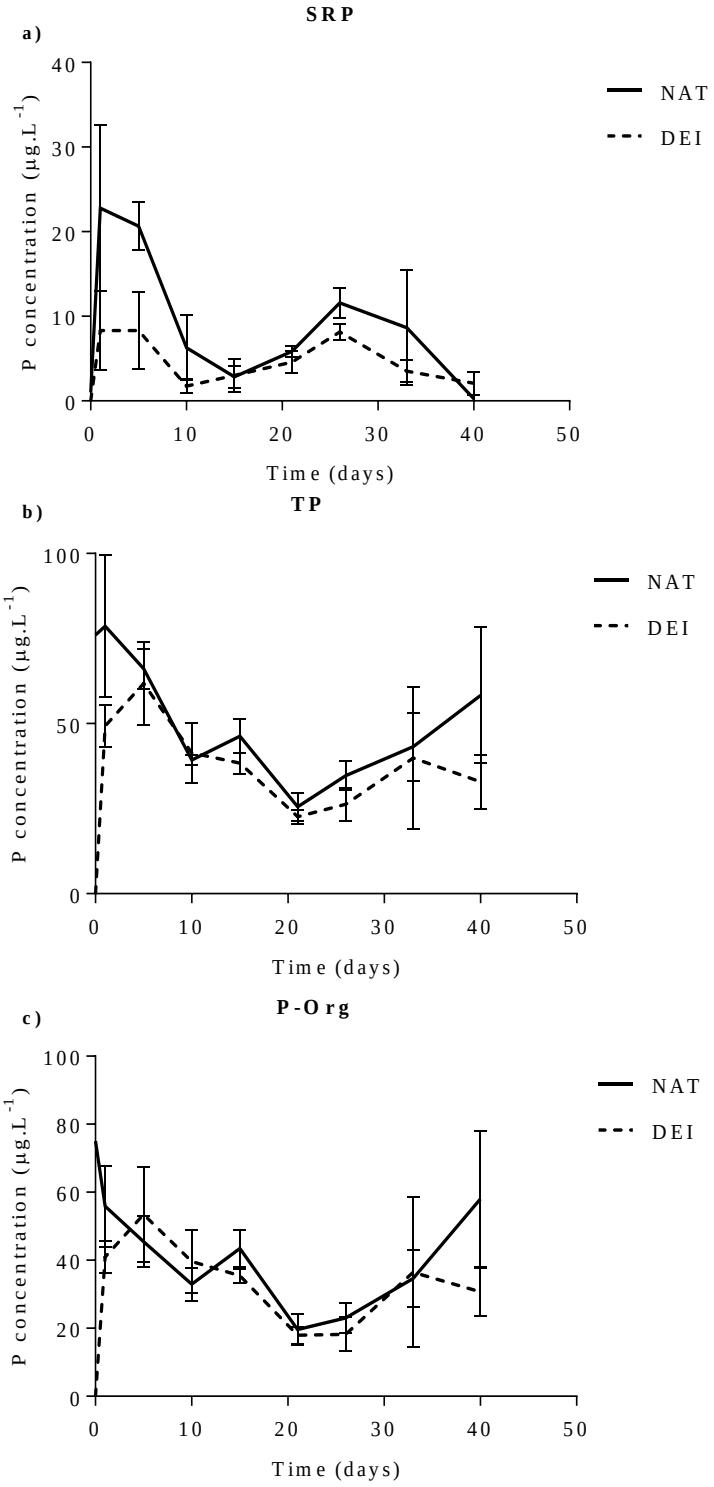

Fig. 6. P concentration in the water overlying the sediment. SRP (a), TP (b) and organic P (c).

This general increase in P concentrations immediately after settling the experiment can be attributed to the initial physical disturbance in the sediment in both NAT and DEI units, similarly to a resuspension (Huang et al., 2015; Søndergaard et al., 1992). Additionally, specifically for DEI units and NAT's SRP, the initial release and positive P fluxes (Fig. 7), can be partially attributed to the initial lack of P in the water. That is, P concentration in the pore water of the sediment, the most mobile fraction, was, initially, higher than the P concentration in the water overlying the sediment, creating a concentration gradient. In this case there's a tendency for that P to be released into the water through diffusion (Golterman, 2004; Roy et al., 2012).

The initial increase in SRP was followed by a decrease that lasted until day 15 for DEI and 10 for NAT (Fig. 6a). TP concentrations in NAT decreased until day 21, reaching its lowest average, 25.5$\mu g.L^{-1}$ (Fig. 6b). The decrease of TP concentration in the DEI units only started on day 5, and carried on till day 21, reaching its lowest value of 22.6 $\mu g.L^{-1}$. Both NAT and DEI P-Org concentrations had a general decrease until day 21 of the experiment (Fig. 6c).

SRP concentrations increased until day 26, in NAT and DEI and then decreased until the end of the experiment (Fig. 6a). From day 21 onwards, NAT's TP concentrations only increased, reaching a final average of 58.25 $\mu g.L^{-1}$. DEI's TP concentrations also increased in that period, but had a slight decrease towards the end, when it got to an average of 32.83 $\mu g.L^{-1}$. From day 21 onwards, P-Org concentrations increased in the NAT units until the end of the experiment, when it reached an average of 58.0 $\mu g.L^{-1}$ (Fig. 6c). P-Org in DEI also increased from day 21 onwards, but, like TP, it decreased in the end, getting to an average of 30.74 $\mu g.L^{-1}$.

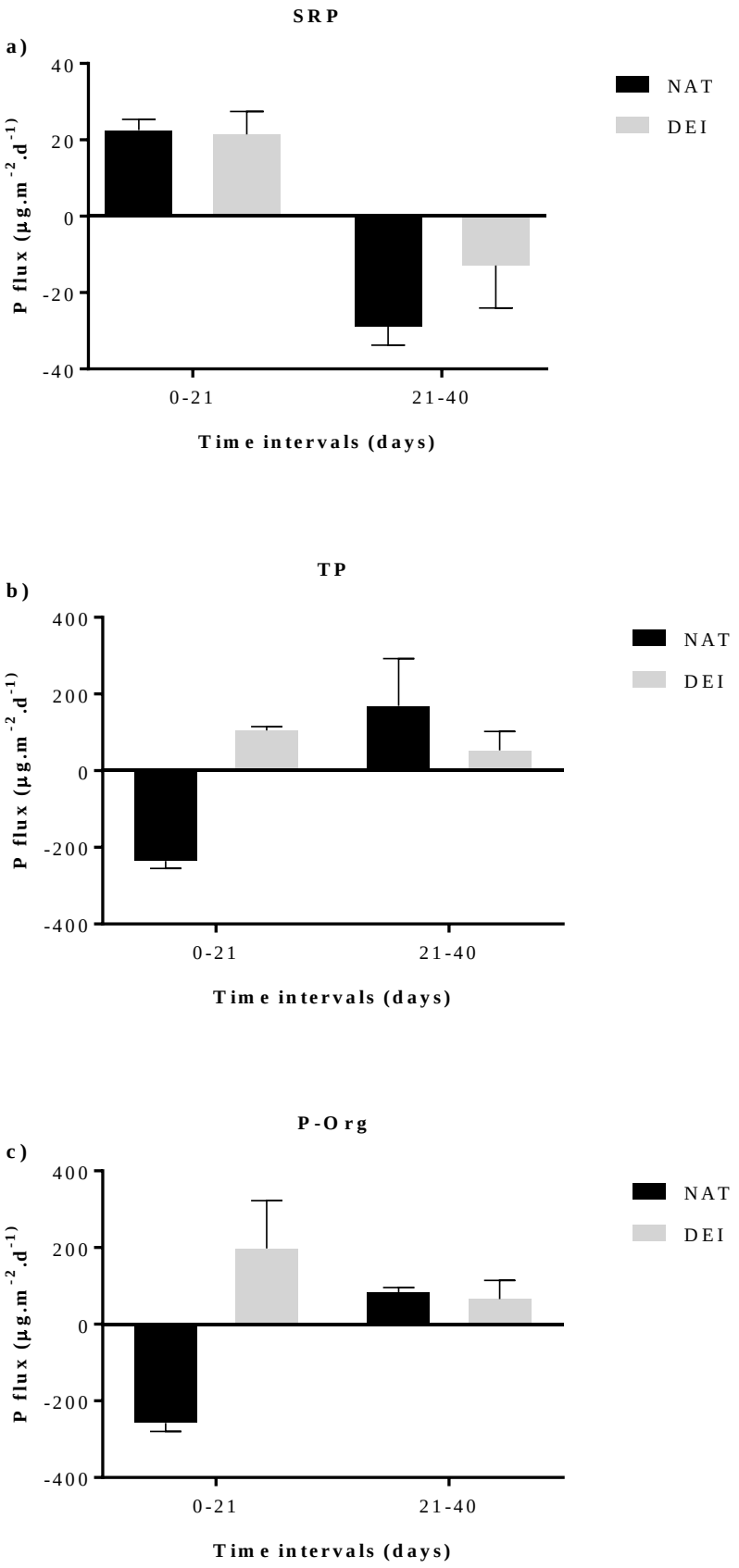

Fig. 7. P fluxes between sediment and water throughout the experiment. SRP (a), TP (b) and P-Org (c). Calculated for the intervals between day 0 to day 21, and day 21 to day 40. Error bars represent the standard deviation.

The second half of the experiment had positive fluxes of TP in all the units, however, the SRP fluxes were negative. Hence, these positive TP fluxes were due to P in organic compounds, as seen in Fig. 7c, rather than inorganic.

P release from sediment is often associated with anoxic conditions (Olszewska et al., 2017; Wang et al., 2006; Zhu et al., 2012). Consequently, the classic release mechanism related to Fe reduction is broadly discussed, due its great relevance. Nonetheless, P can be released under aerobic conditions, because oxygen deficit is not always its prime cause as P release is controlled by a number of factors (Hupfer and Lewandowski, 2008). In aerobic conditions, the temperature seems to be the most important environmental factor influencing P release from sediment (Jensen and Andersen, 1992; Suplee and Cotner, 2002; Wu et al., 2014), and this is most likely related to the influence of temperature on organisms, hence giving more relevance to P-Org in these cases (Jiang et al., 2008) .

The second half of the experiment seems to have been influenced by the rise in temperature, as it was closely followed by an increase in all P concentrations measured in the water. This behaviour is in agreement with the premise that high temperatures increase P release from sediment (Wu et al., 2014). It can happen because high temperature stimulate P release from sediments through different processes such as increasing the solubility of P compounds (Jensen and Andersen, 1992), and increased mineralization of the organic matter and organism metabolism (Wu et al., 2014). We draw attention to the role of organisms in the sediment because, even though the water had been filtered through a 1.2 μm membrane, it is fair to assume that there are still microorganisms, such as bacteria, in the water of the lake. In this case, the increase in SRP and TP in the water is most likely linked to an

increase in bacterial metabolism and biomass, as it's been proven to be the case for dark environments (Jiang et al., 2008).

In the beakers which contained lake sediment covered by filtered lake water, t NAT treatment, P-Org increased along with the temperature until the end of the experiment, while SRP did not. This pattern shows that, at first, the higher temperature stimulated release of both inorganic and organic forms of P, whereupon there was a SPR uptake from bacteria, as they can consume large portions of inorganic nutrients (Kirchman, 1994), possibly resulting in an increased biomass. This did not happen in the beakers where the lake sediment was covered by deionised water, the DEI units, where P-Org did not increase until the end, what is further indication that the processes in NAT were related to organisms that can be found in the lake water but not in deionised.

Regarding the sediment of the experiment, the total amount of P fractions in the sediment measured from the beakers after the experiment has shown no significant difference from what was considered initial (Fig. 8a). However, there were significant differences between P fractions in the sediment, mainly between the initial values and NAT. Among the mobile fractions of P in the sediment of NAT F, two have shown significant difference in relation to the initial values, P-Water (p=0.02488) and P-NaOH (p=0.0008). While, in the non mobile pool, P-Humic and P-HCl were different with p=0.0062 and p=0.0266, respectively. The mobile P pool of NAT was significantly higher than the initial mobile P pool (p=0.03282) (Fig. 8b). Regarding the P fractions in DEI, two have shown significant difference in relation to the initial values, they were P-NaOH (p=0.0378) and P-Humic(p=0.0114).

The fact that P-NaOH, which is partially composed of organic material, and P-Humic were significantly higher in both NAT and DEI sediments at the end of the

experiment can be an evidence of organisms' activity within the sediment. The high temperature stimulates metabolism and biomass growth (Jiang et al., 2008), what happens through immobilization of inorganic nutrients, thus increasing the amount of P bound to organic matter within the sediment.

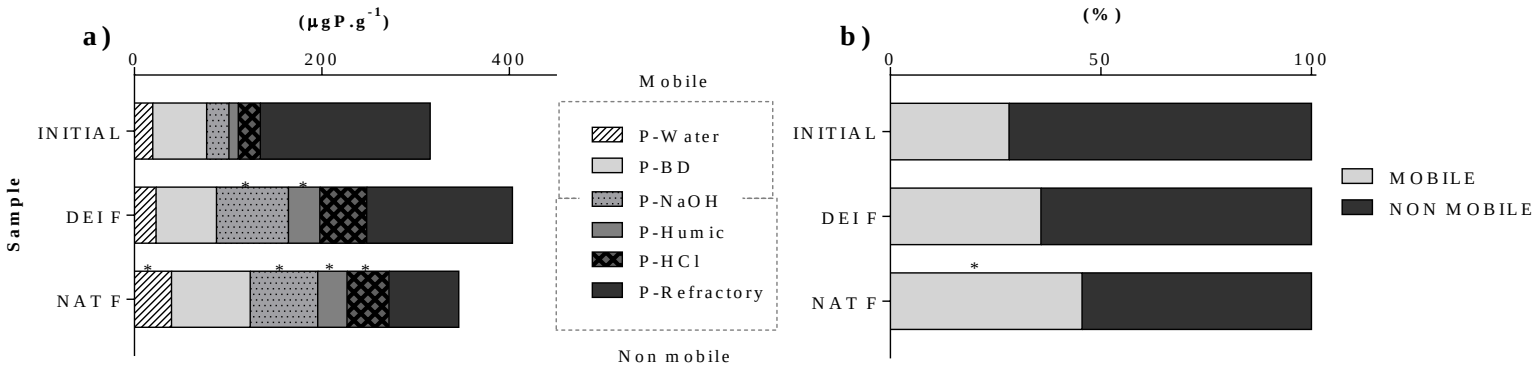

Fig. 8. Content of P forms in the sediment before the experiment (INITIAL) and after the experiment (DEI F and NAT F) (a), and their relative contributions to the mobile and non mobile P pools (b). The * represents significant difference in relation to INITIAL.

Overall, the change in temperature seems to have been the trigger of the release of P from the sediment in the experiment, as OD was always available, and pH either remained neutral or did not cause an effect in the units where it became more acidic. This information implies, for the lake, that P release from sediment is expected to contribute more to P concentration in the water during the warmest time of the year, and P bound to organic compounds have an important role.

Another factor to be considered is climate change. Lake Extremoz is in an area where temperature is expected to increase, even considering optimistic scenarios (IPCC, 2014), and bacterial metabolism is already higher in tropical regions, when compared with temperate (Amado et al., 2013). The consequences of warming on lake metabolism are expected to be felt the most at low latitudes, which is the case for this study area, mainly because the region is already warm and a linear increase in

temperature is expected to have an exponential influence on metabolism (Kraemer et al., 2017). Also, according to the IPCC (2014) reports, it is a region where rainfall is expected to decrease, thus reducing runoff and consequently external loading, hence it seems likely that internal loading will become of more relevance for this system in the future.

Each system has its own characteristics to be considered when it comes to understanding and controlling eutrophication. In Lake Extremoz, the fact that P can go into the water even in oxic conditions indicates that internal loading can contribute to increase the eutrophication hindering the quality of its water. The surrounding population relies on Lake Extremoz for water supply, so, if eutrophication in the lake is not controlled, it will become a problem for the water treatment plant, as it will be required to deal with forthcoming issues, such as algae blooms.

4. Conclusions

- Phosphorus can still be released from sediment into the water column even in the presence of oxygen, seeing as P internal cycling is a complex process which can be influenced by several other factors, such as temperature, physical disturbance, pH and organisms.
- Under oxic conditions, P release is likely to be largely influenced by temperature and its effects on organisms and the balance between mineralisation and immobilisation, giving special relevance to organic P forms.

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