

Magnetic microparticles as a new tool for lake restoration: A microcosm experiment for evaluating the impact on phosphorus fluxes and sedimentary phosphorus pools

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ABSTRACT

In the last decades, magnetic particles (MPs) as adsorbents have gained special attention due to their high adsorption capacity and the possibility of recovering them by applying a magnetic separation gradient. For the first time MPs have been tested as P adsorbents in a microcosm experiment in a context of lake restoration. MPs were added to sediment cores from a hypertrophic lake, at Fe:P_{Mobile} molar ratio of 285:1 and 560:1 under both, oxic and anoxic conditions. We have found that, under anoxic conditions (anoxic), MPs are able to reduce P release rate from the sediment to the overlying water and to reduce sedimentary P_{Mobile} concentration (a 22–25% reduction within 0–4 cm depth compared to controls). Under oxic conditions, the addition of MPs do not affect P fluxes across the sediment and water interface since the lake sediment is naturally rich in iron oxides. However a measured reduction in sedimentary P_{Mobile} concentration (12–16% reduction in 0–10 cm depth) contributes to a potential reduction in long-term P efflux.

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1. Introduction

Eutrophication is subject of concern to managers since it is the main problem that impairs water quality of 30–40% of water resources of all over the world (Hupfer and Hilt, 2008; Søndergaard et al., 2007). Since phosphorus (P) is the nutrient that often limits primary production in freshwater, it is a basic requirement to reduce its concentration in order to combat eutrophication and meet the requirements set by law (Schindler et al., 2008). Therefore, the first measure to consider in lake restoration should be the reduction of P external loading (Cooke et al., 2005; Reitzel et al., 2003). However, a successful reduction of external P loading is not always practical or economically feasible due to the difficulty in controlling external P inputs dominated by non point sources and due to the drastic reduction in external P loading required to accomplish the desired outcome (Marsden, 1989; Istvanovics and Somlyódy, 2001; Deppe and Benndorf, 2002). Moreover, biological

resilience and P release from lake sediments (P internal loading) usually delay ecosystem recovery after a reduction in external P loading (Jeppensen et al., 1991; Søndergaard et al., 2003). In such situations, it is recommended, apart from reducing P external loading, the application of in-lake techniques to decrease internal P loading and accelerate lake water improvement (Lürling and Oosterhout, 2013; Cooke et al., 2005). Some of these techniques are based on preventing P release from sediment by hypolimnetic aeration, nitrate (NO₃) addition or sediment capping (Hupfer and Hilt, 2008). Some other in-lake techniques are focused on enhancing P adsorption capacity of sediment by adding alum (Al), iron (Fe), calcium (Ca) salts, solid phase P-sorbing products (PSPs) coming from industrial waste and also Phoslock® (Cooke et al., 2005; Deppe and Benndorf, 2002; Lewandowski et al., 2003; Meis et al., 2012; Spears et al., 2013b; Yamada et al., 2012). In spite of its widespread application and success achieved, the main drawback about salt addition is that, although inactivated, P remains in sediment and may be released to water column under changing physicochemical and biological conditions such as temperature, pH, redox potential, biological activity or resuspension (Jensen and Andersen, 1992; Søndergaard et al., 1992; Rydin and Welch, 1998; Egemose et al., 2009). Although, in

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general, Al is preferred to Fe (Boers et al., 1992), since it keeps invulnerable to shifts in redox potential at sediment–water interface, Al application has also some limitations. For instance: (i) Al addition is limited to a pH range between 5.5 and 8 to assure the absence of toxicity and the efficiency in P removal (Lewandowski et al., 2003; Reitzel et al., 2013), (ii) Al-rich sediment layers reduce sediment consolidation degree, which hinders the establishment of macrophytes and favors resuspension events and temporal P release (Egemoose et al., 2010) and (iii) the effectiveness of Al addition is time-limited since P maximum adsorption capacity of Al floc is notably reduced by aging (76% of reduction after 3 months; de Vicente et al., 2008a).

To counteract the limitations of using Fe and Al salts, in the mid-1990s an alternative adsorbent, a lanthanum modified bentonite clay, Phoslock[®], was invented for trapping P in aqueous solutions (Robb et al., 2003; Ross et al., 2008; Spears et al., 2013a). However, Phoslock[®] has some drawbacks since P binding capacity declines when pH is above 8.1 and when increasing alkalinity, having some limitations in hardwater systems (Ross et al., 2008; Reitzel et al., 2013). Moreover, chemical interferences with humic substances, similarly to the addition of Al salts (de Vicente et al., 2008b) and of MPs (de Vicente et al., 2011; Merino-Martos et al., 2015), which lastly affect P removal efficiency have been found (Lürling and Faassen, 2012; Reitzel et al., 2013; Lürling et al., 2014). In addition, the high Phoslock[®]: P mass ratio necessary for retaining P, which has been identified as higher than 100:1 (Reitzel et al., 2013), and its high price make this technique specially unviable from an economic point of view in some circumstances.

As a result, new methods may be useful for lake restoration in order to overcome drawbacks of current practices. A large background of laboratory experiments has shown that magnetic particles (MPs) are good and cost-effective pollutant adsorbents (Tang and Lo, 2013). Among the main advantages for using these particles are their high surface area, which is responsible for a high adsorption capacity; a fast adsorption kinetic and their magnetism properties (Huber, 2005; Tang and Lo, 2013). The last characteristic of MPs implies that contaminant-loaded MPs can be efficiently removed from solution by applying a magnetic separation gradient, minimizing alteration in water quality and enabling their reuse in subsequent adsorption processes (de Vicente et al., 2010b; Funes et al., 2014).

In the case of P removal from aqueous solutions, it has been previously tested the convenience of using MPs as P adsorbents in laboratory scale under both batch mode (de Vicente et al., 2010b) and flow conditions (Merino-Martos et al., 2011). Apart from being considered as efficient P adsorbents (P uptake efficiency is always higher than 80% whatever pH value from 6 to 9), MPs present a fast adsorption kinetic (less than 1 h) and keep a high P removal efficiency when reusing them in subsequent removal processes (de Vicente et al., 2010b; Merino-Martos et al., 2014).

In this context, the aim of this study was to assess the effect of adding MPs on P fluxes across the sediment–water interface and on the sedimentary mobile P concentration. To get these purposes, a microcosm experiment using sediment cores and lake water collected from a hypereutrophic wetland (Honda lake, Southeast of Spain) was run under both oxic and anoxic conditions. Similarly to Reitzel et al. (2003), we proposed to add MPs relative to sediment mobile P pool (P_{Mobile}). Microcosm experiments tries to mimic more realistic conditions than the previously performed laboratory experiments (de Vicente et al., 2010b) and although this type of design obviously lacks the complexity of the whole ecosystem (Schindler, 1998), it may constitute a previous and necessary step for a future whole-lake application.

2. Materials and methods

2.1. Study site

Honda lake is a shallow (surface area = 9 ha, mean depth = 1.3 m and maximum depth = 3.2 m), hardwater (alkalinity 3.17–6.21 meq L⁻¹), brackish water (3.09 mS cm⁻¹) and hypertrophic coastal wetland located in Albuferas of Adra lacustrine complex (southeast Spain; Fig. 1). Table 1 includes some information about the general limnological features of the study lake. Despite of being designated as Natural Reserve (1989) and Ramsar Site (1994), among others protection states, its high external and internal P loads have impaired water quality as a result of eutrophication processes (de Vicente et al., 2003). The external P loading (1.73 g P m⁻² year⁻¹) is mostly constituted by diffuse inputs (about 90%; de Vicente and Cruz-Pizarro, 2003; de Vicente et al., 2003). In relation to the relevance of internal P load in this lake, its shallowness and the presence of intense winds cause frequent resuspension events which are lastly responsible for bringing back sediment associated particulate and dissolved nutrients into the water column where then can be released (de Vicente et al., 2010a). Apart from sediment resuspension, the release of nutrients across sediment–water interface may be favored by anoxic conditions at hypolimnion during the weak thermocline established during summer time period (de Vicente et al., 2003). As a result of the inherent wetland characteristics (shallowness, frequent resuspension events and hypolimnetic anoxia) the use of P binding salts commonly used for in-lake restoration techniques (Al or Fe salts) may be not recommended since P is likely to be released during resuspension or under shifting physicochemical conditions. Instead, new techniques intended to restore shallow and polymictic lakes may be focused on increasing P export from the system. In this context, the use of MPs as P adsorbents and its subsequent removal from the ecosystem seems to be a suitable restoration option.

2.2. Materials

Micronized Fe MPs were obtained from BASF (Germany) and

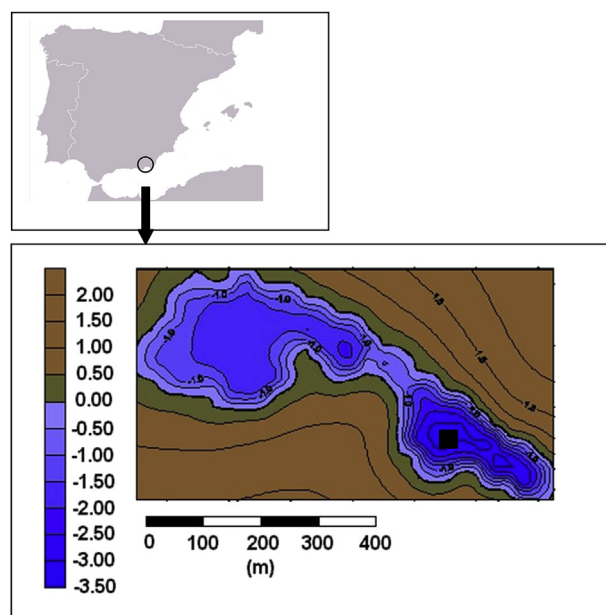


Fig. 1. Geographic location and morphometric map of the study lake. Black square indicates the sampling point at the maximum water depth.

Table 1

General limnological features of the study lake. All data correspond to July 2013 except for DOC which was measured on July 2015. Mean values have been estimated from surface, mid depth (1 m) and bottom samples (2 m). All analysis have been performed following standard methods (APHA, 1989).

	Mean $\pm$ SD
P-PO ₄ ³⁻ ($\mu\text{g L}^{-1}$)	0.59 $\pm$ 0.09
TDP ($\mu\text{g L}^{-1}$)	31.57 $\pm$ 2.77
TP ($\mu\text{g L}^{-1}$)	493.54 $\pm$ 35.99
N-NO ₃ ⁻ (mg L ⁻¹)	0.108 $\pm$ 0.002
TDN (mg L ⁻¹)	4.95 $\pm$ 0.13
TN (mg L ⁻¹)	9.41 $\pm$ 0.45
DOC (mg L ⁻¹)	59.3 $\pm$ 1.49
Chl a ($\mu\text{g L}^{-1}$)	57.2 $\pm$ 19.7

used as P adsorbent. According to the manufacturer, MPs are chemically characterized as follows: 97.5% Fe, 0.9% carbon, 0.5% oxygen, and 0.9% nitrogen. Previous characterization has shown that MPs are spherical in shape and relatively polydisperse in size with a mean particle diameter of 800 ± 10 nm (de Vicente et al., 2010b). Previous data have revealed that MPs surface is negatively charge in the studied pH range (6–9) and the magnitude of charge increases as pH value increases (de Vicente et al., 2010b).

2.3. Sequential extraction procedure of sedimentary P pools

In July 2013, 3 large cores ($\Theta = 5.4$ cm; $h = 50$ cm) were collected, at 2 m depth in Honda lake and sectioned at intervals of 2 cm up to 10 cm obtaining 5 different sediment slices. The three samples of each depth were pooled and homogenized before analysis. A sequential chemical extraction procedure according to (Paludan and Jensen, 1995) was used in order to quantify the concentration of different P pools in the in the upper 10 cm of sediment: P_{→Water} (pore water o-P extracted in distilled water), P_{→BD} (o-P bound to reducible metals such as Fe and Mn extracted in 0.11 M NaHCO₃, 0.11 M Na₂S₂O₄ bicarbonate dithionite solution reagent, P_{→NaOH} (o-P adsorbed to Al oxides, clay minerals and humic acids extracted in 0.1 M NaOH), P_{→NaOH, Humic} (P bound to humic acids precipitated in acidified solution), P_{→HCl} (magnesium and calcium bound o-P extracted with 0.5 M HCl) and P_{→HCl, Res} (refractory organic P extracted with 1 M HCl at 120 °C after combustion at 550 °C, 3.5 h). Finally, organic P labile (Org-P_{labile}) was calculated as the sum of Non-reactive P (NRP) which stems from the difference between Tot-P (wet digestion with 0.18 M K₂S₂O₄) and o-P of the three first steps of extraction. Among all P pools that define total P in sediment, only P_{Mobile} is expected to contribute to internal P loading (Boström et al., 1988b; Rydin, 2000). P_{Mobile} was estimated as the sum of P_{→Water}, P_{→BD} and Org-P_{labile} in the upper 10 cm of sediment (Rydin, 2000; Hansen et al., 2003; Reitzel et al., 2003). Total sediment P (Tot-P_{sed}) and total sediment Fe (Tot-Fe_{sed}) were determined on parallel by ashing the sediment samples (520 °C, 5.5 h) followed by an acid hot digestion with 1 M HCl (120 °C, 1 h). P pools data were normalized according to Tot-P_{sed}, which is supposed to be more accurate.

Soluble reactive P (SRP) was determined spectrophotometrically using the molybdenum blue method proposed by Murphy and Riley (1962). In the same extractants for P measurements, Fe fractions (Fe_{→Water}, Fe_{→BD}, Fe_{→NaOH}, and Fe_{→HCl}) were determined following the spectrophotometric ferrozine method proposed by Gibbs (1979). Finally, sediment was also analyzed for dry weight (DW, %) at 105 °C for 24 h and loss on ignition (LOI, %) at 520 °C for 5.5 h.

2.4. Microcosms experiment with sediment cores

In July 2013, 18 small cores (inner diameter = 5.4 cm, height = 25 cm) were taken at 2 m depth in Honda lake (at the same sampling site as for collecting the 3 large cores mentioned above). Sediment height was adjusted to give 10 cm of the overlying water in all cores. Before running the experiment, and similarly to Rydin and Welch (1999) and Reitzel et al. (2003), we first measured sedimentary P_{Mobile} in three large cores and the mass of adsorbent required was estimated as a function of P_{Mobile} pool. Considering that the maximum P adsorption capacity by MPs (under batch conditions) was 18.83 mg P g⁻¹ Fe (de Vicente et al., 2010b) and that the mass of sedimentary P_{Mobile} in the upper 10 cm of the sediment was 19.51 mg, we obtained that 1.04 g MPs were needed to be added to the cores. As a result, we decided to consider two different treatments, one adding 10 g (T₁) and another adding 20 g (T₂) to check the performance of MPs in excess in order to counteract possible chemical interferences as previous studies have found (de Vicente et al., 2011; Merino-Martos et al., 2015), giving a final Fe: P_{Mobile} molar ratio of 285:1 and 560:1, respectively.

During the experiment, cores were kept in darkness and at room temperature (23 ± 2 °C) for 24 h. In total, six different treatments, which were run in triplicates, were considered. On the one hand, three treatments were bubbled with oxygen (O₂) (oxic treatments): one of them was not amended with MPs, being considered as control (O-Control), while the other two treatments were enriched with 10 g (O-T₁) and 20 g (O-T₂) of MPs. On the other hand, the other three treatments were incubated under anoxic conditions and the same procedure as mentioned before was applied: no addition of MPs (A-Control), addition of 10 g (A-T₁) and addition of 20 g (A-T₂) of MPs. Sediment cores incubated under oxic conditions were continuously bubbled with O₂ during the whole experiment. Anoxic conditions were promoted by adding, at the beginning of the experiment, BD reagent to reach a final concentration of 4 mg L⁻¹, which was previously tested as the right concentration for assuring anoxic conditions. Thus, O₂ concentration was always higher than 4 mg L⁻¹ in all oxic cores and lower than 1 mg L⁻¹ in all suboxic ones during the whole experiment. When MPs were added (T₁ and T₂), they were homogeneously distributed over the entire surface of sediment cores. After 24 h of incubation, MPs were removed from sediment cores by applying a magnetic field gradient exerted by a permanent magnet (volume = 25.6 cm³; NB032, Aiman GZ, Spain). Removal process of MPs was carried out by immersing the magnet twice for 15 s in the cores. Water displaced by magnet immersion was considered in calculations. Initial and final (both before and after removing MPs) P concentrations were determined following the above mentioned method (Murphy and Riley, 1962). P efflux from sediment to water column was finally measured as the change in P concentration in overlying water during 24 h of incubation time. Initial and final (after removing MPs) Fe concentrations were determined for the same period of incubation in order to see the effect of MPs on Fe concentrations in water column. In addition, pH and O₂ concentration (mg L⁻¹) were measured during the experiment using a VWR Symphony multiparametric sensor (VWR International Eurolab S.L.; Spain).

Finally, and in order to assess the effect of adding MPs on changes in sedimentary Fe and P pools (specifically on P_{Mobile} concentration) a sequential extraction procedure described in section 2.3 was carried out in sediment cores from all treatments at the end of the incubation time. In addition, P retention capacity of the sediment was estimated by the molar ratio between Fe_{→BD} and P_{→BD} in the upper 10 cm in the initial fractionation (Jensen et al., 1992).

2.5. Statistical analysis

All data reported in this work have been obtained in triplicates. In order to test significant differences in P fluxes and Fe concentrations in water column as a result of MPs addition, a comparison between control and treatments was carried out using one-way ANOVA and then Least Significant Difference (LSD) post-hoc test. Differences in initial and final Fe concentrations of each treatment and control were tested by applying paired t-test. Significant differences were accepted when $p < 0.05$.

Shapiro–Wilk test and Levene's test were performed to check normality and homogeneity of variances, respectively. In order to satisfy normality assumptions, data were log-transformed before performing statistical analysis. Statistical analysis was done using SPSS software.

3. Results

3.1. Effect of MPs addition on P fluxes across the sediment–water interface

P exchange rates across the sediment–water interface were estimated for two different situations after finishing the incubation period: a) when MPs were still in the sediment; b) after removing MPs from the cores by using magnetic separation. P fluxes across the sediment and water interface are shown in Fig. 2a and Fig. 2b, respectively. When MPs were still in sediment, all treatments amended with MPs evidenced a net P uptake by the sediment in both, oxic and anoxic conditions (Fig. 2a). In particular, P exchanges rates were -1.66 ± 0.34 and $-1.95 \pm 0.19 \mu\text{g cm}^{-2} \text{ day}^{-1}$ in O-T₁ and

O-T₂ respectively; and -0.21 ± 0.58 and $-1.80 \pm 0.34 \mu\text{g cm}^{-2} \text{ day}^{-1}$ in A-T₁ and A-T₂, respectively.

After removing MPs from sediment cores, control and treatments under oxic conditions kept exhibiting a net P uptake by the sediment and no significant differences among neither of them were noticed (Fig. 2b). In anoxic conditions, the highest P release rate ($1.96 \pm 2.52 \mu\text{g P cm}^{-2} \text{ day}^{-1}$) was observed when no MPs were added (A-Control) compared to treatments (A-T₁ and A-T₂). P efflux registered in A-T₂ ($-1.27 \pm 0.28 \mu\text{g P cm}^{-2} \text{ day}^{-1}$) was significantly lower than that found in A-T₁ ($p = 0.043$) and in A-Control ($p = 0.011$). By contrast, no significant differences were found between A-Control and A-T₁.

It is important to consider that P fluxes were measured before and after removing MPs from the cores in order to take into account possible P release during resuspension triggered by MPs removal with the magnet. However, statistical analyses have shown that P exchange rates were not significantly different between these two stages, neither in oxic nor in anoxic conditions in any treatment.

3.2. Effect of MPs addition on Fe concentrations in the water column

In order to assess the effect of MPs addition on Fe concentrations in lake water, Fe concentrations were measured in controls and treatments as initial Fe concentration (before adding MPs) and as final Fe concentration (at the end of the incubation period). While in oxic conditions (both in control and treatments) Fe concentration in the overlying water was always below the detection limit ($1 \mu\text{g Fe l}^{-1}$), in anoxic cores the trend was very different (Fig. 3). Fe concentration did not significantly change in A-Control during the experiment whereas in A-T₁ and A-T₂ treatments there was a significant increase in Fe concentrations from 1.15 ± 0.40 to $8.63 \pm 1.23 \text{ mg L}^{-1}$ in the case of A-T₁ and from 0.88 ± 0.60 to $12.74 \pm 3.43 \text{ mg L}^{-1}$ in the case of A-T₂. As a consequence, at the end of the experiment, Fe concentration in A-T₁ was 10 times higher than in A-Control ($p < 0.001$) whereas in A-T₂ was 15 times higher than in A-Control ($p < 0.001$).

3.3. Sediment characterization

3.3.1. Initial sedimentary P pools

As it can be seen in Fig. 4, Tot-P_{sed} concentration decreased from $1022.26 \mu\text{g P gDW}^{-1}$ at sediment surface to $847.37 \mu\text{g P gDW}^{-1}$ at 10 cm depth. As an average of the first 10 cm, the percentage of each

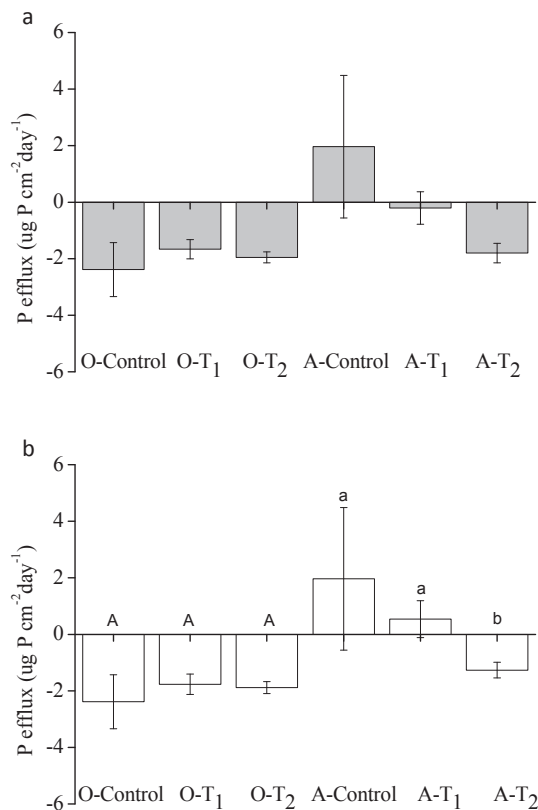


Fig. 2. Sediment P fluxes before (a) and after removing MPs (b). Significant differences ($p < 0.05$) between treatments are indicated with letters. Standard deviation is represented by vertical bars.

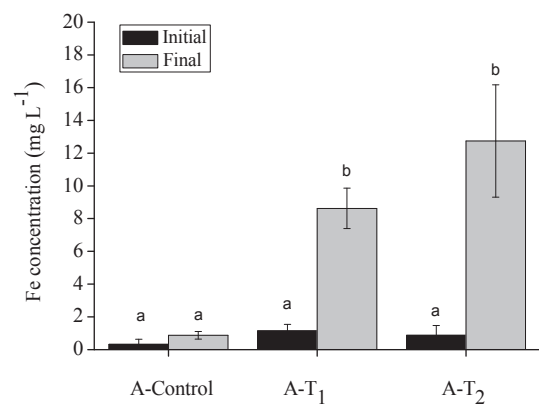


Fig. 3. Fe concentration in water column in control and treatments under anoxic conditions. Standard deviation is represented by vertical bars. Significant differences between initial and final concentrations are written with letters.

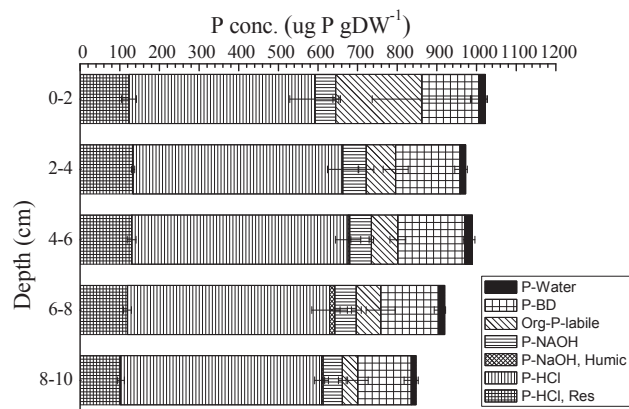


Fig. 4. Initial sedimentary P fractionation of untreated sediment. Standard deviation of each fraction is represented by horizontal bars.

P fraction with respect to Tot-P_{sed} was: 1.6 (P_{→Water}), 16.0 (P_{→BD}), 5.7 (P_{→NaOH}), 0.5 (P_{→NaOH, Humic}), 54.2 (P_{→HCl}), 9.3 (Org-P_{labile}) and 12.8% (P_{→HCl, Res}). Org-P_{labile} concentration reduced with depth. P_{→NaOH, Humic} and P_{→HCl} increased slightly with depth whereas P_{→BD}, P_{→NaOH} and P_{→HCl, Res} fractions kept practically constant at all depths.

3.3.2. Changes in sediment composition induced by MPs addition

The percentage distribution of the seven P pools with respect to Tot-P_{sed} was rather similar in the initial fractionation and the final fractionation in all treatments and controls. This similarity was in accordance to that obtained by Hansen et al. (2003) when applying different treatments (addition of Fe, Al and O₂ application) to sediment cores.

However, some quantitative differences in sedimentary P pools concentrations emerged when comparing treatments and controls in final fractionation. As a way of illustration, Fig. 5 shows P_{Mobile} concentrations at five depth intervals in oxic (Fig. 5a) and anoxic (Fig. 5b) conditions. Controls, both in oxic and anoxic conditions showed higher P_{Mobile} concentrations than treatments (T₁ and T₂) at all depths. Considering the 10 cm of the upper sediment, MPs addition caused a reduction in sediment P_{Mobile} concentration, ranging from 12% in O-T₁ to 16% in O-T₂ with respect to O-Control, and 16% in A-T₁ and the 17% in A-T₂ compared to A-Control. By dividing the sediment in just two depths, the uppermost (0–4 cm) and the deepest layer (4–10 cm), we can see that the highest reduction in P_{Mobile} concentration occurred in the deepest sediment layer in oxic conditions (18% both in O-T₁ and O-T₂). By contrast, an inverse tendency was observed for anoxic conditions where the highest reduction in P_{Mobile} concentration was measured in the upper sediment layer, which reached the 22% and 25% in A-T₁ and A-T₂, respectively.

It is worth to remark that changes in P_{Mobile} pool between treatment and controls were mostly due to changes in Org-P_{labile} fraction, since no differences were noticed for P_{→Water} and P_{→BD} after MPs addition. Because of that, next we focused on Org-P_{labile} fraction. Specifically, considering the upper 10 cm, Org-P_{labile} reduction was 34% in O-T₁ and 44% in O-T₂ compared to O-Control and 32% in A-T₁ and 45% in A-T₂ compared to A-Control. Similarly to what occurred with P_{Mobile} under oxic conditions the higher reduction in Org-P_{labile} took place within the deepest layer accounting for 45% in O-T₁ and 53% O-T₂ compared to O-Control. In anoxic conditions, Org-P_{labile} concentration was reduced in a higher proportion in the upper sediment layer than in the deepest sediment, reaching 37% of Org-P_{labile} reduction in A-T₁ and 54% of

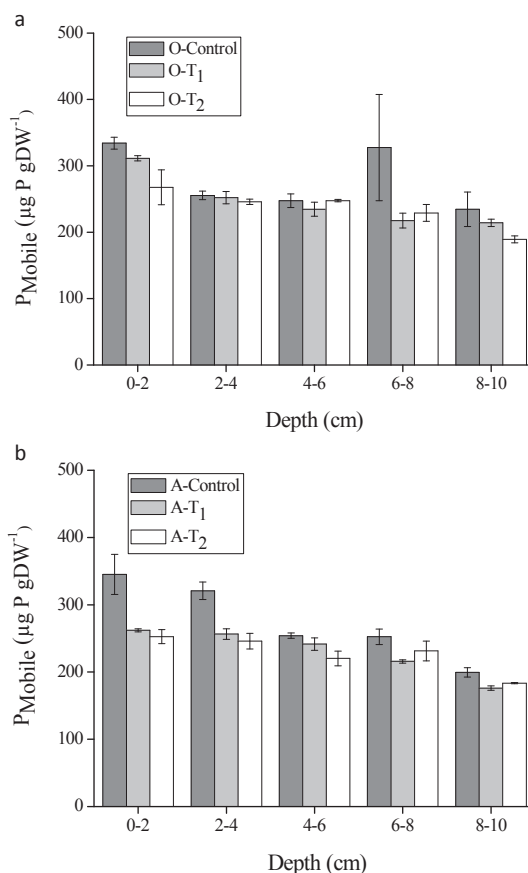


Fig. 5. Changes in P_{Mobile} concentration with depth after removing MPs. Fig. 5a corresponds to oxic treatments and Fig. 5b refers to anoxic treatments. Standard deviation is represented by vertical bars.

reduction in A-T₂. The rest of P fractions do not seem to have suffered any significant change when comparing control and treatments.

Considering sedimentary P_{Mobile} mass that MPs addition (T₁ and T₂) was able to reduce compared to control; we have estimated that, in the whole lake (94,000 m² of surface area and referred to the upper 10 cm of the lake sediment), a total mass of 130, 195, 62

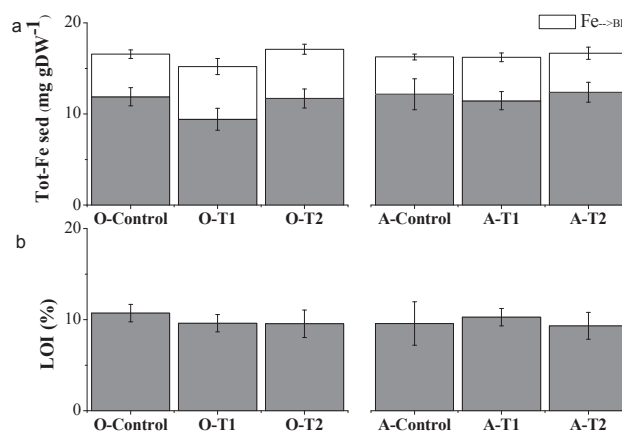


Fig. 6. a) Fe_{BD}, Total sediment Fe (Tot-Fe_{sed}) and LOI (%) in treatments and controls within 0–10 cm depth at the end of the incubation period. Standard deviation (SD).

and 141 kg P in O-T₁, O-T₂, A-T₁ and A-T₂, respectively, would be removed after MPs application.

Changes in Fe_{→BD} and Tot-Fe_{sed} pools as a consequence of MPs performance can be seen in Fig. 6a. By analyzing Fe_{→BD} and Tot-Fe_{sed}, no remarkable differences in Fe concentration were observed between controls and treatments, neither in oxic nor in anoxic conditions over the depth intervals. The same trend was found for the other different Fe fractions (data not shown). Fig. 6b also shows that similar LOL contents were present at the end of incubation period in treatments and controls.

4. Discussion

4.1. Effect of anoxic conditions on P exchange across the sediment and water interface

Comparison of controls (A-Control and O-Control) in which the only different factor was redox potential, highlights the importance of the classical model proposed by Einsele (1936) and Mortimer (1941) which pointed out the close coupling between redox-sensitive Fe compounds and P exchange between sediment–water interface. This classical model has been later confirmed by many other studies such as Boström et al. (1988a), Gomez et al. (1999), Burley et al. (2001) and Hansen et al. (2003).

Under oxic conditions, sediment of Honda lake exhibited a net P uptake. It is very well known that in these conditions, there exists an oxidized microzone in the uppermost sediment layer in which precipitated Fe naturally present in sediment is able to retain P (Mortimer, 1971). It is important to remark that under oxic conditions, sediment P adsorption capacity and thus, P transport across sediment–water interface is mainly controlled by Fe_{→BD}: P_{→BD} molar ratio (Jensen et al., 1992). In Honda lake, this molar ratio was 15:1 which is considerably higher than the molar ratio (8:1) required for trapping P in the sediment (Jensen et al., 1992).

By contrast, in anoxic conditions, P exchange rate across the sediment and water interface was 1.96 $\mu\text{g P cm}^{-2} \text{ day}^{-1}$ (A-Control) which is in the range of those values reported for hypertrophic systems (Carter and Dzialowski, 2012; Nürnberg, 1988, 1997). This positive P efflux and the increase of Fe concentration in water column along the incubation period evidenced the existence of Fe reduction and the subsequent P mobilization from lake sediment to the overlying water (Marsden, 1989; Hupfer and Lewandowski, 2008). In such conditions, P transport from sediment to water column is mediated by the concentration gradient between dissolved P in pore water sediment and overlying water (Eckert et al., 1997; Sondergaard et al., 2001).

As a way of illustration of the relevant effect of internal P loading on the P concentration of the water column, next we present some calculations. Since the lake presents an average of 204 anoxic days per year (de Vicente et al., 2003) and in this study we have measured a P release flux of 1.96 $\mu\text{g P cm}^{-2} \text{ day}^{-1}$ under anoxic condition, the internal P loading is calculated to be responsible for 376 kg P yr⁻¹. However under oxic conditions, natural Fe oxides present in this sediment would retain 360 kg P during this period (161 days yr⁻¹). The net result of both processes would give rise to a P concentration in the water column of 135.6 $\mu\text{g L}^{-1}$, contributing to almost half of the annual mean TP concentration (312 $\mu\text{g L}^{-1}$; de Vicente et al., 2003). However it is important to consider that anoxic conditions promoted by BD addition are likely to be a severe treatment which it may cause an overestimation of these calculations.

4.2. Effect of adding MPs on P exchange fluxes across the sediment–water interface and on Fe concentrations in water column

4.2.1. Oxic treatments

Sediment from Honda lake experienced a net P uptake from the overlying water after MPs amendment (O-T₁ and O-T₂), both before and after removing them from the cores. This behavior highlights the scarce relevance of P release due to the resuspension when removing MPs under oxic conditions. On the other hand, the rather similar P fluxes values in the control and treatments evidenced the negligible effect of adding MPs on P efflux. The reason behind this finding is that in the sediment of the study lake, as it has been already stated, Fe oxides concentration was high enough to trap P under oxic conditions. Regarding Fe concentrations in water column, it was observed that initial and final Fe concentrations kept similar in control and treatments. These data along with the fact that Tot-Fe_{sed} was not significantly increased in treatments compared to control indicates that MPs do not release Fe in oxic conditions.

4.2.2. Anoxic treatments

In anoxic conditions, the addition of MPs caused an important reduction in P fluxes compared to the control (A-Control). While in the case of A-Control P was released from the sediment to the overlying water, in the case of A-T₂ treatment, P mobilized by the reduction of Fe oxides did not go to the water column but was adsorbed on MPs, as it is reflected by a net P uptake by the sediment. Hence, our results have shown that the addition of MPs in a molar ratio of 560:1 respect to P_{Mobile} concentration was enough to inactivate P internal loading. A similar P efflux reduction (100% reduction compared to control) under anoxic conditions has been reported by some authors such as Hansen et al. (2003) (P efflux = $-0.025 \mu\text{g P cm}^{-2} \text{ day}^{-1}$) when using Al: P_{Mobile} molar ratio of 10:1; Reitzel et al. (2003) (P efflux = $-0.097 \mu\text{g P cm}^{-2} \text{ day}^{-1}$) when using Al: P_{Mobile} molar ratio of 4:1 and Gibbs et al. (2011) ($-0.7 \mu\text{g P cm}^{-2} \text{ day}^{-1}$ and $-0.8 \mu\text{g P cm}^{-2} \text{ day}^{-1}$) when adding Phoslock® at a 50:1 and 100:1 Phoslock®: P weight ratio, respectively. It is worth to note that P uptake rate by sediment was a little bit lower in these studies compared to our value. By contrast, P efflux after removing MPs reflected that the 285:1 Fe P_{Mobile} molar ratio was not enough to suppress short-term P efflux (95% of reduction). It is important to remark that P concentration in water column was measured right after removing MPs, and thus higher concentration of P due to resuspension could be measured. Likewise, the 10:1 Fe:P molar ratio proposed by Hansen et al. (2003) as well as the 8:1 Al: P_{Mobile} molar ratio proposed by Reitzel et al. (2003) were not enough to retain P by the sediment (P efflux = $0.053 \mu\text{g P cm}^{-2} \text{ day}^{-1}$ and $0.16 \mu\text{g P cm}^{-2} \text{ day}^{-1}$, respectively) giving a 95% of reduction in both cases.

Final Fe concentrations in water column were remarkably higher in treatments (A-T₁ and A-T₂) compared to A-Control, reflecting that under anoxic conditions MPs were releasing Fe to the water column, probably due to the dissolution of MPs in contact to BD reagent used to guarantee anoxic conditions. Hunt et al. (1995) and Fine et al. (1993) reported that fine grain magnetite (with a similar surface of our MPs) undergo dissolution in the presence of Citrate-BD solution. Fe concentration in freshwater is naturally less than 1 mg L⁻¹, whereas in anaerobic groundwater where the Fe⁺² species predominates it usually ranges 0.5–10 mg L⁻¹ (World Health Organization, 2003; Xing and Liu, 2011). According to some studies, there is no evidence of negative effects of increasing Fe concentrations on the maximum achievable ecological quality for fish, macrophyte and diatom communities although it has been reported a decrease of macroinvertebrate

populations in contact with high total Fe concentrations (WFD-UKTAG, 2012). Therefore, some thresholds have been proposed to guarantee the good state of these communities such as 1 mg L^{-1} total Fe (EPA, 1976). At this point, it is of great importance to consider that the use of BD in this study for achieving anoxic conditions could have increased Fe concentrations more than natural anoxic conditions occurring in lakes, so lower Fe concentrations are likely to be measured when adding MPs in natural anoxic conditions. In addition, it is essential to work in synthesizing new MPs that do not release Fe in anaerobic conditions in order to reduce undesirable effects on biota.

4.3. Effect of adding MPs on sedimentary P pools

From initial sediment fractionation analysis we can conclude that P_{HCl} pool which is not expected to contribute to internal P loading, is by far the most important P form in our sediment. In ecosystems with high alkalinity (as in our case) P can be immobilized in sediment by coprecipitation or adsorption with carbonates at high pH values contributing to the burial of P in sediment (Otsuki and Wetzel, 1972; Eckert et al., 1997). Since in these wetlands the amount of P bound to carbonates is remarkable, potential internal P loading is likely to be closely related to reductions in pH values (Rydin and Welch, 1998). P_{Mobile} pool, which accounted for 8.52 g m^{-2} within the first 10 cm, has an outstanding importance as it can be used for predicting future internal P loading. The three P pools contributing to P_{Mobile} fraction (P_{Water} , P_{BD} , $\text{Org-P}_{\text{Labile}}$) consist of 37% of $\text{Tot-P}_{\text{sed}}$ at surface sediment and decrease with depth up to 21% at 10 cm depth due to the well-known upward transport of P to upper sediment layers (Rydin, 2000), suggesting that these three pools do not contribute to burial flux of P in sediments (Reitzel et al., 2003).

On the other hand, the addition of MPs has caused a reduction in P_{Mobile} concentration both in oxic and anoxic condition even in the deeper sediment layer (10 cm). In fact, the presence of MPs is not restricted to surface sediment as they are characterized by a much higher density (7.8 g cm^{-3}) than sediment (1.1 g cm^{-3}). Moreover, the high ionic strength present in the lake (conductivity of 3.09 mS cm^{-1} , de Vicente, 2004) implies a reduction in the zeta potential value which is involved in electrostatic repulsion interactions between MPs, leading to their aggregation and rapid sedimentation (de Vicente et al., 2011; Gunnars et al., 2002). The high density of MPs compared to the low density of other P-capping agents as Al salts (Lewandowski et al., 2003) entails a different behavior in sediment, causing P inactivation in deeper sediment layers. Phosphorus adsorption mechanisms onto MPs has been previously reported to take place by ligand exchange, in which hydroxyl groups are replaced by P species forming inner-sphere surface complexes at water–oxide interface (de Vicente et al., 2011; Daou et al., 2007). Despite being negatively charged under these experimental conditions of pH ($\text{pH} = 8$), MPs are able to adsorb considerable amounts of P due to specific adsorption (de Vicente et al., 2011; Daou et al., 2007). $\text{Org-P}_{\text{Labile}}$ was the only P sedimentary pool comprising P_{Mobile} which experienced a reduction in treatments compared to controls both in oxic and anoxic conditions. However, no changes in LOI % content between control and treatments have been observed which could be explained by the lower sensibility of the loss on ignition calculation method. The higher affinity of MPs for $\text{Org-P}_{\text{Labile}}$ is likely to be the result of the well-known strong affinity of organic compounds by Fe oxides. In particular, Illés and Tombácz (2003) reported a notable adsorption of organic substances such as fulvic and humic acids (HA) by magnetite at low pH (4.5) but even at higher pH similar to those registered in our experiments (anoxic conditions, $\text{pH} 6.2 \pm 0.18$; oxic conditions, $\text{pH} = 8.15 \pm 0.08$).

Similarly, Merino-Martos et al. (2015) reported a remarkable decrease in P adsorption efficiency, when using the same carbonyl Fe particles as in this experiment, in the presence of high HA concentrations (from 94% when $\text{HA} = 17 \text{ mg C L}^{-1}$ to 12% when $\text{HA} = 35.5 \text{ mg C L}^{-1}$).

4.4. Some considerations for lake restoration

In the framework of the whole available methods for lake restoration, MPs addition could be considered as a method focused on increasing P export for reducing lake P concentration. The use of MPs has several advantages compared with other drastic techniques that aim at increasing P export, such as sediment dredging. High turbidity due to resuspension of finely divided sediment, liberation of nutrients and toxic metals to water column, destruction of benthic fauna and high costs are some of the negative aspects about using sediment dredging (Petersen, 1982). In this sense, MPs minimizes impacts of resuspension and water column since they are more selective with sediment (they have more affinity with sedimentary P forms). Next, we will summarize some advantages of using MPs. First, P can be recovered from the aquatic ecosystem, which allows the later potential use of P as P-containing fertilizers. In this sense, it is nowadays considered that MPs are a non-renewable resource and could be exhausted in the next 50–100 years (Cordell et al., 2009). This situation has become alarming due to the increasing population density, above all in developing and emerging countries, which demands a high food production. So, it is required new challenges to find solutions where the equilibrium P-cycle is reached. Second, MPs can be recovered from the solution reducing both economic costs and toxic effects on the biota. In relation to the economic cost, it is important to consider that before making any whole lake application it is essential to gain also some knowledge about the economic balance. For making a economic balance, we have compared some crucial characteristics (price and P removal efficiency) of MPs and some of the most commonly used P adsorbent for lake restoration such as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (i.e. Rydin, 2000; Reitzel et al., 2005; Egemose et al., 2011) and Phoslock® (i.e. Robb et al., 2003; Lürling and Tolman, 2010). In brief, we can conclude that when re-using MPs more than 2 times it is economically worth to use this adsorbent instead of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or Phoslock®. In relation to the toxic effect on the biota, recent studies have found that MPs concentration have to be added in high concentration to cause negative effect on planktonic and benthonic organisms. In particular, Álvarez-Manzaneda et al. (unpublished results) have measured that the concentration of MPs that produces the immobilization of 50% of the individuals during exposition period (CE_{50} ; OCDE, 2004) was 0.9 and 0.4 g L^{-1} for *Daphnia magna* and *Chironomus* sp., respectively. At this point, it is relevant to note that, considering the MPs: P ratio reported in previous studies (de Vicente et al., 2010; Merino-Martos et al., 2011), the addition of 0.4 g L^{-1} would not be required as it corresponds to extremely high P concentrations. As a result, it is expected that in a whole lake application, MPs will not cause any toxic effect on the biota.

5. Conclusions

Despite the broad use of P-binding compounds for restoring eutrophicated waters, up to date, there is not a universal adsorbent for applying in whatever physico-chemical conditions (i.e. pH, redox potential) and therefore more research in new adsorbents is required. This study has evidenced that internal P loading during the anoxic period contributes to half of the annual mean P concentration in the water column of the study lake. In this sense, the

use of MPs seems to be a suitable technique to apply since it is able of completely suppressing the short-term P efflux under the most undesirable conditions (anoxic) at the 560:1 MPs: P_{Mobile} ratio. However, when Fe oxides naturally present in sediment are enough to uptake P from water column, MPs do not show any effect on P fluxes. Apart from the effect of MPs on P efflux under anoxic conditions, MPs also reduces sedimentary P_{Mobile} concentration in both oxic and anoxic conditions, leading to a reduction in long-term P efflux. The best results have been found when adding MPs at the Fe: P_{Mobile} molar ratio of 560:1, which conducted to the removal of 141 kg of sedimentary P in anoxic and to 191 kg P under oxic conditions for the whole lake area.

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