An enclosure experiment for testing the consequences of using magnetic microparticles on water quality and sediment phosphorus pools

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Abstract

By using microcosm enclosures containing brackish water (6000 µS cm^{-1}) and natural surface sediment from an hypertrophic aquatic ecosystem, this study assessed the effects of adding iron (Fe) magnetic microparticles (MPs) on water quality, with special focus on P concentrations in water column and in the sediment. Two different treatments were considered for a constant 85:1 MPs:P_{Mobile} molar ratio: T-W, where MPs were applied above the surface layer of water, and T-S, where MPs were added directly above the sediment. Our study demonstrated the convenience of adding MPs for reducing both P concentrations in lake water and lake sediment. Both, T-W and T-S exhibited a reduction of 68 ± 6% in dissolved inorganic P concentration (DIP) on average for a 70-days oxic period and a reduction of 80 ± 8% (T-W) and 80 ± 4% (T-S) for a 5-days anoxic period. MPs also decreased reactive silicate (Si) concentration approx. by 50% on average for both periods whereas dissolved organic carbon (DOC) was only reduced by 15% after 24 h of MPs addition. Despite the drastic reduction in DIP concentration due to MPs addition, chlorophyll *a* (Chl *a*) was not reduced because total P (TP) concentration after treatments (> 200 µg L^{-1}; before treatments: > 700 µg L^{-1}) was still higher than that required (0.05–0.1 mg L^{-1}) to see changes in biological community. P bound to Al oxides, clay minerals and humic substances ($P_{\rightarrow NaOH}$) and easily degradable organic P (Org-P_{Labile}) showed a reduction of 15% and 12%, respectively in T-S compared to control. P bound to humic substances ($P_{\rightarrow NaOH,\ Humic}$) was reduced by 11-22% in both treatments. Finally, considering the efficiency in P and MPs removal in both treatments (T-W and T-S), we recommend T-W treatment for a future whole-lake application to ensure the effectiveness of P export (in water and sediment) and the recovery of MPs.

1. Introduction

For combating the worldwide spread problem of eutrophication, large investments in improving wastewater treatment combined with the implementation of other measures to reduce, in particular, the phosphorus (P) input to aquatic ecosystems have been accomplished (Jeppesen et al., 1999; Gulati and Van Donk, 2002; Søndergaard et al., 2005). Although some lakes may respond fast to a reduction in external P loading (Sas, 1989), many other lakes are still eutrophic and exhibit an unsatisfactory water quality (Marsden, 1989; Jeppesen et al., 1991; van der Molen and Boers, 1994). The delayed recovery could be caused by a fish community dominated by zooplanktivorous species which make weaker the top-down control on algal biomass (Benndorf, 1990; Hansson et al., 1998), but also by a continued P release from the sediment (Marsden, 1989; Jeppesen et al., 1991; Søndergaard et al., 2001). As the internal P loading may have a very significant impact on lake water P concentrations and subsequently on lake water quality (Phillips et al., 1994), many restoration focus on increasing P retention by the sediment. Among these methods, we highlight the next: hypolimnetic aeration (Liboriussen et al., 2009), calcium addition (Dittrich et al., 2011), nitrate (NO_3^-) addition (Foy, 1986), iron (Fe) addition (Boers et al., 1992), aluminum (Al) addition (Egemose et al., 2011) and Phoslock® addition (Spears et al., 2013, 2015).

Among all of the above mentioned methods, those most frequently used today are based on increasing sedimentary P binding capacity (P inactivation methods) by the addition of different compounds. However, the P removal efficiency of most P sorbing materials is typically related to pH, potential redox and the presence of other dissolved ions (Westholm, 2006; de Vicente et al., 2008; Vohla et al., 2011; Lürling et al., 2014). In particular most frequently used adsorbents (Al and Phoslock®) do not efficiently remove P at high pH values (Ross et al., 2008; Reitzel et al., 2013) which are typically encountered in typical hypereutrophic aquatic ecosystems. Moreover, after P inactivation, adsorbents remain within the sediment, and this implies that they could be eventually released to the 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).

In this context, several studies have recently proposed the convenience of using magnetic particles (MPs) for removing P from aqueous solutions by first adsorbing P and by the later application of a magnetic separation gradient, minimizing alteration in water quality and enabling their reuse in subsequent adsorption processes (de Vicente et al., 2010). Some of the advantages of using MPs for lake restoration are as follows: (i) MPs can efficiently adsorb P under both batch and flow conditions (de Vicente et al., 2010; Merino-Martos et al., 2011) so they can be used for trapping P in rainfall ponds and hence for controlling P input through run-off. Also, they can be applied in water treatment plants and/or point sources under continuous flow conditions; (ii) MPs are able to adsorb considerable amounts of P for pH > 7, despite being negatively charged, due to specific adsorption (Daou et al., 2007; de Vicente et al., 2010) (iii) P adsorption by MPs does not depend on redox conditions (Funes et al., 2016); (iv) MPs addition causes a reduction in sedimentary P_{Mobile} concentration (under both oxic and anoxic conditions) hence contributing to a potential reduction in long-term P efflux; (v) Based on a preliminary economic balance, Funes et al. (2016) found that when re-using MPs more than 2 times, it is economically worth to use this adsorbent instead of $AlCl_3 \cdot 6H_2O$ or Phoslock® and (vi) No toxic effect on the planktonic and benthonic organisms are expected to be caused after MPs addition (Alvarez-Manzaneda et al., unpublished results).

Before using MPs in a whole-lake restoration project, it is also important to remark that some of the major ions present in natural waters, in particular humic acid (HA) and reactive silicate (Si), cause a reduction in the effectiveness of P adsorption by MPs. In the context of the MPs used in this work, this has been observed both in complex natural matrices (de Vicente et al. 2011) and single-ion laboratory experiments (Merino-Martos et al. 2015). With this in mind, it would not be surprising that the addition of MPs may influence not only P cycling but also the cycling of other nutrients.

The goal of this study was to assess the effectiveness of MPs application on improving water quality of a hypertrophic Mediterranean lake. For this aim, a large enclosure, containing both lake water and lake sediment, was undertaken. During the experiment, which lasted for 84 days, oxic and anoxic conditions were simulated and physico-chemical and biological variables were monitored in order to evaluate the long-term effect of MPs addition on nutrient cycling; especially on P cycle. The specific objectives of the study include: (i) to test the effect of MPs addition on lake water P concentration; (ii) to evaluate the effect of MPs application on sedimentary P pool; (iii) to assess the effects of MPs addition on nutrient cycling (carbon C, nitrogen N, Si) and (iv) to establish the best working conditions for achieving both the highest MPs removal and the highest improvement in water quality.

2. Materials and Methods

2.1 Sampling site

Honda lake is a shallow (surface area = 9 ha, Z_{mean} = 1.3 m; Z_{max} = 3.2 m), hypertrophic and brackishwater (6000 µS cm^{-1}) wetland situated in the coast of Almería (Southeast of Spain; de Vicente et al., 2003; Funes et al., 2016). The catchment area is principally dominated by intensive agricultural areas although the lake was designated as Natural Reserve (1989) and Ramsar Site (1994). Apart from the high external P inputs, internal P loading has also special importance due to frequent resuspension events and the anoxic periods during summer in which a large amount of sedimentary P is continuously released to the overlying water (de Vicente et al., 2006).

2.2 Materials

MPs used as P adsorbents (HQ grade, BASF, Germany) were micronsized soft magnetic spherical particles with negligible coercitive field and remnant magnetization (i.e. magnetization becomes zero when removing the magnetic field). More details on the particles used can be found in de Vicente et al. (2010) and Merino-Martos et al. (2011).

A specially designed device was constructed to remove MPs from the sediment in the enclosures (Fig. 1). This device essentially consists in a magnetic rake (Fig. 1a). It has a maximum diameter of 20 cm and contains a platform (with a handle) provided with an array of 89 cylindrical Neodimium magnets individually inserted on its base. A one-piece hard-plastic shell (1 mm thickness) protected the magnets from the direct contact with MPs in order to facilitate MPs recovery and cleaning. A detail of the base and hard –plastic shell is provided in Fig. 1b. In Fig. 1c we show a surface plot of the magnetic field density on the hard –plastic shell. Fig. 1d shows the magnetic field density profiles in the x- and diagonal (45º) directions. Figs. 1c and 1d demonstrate that the interference between the magnets is minimal. The size of the magnets (diameter 4 mm, height 25 mm), arrangement (cubic array) and separation between them (14 mm) were modeled with Comsol Multiphysics software (COMSOL Inc., Burlington, MA) in order to ensure an optimum magnetic flux density gradient of approximately 20 T/m to remove the maximum number of MPs.

2.3 Microcosm enclosures experiment

On July 2015, 100 dm^3 of surface sediment were collected with an Ekman dredge at the deepest site of the lake. Surface water was also collected near the shore with a peristaltic pump and kept at 14 ºC until use. Sediment was thoroughly homogenized in a big tank before dividing it up among fifteen PVC enclosures (Ø = 38 cm; h = 58 cm). Once in the laboratory, 6600 cm^3 of surface sediment and 40 L of surface lake water were added to each enclosure. These enclosures were randomly distributed through space in an out-door roofed area to avoid any bias.

After one-week of stabilization period (at day 0), the physico-chemical parameters were measured and the enclosures were subjected to their corresponding treatment. This physico-chemical analysis reflects the initial state prior to the treatments application. Three different treatments (n = 5 replicates per treatment) were considered: (1) MPs addition over the surface water (T-W); (2) MPs addition over the surface sediment (T-S); and (3) No addition of MPs. The later treatment (#3) served as the control. MPs were added to the enclosures in aqueous dispersion (distilled water, 120 g L^{-1}) by using a peristaltic pump and a grid to guarantee a homogeneous distribution of the MPs in the replicates. The MPs:P_{Mobile} molar ratio applied was 85:1. This is three times higher than that proposed by de Vicente et al. (2010) when testing P adsorption efficiency by MPs in batch experiments. We decided to overdose the proposed ratio to counteract possible chemical interferences effects (de Vicente et al., 2011).

After a contact time of 24 h (at day 1), P loaded MPs were removed by fully immersing the magnetic rake into the enclosures just over the sediment surface. For consistency, the rake was passed only once as this already resulted in a MPs removal above 90%. Of course, passing the rake more than one would result in a removal enhancement.

In the following days the enclosures were subjected to an intensive study by monitoring the time evolution of physico-chemical parameters. The whole subsequent experiment comprised two stages: an initial 70 days-oxic period (from day 0 to day 70) in which the enclosures were continuously air bubbled, and a 5 days-anoxic period (from day 79 to day 84) where the enclosures were continuously N_2 bubbled. It is worthy to highlight that from day 70 enclosures were N_2 bubbled until stable anoxic conditions were reached at day 79.1.5 L of water was sampled from each enclosure on days: 2 (i.e. 24 h after MPs removal), 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 79, 81 and 84 to analyze physico-chemical parameters. Water removed by sampling and evaporation was weekly replaced by previously filtered (30 µm) lake water. Temperature, pH, dissolved oxygen (DO) concentration, conductivity and total dissolved solids (TDS) were measured with a multi-parameter probe (Hanna Instrument, HI 9829). Total suspended solids (TSS) were determined by filtering 50 mL of water sample through pre-weighed filters (Whatman GF/F, 0.7 µm pore size). The residue retained in the filters was dried at 105 ºC for 24 h and the TSS was estimated. Determination of chlorophyll *a* (Chl *a*) was achieved by filtering 50 mL of water sample (Whatmann GF/F, 0.7 µm pore size). The filters were placed in a glass vial with 5 mL of 90% acetone at 4º C in darkness for 24 h. Extract was filtered and measured in a spectrophotometer (Biochrom-Libra S50) at 630, 645, 665 y 750 nm. Chl *a* was calculated according to Jeffrey and Humphrey (1975):

$$Chl\,a = \frac{(11.85\,E_{665\,o} - 1.54\,E_{645\,o} - 0.08\,E_{630\,o})\,v}{V Z} \quad (1)$$

Here $E_{665\,o}$, $E_{645\,o}$ and $E_{630\,o}$ correspond to the absorbances (corrected for turbidity at 750 nm) at 665, 645 and 630 nm, v is the extracted volume (5 mL), V is the volume of filtered water (0.05 L) and Z is the cuvette pathlength (1 cm). Color samples were filtered (Whatman GF/F, 0.7 µm pore size) and measured in a spectrophotometer at 440 nm in 1-cm cuvettes. Water color was expressed as absorption coefficient (a_{440}) in units of inverse meters (m^{-1}) according to the following equation (Reche and Pace, 2002):

$$a_{440} = \frac{2.303\, A_{440}}{Z} \tag{2}$$

where A_{440} is the measured absorbance at 440 nm and Z is the optical pathlength in m. Dissolved organic C (DOC) was only measured at days 0, 2 and 7, by filtering the samples through precombusted Whatman filters GF/F, acidified to pH < 2 and measured with a total organic C analyzer (Shimadzu TOC-V, CSH, Japan). Total dissolved Fe (Tot-Fe_{dis}) was measured by the ferrozine method (Gibbs, 1979). Dissolved inorganic P (DIP) was analyzed by molybdenum blue method (Murphy and Riley, 1962). Total P (TP) and total dissolved P (TDP) were determined after the digestion of unfiltered/filtered aliquots, respectively, with potassium persulphate (APHA, 1995). Dissolved organic P (DOP) was calculated by subtracting DIP to TDP. Total particulate P (TPP) was calculated as the difference between TP and TDP. In relation to the dissolved inorganic N (DIN) pool, NH_4^+-N was determined by phenate method (Rodier, 1989), NO_3^--N was determined by ultraviolet spectrophotometric screening method (APHA, 1995) and NO_2^--N was analyzed by sulfanilamide method (Rodier, 1989). Total N (TN) and total dissolved N (TDN) were determined by ultraviolet method after digestion of unfiltered/filtered aliquots, respectively (APHA, 1995). Dissolved organic N (DON) was determined by subtracting DIN to TDN. Total particulate N (TPN) was calculated as the difference between TN and TDN. Major cations [sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+})] and anions [sulphate (SO_4^{2-}) and chloride (Cl^-)] were measured by ion cromatography (IC; 940 Professional IC Vario, Metrohm). Finally, reactive Si was determined by using a spectrophotometric method described by Koroleff (1983), after a reaction with ascorbic acid and molybdate.

Sedimentary P fractions were also determined within the first 6 cm of sediment, at the beginning (initial fractionation) and at the end of the experiment, following Paludan and Jensen (1995). In particular, the following fractions were obtained: orthophosphate (o-P) extracted from porewater in distilled water ($P_{\rightarrow Water}$), o-P bound to reducible metals such as Fe and Mn ($P_{\rightarrow BD}$) extracted in 0.22 M bicarbonate dithionite solution (BD), P adsorbed to Al oxides, clay minerals and humic acids extracted in 0.1 N NaOH ($P_{\rightarrow NaOH}$), P bound to HA precipitated in acidified solution ($P_{\rightarrow NaOH, Humic}$), o-P bound to magnesium and calcium extracted in 0.5 N HCl ($P_{\rightarrow HCl}$), and refractory organic P extracted with 1M HCl at 120 ºC after combusting the pellet at 550 ºC for 3.5 h ($P_{\rightarrow HCl, Res}$). Finally, organic P labile (Org-P_{Labile}) was calculated as the sum of non-reactive P (NRP) coming from the three first steps of extraction which resulted from substracting o-P to Total P (wet digestion with 0.18 M $K_2S_2O_4$). P_{Mobile}, the only fraction that is expected to contribute to internal P loading, was calculated as the sum of $P_{\rightarrow Water,}$ $P_{\rightarrow BD}$ and Org-P_{Labile} within 6 cm depth. Additionally, sedimentary Fe fractions were similarly determined in the sequential fractionation. Sedimentary total P (Tot-P_{sed}) and sedimentary total Fe (Tot-Fe_{sed}) were measured on parallel extractions by combusting the sediment samples (520 ºC, 5.5 h) followed by acid hot digestion with 1 M HCl (120 ºC, 1 h). P and Fe data were normalized with Tot-P_{sed} and Tot-Fe_{sed} data.

2.4 Data analysis

Statistical analyses were done with Statistica 7.1 software (Stat Soft Inc., Tulsa, USA). Differences in water chemical parameters due to treatments application over time (split plot design: one between-subjects factor and one within-subjects factor) were tested by using repeated measures ANOVA (RM ANOVA) with Fisher´s Least Significance Difference (LSD) post hoc test. The effect of a specific treatment on a dependent variable was assumed significant when inter-treatments significant differences were found in more than 2 consecutive sampling days. Since sphericity assumption was usually violated, the Greenhouse-Geissler correction of the degrees of freedom was used (when epsilon < 0.75). Changes in sedimentary P and Fe pools were explored with one-way ANOVA and LSD post hoc test and considered significant when $p < 0.05$.

3. Results

3.1 Changes in water column

Table 1 shows the averaged values of all physico-chemical and biological parameters (Chl *a* concentration) measured in the overlying water during the oxic and the anoxic period. For completeness, the associated statistical results are contained in Table 2.

With regards to P, the time-evolution of DIP, TDP and TP for control and treatments is shown in Fig. 2. A significant effect of treatments on DIP concentrations and also a significant variation of DIP concentrations over time were observed (c.f. Table 2). DIP concentration was substantially reduced in T-W and T-S as compared to control during several sampling days (see Fig. 2). It is noteworthy to highlight that DIP concentrations were similar in all enclosures before treatments application (day 0), however a notable reduction took place in T-S and T-W (65% of reduction) compared to control just 24 h after MPs removal (day 2). On average, DIP was reduced 68% in both MPs treatments compared to control for the 70-days oxic period whereas a reduction even greater was found for the 5-days anoxic period in which DIP was reduced 80%. Treatment x time interaction was also significant (c.f. Table 2) suggesting that the magnitude of the differences between treatments and control are influenced by time, being the magnitude of the differences higher over time. Data suggest that although differences in DIP between control and MPs treatments existed within the first two weeks, the most remarkable differences took place from day 56 onwards. No significant differences in DIP were noted between amended MPs treatments (T-W and T-S). In terms of accumulated DIP fluxes (data not shown), values changed from 14.0 µg cm^{-2} in control to 4.6 µg cm^{-2} in T-W and to 2.9 µg cm^{-2} in T-S, (67% and 79% of P flux reduction, respectively) in the oxic period, and from 5.2 µg cm^{-2} in control to -2.2 in T-W and -0.9 in T-S (100% of P efflux reduction) in the anoxic period. Inter-treatments differences in TDP and TP were mostly due to changes in DIP concentrations since neither differences between treatments nor treatment x time interaction were found for TPP and DOP (data not shown). On average, TDP and TP were reduced 62% in both T-W and T-S compared to control for the oxic period whereas for the anoxic period a reduction of 70% and 77% was found for T-W and T-S, respectively.

Changes in the concentration of the different N fractions (DIN, TDN and TN) over time are shown in Fig. 3. No significant effect of treatments were found for any N pool as significant inter-treatment differences were only found at 2 sampling days for DIN and TN (see Table 2). Specifically, at day 7 T-W and T-S showed higher DIN and TN than control, and on day 21 DIN was higher in T-S than in control. Changes in TN between treatments were attributed mostly due to changes in DIN since treatments did not have any effect on DON and TPN (data not shown). It is noteworthy that all N forms varied synchronically over time in all the enclosures. In particular, the average DIN, TDN and TN concentrations narrowly ranged between 1.5-1.8 mg L^{-1}, 2.5-2.7 mg $L^{-1}$and 3.3-3.8 mg L^{-1}, respectively, in all enclosures.

Si concentration was significantly affected by treatments in almost all sampling days (Fig. 4a) and it also changed over time (Table 2). On average, Si was reduced 45% in both MPs treatments compared to control for the oxic period. In the anoxic period, Si concentration was 61% lower in T-W and 68% in T-S compared to control. However, no differences in Si between MPs treatments were noticed. A significant effect of treatment x time interaction was observed, indicating a significant effect of time on the magnitude of the differences between treatments which tend to increase over time.

In relation to DIN:DIP molar ratio, a sharp increase of 4-fold in T-W and 3-fold in T-S compared to control took place 24 h right after MPs removal and it was maintained at a high level in both MPs treatments through all the oxic period with an average of 48:1 and 52:1 respectively (Fig. 4b). In the anoxic period the DIN:DIP molar ratio changed to 27:1 and 33:1 in T-W and T-S, respectively. In the control, DIN:DIP molar ratio was much lower than in treatments with an average of 13:1 for the oxic period and 6:1 for the anoxic period.

Temporal changes in Chl *a* concentration are represented in Fig. 5. Chl *a* was not significantly affected when adding MPs but it synchronically changed over time in all enclosures (Table 2). No significant effect of treatment x time interaction has been found.

In relation to the physico-chemical variables, a gradual reduction in temperature over time was registered in all the enclosures due to seasons change from summer to autumn. pH was not significantly affected by treatments (Table 2) being in all enclosures very close to 9 (Table 1). Dissolved O_2 concentrations kept constant at 7.5 mg L^{-1} and 1 mg L^{-1} during the oxic and anoxic conditions, respectively. Conductivity, TDS, TSS, color and major cations and anions concentration significantly changed over time but no significant differences were found between treatments (Table 2). A significant effect of MPs addition on DOC concentration was also observed (Table 2). DOC significantly changed from 77.7 mg L^{-1} (control) to 65.0 mg L^{-1} in T-W (LSD p = 0.0039) and T-S

(LSD p = 0.0033) at day 2 (24 h after MPs removal), giving a 15% of DOC reduction in both MPs treatments. A visible change of DOC over time was also noticed but no effect of treatment x time interaction on DOC was observed. Tot-Fe_{dis} concentration was negligible (below the detection limit) not only in the oxic but also in the anoxic period in treatments and control (see Table 1). Inter-treatment differences in SO_4^{2-} and water color were only noticed on day 84 (SO_4^{2-}: LSD p = 0.0010; Water color: LSD p = 0.0181). Specifically, SO_4^{2-} was higher in control (853 mg L^{-1}) than in T-S (687.89 mg L^{-1}). Similarly, water color was high in control (4.2 m^{-1}) compared to T-S (3.1 m^{-1}). However, no significant effect of treatment on these two variables was considered because they were isolated cases.

3.2 Changes in sedimentary pools

Initial fractionation of the sediment (data not shown) revealed a Tot-P_{sed} of 810.42 µg P g DW^{-1} within 6 cm depth. P_{Mobile} pool accounted for 23.7% of the Tot-P_{sed}. The higher amount of P was contained in $P_{\rightarrow HCl}$ (52.2% of Tot-P_{sed}) and in $P_{\rightarrow BD}$ fraction (19.8% of Tot-P_{sed}) followed by $P_{\rightarrow HCl,\ Res}$ (13.4% of Tot-P_{sed}), $P_{\rightarrow NaOH,\ Humic}$ (6.4% of Tot-P_{sed}), $P_{\rightarrow NaOH}$ (4.4% of Tot-P_{sed}), Org-P_{Labile} (3.4% of Tot-P_{sed}) and $P_{\rightarrow Water}$ (0.6% of Tot-P_{sed}). Tot-Fe_{sed} was 15.78 mg g DW^{-1} with most of the Fe in $Fe_{\rightarrow HCl,\ Res}$ (40.5% Tot-Fe_{sed}), in $Fe_{\rightarrow BD}$ (36.1% of Tot-Fe_{sed}) and in $Fe_{\rightarrow HCl}$ (18.1% of Tot-Fe_{sed}). The rest of Fe pools accounted for less than 3% of Tot-Fe_{sed}.

Sequential fractionation of P pools at the end of the experiment showed a similar P fractions distribution between treatments (Fig. 6a). No significant differences were found in Tot-P_{sed} concentration between control (1150.5 µg P cm^{-2}) and T-S (1152.3 µg P cm^{-2}). Although not statistically significant, a slightly less Tot-P_{sed} concentration was observed in T-W (1072.3 µg P cm^{-2}) compared to control and T-S. $P_{\rightarrow NaOH,\ Humic}$, $P_{\rightarrow NaOH}$, and

Org-P_{Labile} fractions were significantly lower in T-S (21%, 15% and 12%, respectively) than in control. $P_{\rightarrow NaOH,\ Humic}$ fraction was also decreased in T-W (11%) compared to control. In T-S, $P_{\rightarrow HCl,\ Res}$ fraction was 5% higher than T-W but not than control. No significant changes were observed for the other P fractions.

In contrast, important changes in the final fractionation were measured for Fe pools (Fig. 6b). Tot-Fe_{sed} concentration was not significantly different between T-W (23.6 mg cm^{-2}) and control (19.4 mg cm^{-2}) whereas Tot-Fe_{sed} in T-S (54.5 mg cm^{-2}) was 3-fold higher than in control and twice higher than in T-W. This outstanding increase of Fe concentration in T-S was specifically found in $Fe_{\rightarrow BD}$ and $Fe_{\rightarrow HCl}$ fractions. In particular, an increase of 20.2 mg Fe cm^{-2} in $Fe_{\rightarrow HCl}$ was measured for T-S compared to control and T-W. Although $Fe_{\rightarrow BD}$ in T-W was also significantly higher than in control (increase of 3.4 mg cm^{-2}), T-S showed the highest increase in $Fe_{\rightarrow BD}$ compared to control (increase of 14.4 mg cm^{-2}). No significant differences were observed for the rest of Fe fractions.

Finally, and in relation to the recovery of MPs in T-W and T-S by using the magnetic rake, 91% of the MPs were recovered in T-W while, as expected, a much lower MPs recovery efficiency was noted for T-S (32%).

4. Discussion

Up to date, there exists a wide variety of methods for restoring eutrophic aquatic ecosystems but no universal and efficient method has been already proposed, so more knowledge about novel restoration tools is required. In addition, only very few studies (Egemose et al., 2011; Lürling and van Oosterhout, 2013) have monitored the effects of adding P sorbing materials on nutrient cycling apart from P cycle during lake restoration. Therefore, and previous to a whole-lake restoration strategy, it is imperative to assess the final effect of any P adsorbent on water quality.

4.1 Changes in water column

This study confirmed the convenience of adding MPs for reducing P concentration in lake water and lake sediment. Similarly to what occurs with most P adsorbents, after the addition of MPs, a sharp decrease in DIP concentrations has been observed in both treatments but no effect on other P fractions, such as DOP or TPP, have been found. However, other studies have reported that adsorbents such as Al hydroxide [$Al(OH)_3$] adsorbs and precipitates both DIP and dissolved organic-P compounds (Reitzel et al., 2009).

It is important to consider that although sedimentary Fe_{BD}:P_{BD} molar ratio was 19:1 which according to Jensen et al. (1992) reflect that internal P-loading may be controlled by P adsorption onto oxidized surface sediments, lake water DIP concentrations were quite high (> 200 µg L^{-1}) in control during oxic conditions. The addition of MPs drastically reduced P fluxes (67-79% in T-W and T-S, respectively) during the oxic period and a net P sedimentary uptake was recorded during anoxic conditions. These results are in agreement with those found by Funes et al. (2016) who observed that when adding MPs, in anoxic conditions, sediment act as a sink for P. If we keep in mind that typical hypertrophic aquatic ecosystem, the most imperious systems to be restored, are characterized apart from the high pHs, as mentioned before, by prevailing anoxic periods, it is decisive to assess the ability of the selected P adsorbent to retain P under such adverse conditions. In this sense, it is fair to recognize that both Al (Hansen et al., 2003) and Phoslock® (Ross et al., 2008) have been also verified to be able to trap P in anoxic conditions.

Changes in water quality may be the result of external forcing instead of the MPs addition. In fact the synchrony of a given parameter among spatially distant ecosystems is considered indicative of a significant (external) climatic control in the region (Baines et al., 2000). In our case, the circumstance that a certain parameter is significant and positively related in treatment and control may suggest the existence of an external forcing. In particular, we found synchronous dynamics in Chl *a* concentration for all treatments and control ($p < 0.05$) and the slope of the regression line was for all cases close to 1 (0.84 ± 0.11). A similar pattern was observed for NO_3^-, DIN and TN fractions, where a significant and positively relationship was detected between treatments and controls. However, no effect of MPs addition on N forms and Chl *a* concentration have been found.

The absence of any effect of MPs addition on Chl *a* is coherent with the lack of effect on TPP concentrations. It is very well-known the strong relationship between TP concentrations and Chl *a* in lake water, so reducing the P concentrations in the lake water is the most important strategy for eutrophication control (Hupfer and Hilt, 2008). Despite this worldwide accepted tendency, there exists a high variance between one specific P concentration and the resulting Chl *a* concentration illustrating that other environmental factors and different feedbacks can also affect the primary production (Hupfer and Hilt, 2008). In addition, MPs addition caused an important and significant reduction in DIP and consequently on TP concentrations, but TP concentrations were still very high in treatments (> 200 $\mu g\ L^{-1}$). Previous studies have reported that significant and sustained changes in the biological community and water transparency of shallow, temperate, freshwater lakes may not appear unless TP is reduced below 0.05–0.1 $mg\ L^{-1}$ (Jeppesen et al., 2000) or, for deep lakes, 0.02–0.03 $mg\ P\ L^{-1}$ (Sas, 1989). As a result, in order to get a significant reduction in Chl *a* concentration it would be necessary to: (i) continue long-term monitoring of changes in water quality, (ii) repeat MPs addition or (iii) add a higher MPs dose in the first application.

As DIN concentrations were rather similar in control and treatments but DIP concentrations were lower in treatments than in control, DIN:DIP ratio was notably higher in treatments than in control. According to the Redfield 16:1 N:P molar ratio to meet the phytoplankton´s metabolic requirements, the average DIN:DIP molar ratio in control for the whole period (oxic and anoxic) suggested N limitation. By contrast, the average DIN:DIP molar ratio in both treatments (T-W and T-S) exceeded well above the Redfield ratio, pointing out a potential change in limiting nutrients from N (in control treatment) to P in microcosms treated with MPs. However, in terms of absolute concentration, there is no nutrient deficiency in enclosures treated with MPs since the average DIP and DIN concentrations for the whole period surpassed the minimum concentrations needed for phytoplankton growth proposed by Reynolds (1992, 1999), being those 3 µg P L^{-1} for DIP and 80 µg N L^{-1} for DIN concentrations.

Nutrient-loading ratios can exert a strong selective effect on natural communities of phytoplankton and, in turn, can affect the biomass yield for the nutrient limiting most species (Smith, 1982; Hecky and Kilham, 1988). Del Arco et al. (unpublished results) have found that during this particular study, microcosms were dominated by cyanobacteria, even thought there was a significant decrease of P in the treatments (around 70% with respect to the controls in DIP), it did not yield a phytoplankton abundance decrease neither a community change. Nevertheless, there were marginal (p-value ranged between 0.05 and 0.1) decrease of cyanobacteria on T-S on specific sampling days. It may suggest that cyanobacteria were sensitive to the decrease of nutrients availability but need longer period to show relevant community changes.

MPs addition led to significant changes not only in lake water P concentrations but also in Si concentrations. This result is not surprising. In fact, similar observations were described by de Vicente et al. (2011) and Merino-Martos et al. (2015) when using the same MPs in natural waters (complex matrix) and in single-ion experiments, respectively. These authors observed that P removal efficiency was reduced from 81% to 22% when the Si concentration increased from 5 to 10 mg L^{-1}. In the literature it is very well documented that Si and P have the same specific adsorption behavior, and competition for adsorption sites should occur (Sigg and Stumm, 1981; Cornell and Schwertmann, 1996; Hartikainen et al., 1996). For example, de Vicente et al. (2008) concluded that Si significantly decreased the effectiveness of P adsorption by $Al(OH)_3$ in single-ion experiments. In a whole-lake experiment, Egemose et al. (2011) observed that after Al treatment to a eutrophic lake (Lake Nordborg, Denmark), the concentration of Si was significantly reduced from 1.5-4.4 mg L^{-1} to 0.2-0.5 mg L^{-1}. Despite of the strong influence of MPs addition on Si cycle, Si concentration was always higher than 2 mg L^{-1} during our microcosm experiment in both T-S and T-W, so no limitation for diatom was likely to occur. Although different diatom species have different Si requirements, Pearson et al. (2016) assumed values of 0.04-0.1 mg Si L^{-1} as the likely range of diatom Si limitation. Moreover, concentrations of Si must be lower than 0.23 mg L^{-1} (0.5 mg L^{-1} SiO_2) to promote the abrupt decline of diatom dominance during the phytoplankton spring maximum (Wetzel, 2001).

Apart from Si, MPs addition also caused changes in DOC concentration while no significant changes in water color have been detected. DOC initial concentration in the study lake (67.0 mg C L^{-1}) was much higher than other used in previous single-ion experiment (17 and 35.5 mg C L^{-1}; Merino-Martos et al. (2015). In spite of it, MPs addition promoted a reduction in P concentration, as it is mentioned before, of 68%. In relation to changes in DOC, 24 h after MPs removal, a 15% reduction of DOC concentration was detected. The adsorption of HA on Fe oxides (Zhang et al., 2009), $Al(OH)_3$ (de Vicente et al., 2008) and Phoslock® (Lürling et al., 2014) has been widely reported in literature and it is known that HA can bind metals over the entire pH range. However, it is fair to recognize that there are also publications that demonstrated negligible interactions between HA and P adsorption (Borggaard et al., 1990, 2005). In this sense, a very recent study has evidenced that P adsorption by Fe_3O_4@SiO_2 coated magnetite nanoparticles functionalized with hydrous lanthanum oxide is scarcely dependent on HA concentration (Lai et al., 2016). In fact, P removal efficiency was reduced only 7% in the presence of 50 mg C L^{-1}.

4.2 Changes in sedimentary pools

Probably, the major advantage of using MPs particles compared to sediment capping/inactivating agents is that P is permanently removed from the ecosystem. Following the addition of MPs, no significant changes in Tot-P_{sed} concentration was observed in treatments compared to control. However, a significant reduction in some sedimentary P pools was noticed. As a rough estimation, we have calculated that MPs addition in T-W compared to control, considering 94,000 m^2 as lake area (de Vicente et al., 2003) and referring to the upper 6 cm of the lake sediment, would contribute to a removal of a total mass of 73.4 kg P. By contrast, from the comparison of Tot-P_{sed} concentration in T-S and control, we can infer that no changes in the total mass of sedimentary P occur. The explanation for this observation is that in T-S, and due to the much lower percentage of MPs recovery (31%), most of MPs are still retained in the sediment together with the adsorbed P. For a complete removal of the MPs, the magnetic rake had to be used at least twice. At this point, it is necessary to consider that Funes et al. (2016)

found, in a laboratory experiment with sediment cores collected from the same study lake, a higher reduction in the total mass of P (ranging from 62 to 195 kg P referred just to the P_{Mobile} and to the first 10 cm sediment layer) but a much higher MPs dose was applied (MPs:P_{Mobile} molar ratio of 285:1 and 560:1 compared to 85:1 of the present study).

It is also important to note that the addition of MPs also affected Tot-Fe_{sed} concentration. In particular, a significant increase in T-S compared to the control was observed due to the low percentage of MPs recovery (31%). In view of our results we can conclude that P bound to MPs are likely to be extracted in BD and in HCl as significant differences were observed in these Fe fractions. Despite of these results, no effect of MPs addition on dissolved Fe concentration in the water column was noticed either in oxic or anoxic condition in any of the amended treatments. So, no toxic effects linked to the presence of dissolved Fe are expected to be caused when adding MPs.

5. Conclusions

This study confirms the convenience of adding MPs (T-W or T-S) for reducing, in a long-term, P concentration in lake water and lake sediment in oxic and anoxic conditions, even at a lower dose than those used in previous studies (Funes et al., 2016).

From the comparison of both treatments, and in order to recommend a future whole-lake application, we can conclude that the best option of adding MPs to the system is T-W due to two main advantages i) a high percentage of MPs recovery (91%) compared to the low recovery of T-S (31%), therefore reducing economic cost and potential toxicity on aquatic biota and (ii) an easier operation in a whole-lake application compared to adding the MPs directly on the upper sediment (see below).

Apart from the P cycle, and similarly to other P adsorbents (Phoslock® and $Al(OH)_3$), MPs addition caused an important effect on Si and C cycles. Despite the drastic reduction in DIP concentrations, Chl *a* was not reduced after MPs addition due to still high TP concentrations (> 200 µg L^{-1}) than those required to see changes in biological community (0.05–0.1 mg L^{-1}; Jeppesen et al., 2000). As a result, in order to get a significant reduction in Chl *a* concentration it would be necessary to: (i) continue long-term monitoring of changes in water quality, (ii) repeat MPs addition or (iii) add a higher MPs dose in the first application.

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Figures

Fig.1. Design of the magnetic rake for MPs removal. a) Schematics of the magnetic rake. b) Detail of the base and hard-plastic shell protecting the magnets. c) Surface plot of the magnetic field density in perpendicular direction to the platform on the surface of the shell (1 mm distance from the top of the magnets). d) Magnetic field density profiles in the x- (1) and diagonal (45º) directions (2).

Fig.2. Temporal evolution of DIP (a), TDP (b) and TP (c) in lake water for control (closed squares), T-W (closed circles) and T-S (open triangles). Red-downwards arrows indicate the moment (day 0) when MPs were added, while black-upwards arrows reflect MPs removal (after 24 h). Significant differences ($p < 0.05$) between treatments and control, for DIP fraction, are indicated by letters: a (control and T-W) and b (control and T-S). Not-shadowed area represents the oxic period (70 days; n = 12); shadowed area represents the anoxic period (5 days; n = 3).

Fig.3. Temporal evolution of DIN (a), TDN (b) and TN (c) in lake water for each treatment and control. Symbols and arrows are the same as described in Fig. 2. Significant differences ($p < 0.05$) between treatments and control, for DIN fraction, are indicated by letters: a (control and T-W) and b (control and T-S). Not-shadowed/shadowed areas illustrate the same as in Fig. 2

Fig.4. Changes of DIN: DIP molar ratio (a) and Si concentration (b) in the water column over time. Symbols, letters for significant differences in Si concentration, arrows and not-shadowed/shadowed are the same as described in Fig. 2.

Fig.5. Temporal changes in Chl *a* concentration. The meaning of vertical arrows and not-shadowed/shadowed areas is the same as described in Fig. 2

Fig.6. P (a) and Fe (b) sedimentary pools in treatments and control after the experiment.

Fig. 1

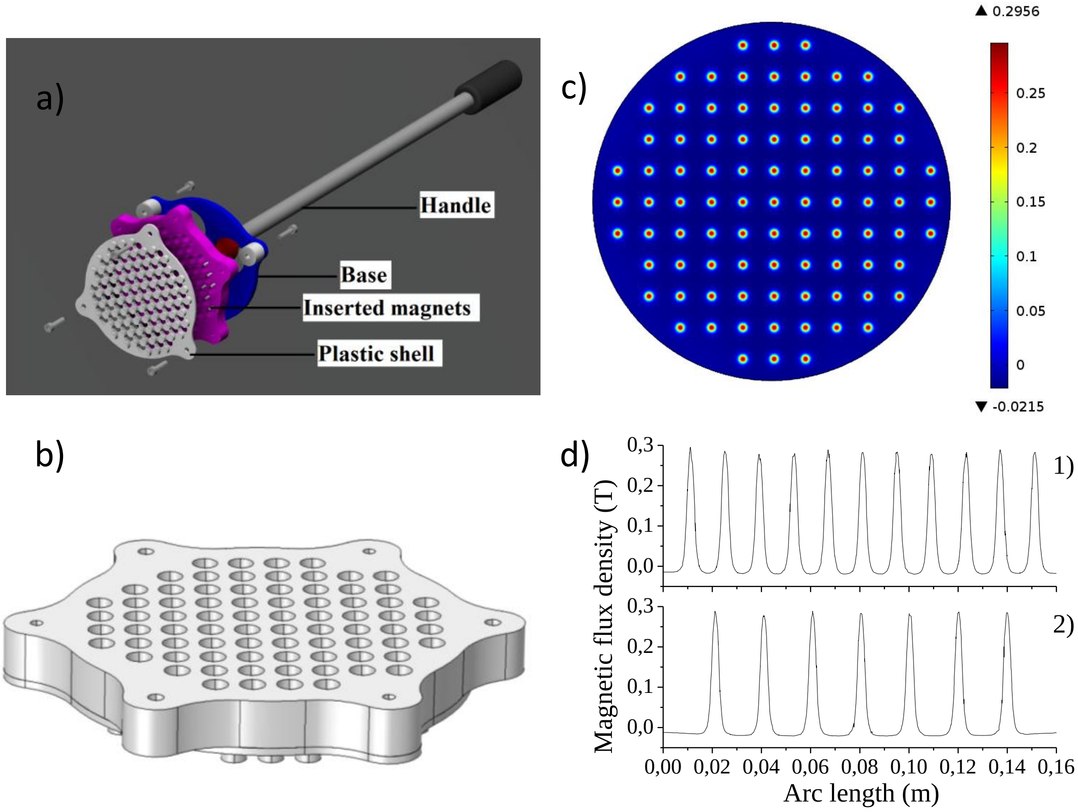

a)
Handle
Base
Inserted magnets
Plastic shell
b)
c)
0.2956
0.25
0.2
0.15
0.1
0.05
0
-0.0215
d)
1)
2)
Magnetic flux density (T)
0,0
0,1
0,2
0,3
Arc length (m)
0,00
0,02
0,04
0,06
0,08
0,10
0,12
0,14
0,16

Fig. 2

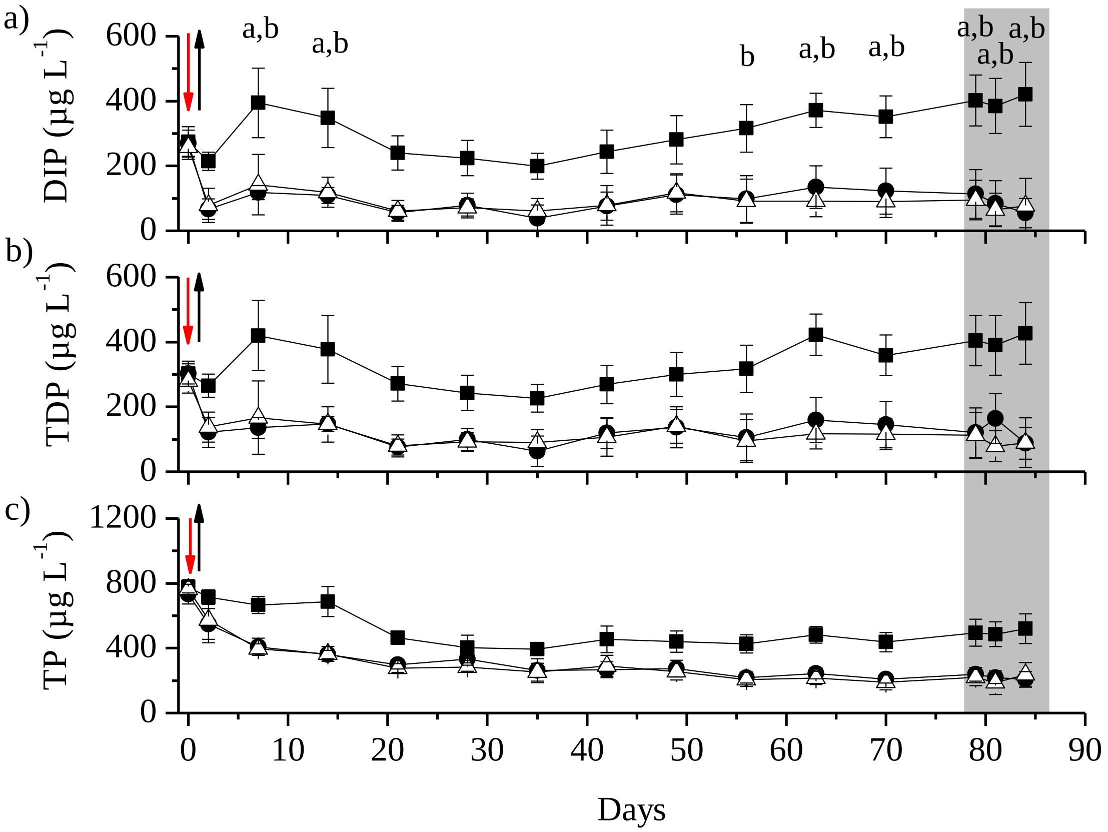

a)
DIP (µg L^{-1})
600
400
200
0
a,b
a,b
b
a,b
a,b
a,b
a,b
a,b
b)
TDP (µg L^{-1})
600
400
200
0
c)
TP (µg L^{-1})
1200
800
400
0
0
10
20
30
40
50
60
70
80
90
Days

Fig. 3

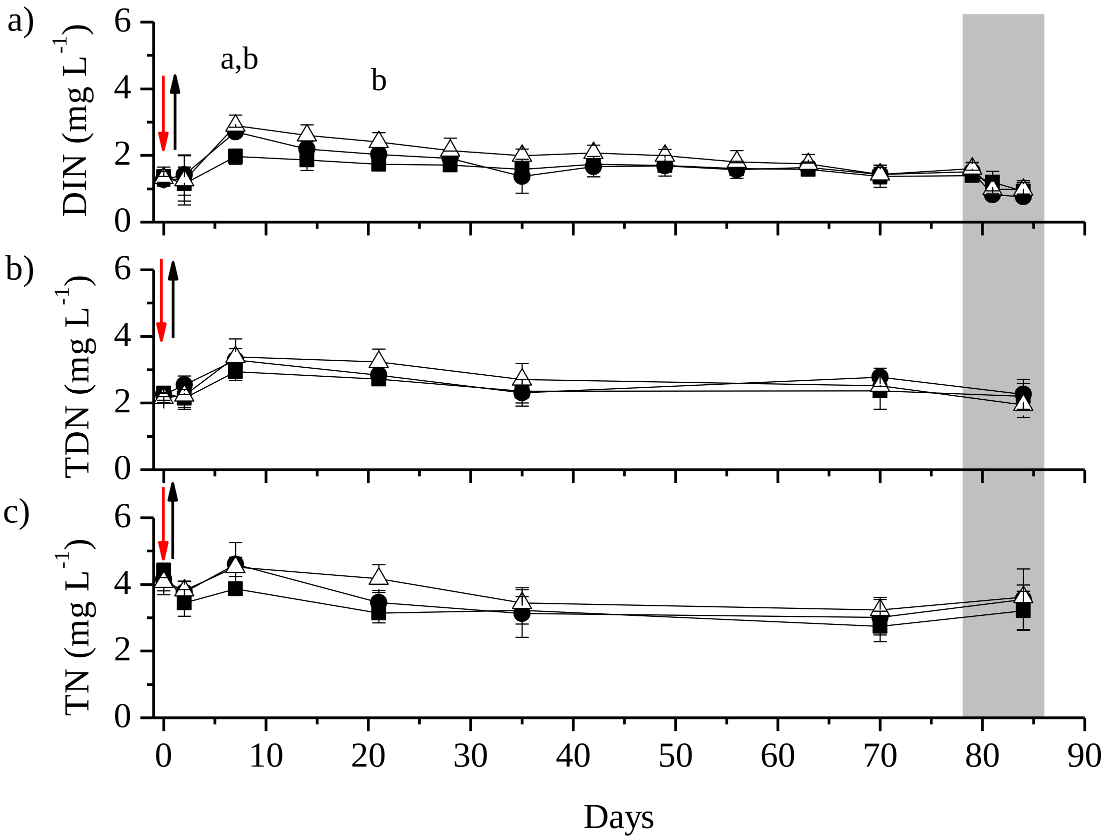

a)
b)
c)
DIN (mg L^{-1})
TDN (mg L^{-1})
TN (mg L^{-1})
a,b
b
0
2
4
6
0
10
20
30
40
50
60
70
80
90
Days

Fig. 4

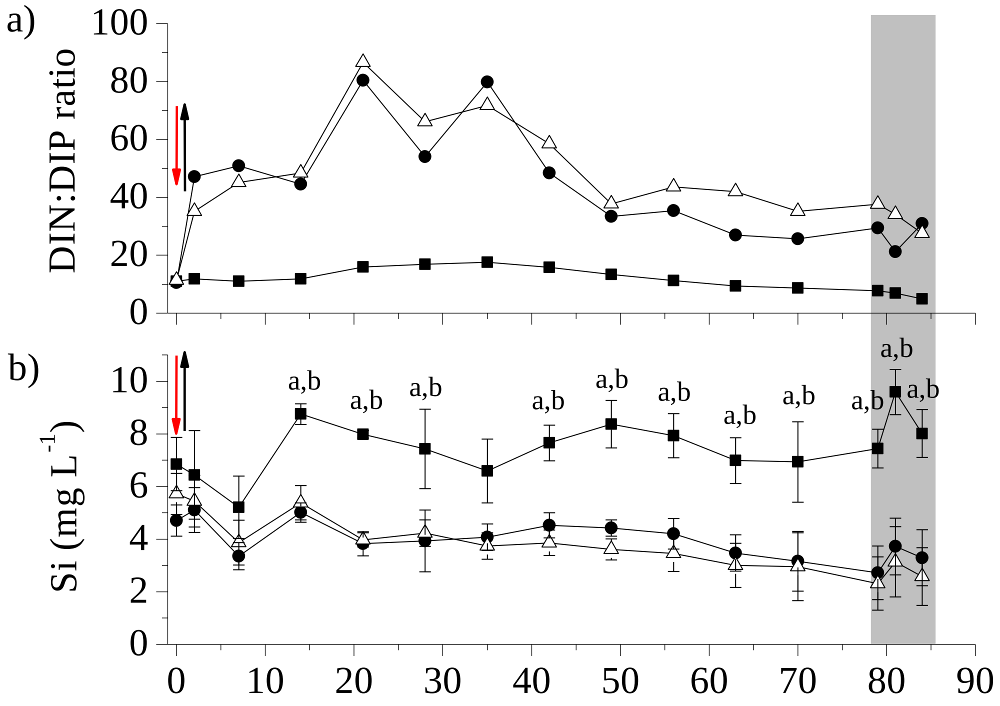

a)
DIN:DIP ratio
100
80
60
40
20
0
b)
Si (mg L^{-1})
10
8
6
4
2
0
a,b
0
10
20
30
40
50
60
70
80
90

Fig. 5

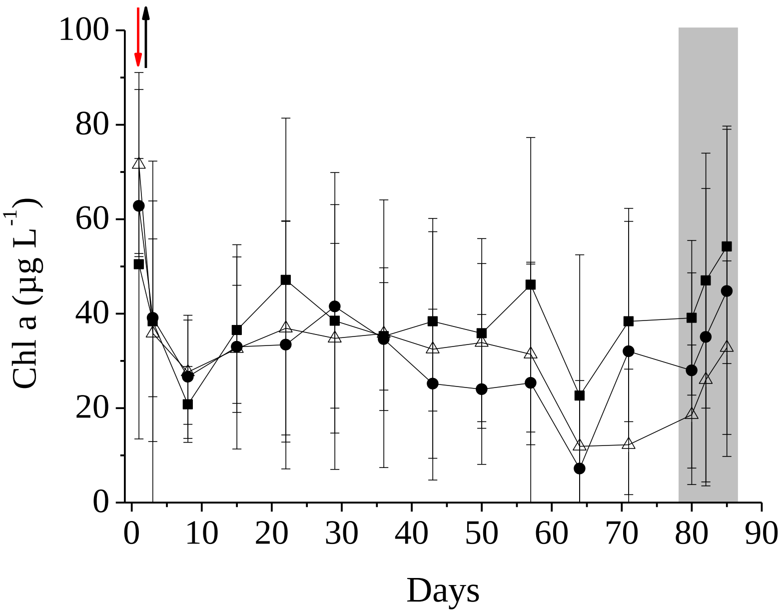
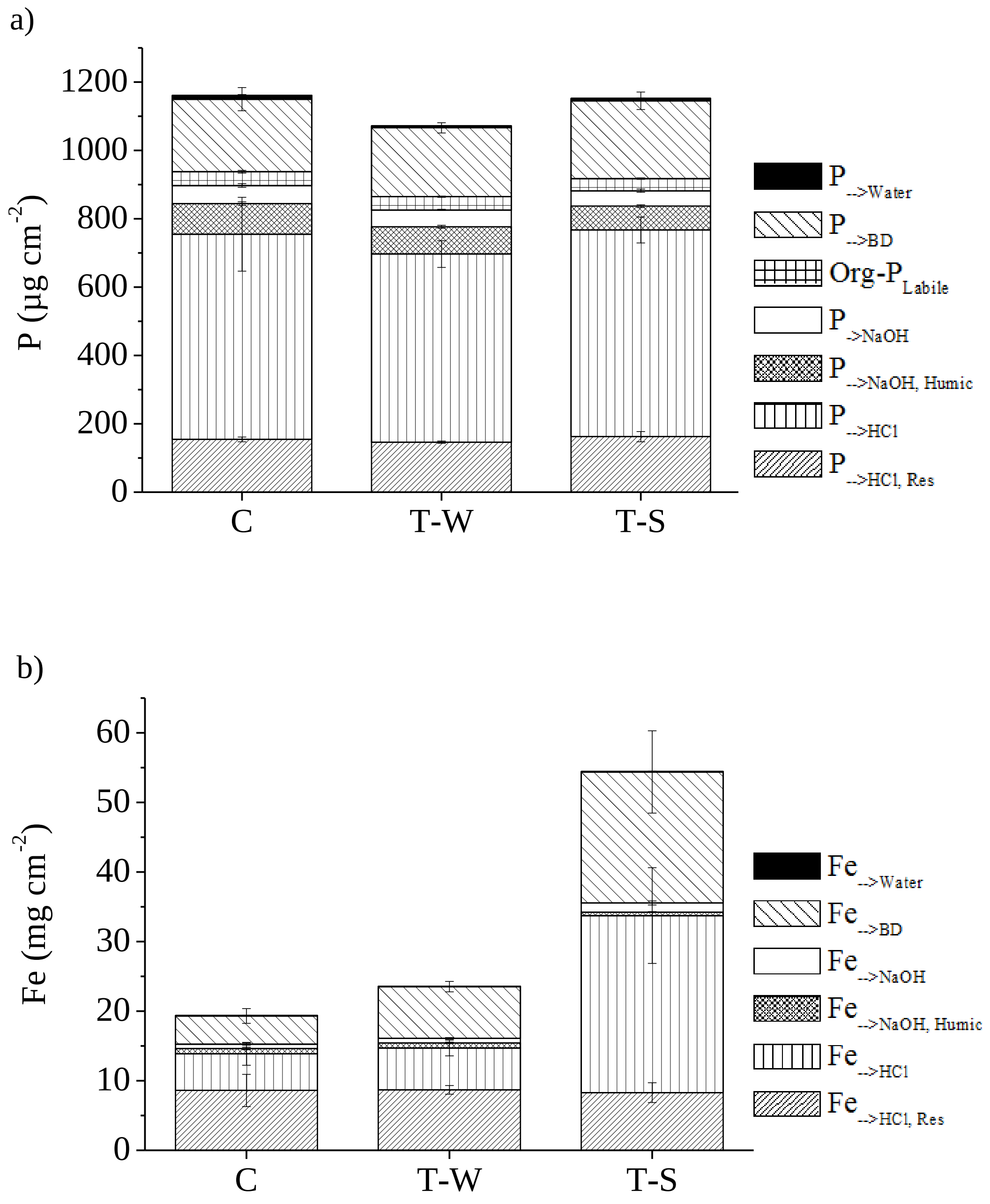


Fig. 6.


a)
P (µg cm^{-2})
0
200
400
600
800
1000
1200
C
T-W
T-S
P$_{-->Water}$
P$_{-->BD}$
Org-P$_{Labile}$
P$_{->NaOH}$
P$_{-->NaOH, Humic}$
P$_{-->HCl}$
P$_{-->HCl, Res}$
b)
Fe (mg cm^{-2})
0
10
20
30
40
50
60
C
T-W
T-S
Fe$_{-->Water}$
Fe$_{-->BD}$
Fe$_{-->NaOH}$
Fe$_{-->NaOH, Humic}$
Fe$_{-->HCl}$
Fe$_{-->HCl, Res}$

Tables

Table 1. Average values and standard deviations of the physico-chemical and biological parameters measured in the water column during the oxic (70 days; n=12) and the an-oxic period (5 days; n=3).

Table 2. Statistical results of the repeated measured ANOVA model. df = degrees of freedom) and p value= * (<0.05); ** (<0.005); *** (<0.0005).

Table 1

	Control		T-W		T-S	
	Oxic	**Anoxic**	**Oxic**	**Anoxic**	**Oxic**	**Anoxic**
T (ºC)	21.2 ± 3.9	14.6 ± 1.3	21.2 ± 4.0	14.5 ± 1.3	21.2 ± 3.9	14.4 ± 1.4
pH	9.0 ± 0.3	9.0 ± 0.0	9.0 ± 0.3	9.1 ± 0.0	9.0 ± 0.3	8.7 ± 0.7
O_2 (mg L^{-1})	7.5 ± 0.8	0.9 ± 0.1	7.5 ± 0.8	0.8 ± 0.1	7.4 ± 0.9	0.9 ± 0.2
Conductivity (µS cm^{-1})	6625 ± 469	6750 ± 485	6516 ± 423	6958 ± 89	6437 ± 392	6838 ± 81
TDS (mg L^{-1})	3369.0 ± 357.4	3255.1 ± 460.4	3306.5 ± 276.7	3483.6 ± 48.7	3226.5 ± 194.9	3427.3 ± 52.8
TSS (mg L^{-1})	83.1 ± 38.3	45.6 ± 2.0	79.8 ± 28.1	47.2 ± 2.9	84.5 ± 37.6	46.1 ± 6.9
Chl *a* (µg L^{-1})	39.2 ± 11.3	46.8 ± 7.6	32.8 ± 13.4	35.9 ± 8.4	34.1 ± 14.9	25.8 ± 7.1
Color (m^{-1})	4.4 ± 0.8	4.2 ± 0.4	3.9 ± 0.9	4.0 ± 0.1	4.1 ± 0.7	3.1 ± 0.5
DOC (mg L^{-1})	67.0 ± 15.0	-	58.9 ± 9.0	-	61.5 ± 4.8	-
Tot-Fe_{dis} (mg L^{-1})	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
DIP (µg L^{-1})	289.5 ± 69.5	402.5 ± 18.2	91.7 ± 30.7	84.3 ± 29.2	91.2 ± 25.5	78.9 ± 15.3
TDP (µg L^{-1})	315.6 ± 69.3	406.8 ± 18.5	119.0 ± 30.3	124.1 ± 38.7	116.9 ± 27.7	93.4 ± 17.0
TP (µg L^{-1})	506.5 ± 121.0	500.5 ± 17.2	311.6 ± 99.3	221.6 ± 16.5	300.5 ± 110.2	214.9 ± 25.2
DIN (mg L^{-1})	1.6 ± 0.2	1.2 ± 0.2	1.8 ± 0.4	1.0 ± 0.4	2.0 ± 0.5	1.2 ± 0.4
TDN (mg L^{-1})	2.5 ± 0.3	2.2 ± 0.0	2.8 ± 0.4	2.3 ± 0.0	2.8 ± 0.5	1.9 ± 0.0
TN (mg L^{-1})	3.3 ± 0.4	3.2 ± 0.0	3.6 ± 0.6	3.6 ± 0.0	3.8 ± 0.5	3.6 ± 0.0
Si (mg L^{-1})	7.3 ± 1.0	8.3 ± 1.1	4.1 ± 0.6	3.2 ± 0.5	4.0 ± 0.8	2.7 ± 0.4
Na^+ (mg L^{-1})	838.35 ± 17.5	958.75 ± 0.0	831.72 ± 76.7	981.46 ± 0.0	846.89 ± 1.3	894.8 ± 0.0
K^+ (mg L^{-1})	115.1 ± 6.6	126.8 ± 0.0	111.0 ± 6.4	130.1 ± 0.0	115.3 ± 8.1	114.1 ± 0.0
Mg^{2+} (mg L^{-1})	30.7 ± 3.3	22.0 ± 0.0	26.7 ± 2.4	10.2 ± 0.0	26.3 ± 8.3	7.2 ± 0.0
Ca^{2+} (mg L^{-1})	215.73 ± 121.1	352.10 ± 0.0	195.48 ± 4.9	347.21 ± 0.0	276.14 ± 30.0	308.31 ± 0.0
Cl^- (mg L^{-1})	1451.6 ± 45.7	1676.0 ± 0.0	1448.7 ± 130.3	1708.6 ± 0.0	1434.6 ± 0.3	1569.2 ± 0.0
SO_4^{2-} (mg L^{-1})	712.3 ± 10.6	853.9 ± 0.0	696.7 ± 59.5	771.8 ± 0.0	666.6 ± 45.8	687.9 ± 0.0

Table 2

	TREATMENT				TIME				TREATMENT x TIME			
	df 1	**df 2**	**F**	**p value**	**df 1**	**df 2**	**F**	**p value**	**df 1**	**df 2**	**F**	**p value**
T (ºC)	-	-	-	-	-	-	-	-	-	-	-	-
pH	2	12	0.6	no sig	1.3	15.9	7,0	*	2.6	15.9	1.1	no sig
O$_2$ (mg L^{-1})	-	-	-	-	-	-	-	-	-	-	-	-
Conductivity (µS cm^{-1})	2	10	0.7	no sig	1.4	13.9	27.5	***	2.8	13.9	0.9	no sig
TDS (mg L^{-1})	2	12	0.8	no sig	2.2	26.7	3.7	*	4.4	26.7	0.8	no sig
TSS (mg L^{-1})	2	9	0.4	no sig	2.0	18.3	6.7	*	4.1	18.3	0.6	no sig
Chl *a* (µg L^{-1})	2	8	1.5	no sig	3.2	25.9	3.2	*	6.5	25.9	0.9	no sig
Color (m^{-1})	2	11	4.3	*	2.5	27.9	15.0	***	5.1	27.8	0.7	no sig
DOC (mg L^{-1})	2	12	5.1	*	2.0	24.0	14.6	***	4.0	24.0	1.6	no sig
Tot-Fe$_{dis}$ (mg L^{-1})	-	-	-	no sig	-	-	-	no sig	-	-	-	no sig
DIP (µg L^{-1})	2	12	40.2	***	3.5	42.3	15.7	***	7.0	42.3	6.6	***
TDP (µg L^{-1})	2	12	39.0	***	4.4	52.9	13.1	***	8.8	52.9	5.6	***
TP (µg L^{-1})	2	12	44.3	***	5.0	59.5	139.8	***	9.9	59.5	5.7	***
DIN (mg L^{-1})	2	12	7.0	*	2.6	31.6	41.8	***	7.1	42.8	2.4	*
TDN (mg L^{-1})	2	11	2.9	no sig	6.0	66.0	16.8	***	12.0	66.0	1.3	no sig
TN (mg L^{-1})	2	12	7.6	*	6.0	72.0	16.4	***	12.0	72.0	1.4	no sig
Si (mg L^{-1})	2	12	61.0	***	2.8	33.2	13.0	***	5.5	33.2	7.4	***
Na^{+} (mg L^{-1})	2	12	0.2	no sig	3.0	36.0	11.1	***	6.0	36.0	0.9	no sig
K^{+} (mg L^{-1})	2	9	0.1	no sig	3.0	27.0	6.0	**	6.0	27.0	1.0	no sig
Mg^{2+} (mg L^{-1})	2	6	3.4	no sig	1.2	7.3	11.6	*	2.4	7.3	0.9	no sig
Ca^{2+} (mg L^{-1})	2	12	0.6	no sig	1.4	16.6	7.6	*	2.8	16.6	1.5	no sig
Cl^{-} (mg L^{-1})	2	12	0.6	no sig	1.6	18.8	11.9	**	3.1	18.2	1.1	no sig
SO$_4^{2-}$ (mg L^{-1})	2	12	4.9	*	1.9	22.2	8.1	**	3.7	22.2	2.4	no sig