

Title:

Evaluating the effect of CFH-12[®] and Phoslock[®] on phosphorus dynamics during anoxia and resuspension in shallow eutrophic lakes

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1 **Abstract**

2 Laboratory experiments with intact sediment cores from a hypertrophic very windy
3 exposed shallow lake were conducted to assess the combined effect of anoxia and
4 sediment resuspension on phosphorus (P) dynamics after adding different P adsorbents
5 (CFH-12[®] and Phoslock[®]). Both adsorbents significantly reduced the P release from the
6 sediments after a 54 days-anoxic incubation period (CFH-12[®] by 85% and Phoslock[®]
7 by 98%) and even after resuspension events (CFH-12[®] by 84% and Phoslock[®] by 88%),
8 indicating that both adsorbents are suitable P inactivating agents for restoring shallow
9 eutrophicated lakes under such circumstances. CFH-12[®] did not release dissolved Fe to
10 the water column neither after the anoxic period nor after resuspension events compared
11 to Control (no adsorbents addition). The La concentration was significantly higher in
12 Phoslock[®] (3.5-5.7 $\mu\text{g L}^{-1}$) than in Control at all sampling days but it was not affected
13 by resuspension. The high efficiency in P removal under anoxia and resuspension, the
14 low risk of toxicity and the high maximum adsorption capacity makes CFH-12[®] a
15 promising adsorbent for lake restoration. Nevertheless, further research about the
16 influence of other factors (i.e. pH, alkalinity, interfering substances) on the performance
17 of CFH-12[®] is needed.

18 **1. Introduction**

19 The addition of adsorbents to inactivate phosphorus (P) in the sediment is a common
20 management tool for eutrophic lakes (Søndergaard et al., 2003; Cooke et al., 2005).
21 Actually, there is not a universally valid P adsorbent as the effectiveness to remove P of
22 most P-sorbing materials is strongly dependent on the physic-chemical characteristics of
23 the lake (e.g. potential redox, pH and/or presence of other dissolved ions) (Westholm,
24 2006; de Vicente et al., 2008; Vohla et al., 2011; Lürling et al., 2014). Especially
25 sensible to redox conditions are iron (Fe) salts (Cooke et al., 1993) while the
26 effectiveness of aluminium (Al) salts and Phoslock[®], a modified bentonite clay, is
27 reduced at the high pH values typically encountered in hypereutrophic aquatic
28 ecosystems (Ross et al., 2008; Reitzel et al., 2013). As Funes et al. (2017) suggested,
29 although some of these adsorbents could represent a long-lasting sink for P, changes in
30 physic-chemical conditions or resuspension events can lead to undesirable P release to
31 water column along with toxic substances stemming from the adsorbent composition
32 (Egemose et al., 2009; Zamparas and Zacharias, 2014).

33 Among all physical, chemical and biological processes driving the internal P loading in
34 natural eutrophic ecosystems, the reduction of Fe (oxyhydr)oxides during anoxic
35 conditions and sediment resuspension are the most essential ones (e.g. Boström, 1982).
36 Accordingly, it is of outstanding importance to assess the stability of novel P adsorbents
37 under both anoxia and sediment resuspension.

38 At first, since results from Einsele (1936) and Mortimer (1941), it is well accepted the
39 tight coupling between the Fe and P cycle considering that Fe (oxyhydr)oxides act as
40 efficient sorption agents for dissolved P under oxic conditions, when P is trapped and
41 surface sediments can act as a barrier for upward diffusing P. However, under anoxic
42 conditions, reduction of Fe (oxyhydr)oxides may result in the release of P into the

43 overlying water column. Nevertheless, it is also worth to note that cycling of sulfur (S)
44 is closely coupled to the transformations of P and Fe and the long-term retention of P
45 under anoxic conditions may also occur due to the formation of stable reduced Fe
46 phosphate minerals such as vivianite (e.g. März et al., 2008; Rothe et al., 2014, 2015).

47 On the other hand, sediment resuspension is a key process governing P cycle in shallow
48 polymictic lakes where the sediment-water interaction is of critical importance due to
49 the high sediment surface: water column ratio (Sondergaard et al., 2003). Wind-induced
50 sediment resuspension occurs frequently promoting increase of turbidity (and reduction
51 of light penetration), changes in nutrients concentrations in the water column (de
52 Vicente et al., 2010) or the redistribution of sediment (Sondergaard et al., 1992). Apart
53 from the evident external forcing caused by the wind stress, there are several in-lake
54 properties (e.g. sediment grain size, lake morphometry and activity of benthic
55 organisms) which lastly influence sediment resuspension consequences (Kleeberg et al.,
56 2007). Even more, it is well accepted that the final effect of resuspension events is, to
57 some extent, lake-specific (Søndergaard et al. 1992) and sediment resuspension and
58 nutrient fluxes across the sediment-water interface are complex processes which can be
59 influenced by a multiplicity of factors (de Vicente et al., 2010). Furthermore, it is
60 essential to consider that sediment resuspension does not only occur in shallow lakes
61 but also in stratified lakes due to internal seiches (Ostrovsky et al., 1996), where the
62 sustained oscillations of water over the bed contribute to the generation of a benthic
63 boundary layer enhancing sediment resuspension (Gloor et al., 1994; Pierson and
64 Weyhenmeyer, 1994). In this situation, sediment resuspension and hypolimnetic anoxia
65 can clearly take place at the same time.

66 Despite the significant role of anoxia and sediment resuspension in shallow
67 eutrophicated lakes, there are only few publications assessing their effects on P

68 dynamics after adding different P adsorbents (Egemose et al., 2009; 2010; Yin et al.,
69 2016; Fuchs et al., 2018). More specifically, the resuspension behaviour of Al has been
70 studied by Egemose et al. (2009) by using a laboratory resuspension experiment with a
71 calibrated erosion chamber. These authors concluded that newly applied Al reduced
72 surface sediment stability and dissolved Al increased markedly after resuspension
73 events but dissolved P concentration was constantly low due to excess binding capacity
74 of the Al floc. Later, Egemose et al. (2010) assessed the effect of adding Al, Phoslock[®]
75 and a combination of Al covered with bentonite (Al/Ben) on P removal, sediment
76 stability, sediment consolidation and color reduction over time. They found that
77 although all treatments effectively reduced the P concentration in the water, the
78 treatments containing Al reduced the P concentration immediately after resuspension,
79 whereas Phoslock[®] required several days after resuspension to reduce the P
80 concentration. In other experiment, Yin et al. (2016) found that adding Phoslock[®] and
81 thermally-treated calcium-rich attapulgite can enhance the stability of surface sediment
82 and reduce the erosion depth caused by wind accordingly. However, only the
83 experiment carried out by Fan et al. (2017) studied the effect of both anoxia and
84 sediment resuspension on the stability of a P adsorbent. They reported that capping
85 sediment with zeolite/hydrous zirconia (ZHZ) increased sediment stability and reduced
86 soluble reactive P from the water column in greater extent than Al treatment after
87 sediment resuspension. Apart from Phoslock[®], a novel P adsorbent has been recently
88 proposed for lake restoration: CFH-12[®], a granular and amorphous ferric oxy-
89 hydroxide. Although there is no previous information about its stability under sediment
90 resuspension events, Fuchs et al. (2018) found that CFH-12[®] reduced the P efflux from
91 the sediment between 43 and 70% under anoxic conditions in three Danish lakes while
92 the Fe²⁺ efflux remained unchanged compared to the untreated cores. Regardless these

93 promising results, before using CFH-12[®] in a real-whole lake application, it is required
94 to test if P bound to CFH-12[®] is likely to be release to the overlying water when
95 sediment resuspension occurs.

96 In this study we hypothesize that the addition of geoengineering materials will increase
97 P retention in the sediment even at the worst physic-chemical conditions such as anoxia
98 and sediment resuspension. We aim on assessing the impact of two lake geoengineering
99 materials (CFH-12[®] and Phoslock[®]) recently proposed for lake restoration, on P
100 dynamics in a eutrophicated very windy exposed shallow lake (Honda, Almería, SE
101 Spain). We simulate, under laboratory conditions and using intact sediment cores, the
102 combination of summer anoxia and the subsequent resuspension events occurring
103 during the autumn. The specific goals were: (i) to analyse the effect of both composites
104 on P fluxes and sediment stability during anoxia and subsequent resuspension and (ii) to
105 determine potential liberation of dissolved Fe or La from the adsorbents. Finally, we
106 would like to stress the novelty of this study as, up to date, there are no studies focused
107 on assessing the combined effect of both anoxia and sediment resuspension on the
108 effectiveness of CFH-12[®] and Phoslock[®] for retaining P.

109

110 **2. Material and methods**

111 *2.1. Study site*

112 Honda lake is a shallow (surface area=9 ha, $Z_{\text{mean}}=1.3\text{m}$; $Z_{\text{max}}=3.2\text{ m}$), hypertrophic, and
113 brackish water ($6000\ \mu\text{S cm}^{-1}$) wetland in Southeast Spain (de Vicente et al. 2003).
114 Besides high external P inputs, the summer anoxic periods and the frequent
115 resuspension events cause an important sedimentary P release into the water column (de
116 Vicente et al. 2006; Funes et al., 2016). Specifically, by using sediment cores, Funes et
117 al. (2016) estimated an extremely high P release rate ($1.96\pm 2.52\ \text{mg P cm}^{-2}\ \text{day}^{-1}$) under

118 anoxic conditions. Similarly, by using a combination of field measurements, modelling
119 and laboratory experiments, de Vicente et al. (2010) evaluated the potential impact of
120 sediment resuspension on P dynamics in both adjacent shallow lakes (Honda and
121 Nueva) comprising Albuferas de Adra (Almería). Due to their geographic proximity
122 (only 200 m apart), they both are subject to equal meteorological forcing and represent
123 ideal systems to study how morphometry and sediment properties relate to wind events.
124 Those results evidenced that Honda lake was much more affected by resuspension
125 events than Nueva lake due to lake morphometry and sediment grain size distribution.
126 In Honda lake, the average concentration (0-15 cm) of total Fe is 34 mg g DW^{-1} , being
127 51% Fe oxides. The concentration of Fe oxides in the surface sediment (0-5 cm) is high
128 (3.91%). The granulometric composition corresponds to sand ($\phi < 50 \mu\text{m}$) 2.6%; sandy
129 silt ($20 < \phi > 50 \mu\text{m}$) 3.1%; silty clay ($2 < \phi > 20 \mu\text{m}$) 55.6% and clay ($\phi < 2 \mu\text{m}$) 41.3%. The
130 high values of turbidity (due to the frequent resuspension events) drastically limit the
131 existence of macrophytes and benthic algae, that otherwise would contribute to
132 sediment consolidation and cohesion (de Vicente, 2004).

133 *2.2. Materials*

134 CFH-12[®] (Kemira, Finland) is a dry, granular and amorphous ferric oxy-hydroxide with
135 a Fe content of ~44%. The 93% of its weight presents a grain size of 0.85-2 mm and the
136 6% is smaller than 0.85 mm (Fuchs et al., 2018). Further details about CFH-12[®]
137 chemical composition are reported by Lyngsie et al. (2014a). Phoslock[®] is a dry and
138 granular compound consisting of lanthanum (La)-modified clay. According to the
139 manufacturer, 95% of its weight corresponds to clay and 5% to La (Reitzel et al., 2013).

140 *2.3 Characterization of the adsorbents*

141 The morphology and elemental composition of the adsorbents was ascertained by ion
142 beam field-emission scanning electron microscopy (FIB-FESEM, AURIGA, Carl Zeiss

143 SMT Inc.). In order to have a fine powder for SEM analysis, a sample of CFH-12[®] and
144 Phoslock[®] was crushed in a mortar. X-ray photoelectron spectroscopy (XPS, Kratos
145 Axis Ultra-DLD) with monochromatic Al K α radiation was also used to analyse the
146 chemical composition of the adsorbents. The wide spectrum (pass energy 160 eV) and
147 the spectra of each element (pass energy 20 eV) were obtained using hybrid lens. The
148 La content in Phoslock[®] was analysed by inductively coupled plasma-mass
149 spectroscopy (ICP-MS; Perkin Elmer NexION 300D) after sample digestion with HNO₃
150 + HF.

151 *2.4 Cores incubation experiment*

152 On July 2016, 12 small sediment cores (h=25 cm; Ø=5.4 cm) and lake water were
153 collected at the deepest site of Honda lake (Almería, Spain). Sediment height was
154 adjusted in all the cores (10 cm of sediment and 15 cm of water). Before applying the
155 treatments, all the cores were N₂-bubbled for 48 h, and afterwards, physic-chemical
156 parameters were determined as pre-treatment conditions. Three different treatments with
157 four replicates each were applied to the cores: addition of (i) CFH-12[®], (ii) Phoslock[®]
158 and (iii) control/no addition. 0.7 g of CFH-12[®] or 2.0 g of Phoslock[®] were mixed with
159 100 mL of lake water and added to each core as slurries on day 0. The adsorbent dosage
160 was calculated according to mobile P pool (sum of pore water P, P bound to reducible
161 metals and organic P labile) in the first 10 cm of the sediment (19.5 mg P) and the
162 maximum P adsorption capacity (q_{max}) of each adsorbent indicated in the literature
163 [CFH-12[®]: 27.59 mg P g⁻¹ (Lyngsie et al., 2014b) and 30 mg P g⁻¹ (Fuchs et al., 2018);
164 Phoslock[®]: 10 mg P g⁻¹ (manufacturer, CSIRO)]. Slurries were gently added to the cores
165 with simultaneous N₂-bubbling of the water column to avoid undesired oxygenation.
166 Cores were then covered with a lid and left for incubation in anoxic conditions at 23 °C.
167 Water column was sampled on days 5 and 54 to measure physic-chemical parameters.

168 Water removed during sampling was replaced with unfiltered anoxic bottom lake water.
169 Temperature (T), pH and dissolved oxygen (DO) concentration were measured with a
170 multi-parameter probe (Hanna Instrument, HI 9829). Dissolved inorganic P (DIP) was
171 determined by the molybdate-blue colorimetric method (Murphy and Riley, 1962).
172 Total dissolved Fe and total dissolved La were measured by the ferrozine method
173 (Gibbs, 1979) and by ICP-MS (Perkin Elmer NexION 300D), respectively. Finally,
174 water turbidity was determined using a turbidity meter (LW-TN3024, Luton
175 Electronics) by measuring the light scattered by the water sample at an angle to the
176 incident beam.

177 *2.5 Cores resuspension experiment*

178 The resuspension experiments were performed using a resuspension chamber (Fig. 1). It
179 consisted of an electrical stirrer paddle connected to a motor and placed just 1.5 cm
180 above the sediment surface of the core. On day 62, the sediment was exposed to a weak
181 resuspension (133 ± 5 rpm; linear velocity 0.4 m s^{-1}) for 2 min. Immediately afterwards,
182 the water column was sampled to measure the following parameters: pH, DIP, total
183 dissolved Fe, total dissolved La and turbidity. The next day (day 63), the water column
184 was again resuspended but more vigorously (315 ± 5 rpm; 0.95 m s^{-1}) for 2 minutes and
185 the water column was sampled to determine the same parameters as described above.
186 This stronger resuspension is similar to that applied by Fan et al. (2017) in recent
187 resuspension experiments. The resuspension intensities in the present study are justified
188 by the fact that Honda lake is exposed to extremely high maximum wind speeds (de
189 Vicente et al., 2010) and we simulated the last effect of the most harmful circumstances
190 on P exchange across the sediment-water interface after P inactivation.

191 *2.6. Statistical analysis*

192 Differences in water chemical parameters among treatments over time were tested by
193 using repeated measures ANOVA (RM-ANOVA: split plot design with one between
194 subjects factor and one within-subjects factor) with Fisher's least significance difference
195 (LSD) post-hoc test. The Greenhouse-Geisser correction of degrees of freedom was
196 used when the sphericity assumption was violated ($\epsilon < 0.75$). Statistical analyses
197 were performed with Statistica 7.1 software (Stat Soft Inc., Tulsa, USA).

198

199 **3. Results and discussion**

200 *3.1. Characterization of the adsorbents*

201 Fig. 2a and Fig. 2b show SEM images of CFH-12[®] and Phoslock[®], respectively. As
202 observed, both adsorbents present an irregular and rough surface. However, differences
203 are also clear. CFH-12[®] is constituted by quasi-spherical aggregated particles whereas
204 Phoslock[®] presents the typical layer structure of bentonite clay.

205 The XPS analysis of adsorbents is displayed in Table 1. As specified for CFH-12[®], O
206 and Fe represent almost the 90% of its surface chemical composition. The presence of C
207 could be explained by environmental adventitious contamination. Little amounts (<3%)
208 of Mg, Ca and S are also present in the surface of CFH-12[®]. Values for Mg and Ca are
209 lower than those obtained by Lyngsie et al. (2014b) using energy-dispersive X-ray
210 spectroscopy (EDS). This difference is not surprising because XPS gives the chemical
211 composition at the surface (around 10 nm penetration) while EDS reaches deeper
212 regions (around 1 μm penetration). In Phoslock[®], O, Si and Al represent the 90% of the
213 atomic surface concentration. The presence of surface La was expected because it can
214 be complexed with the bentonite and adsorbed onto its surface (Lürding and Tolman,
215 2010). The ICP-MS analysis revealed a total La content of 4% in Phoslock[®], which is
216 very similar to that reported by the manufacturer.

217 3.2 Anoxic incubation and resuspension experiments

218 The aim was to mimic real conditions in which a hypertrophic polymictic lake becomes
219 anoxic during summer and several resuspension events take place. With this in mind,
220 the experimental protocol consisted in a whole incubation period of 68 days, that
221 includes a first anoxic incubation period (days 0-54), two subsequent resuspension
222 events on days 62 and 63 and a final sampling on day 68. Anoxia, or near anoxia, in the
223 cores was ensured since DO concentration in the water column was close to $1 \text{ mg O}_2 \text{ L}^{-1}$
224 for the whole incubation period (see Table 2). Additionally, pH was especially high at
225 the beginning of the experiment ($\text{pH} > 9$), in control and in all treatments, and it came
226 down along the incubation period.

227 Fig. 3 shows the accumulated P efflux for the incubation period of 68 days. Firstly, we
228 will analyse the effect of anoxia and sediment resuspension on the P efflux of each
229 treatment, separately. To do so, P efflux has been compared as follows: (i) P efflux at
230 the beginning (day 0) and at the end of the anoxic period (day 54); (ii) P efflux prior to
231 resuspension (day 54) and after the weak resuspension (day 62); (iii) and P efflux after
232 the weak (day 62) and after the strong resuspension (day 63). Statistical analysis
233 showed that P efflux changed over time (RM-ANOVA: $F(1.8,16.5)=93.19$, $p < 0.001$) for
234 the whole incubation period. In Control, P efflux remarkably increased in the first 54
235 days of the anoxic period. Similarly, it significantly increased after the weak (by 29%;
236 $\text{LSD } p < 0.001$) and the strong (by 16%; $\text{LSD } p < 0.001$) resuspension events. This
237 suggests P release induced by sediment Fe reduction (under anoxia) and resuspension
238 (under stirring). Therefore, our results confirmed those obtained by Welch and Cooke
239 (2005) who pointed out that both periodic anoxia and wind induced resuspension are
240 two of the most important processes controlling internal P loading in shallow lakes. As
241 an illustration, Søndergaard et al. (1990) estimated that reducing conditions caused an

242 increase in short-term water column rates over $100 \text{ mg P m}^{-2} \text{ day}^{-1}$ in the Danish
243 eutrophic Søbygaard lake. This is approximately 25 times larger than our observations.
244 Additionally, there are many studies reporting an increase in DIP concentration in the
245 deep water column coincident with low DO concentration (e.g. Welch et al., 1988). In
246 Honda lake, P bound to reducible metals is an important pool (16% of total P sediment,
247 Funes et al., 2016) that could be released to sediment pore water upon Fe reduction and
248 subsequently to the water column after resuspension. In fact, our results are in
249 agreement with those obtained by Funes et al. (2016). Using sediment cores from the
250 same study site, Honda lake, they estimated a much higher P release rate under anoxic
251 ($1.96 \pm 2.52 \text{ } \mu\text{g P cm}^{-2} \text{ day}^{-1}$) than under oxic conditions, where a net P retention was
252 observed. Under oxic conditions, sediment P adsorption capacity and thus, P transport
253 across sediment water interface is mainly controlled by $\text{Fe}_{\rightarrow\text{BD}}: \text{P}_{\rightarrow\text{BD}}$ molar ratio
254 (Jensen et al., 1992). In Honda lake, this molar ratio was 15:1 (Funes et al., 2016) which
255 is considerably higher than the molar ratio (8:1) required for trapping P in the sediment
256 (Jensen et al., 1992). However, our results contrast to those obtained by Fan et al.
257 (2017) who reported not an increase but a high and almost constant concentration of
258 dissolved P in the water column for the 28-days anoxic incubation period when using
259 ZHZ. In addition to periodic anoxia, sediment resuspension is a key process in P cycle
260 in Honda lake as the winds over the lake are episodic with peak values of 15 m s^{-1} and
261 even larger (de Vicente et al., 2010). In relation to our resuspension results, Egemose et
262 al. (2009) also reported an increase of particulate P (from 5 up to 13 mg g^{-1}) in the water
263 column of untreated sediment cores during the application of a lower resuspension
264 velocity ($\approx 1.4 \text{ cm s}^{-1}$) than the one applied in this study.
265 Even more important is the fact that contrarily to what was observed for Control, P
266 efflux in CFH-12[®] and Phoslock[®] did not increase at the end of the anoxic period (on

267 day 54) nor did it after the weak and strong resuspension events (LSD $p>0.05$). Only in
268 Phoslock[®] treatment, P efflux significantly increased by 8 times (LSD $p=0.035$) after
269 the strong resuspension (on day 63) compared to day 62.

270 Secondly, we will compare the effect of CFH-12[®] and Phoslock[®] (in relation to Control)
271 on P efflux under anoxic conditions and sediment resuspension. Statistical analysis
272 showed that treatments had significant effects on P efflux (RM-ANOVA: $F(2,9)=48.72$,
273 $p<0.001$) for the whole incubation period. When comparing treatments with post hoc
274 analysis, it can be seen that P efflux was significantly higher in Control compared to
275 CFH-12[®] and Phoslock[®] treatments at all sampling days, except for day 5. However, P
276 efflux was not significantly different at any sampling day between both treatments. The
277 *time x treatment* interaction was significant (RM-ANOVA: $F(8,36)=43.33$, $p<0.001$)
278 indicating that the differences in P efflux between Control and treatments increased over
279 time. At the end of the anoxic period (on day 54), accumulated P release was reduced by
280 85% in CFH-12[®] and by 98% in Phoslock[®] compared to Control (LSD $p<0.01$ and
281 $p<0.005$, respectively). In agreement with our results, previous studies found that the
282 effectiveness of CFH-12[®] (Fuchs et al. 2018) and Phoslock[®] (Ross et al., 2008) for
283 trapping P was not dependent on redox conditions. Fuchs et al. (2018) reported a
284 remarkable DIP release reduction of 43% for a 85 days-anoxic incubation period when
285 working with sediment cores from the hypertrophic hardwater shallow lake Sønderby
286 (Denmark). After the weak resuspension event, the reduction of P efflux relative to
287 Control was 84% in CFH-12[®] and 98% in Phoslock[®] (LSD $p<0.005$ for both). After the
288 strong resuspension event, the P efflux reduction was 84% and 88%, respectively for
289 each adsorbent (LSD $p<0.005$ for both). No differences in P efflux were found at the
290 end of the anoxic period or at the end of the resuspension events between both
291 adsorbents. At the end of the incubation period (on day 68), the accumulated P efflux

292 for Control ($28.6 \mu\text{g cm}^{-1}$) was significantly higher than those found for CFH-12[®] (6.9
293 $\mu\text{g cm}^{-1}$; LSD $p < 0.001$) and Phoslock[®] ($3.3 \mu\text{g cm}^{-1}$; LSD $p < 0.001$), respectively.
294 Specifically, the CFH-12[®] reduced the P release by 76% whereas Phoslock[®] reduced it
295 by 89% compared to Control, being both efficient P adsorbents under the conditions
296 studied in this experiment.

297 Based on our results, we can assert that even under the worst conditions such as anoxia
298 and resuspension events (at both weak and strong intensities), CFH-12[®] and Phoslock[®]
299 significantly reduced the accumulated P release. But apart from reducing P internal
300 loading, when selecting the most appropriate P adsorbent for a whole-lake application,
301 it is essential to get some knowledge about the economic cost of the lake restoration
302 strategy. As Funes et al. (2016) considered, the total cost of adding a P adsorbent to the
303 lake depend on both (i) its price and (ii) its maximum P adsorption capacity. CFH-12[®]
304 presents much more P adsorption capacity than Phoslock[®]. However, to calculate their
305 prices, it would be essential to know the exact amount of adsorbent to be added since
306 the prices fluctuate on account of the quantity purchased.

307 Before adding an inactivating P agent for restoring a eutrophicated lake, it is crucial to
308 consider that some elements can come into solution such as the case of dissolved Fe
309 when adding CFH-12[®] or dissolved La when adding Phoslock[®]. Results on dissolved Fe
310 release are shown in Fig. 4. In our case, accumulated Fe release did change over time
311 (RM-ANOVA: $F(3,27)=33.14$, $p < 0.0001$). In all treatments, accumulated Fe efflux
312 increased during the anoxic period. After the weak and strong resuspension events it did
313 not significantly change in Control and Phoslock[®] treatment. In CFH-12[®], Fe efflux
314 significantly increased after the weak resuspension (LSD $p < 0.05$) and then significantly
315 decreased after the strong resuspension (LSD $p < 0.05$). However, Fe efflux was not
316 significantly different between Control and treatments nor at the end of the anoxic

317 period neither after any of the two resuspension events (LSD $p > 0.05$) evidencing that
318 the addition of CFH-12[®] does not promote an increase in dissolved Fe during anoxia or
319 resuspension. Similarly to our results, Fuchs et al. (2018) reported the absence of Fe
320 release from CFH-12[®] in a long term anoxic core experiment. Even more, at the end of
321 the experiment, total dissolved Fe concentrations were below 0.1 mg L^{-1} for CFH-12[®],
322 0.2 mg L^{-1} for Phoslock[®] and 0.3 mg L^{-1} for Control (on average for all the treatments
323 0.25 mg L^{-1}). These values are similar to the dissolved Fe concentrations naturally
324 found in freshwaters (less than 1 mg L^{-1} ; Xing and Liu, 2011). Moreover, these values
325 do not exceed the threshold of 1 mg L^{-1} for total Fe established by EPA (1986) to
326 protect aquatic organisms.

327 Despite Phoslock[®] has been classified as riskless, La ions may be released from the
328 modified bentonite-clay in contact with water and be toxic for some aquatic organisms
329 (Lürling and Tolman, 2010). Because of this, it is of importance to evaluate the La
330 concentrations during the incubation period, with special emphasis after the
331 resuspension events, since Phoslock[®] is not redox-sensitive. Results on dissolved La
332 release are shown in Fig. 5. As seen, La concentration did not change over time (RM-
333 ANOVA: $F(1.4, 8.5) = 1.4$, $p = 0.287$), indicating that resuspension did not have any effect
334 on La concentration. Nevertheless, as expected, La concentrations were significantly
335 higher in Phoslock[®] than in Control at all sampling days (RM-ANOVA: $F(1, 6) = 117.8$,
336 $p < 0.00005$; LSD $p < 0.0005$). For the whole incubation period, the La concentration in
337 Phoslock[®] treatment was between $3.5\text{-}5.7 \text{ } \mu\text{g L}^{-1}$. At these low concentrations, no
338 remarkable toxic effects are expected for aquatic organisms since the EC_{50} values,
339 which is the concentration that causes an effect in 50% of the individuals during the
340 exposure period for some species of cladocerans, rainbow fish or algae reported in
341 several studies of acute toxicity are all well above ($\geq 40 \text{ } \mu\text{g La L}^{-1}$; Groves, 2010).

342 Finally, turbidity results are shown in Fig. 6. The turbidity measured in the water
343 column increased over time (RM-ANOVA: $F(1,94, 17.46)=11.36$, $p<0.001$). More
344 specifically, turbidity was significantly higher in Control after the strong resuspension
345 (LSD: day 62 $p=0.119$; day 63 $p<0.001$ and day 68 $p=0.072$). In the case of Phoslock[®],
346 turbidity increased only after the weak resuspension (LSD: day 62 $p<0.05$; day 63
347 $p=0.219$; day 68 $p=0.934$). However, turbidity did no increase significantly after
348 resuspension events (LSD: day 62 $p=0.260$; day 63 $p=0.624$; day 68 $p=0.789$) in the
349 case of CFH-12[®]. On the other hand, turbidity was not significantly different between
350 Control and treatments (RM-ANOVA: $F(2,9)=0.81$, $p=0.473$). Therefore, CFH-12[®] and
351 Phoslock[®] did not influence sediment stability. Contrarily to what was reported in other
352 studies using Phoslock[®] in resuspension experiments (Egemose et al., 2010), it seems
353 that Phoslock[®] did not increase sediment stability during resuspension. Presumably, it
354 can be explained by the higher intensities of resuspension applied in this work (0.4 and
355 0.95 m s^{-1}) compared to the maximum velocity reached by Egemose et al. (2010; 0.2 m
356 s^{-1}).

357

358 **4. Conclusions**

359 For the first time, a laboratory experiment is performed to compare the efficiency of two
360 novel P adsorbents (CFH-12[®] vs Phoslock[®]) for trapping P under two most frequent
361 circumstances prevailing in shallow eutrophicated lakes such as anoxia and sediment
362 resuspension. When selecting the most appropriate P adsorbent for a whole-lake
363 restoration strategy, it is essential to consider several aspects in relation to the
364 adsorbents, such as their efficiency under different circumstances (i.e. anoxia or
365 resuspension) the potential release of undesirable products and the economic cost. Both,
366 CFH-12[®] and Phoslock[®] significantly reduced accumulated P release during long term

367 anoxia and sediment resuspension. The use of Phoslock[®] may entail the release of La to
368 the water column, although the concentration in this study is low enough to avoid
369 toxicity to aquatic organisms. The release of Fe from CFH-12[®] is negligible both in oxic
370 and anoxic conditions. CFH-12[®] presents higher maximum P adsorption capacity than
371 Phoslock[®] but the total cost of each one will finally depend on the purchase price. In
372 order to ascertain the best option for the application in lakes, it is crucial to perform
373 further research to evaluate effect of other factors (e.g. pH, alkalinity, interfering
374 substances) on the performance of both adsorbents, but most of all on CFH-12[®], since
375 its behavior as P adsorbent is less studied in the literature.

376

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383

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521

Figures

Fig. 1. Picture of the experimental set-up for the resuspension experiment with intact sediment cores.

Fig. 2. SEM images of a) CFH-12[®] and b) Phoslock[®].

Fig. 3. Accumulated P release for 68 days. R1 (weak resuspension on day 62). R2 (strong resuspension on day 63). Standard deviation is represented by vertical bars.

Fig. 4. Accumulated Fe release for 68 days. R1 (weak resuspension on day 62). R2 (strong resuspension on day 63). Standard deviation is represented by vertical bars.

Fig. 5. La concentration in water column at sampling days. R1 (weak resuspension on day 62). R2 (strong resuspension on day 63). Standard deviation is represented by vertical bars. Statistically significant differences between treatments at each sampling day are indicated by letters.

Fig. 6. Turbidity in water column at all sampling days. R1 (weak resuspension on day 62). R2 (strong resuspension on day 63). Standard deviation is represented by vertical bars.

Fig. 1

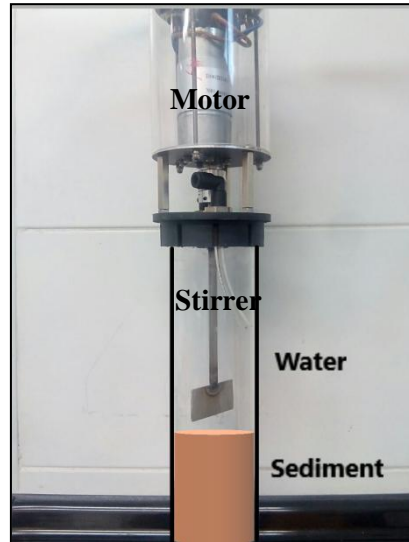
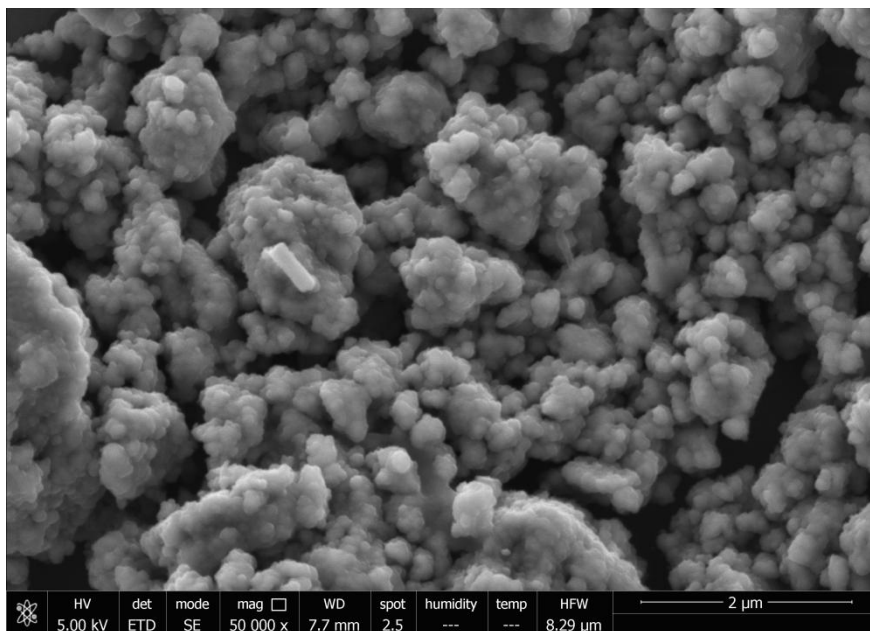


Fig. 2

a)



b)

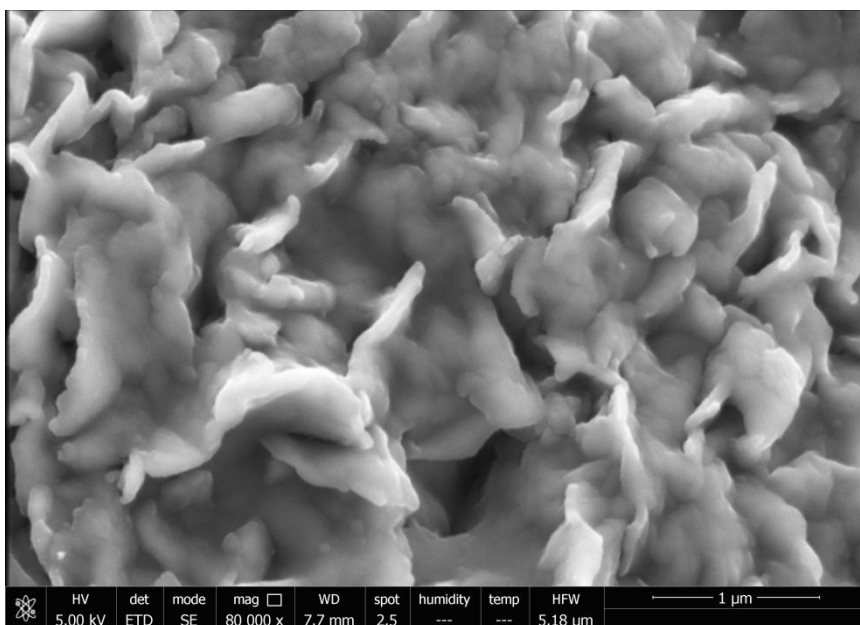


Fig. 3

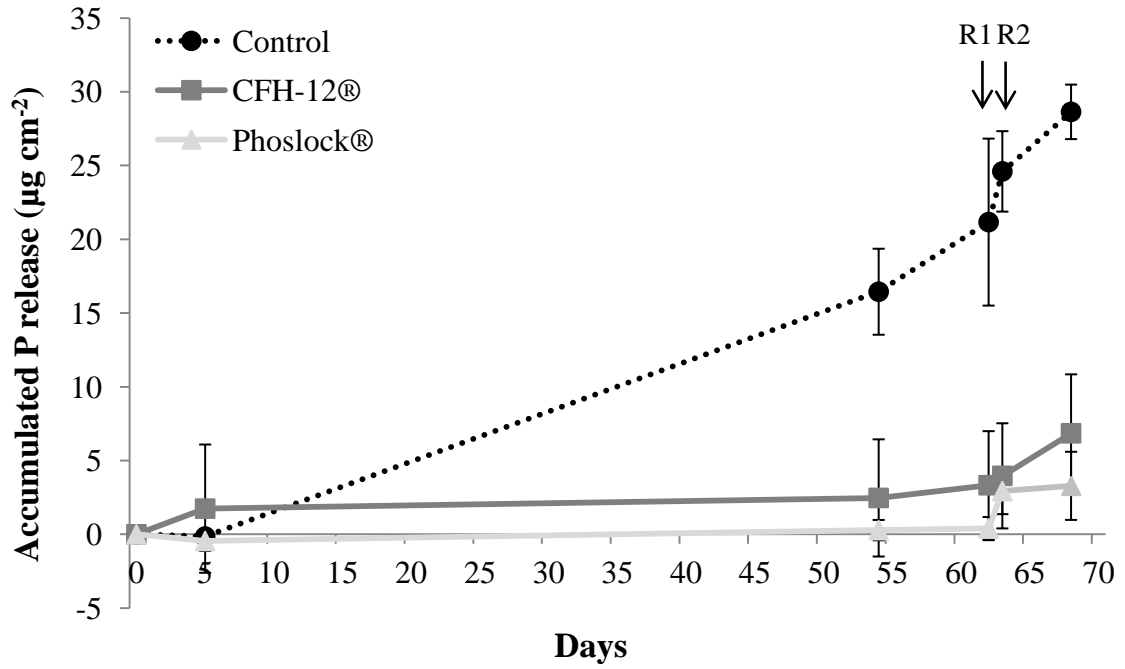


Fig. 4

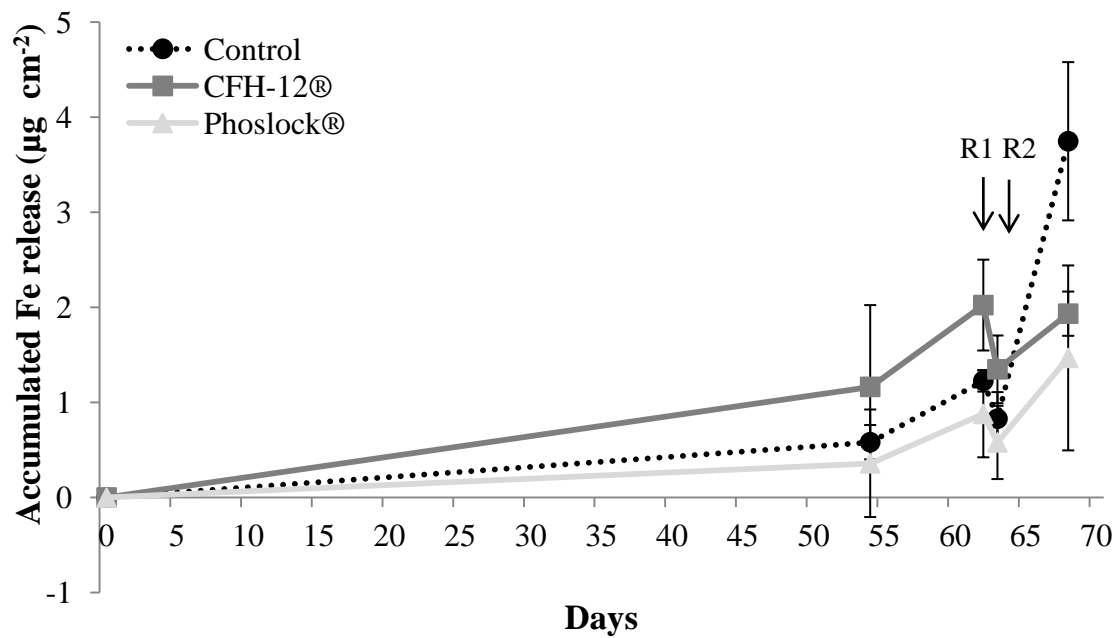


Fig.5

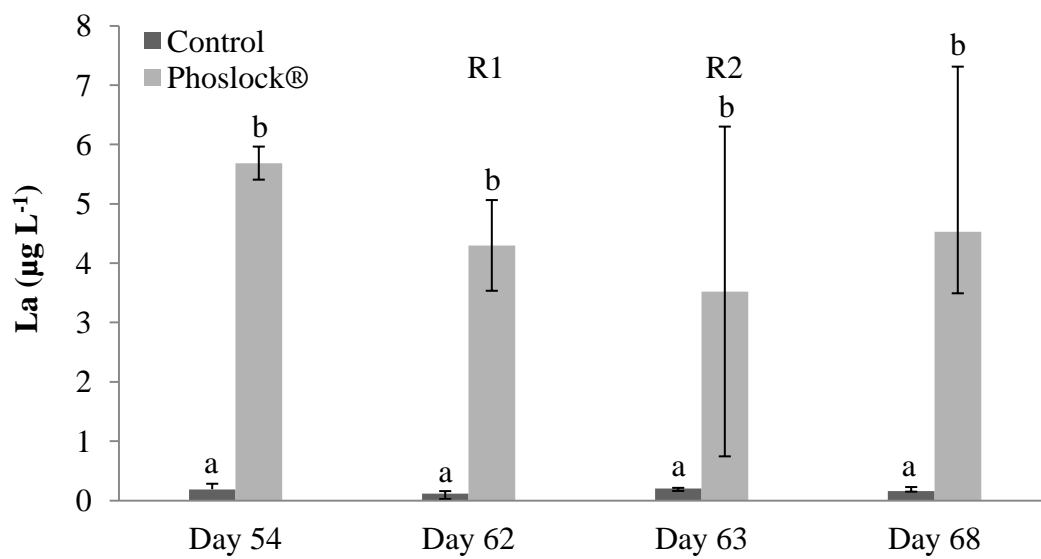
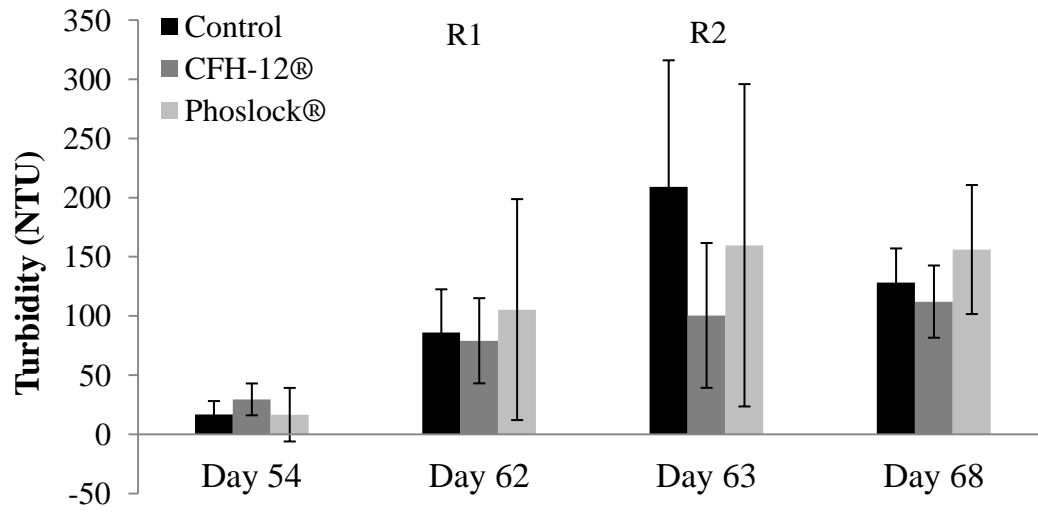


Fig. 6



Tables

Table 1. Surface chemical composition (in %) of the adsorbents by XPS technique.

Table 2. Physic-chemical parameters measured in the water column at sampling days. T: temperature; DO (dissolved oxygen). *missing data.

Table 1

Atomic surface concentration (%)										
	Fe	O	C	Si	La	Na	Mg	Al	Ca	S
CFH-12[®]	28,41	59,34	9,27	-	-	-	0,51	-	0,34	2,13
Phoslock[®]	0,96	65,75	5,61	19,20	0,73	0,84	1,33	4,78	0,81	-

Table 2

	<i>Day 0</i>	<i>Day 5</i>	<i>Day 54</i>	<i>Day 62</i>	<i>Day 63</i>	<i>Day 68</i>
	<i>(Adsorbents addition)</i>	<i>(Anoxic sampling)</i>	<i>(Anoxic sampling)</i>	<i>(weak resuspension)</i>	<i>(strong resuspension)</i>	<i>(final sampling)</i>
T (°C)	22.9 ± 0.2	21.2 ± 0.3	21.8 ± 0.1	22.4 ± 0.1	22.1 ± 0.2	21.5 ± 0.0
Control						
DO (mg L ⁻¹)	0.5 ± 0.1	0.5 ± 0.0	1.1 ± 0.0	1.0 ± 0.0	0.5 ± 0.0	0.9 ± 0.0
pH	9.2 ± 0.1	*	8.0 ± 0.2	8.1 ± 0.1	8.3 ± 0.1	8.2 ± 0.1
T (°C)	22.4 ± 0.1	21.7 ± 0.1	21.3 ± 0.1	22.1 ± 0.2	22.2 ± 0.2	21.3 ± 0.1
CFH-12[®]						
DO (mg L ⁻¹)	0.5 ± 0.1	0.9 ± 0.0	1.3 ± 0.0	0.9 ± 0.0	0.5 ± 0.0	1.0 ± 0.1
pH	9.3 ± 0.1	*	7.9 ± 0.1	8.1 ± 0.1	8.4 ± 0.0	8.5 ± 0.2
T (°C)	22.5 ± 0.1	21.1 ± 0.1	21.8 ± 0.2	22.5 ± 0.2	22.1 ± 0.1	21.3 ± 0.1
Phoslock[®]						
DO (mg L ⁻¹)	0.4 ± 0.1	0.8 ± 0.0	1.0 ± 0.0	1.0 ± 0.0	0.5 ± 0.1	1.0 ± 0.0
pH	9.4 ± 0.0	*	7.8 ± 0.1	8.1 ± 0.1	8.2 ± 0.2	8.3 ± 0.1