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Release of phosphorus under reducing and simulated open drainage conditions from overfertilised soils.

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(Article begins on next page)

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Manuscript Number: CHEM28299R1

Title: Release of phosphorus under reducing and simulated open drainage conditions from overfertilised soils

Article Type: Research Paper

Section/Category: Environmental Chemistry

Keywords: anaerobic conditions; anoxic; redox; mixed resins; HCO₃⁻ resins

Corresponding Author: Dr. Riccardo Scalenghe, PhD

Corresponding Author's Institution: Università degli Studi di Palermo

First Author: Riccardo Scalenghe, PhD

Order of Authors: Riccardo Scalenghe, PhD; Anthony C Edwards, PhD; Elisabetta Barberis, Professor; Franco Ajmone-Marsan, Professor

Response to Reviewers: Dear Editor,

We hereby submit the revised manuscript CHEM28299 "Release of phosphorus under reducing and simulated open drainage conditions from overfertilised soils". It has been revised according to the annotations and recommendations of both referees.

The page limitation was followed through the text and the number of tables plus figures does not exceed seven. We have defined acronyms when they first appear and then used in the subsequent text.

We did not create new acronyms but we quoted directly those from existing literature.

Our detailed reply to individual comments (in italics) are shown below.

Reviewer #1:

- Paper needs language editing. The ms has been thoroughly revised.

- What about Quality Assurance / Quality Control design?

Within the research project – which was carried out in four research institutions - a laboratory quality control was designed to reduce and correct potential deficiencies in the analytical process. To verify the quality of the results a P solution was circulated among the four laboratories and after a ring test for calibration it was utilised for running all the experiments. As a quality assurance all the basic analyses on the oxic status of all the soil samples were cross-checked between the laboratories. A laboratory quality control material was run within each experiment. The stability for the whole period of time of all the experiment was checked and it was always within upper and lower limits of one standard deviation.

All redox measurements were carried out through independent experiment and cross-checked at fixed period of time.

- Give a map showing the soil sampling sites and describe the sites in a related table in terms of geographical position, soil characteristics, land use and further variables which might be of importance for the interpretation of measurements.

As the number of tables and figures is limited we decided do not provide a visual representation of the study area (i.e. the European Union). We added the geographical coordinates, soil classification and main agricultural crops to Appendix A into the Supplementary Information. Actually, a static symbolic

depiction highlighting relationships among 12 elements within a space of more than 4 million square kilometres it seems not very meaningful. With modern and dynamic technologies for the visualization of geographical data we feel a table of data is more useful than a static map. A kmz file could be easily customised directly and effectively by the Reader.

Please, give the page number you are referring to. I looked for respective information on soils in that publication but I did not find nothing that could be referenced to your study.

We have added these details.

- Describe soil sampling.

The area sampled were all of them as uniform as possible in terms of soil type and cropping and fertilizing history. We collected a number of cores higher than 20 by walking in a zig-zag random pattern over each individual area. We sampled about 50 kg of soils by pushing the blade of a spade into the soil to a maximum depth of 50 cm, as a lower limit of the Ap horizon. We mixed all cores thoroughly in a clean pail for the composite lab sample.

- Conclusions: Ecological implications and recommendations for management should be discussed.

Some recommendations for management have been included into the Conclusion section.

Reviewer #2:

In general:

- I recommend the splitting of the 'results and discussion' section into separate 'results' and 'discussion' sections. As written, the section is confusing. Many of the sentences are long and blend description and interpretation of the data. Several times I had to re-read sentences to see if they concerned results of the authors of the current paper, results of the authors from a previous paper, or results of other authors of a previous paper. Creating a separate results section will make the data from the current research effort much more clear.

Done

- Separate out the analyses done in MINTEQ. As it is the 'results and discussion section' is not easily readable.

Done

- The long and complicated sentences of the 'results and discussion' section are characteristic of the writing throughout. Sentence length and complexity is not at the service of readability or interpretability. Therefore I recommend a sentence-by-sentence revision of the document. For example the first sentence of the paper itself (lines 37-40) is not even a sentence.

We rewrote most of the text, sentence-by-sentence. And we thank both reviewers for their careful revision of our previous manuscript.

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The number of figures and/or tables should not exceed a total amount of seven in Chemosphere. For this reason we have included the information required by Reviewer #2 as Appendix A into the Supplementary Information (SI). We will mention their existence explicitly through the text.

- How many replicates were allocated to the anionic resin, and the control treatments?

Four replicates it was stated at the beginning of line 102 at page 5, however we have included more specific detail.

- There is a conspicuous absence of the use of statistics throughout this paper. As a result differences are claimed between treatments but these differences are not justified.

We added the required statistics and we have modified the text accordingly, where necessary.

- 127: Include Eh and pH data from this experiment.

We added a table as Appendix B reporting redox measurements in soils at the beginning of the experiment (oxic conditions) and after 32 days of reduction.

During the experiment the pH of these soils have been modified by an average of 0.8 ± 0.6 pH units while the redox potential was lowered in average 9.6 ± 1.3 pe units (Appendix B, SI). Initial pe+pH of these soils is on average higher than 13.3 ± 1.3 while after reduction it falls to 4.5 ± 0.4 .

- 132-136: The data here are not referenced to a table or figure.

Added in the text: Figure 3 in Scalenghe et al. (2002)

- 140: 'This can be, in fact, unrealistic: if, on the one hand, an anionic...' an example of unnecessary language. Rather: "However this can be unrealistic. An anionic..."

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Highlights

- ▶ The response of 12 contrasting soils to reduction was tested in term of P release
- ▶ Laboratory simulation of open drainage was carried out using ion-exchange resins
- ▶ Ca plays a major role in controlling P dynamics even in acid soils
- ▶ The potential for P loss is increased by soil reduction-oxidation

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2 **soils**

3 **SCALENGHE Riccardo** (corresponding author: riccardo.scalenghe@unipa.it, skype [riccardo_daat](#))
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12 **AJMONE-MARSAN Franco** Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università degli
13 Studi di Torino, via Leonardo da Vinci 44, 10095 Grugliasco IT

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16 ► Laboratory simulation of open drainage was carried out using ion-exchange resins ► Ca plays a
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18 reduction-oxidation

19

20 **Abstract** Does removal of cations from soil solution during soil reduction stimulate phosphorus (P)
21 release? An ion-exchange resin system was employed to provide a sink during the incubation of
22 twelve soils under fully reducing conditions. ~~It was thought that~~ this experimental design was
23 considered to might better simulate the ~~possible~~ loss of ~~cations and anions~~ likely to which might
24 occur under field conditions than. ~~The~~ more routine batch type closed extraction systems
25 where allows solutes ~~the build-up of ions~~ build-up in the extracting solution. ~~Solution composition~~
26 ~~and soil P forms were identified by sequential extraction.~~ The small solute concentrations that
27 remaining in the equilibrating solution suggest the mixed resin system ~~effectively~~ acted as an
28 effective sink over the whole experimental period. By maintaining a small P ~~When the~~ concentration
29 ~~of P is lowered by~~ the resin system, ~~mimics~~ mimicking soil drainage conditions and encourages P
30 release from soil ~~increases~~. Measurement of soil P forms by sequential extraction after the
31 incubation period indicated an increase in the amorphous forms present. ~~Here,~~ we show that even
32 if the P-containing solution is retained by the soil, the potential for a subsequent P loss is increased
33 under aerobic conditions. The management of drainage systems should try and avoid the onset of
34 anaerobic conditions ~~in topsoil as this is likely to increase the solubility of P leading to the potential~~
35 ~~degradation of the quality of surface waters.~~ Eventually, magnesium- and calcium-based
36 precipitation products could recapture P from drains recycling it in topsoils as fertilizer.

37

38 **Keywords** anaerobic conditions; anoxic; redox; mixed resins; HCO₃⁻ resins

39

40 1. Introduction

41 ~~Phosphorus (P) release from soils to waterbodies is a matter of environmental concern particularly~~
42 ~~in terms of eutrophication of surface waters (Carpenter, 2005); today, in fact t~~The preeminent way
43 ~~in managing P excesses lies in recapturing P and recycling it again decelerating global P flows (Ashley~~
44 ~~et al., 2011; Cordell et al., 2009; Köiv et al., 2012; Rittmann et al., 2011; Ryan et al., 2012; Scholz and~~
45 ~~Wellmer, 2013).~~

46 The ~~P-reactivity~~ of phosphorus (P) in the environment through its association with Fe and Mn oxides
47 is influenced directly by the ~~reduction-oxidation (redox) state of topsoil components~~ as a significant
48 ~~proportion of it is associated with Fe and Mn oxides that can become reduced in the soil~~
49 ~~environment~~ (Hartikainen et al., 2010). ~~Phosphorus can be released when~~ if the environment
50 becomes anaerobic, oxides are ~~reduced and~~ solubilized and P associated with them is brought into
51 solution (Obour et al., 2011). Once in solution, P can be retained in the soil matrix by subsequent re-
52 sorption or can be removed ~~through (leaching) of~~ when the soil solution ~~is drained~~. While this is
53 generally inconsequential for soils that are submerged for long periods, soils that experience short-
54 term reduction ~~(Edwards and Withers, 2007)~~ can become potential sources of ~~P~~ phosphorus
55 ~~(Edwards and Withers, 2007)~~. Ajmone-Marsan et al. (2006) ~~have in fact~~ reported that ~~after~~ on
56 ~~repeated subsequent redox cycles of oxidation and reduction soil P chemical chemistry fractions~~
57 ~~tends~~ to shift towards more labile forms that would be more easily released on a subsequent
58 submersion and reduction cycle.

59 ~~Artificial d~~ Soil drainage of agricultural land is a management practice that provides some
60 control over the water regime, particularly of soils that experience ~~temporary transient~~ high water
61 tables and saturation. Under anoxic conditions, however, ~~the~~ artificial soil drainage may not be
62 recommended in view of the increased potential for transport and loss of nutrients (Schröder et al.,
63 2010). In addition to losses in solution P can move through the soil associated with transported
64 particles (e.g. Ashley et al., 2011; Beauchemin et al., 2003) and which would potentially accumulate
65 as within a drain or a ditch and function as a sink or source of nutrients accor depending ton the

66 ~~prevailing redox conditions, where soil particles tend to accumulate.~~ Normally, P-deficient ~~sub-~~soils
67 limit the movement of P from a highly concentrated solution toward drains (Allen et al., 2012). ~~but it~~
68 ~~can become a~~One particular ~~situation may occur~~issue where soils have been overfertilized with P
69 and anoxia ~~develops as a result of~~~~is attained with~~ overlying stagnant water combined with an
70 adequate supply of organic material (Hill and Robinson, 2012; Mukhtar et al., 1996).

71 In previous experiments conducted on a range of European soils overfertilized with P ~~we~~
72 ~~was~~ ~~have~~ observed that P is released under reduction and that more P is released under pulsed
73 redox conditions, i.e. on alternating wet-dry cycles (Scalenghe et al., 2012). In those experiments,
74 however, the concentration of P in solution rapidly ~~reached a~~ peaked and then decreased, ~~most~~
75 ~~likely due to re-adsorption on the soil matrix.~~ The decrease in soluble P concentration can be
76 explained by soil re-adsorption as crystalline Fe-oxides are not completely dissolved by the reduction
77 ~~and while~~ retain ~~part of~~ ~~ing~~ their sorption capacity (Demello et al., 1998). Also, new sorption sites
78 may ~~result~~derive from the dissolution of Fe ~~coatings~~oxides that exposes ~~fresh~~new adsorbing surfaces
79 ~~on clay minerals~~, onto which Fe oxides are often precipitated, and from iron ~~precipitates~~oxides that
80 ~~can be~~formed under anoxia (Willett and Higgins, 1978; Willett, 1989; Barberis et al., 1992). ~~In an~~
81 ~~extension of earlier experiments (Scalenghe et al., 2002 and 2012) these conditions were simulated~~
82 ~~by introducing a sink for reactants and simulating non equilibrium conditions in an attempt to better~~
83 ~~quantify the potential release of P (Fernández et al., 2008).~~The 'closed system' experimental
84 approach used in those studies (e.g. Scalenghe et al., 2002; Obour et al., 2011) could have ~~in fact~~
85 influenced the extent to which elements released to the ~~surrounding~~ solution subsequently interact
86 with the soil mineral phase.

87 ~~While U~~nder field conditions, ~~however in fact, while~~ it is possible that the soil solution
88 remains in contact with the soil matrix, it is also likely to infiltrate through the *solum*, leaching P and
89 other ions in solution towards the water table ~~and promoting further release.~~ ~~By introducing a sink~~
90 ~~for reactants and simulating non-equilibrium conditions Fernández et al. (2008) attempted to better~~
91 ~~quantify the potential release of P.~~

92 The aim of this paper is to appraise P release from overfertilized soils under reducing
93 conditions in the presence of a sink (ion-exchange resin) ~~which~~ better simulates the removal of
94 elements that might occur during leaching.

95

96 **2. Material and Methods**

97 The soils involved in this study ~~are taxonomically representative of one thirds of the World~~
98 ~~Reference Base Groups (IUSS Working Group WRB, 2007). They~~ span geographically from parallel 38
99 to 57 N and from meridian 6 W to 11 E, and pedologically from the cooler Chernozems to the
100 warmer Vertisols, and to Regosols ~~(IUSS Working Group WRB, 2007)~~. Mean annual air temperature
101 varies from 7.5 to 18.5 °C and mean annual rainfall from 490 to 900 mm. The selected ~~agricultural~~
102 soils are intensively farmed (OECD, 2007) and 'overfertilised' by having at least twice the optimum
103 concentration of available P. All sampled Ap horizons were sieved to <2 mm and stored in an air-dry
104 condition. The soils and their relevant general properties ~~have been~~ are described in Barberis et
105 al. (1996) ~~(Supplementary Information (SI), Appendix A) and~~ while basic the redox relevant ~~basic~~
106 information ~~can be found~~ in Scalenghe et al. (2002) ~~(SI, Appendix B)~~. According to Delgado and
107 Torrent (1997), these soils ~~can behave been~~ grouped into calcareous, C, (E1, E2 and I3), slightly acid,
108 SA, (D1, D2, E3 and I2), acid and rich in organic matter, AOMR, (G3, G6 and G9), and acid and light-
109 textured, ALT, (D3 and I1) ~~(Supplementary Information, Appendix A)~~. The latter group contains two
110 soils with very different properties: D3 is a sandy soil with a large amount of extractable P and I1 was
111 sampled from a rice ~~fieldgrowing region~~, and therefore ~~it undergoes will have experienced~~ periodic
112 flooding as a routine agronomic practice. The general properties of soils include a pH ranging from
113 4.6 to 7.8 and organic carbon from 7 to 39 g kg⁻¹. Extractable forms of Fe and Al differ widely; the
114 oxalate/dithionite extractable iron, Fe_{ox}/Fe_d ratio ~~(an index of the degree of iron crystallinity~~
115 ~~proposed by Delgado and Torrent, (1997),~~ ranged from 0.07 to 0.77 being >0.5 in three soils only
116 (G3, D3 and I1).

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117 ~~Four replicates~~Quadruplicate of 0.25-g each soil samples were incubated in 120 mL vials with
118 2.5 g of HCO₃⁻-resin (Dowex 1x4-50), 0.8 g of H⁺-resin (Dowex 8x5-50) and 100 mL of deionized water
119 (pre-purged with N₂) sealed and stored in an anaerobic box. ~~A~~The similarame experiment with the
120 anionic resin only was performed with four replicates (including the control treatments) as described
121 by Sibbesen (1977 and 1978). A gas mixture of pN₂=0.88; pCO₂=0.08; pH₂=0.04 was chosen to best
122 simulate the components most likely to be present under naturally anoxic conditions. Hydrogen was
123 flushed through a Pd catalyser to remove the residual O₂. All vials were subjected to a reduction
124 period of 32 days at 298 K. This saturation period was chosen as this was known from previous
125 studies to approximate full reduction for these soils (Scalenghe et al., 2002). A control series of
126 samples were maintained in an aerobic condition by flushing each vial every day with ~~in~~ air for 30
127 minutes. Redox parameters (Eh and pH) were measured within the anaerobic box on the reduced
128 series. All the vials were shaken on an end-over-end shaker at 150 rpm every day for 20 minutes
129 during the reduction period. ~~After 32 days~~the end the sealed vials were centrifuged at 1800 g then
130 5 mL of the supernatant were sampled using a syringe and acidified to pH<3 in order to minimise the
131 precipitation of oxidized species.

132 Soil P fractions ~~in the soils of the oxic and anoxic experiments~~ were quantified by sequential
133 extraction (Olsen and Sommers, 1982) on all samples at the end of the incubation period. In brief the
134 method includes (1a) 1 M NaOH, P_{NaOH}, to remove P associated to Fe and Al (hydr-) oxides (1b)
135 citrate bicarbonate, P_{CB}, to remove P adsorbed by carbonates during the previous extraction, (2) Na
136 citrate-bicarbonate-dithionite, P_{CBD}, to remove occluded P within the Fe oxides, and (3) 1 M HCl, P_{HCl},
137 to remove P bound to Ca. Phosphorus in the solutions (molybdate-reactive P, ~~e~~ MRP) was
138 determined using either the method of Murphy and Riley (1962) or by the malachite green method
139 of Ohno and Zibilske (1991) as modified by Barberis et al. (1998) for lower concentrations. Calcium,
140 Fe and Mn were determined by atomic adsorption spectrometry.

141 Solutions and solid phases were analyzed following the standard analytical methods
142 described in Barberis et al. (1996) and Scalenghe et al. (2002). Activity calculations were made using
143 the chemical speciation program MINTEQA3 (Gustafsson, 2012).

144

145 3. Results

146 The onset of anoxic condition was reached within one week and values of Eh and pH corresponded
147 to those obtained in previous experiments with the same soils (Scalenghe et al., 2002). At the end of
148 the present experiment the pH of these soils was modified by an average of 0.8 ± 0.6 pH units while
149 the redox potential was lowered on average by 9.6 ± 1.3 pe units (Appendix B, SI). The initial pe+pH of
150 these soils was on average higher than 13.3 ± 1.3 while it fell to 4.5 ± 0.4 after reduction.

151 The amount of P extracted in the presence of mixed resins was higher than that extracted
152 when using anionic resins only. In Figure 1 the amount of P that remains in solution without any
153 resin and that adsorbed by resins are compared. These data confirm a better efficiency of the mixed
154 resins in extracting P from soils under anoxic conditions, although not statistically significant. The
155 amount of cations and anions left in the solution is nevertheless measurable and is higher for the
156 anoxic samples in the case of Ca for all soils, Fe and Mn in more acidic soils and P in calcareous soils
157 (FigureTable 12).

158 When the release of elements to mixed resins under anoxic conditions is compared with oxic
159 conditions (Table 24), a general increase of P removal from all anoxic soils is observed and it
160 corresponds to the excess P fertilizers these soils have received (Delgado and Torrent, 1997). One
161 origin for this P appears to be related to the solubilization of Ca compounds. In calcareous soils the
162 removal of Ca is also the result of the lowering of the pH under anaerobiosis. The release of P
163 appears to be the result of many factors. The reduction of the oxides and the consequent maximum
164 release of Fe, Mn, and the associated Al and Ca is up to around $700 \text{ mg Fe kg}^{-1}$, $300 \text{ mg Mn kg}^{-1}$, 100
165 mg Al kg^{-1} and about 38 g kg^{-1} for Ca (calculated as difference between anoxic and oxic release as a
166 sum of both the concentration in Table 1 and Figure 12).

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167 Figure 23 shows Quantity-Intensity (Q/I) relationships, where Q is the P desorbed by the
168 resin and I is the P that remains in solution. Soil groupings had no influence on this relationship ($p <$
169 >0.05) and the Q/I relationship in the oxidized environment follows a linear trend. Under reducing
170 conditions there is no relationship between Q and I.

171 Analysis of the solid P phase determined after re-oxidation at the end of the experiment
172 (Figure 34) show that for SA and ALT soils a decrease of P_{NaOH} is evident while I3, a carbonate-rich C
173 soil, is marked by a decrease in P_{HCl} . A decrease of occluded P (P_{CBD}) is also evident. While, the
174 simultaneous increase of P_{NaOH} , and P_{CB} is probably due to re-adsorption phenomena.

175

176 **4. and Discussion**

177 The release of P is released in into solution under when the soil becomes anoxic conditions has been
178 demonstrated by several authors for a range of soil and sediment (Davison, 1993; Demello et al.,
179 1998; Ajmone-Marsan et al., 2006; Scalenghe et al., 2012).

180 In our soils the onset of anoxic condition was reached within one week. The values of Eh and pH
181 (data not shown Supplementary Information, SI) corresponded to the values obtained in previous
182 experiments with the same soils (Scalenghe et al., 2002). At the end of the present experiment the
183 pH of these soils were have been modified by an average of 0.8 ± 0.6 pH units while the redox
184 potential was lowered on average by 9.6 ± 1.3 pe units (Appendix B, SI). The initial pe + pH of these
185 soils was on average higher that 13.3 ± 1.3 while after reduction it fealls to 4.5 ± 0.4 after reduction.

186 In the previous ese experiments using these soils (Scalenghe et al., 2002), Pphosphorus was released
187 from all soils under anaerobic conditions and peaked after 32 days, after which concentrations in
188 solution decreased. At the onset of anaerobiosis the dissolution of Fe and Mn oxides was
189 demonstrated by an increase of their solution concentration. One third of the Fe_0 was solubilized by
190 the effect of the reduction in SA, AOMR and ALT soils ($14 \pm 4\%$ of the initial P_{CBD} CBD extractable iron).
191 In C soils around 14% per cent of Fe_0 passed in solution which corresponds to 3% of the initial
192 P_{CBD} CBD extractable iron. This was accompanied by a substantial remarkable release of P as a

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193 consequence of the dissolution of the Fe-Mn oxide surfaces where the P ~~was~~ adsorbed (Figure 3 in
194 Scalenghe et al., 2002, page 443). For this reason ~~we have designed the current experiments were~~
195 ~~designed with a period of 32 days of anoxia.~~

196 ~~Various authors have~~ ~~it has been~~ observed that the addition of a P (anion) sink in the
197 experimental system maintains the P concentration in ~~the~~ solution close to zero and ~~limits restricts~~
198 the re-adsorption of P by the soil (Agnébin and van Raij, 2001; Amery and Smolders, 2012; Bache
199 and Ireland, 1980; Barrow and Shaw, 1977; Sibbesen, 1977). ~~However, this may not be~~
200 ~~representative of natural conditions be unrealistic as the.~~ ~~An~~ This can be, in fact, unrealistic: if, on the
201 ~~one hand, an~~ anionic resin ~~would~~ ~~would~~ competes ~~with the positively charged surfaces of the soil~~ for
202 P adsorption, ~~thus~~ shifting the ~~P equilibrium~~ towards the solution, ~~but, on the other hand~~ it would
203 not hinder the dissolution-precipitation of Ca-P compounds ~~that would predominate, for example, in~~
204 ~~a calcareous soil.~~ In order to obtain a more ~~accurate realistic~~ picture by including these ~~latter~~
205 reactions in our system, the experiment was run in the presence of a mixed - cationic and anionic -
206 resin. The mixed resin has the effect of removing the principal anions and cations from the solution,
207 ~~reducing preventing the likelihood of~~ any precipitation with P (Curtin et al., 1987); ~~in turn,~~ this ~~would~~
208 mimics ~~the a~~ removal of ions from solution under field conditions in response to drainage.

209 ~~In our twelve soils the amounts of P extracted using mixed resins was higher than that~~
210 ~~extracted using anionic resins only. In Figure 1 the amount of P that remains in solution without any~~
211 ~~resin and that adsorbed by resins are compared. These data show the confirm a better efficiency of~~
212 ~~the mixed resins in extracting P from soils under anoxic conditions, although not statistically~~
213 ~~significant. The amount of cations and anions left in the solution is nevertheless measurable and is~~
214 ~~again higher for the anoxic samples in the case of Ca for all soils, Fe and Mn in more acidic soils and P~~
215 ~~in calcareous soils (Figure 2).~~

216 ~~When the release of elements to mixed resins under anoxic conditions is compared with oxic~~
217 ~~conditions (Table 1), a general increase of anoxic P removal from all soils is observed and it is in line~~
218 ~~with the excess P fertilizers these soils have received (Delgado and Torrent, 1997). Part of this~~

219 ~~release appears to be connected with~~related to the solubilization of Ca compounds. In calcareous
220 ~~soils the removal of Ca is also the result of the lowering of the pH following the~~under anaerobiosis.
221 ~~This contributes to the release of P by preventing the precipitation of Ca-P compounds.~~

222 The release of phosphorus appears to be the is a result of many factors. All these factors
223 ~~appear to have contributed to the release of phosphorus. The reduction of the oxides and the~~
224 ~~consequent maximum release of Fe, Mn, and the associated Al and Ca is up to around 700 mg Fe kg⁻¹~~
225 ~~, 300 mg Mn kg⁻¹, 100 mg Al kg⁻¹ and about 38 g kg⁻¹ for Ca (calculated as difference between anoxic~~
226 ~~and oxic release as a sum of both the concentration in Table 1 and Figure 1). The release of nearly 2~~
227 ~~times the amount of P under reduction is paralleled by the release of Fe. While~~Usually Fe is by
228 ~~far the dominant role in P retention but a role should not be excluded for Mn also appears to be~~
229 ~~involved in our soils. In general~~The reduction doubles the amount of favours the release of about two
230 ~~times the~~Mn with respect to the oxic environment (and up to 11 and 13 times for D2 and I1,
231 respectively). The~~An~~influence of Mn on P sorption has been suggested for soils of temperate areas
232 (Zaidel'man et al., 2009) although this~~it~~was not confirmed for tropical soils (Gonçalves et al., 2011).

233 ~~The release of high amounts of P appears to be accompanied by an increase of Al concentration in~~
234 ~~solution. The reduction of the oxides and the consequent maximum release (calculated as difference~~
235 ~~between anoxic and oxic release) of Fe, Mn, and the associated Al and Ca is up to around 700 mg Fe~~
236 ~~kg⁻¹, 300 mg Mn kg⁻¹, 100 mg Al kg⁻¹ and about 38 g kg⁻¹ for Ca. The effect of reduction favours the~~
237 ~~release of about two times the manganese with respect to the oxic environment (and up to 11 and~~
238 ~~13 times for D2 and I1, respectively). The amount of Fe and Al adsorbed by the resins,~~on the
239 ~~contrary,~~ appears to be independent ~~on~~from the soil type. In general, however, an increase of the
240 release of Al is observed. Soluble Al can derive from a combination of Al-substituted Fe oxides
241 (Adhami et al., 2012; Cessa et al., 2009), or from organic molecules that are being oxidized
242 (Pizzeghello et al., 2011). Previous findings (Scalenghe et al., 2002; Wang et al., 2013) postulated an
243 involvement of Al in the ~~P cycle of P~~ under reduction although this element is not directly affected by
244 redox reactions. Also, the decrease of the pH in calcareous soils associated with the reduction

245 increases the solubility of Al; its displacement can in turn favour the dissolution of Al-silicates or
246 strengite. ~~An influence of Mn on P sorption has been postulated for soils of temperate areas~~
247 ~~(Zaidel'man et al., 2009) but this was not confirmed for tropical soils (Gonçalves et al., 2011). In our~~
248 ~~soils a role of Mn in the P retention should also be taken into account.~~

249 ~~Phosphorus loss from soils can occur under diverse conditions and commonly~~ The ratio
250 between soil mass and water is ~~an assumed to be the most~~ important factors influencing P release
251 ~~from soil~~ soil P loss ~~the process~~. In our soils, independently of their groupings, the amount of P
252 desorbed to a dilute electrolyte is correlated with P concentration in the 1:1 water-to-soil-ratio
253 extract raised to a power that decreases with widening of increasing the water-to-soil-ratio, as
254 ~~observed by~~ (Torrent and Delgado, 2001). These ~~a~~ Authors concluded that under oxic conditions it is
255 the Quantity (Q) that controls the system. ~~Figure 3 shows Quantity Intensity (Q/I) relationships,~~
256 ~~where Q is the P desorbed by the resins (the quantity that actually is adsorbed onto the resin) and I~~
257 ~~is the phosphorus that remains in solution. Soil groupings are not relevant ($p < 0.05$) and the Q/I~~
258 ~~relationship in the oxidized environment follows an equation of the etm-type a linear trend. Otherwise~~
259 ~~Under reducing conditions there is no relationship between Q and I quantity and intensity,~~
260 ~~confirming that, while in~~ The difference in behaviour and relationship between Q and I (Figure 23)
261 may be explained as under oxic conditions part of the P solution concentration ~~in solution~~ is
262 controlled by the solid phase, while under anoxia the dissolution of the oxides ~~of surfaces~~ brings
263 about a variety of precipitation reactions ~~which that~~ prevents any clear relationship from being
264 observed.

265 ~~Analysis of the solid P phase determined after re-oxidation (Figure 4) at the end of the~~
266 ~~experiments (Figure 4) show that in SA and ALT soils, where the release of P is likely being controlled~~
267 ~~by Fe (hydr)oxides, a decrease of P_{NaOH} is evident while with congruence in I3, a carbonate-rich C~~
268 ~~soils is marked by a decrease in P_{HCl}. A decrease of occluded phosphorus, P_{CBP} is also observed.~~
269 ~~While, The simultaneous increase of P_{NaOH} and P_{CB} is probably due to re-adsorption phenomena. A~~
270 ~~decrease of occluded phosphorus, P_{CBP} is also observed.~~ Various soil P fractions, particularly those in

271 newly accreted materials, are highly unstable and could be released in a more available form when
272 ~~newly accreted~~ soils undergo subsequent rewetting after drying. It appears in fact that reduction
273 brings about an overall transformation of P forms towards more labile forms confirming earlier
274 results findings obtained by other researchers on different soils (Ajmone-Marsan et al., 2006; Olila et
275 al., 1997). For these
276 ~~in our soils, it had been observed that~~ if a new anoxic environment develops the potential
277 release of P ~~is was~~ increased ~~during time is pulsed reducing condition occurs well~~ (Figure 1 in Figure
278 1 at page 143 in Scalenghe et al., 2012, Figure 1, page 143). ~~A proof~~ This response evidence is
279 explained here comes from by the considerable amount of Fe and Mn precipitated in amorphous
280 (oxalate extractable) forms ~~extraction of amorphous Fe forms after the experiments of 32 days of~~
281 incubation in the presence of mixed resins. ~~The data in (Table 2) clearly show that, after the~~
282 ~~experiment with mixed resins, a considerable amount of Fe – and Mn – is precipitated in amorphous~~
283 ~~(oxalate extractable) forms together with some P, most probably the P that remained in solution~~
284 ~~during the anoxic experiment.~~ – No relationship is apparent between P and Fe, and Mn in oxic
285 conditions, in Table 2. Nevertheless, the difference between oxalate extractable elements under oxic
286 and reducing conditions after incubation with mixed resins shown in (Table 3) – explains the
287 relationship between P bound to the resin after 32 days of submersion as a Q factor and P in
288 solution, highlighted in Figure- 2. The progressive increase in amorphification components of the
289 absorbing complex alternating oxic c conditions under anoxia provokes the dissolution of the oxides
290 and carbonates that in turn cause the release of P. Nevertheless their presence of P in solution
291 does not appear to be controlled by the solid phase in accordance with the data of Figure 3. Quang
292 and Dufey (1995) ~~observed the same phenomenon~~.

294 4.1 Theoretical prediction of P precipitates

295 The possibility that P in solution ~~is maybe~~ lowered by precipitation was also considered. Due
296 to overfertilization polyphosphates occur largely in agricultural soils and tend to transform into β -

297 | $\text{Ca}_2\text{P}_2\text{O}_7$. Pyrophosphates are unstable in soils and eventually ~~are converted~~~~turn—in~~ to
298 | orthophosphates. In oxic environments, the theoretical threshold stability of magnetite occurs when
299 | $\text{pe}+\text{pH}>11.53$: the availability of ionic Fe—~~definitely~~ controls soil mineral stability, below that
300 | threshold Ca prevails (Lindsay, 1979). Strongly reduced environments are again controlled by Fe, but
301 | $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ is converted into $\text{Fe}_2\text{P}_2\text{O}_7$ only at $\text{pe}+\text{pH}<3$.

302 | In the presence of free O_2 our soils show an average $\text{pe}+\text{pH}$ of 13.3 ± 0.9 , which drops to
303 | 4.5 ± 0.4 after 32 days under reducing conditions. When ~~the~~our soils become anoxic, without resins,
304 | the co-precipitation of the most common Fe and P compounds is unlikely despite the large
305 | concentration of Fe and P; the decrease of Fe and Mn concentration in solution is, in fact,
306 | presumably due to the formation of Fe and Mn precipitates not in association with P ([Figure 4 in](#)
307 | [Scalenghe et al., 2002, page 443](#)). By mimicking the ~~effect of losing elements through~~ ~~drain~~~~ageing of~~
308 | ~~our soils~~ under anoxia, the selective removal of ions ~~by the drains~~ produces conditions that, contrary
309 | to a closed system, could induce the precipitation of phosphates (Table [43](#)). Hydroxyapatite ~~could be~~
310 | ~~expected~~ in C and SA soils, ~~with~~ MnHPO_4 in C, SA and AOMR soils, and vivianite in all soils.
311 | Manganese and iron phosphates are normally insignificant ~~under closed laboratory conditions~~ but
312 | ~~in the resin based~~ open systems ~~used here~~ may increase their relative importance (Green et al.,
313 | 1989). [For instance](#), Walpersdorf et al. (2013) have recently confirmed that vivianite may control P
314 | concentration in solution under soil anaerobic conditions.

315 | [In many ecosystems P is often the limiting nutrient, even in intensively managed agricultural](#)
316 | [systems where P is a regular addition the general view is that the bioavailability of P gradually](#)
317 | [declines with time. Various mechanisms have been proposed to explain this observation and these](#)
318 | [include the formation of more stable P-oxide precipitates together with a physical migration of P](#)
319 | [deeper into soil aggregates. Here we describe some simple laboratory simulations employing](#)
320 | [changes in local redox and leaching environment where the opposite situation might be expected. In](#)
321 | [widely contrasting soils it has been demonstrated that the resulting fresh P containing precipitates](#)
322 | [which readily formed after short-term periods of reduction. If the frequency and geographical](#)

323 distribution of soils likely to experience reducing conditions is increasing as a result of climate
324 change and increased management induced soil compaction then there is the possibility that
325 temporary increases in the bioavailability of soil P may be the result.

326 Maintaining the efficiency land drains where present remains an important management
327 strategy. While in certain situations this might increase the risk of P leaching novel capture and
328 recovery techniques (e.g., Erickson et al., 2012; Kõiv et al., 2012; Liu et al., 2013) are being
329 suggested. Rittmann et al. (2011) have reviewed the current options being suggested for P recovery,
330 which include precipitation as Al-, Fe-, Mg- (e.g. struvite) or Ca- (e.g. hydroxyapatite) based products
331 that also have qualities potentially equivalent to conventional fertilizers. Phosphorus recovery could
332 also involve adsorption (metal-based adsorbents), ion exchange (phosphate-selective solids), or
333 uptake (photosynthetic microorganisms or P-selective proteins).

334
335

336 **54. Conclusions**

337 The provision of a sink for cations and anions during the development of reducing conditions
338 over a 32 day period modified the degree of solubilisation that occurred in wide range of
339 overfertilised soils. In general anoxic conditions brought about the release of P to various degrees.
340 When the concentration of P is lowered by providing a resin sink, mimicking a draining solution, the
341 amount of P released (solubilised) increases. The amount of additional P that can be solubilised from
342 a 20 cm soil layer is as much as 0.5 kg ha⁻¹, especially from light textured soils which are also more
343 prone to leaching although less prone to waterlogging. The choice of experimental conditions
344 imposed during laboratory incubations is shown to significantly influence the solubility of P. After
345 the incubation period soils were allowed to dry out and effects continued to be apparent in the
346 forms of P present in the solid phase. ~~Overfertilised soils of diverse location in Europe were~~
347 ~~confirmed to contribute a threat for water quality. In general anoxic conditions brought~~brings about
348 the release of P to various degrees in overfertilized soil. When the concentration of P is lowered by

349 ~~providing a the resin sink, mimicking a draining solution, P release increases. The amount of~~
350 ~~additional P that can be solubilised from lost by a 20 cm soil layer of 20 cm is as much as half a kg0.5~~
351 ~~kg per ha⁴, especially in particular from light textured soils which are also more prone to leaching~~
352 ~~(although less prone to waterlogging). Obviously, not all P is lost with the soil solution as part of it~~
353 ~~can be removed by particles that are eluviated with the draining solution, so it is difficult to achieve~~
354 ~~accurate predictions in terms of P concentrations in tile drainage water (Beauchemin et al., 2003).~~
355 ~~In those soils where the possibility of reaching anoxic condition is likely, i.e. where there is an excess~~
356 ~~precipitation (or irrigation) over evapotranspiration (or irrigation) or a fluctuating dynamic~~
357 ~~watertable, soil drainage is an obvious solution. In those cases one might wonder if it would be~~
358 ~~better to let the soil solution to drain freely drain, and lose some P or to limit water percolation to~~
359 ~~avoid P losses. The latter would however induce reduction and would eventually result end up in a~~
360 ~~possible greater loss of P. Here, we have also shown that even if the P-containing solution is retained~~
361 ~~by the soil closing by the drains the potential for a subsequent P loss is increased under anaerobic~~
362 ~~conditions. The main soil P losses originate, in fact, from a little part of critical areas characterised by~~
363 ~~a great release P potential (Huang et al., 2012) and although those losses by leaching appears to be~~
364 ~~inevitable in aerobic systems, it would be much worse if those soils go anaerobic, even for a short~~
365 ~~period. The management of drainage systems should avoid the onset of anaerobic conditions as~~
366 ~~much as possible, as that would increase the potential degradation of the quality of the draining~~
367 ~~water.~~

368

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371

372 **Appendix A. Supplementary material**

373 | Supplementary data [on sampling, soil characteristics, and redox parameters which might be of](#)
374 | [importance for the ~~interpretation~~interpretation of these results are](#) associated with this article [and](#)
375 | can be found, in the online version, at [URL...](#)
376 |

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511 **Table 1**

<u>Group†</u>	<u>control (oxic)</u>					<u>reduced</u>					
	<u>P</u>	<u>Mn</u>	<u>Fe</u>	<u>Al</u>	<u>Ca</u>	<u>P</u>	<u>Mn</u>	<u>Fe</u>	<u>Al</u>	<u>Ca</u>	
<u>C</u>	<u>E1</u>	<u>45</u>	<u>n.d.</u>	<u>179</u>	<u>n.d.</u>	<u>1954</u>	<u>48</u>	<u>24</u>	<u>62</u>	<u>n.d.</u>	<u>3048</u>
	<u>E2</u>	<u>33</u>	<u>n.d.</u>	<u>72</u>	<u>n.d.</u>	<u>2240</u>	<u>37</u>	<u>24</u>	<u>62</u>	<u>n.d.</u>	<u>7948</u>
	<u>I3</u>	<u>25</u>	<u>n.d.</u>	<u>20</u>	<u>n.d.</u>	<u>1071</u>	<u>50</u>	<u>6</u>	<u>75</u>	<u>n.d.</u>	<u>2073</u>
<u>SA</u>	<u>D1</u>	<u>39</u>	<u>n.d.</u>	<u>113</u>	<u>n.d.</u>	<u>71</u>	<u>48</u>	<u>n.d.</u>	<u>53</u>	<u>n.d.</u>	<u>625</u>
	<u>D2</u>	<u>27</u>	<u>n.d.</u>	<u>18</u>	<u>n.d.</u>	<u>23</u>	<u>30</u>	<u>18</u>	<u>32</u>	<u>n.d.</u>	<u>290</u>
	<u>E3</u>	<u>25</u>	<u>n.d.</u>	<u>233</u>	<u>n.d.</u>	<u>50</u>	<u>43</u>	<u>18</u>	<u>122</u>	<u>n.d.</u>	<u>317</u>
	<u>I2</u>	<u>28</u>	<u>6</u>	<u>51</u>	<u>n.d.</u>	<u>2</u>	<u>31</u>	<u>12</u>	<u>90</u>	<u>n.d.</u>	<u>104</u>
<u>AOMR</u>	<u>G3</u>	<u>24</u>	<u>n.d.</u>	<u>12</u>	<u>n.d.</u>	<u>31</u>	<u>25</u>	<u>24</u>	<u>63</u>	<u>n.d.</u>	<u>71</u>
	<u>G6</u>	<u>26</u>	<u>n.d.</u>	<u>9</u>	<u>n.d.</u>	<u>2</u>	<u>32</u>	<u>18</u>	<u>84</u>	<u>1</u>	<u>90</u>
	<u>G9</u>	<u>26</u>	<u>n.d.</u>	<u>14</u>	<u>n.d.</u>	<u>23</u>	<u>25</u>	<u>24</u>	<u>54</u>	<u>n.d.</u>	<u>110</u>
<u>ALT</u>	<u>D3</u>	<u>27</u>	<u>n.d.</u>	<u>12</u>	<u>n.d.</u>	<u>8</u>	<u>31</u>	<u>n.d.</u>	<u>36</u>	<u>n.d.</u>	<u>221</u>
	<u>I1</u>	<u>25</u>	<u>6</u>	<u>18</u>	<u>n.d.</u>	<u>n.d.</u>	<u>40</u>	<u>6</u>	<u>155</u>	<u>n.d.</u>	<u>77</u>

512 † C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured

513

514

[Table 2](#)

Group†	control (oxic)					R _r reduced					
	P	Mn	Fe	Al	Ca	P	Mn	Fe	Al	Ca	
C	E1	5.8	0.4	2.4	1.4	868	8.8	3.4	4.7	3.1	1390
	E2	5.9	0.2	1.6	1.4	910	6.4	2.2	3.4	4.6	1850
	I3	2.3	0.2	2.9	2.0	458	4.2	2.5	3.3	4.6	785
SA	D1	1.8	0.6	1.8	1.0	56	7.0	1.4	3.5	4.1	70
	D2	7.0	1.3	2.3	1.5	45	8.0	2.3	4.0	3.7	49
	E3	0.7	0.4	1.3	0.8	40	0.7	0.8	1.6	3.0	43
	I2	3.2	1.1	2.5	1.0	24	5.6	1.9	5.2	3.7	24
AOMR	G3	1.1	0.5	3.3	4.5	42	1.4	2.0	4.6	5.8	43
	G6	2.0	0.5	2.1	2.2	25	3.5	1.3	7.8	7.1	25
	G9	2.1	0.4	2.0	2.5	28	2.4	1.4	3.9	5.0	30
ALT	D3	3.2	0.3	1.9	1.1	17	5.9	0.6	3.7	3.4	18
	I1	2.6	0.7	3.2	1.3	21	8.1	1.1	15.5	4.1	23

515

† C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured

516

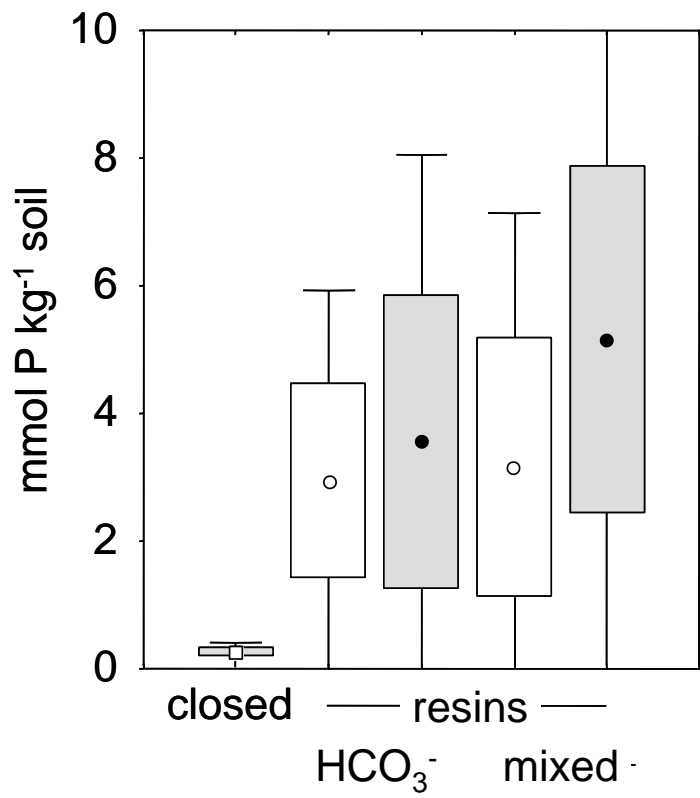
Group†		P	Fe	Mn
C	E1	5.4	3.6	3.8
	E2	1.1	1.8	1.6
	I3	3.4	1.8	3.5
SA	D1	3.3	5.4	2.7
	D2	1.4	35.7	5.1
	E3	1.7	1.8	0.5
	I2	2.1	25.0	0.5
	G3	0.6	32.1	2.2
AOMR	G6	2.4	46.4	1.8
	G9	0.4	19.6	0.9
ALT	D3	1.0	5.4	0.4
	I1	1.9	39.3	0.7

518 † C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured

519 | **Table 3-4**

	C		SA		AOMR		ALT	
	oxic vs reduced		oxic vs reduced		oxic vs reduced		oxic vs reduced	
Hydroxyapatite	4	5	-6	3	-17	-4		
Vivianite	6	5	2	5	-6	2	-4	4
MnHPO ₄ (s)		4		3		3		
βCa ₃ (PO ₄) ₂	-1	-1	-8	-2	-14	-6		-4
Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-3	-2	-11	-4	-19	-9		-6
CaHPO ₄ (s)	-1	-1	-3	-2	-5	-3		-2
CaHPO ₄ ·2H ₂ O(s)	-2	-2	-3	-2	-5	-3		-2
Lime	-22	-22	-25	-22	-27	-24		-23
Fe(OH) ₂ (am)	-3	-3		-4	-8	-5		-4
Fe(OH) ₂ (c)	-2	-3		-3	-8	-4	-8	-4
Mn ₃ (PO ₄) ₂ (s)		-10		-12		-14		
Portlandite	-12	-12	-15	-12	-17	-14		-13
Pyrochroite		-5		-6		-7		

520



521

522 Fig. 1.

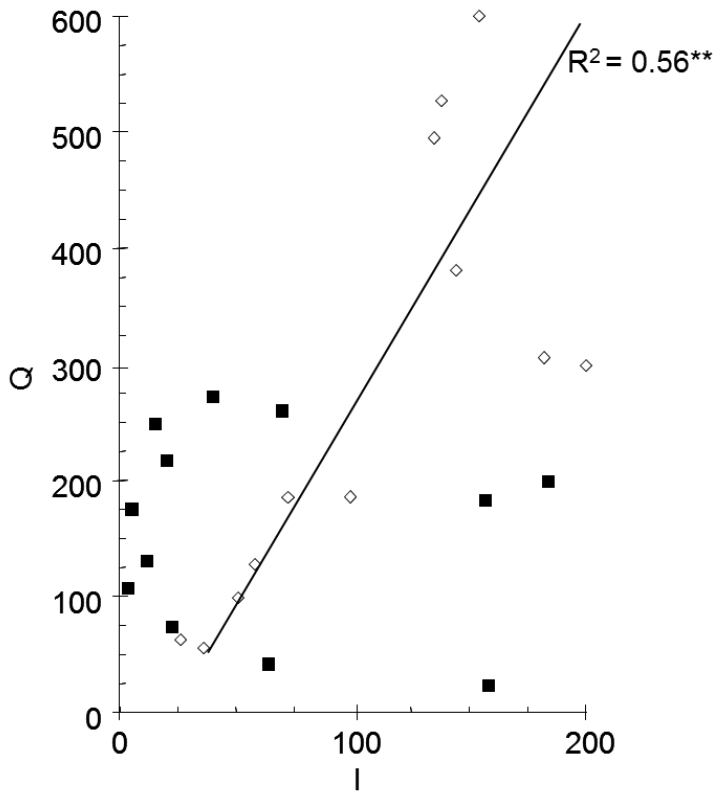
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Fig-2.



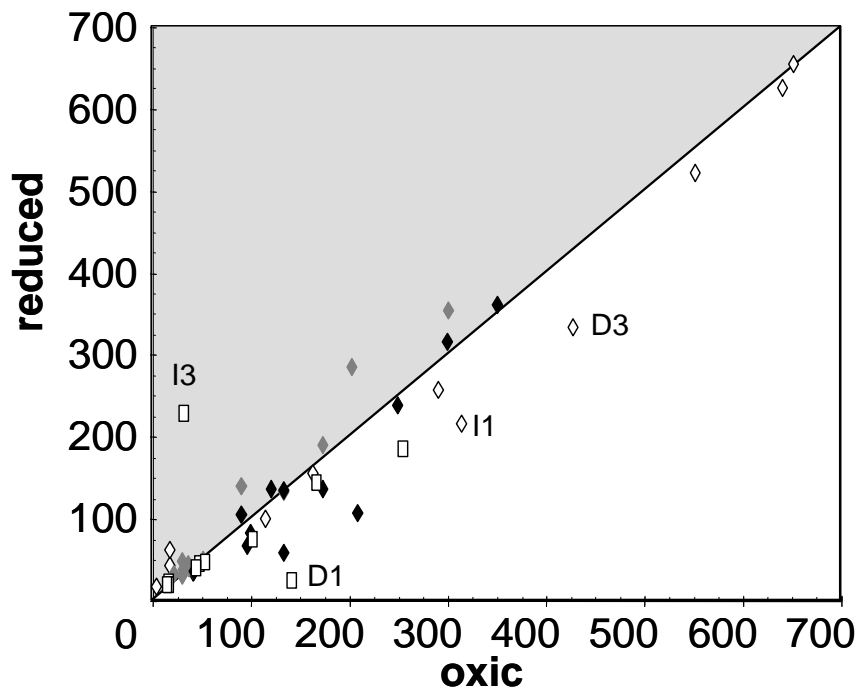
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528

529 Fig. 32.

530



531

532 | Fig. 43.

533 CAPTION TO TABLES AND FIGURES

534 ~~Table 1~~ Element adsorbed onto mixed resins after 32 days of submersion. Data expressed in mmol
535 kg⁻¹ soil. Student *t* test is significant in the case P vs Mn only, both under oxic and reduced conditions
536 ($p < 0.05$).

537 ~~Table 12~~ Elements measured in solution in the presence of mixed resins after 32 days of submersion.
538 Data expressed in $\mu\text{mol kg}^{-1}$ soil. Student *t* test oxic vs reduced is significant for in the case P ($p <$
539 0.008) and -Mn ($p < 0.001$) only. n.d. – not detectable.

540 ~~Table 2~~ Element adsorbed onto mixed resins after 32 days of submersion. Data expressed in mmol
541 kg⁻¹ soil. Student *t* test is significant in the case P vs Mn only, both under oxic and reduced conditions
542 ($p < 0.05$).

543 ~~Table 3~~ Difference between oxalate extractable elements (mmol kg^{-1}) under reducing conditions
544 minus that extracted by control soils (oxic) after incubation with mixed resins. ~~Data in mmol kg⁻¹.~~

545 ~~Table 3-4~~ Ion activity product (IAP) calculated on the basis of the stoichiometry of the species
546 remained in solutions in the presence of mixed resins at measured pe+pH stages. Values are
547 expressed as logarithm of the IAP. ~~Numbers in **†**-bold~~ show oversaturated species.

548
549 ~~Figure 1.~~ Phosphorus in solution (closed system) and on anionic HCO₃⁻ and mixed resins after 32
550 days of reducing conditions (n=12). Where symbols represent the median (open square indicate a
551 close system without resins while circles P desorbed by resins), the box indicates the interquartiles,
552 and whisker the means \pm 1,96·SD, respectively. Grey boxes indicate an anoxic environment, open
553 boxes indicate oxic conditions. All results are expressed as mmol kg⁻¹ soil. All treatments show a
554 significant difference ($p < 0.01$) between the initial oxic condition (closed system, bar on the left side)
555 and the 32 days incubation data. Between treatments a *t* test does not prove ~~duce~~ significant
556 differences ($p < 0.05$).

557 ~~Figure 2.~~ Elements measured in solution in the presence of mixed resins. Results are expressed as
558 mmol in solution with respect to 1 kg of soil. Soil grouping: C calcareous, SA slightly acid, AOMR

559 acid-organic matter rich, ALT acid light textured. Empty bars are soils in oxic conditions while filled
560 bars represent soils after 32 days of reducing conditions ($p_e + pH < 5$) [Element Ca under oxic
561 conditions have been divided by 2 in slightly acid soils and by 20 in calcareous soils]. Bars marked
562 with an a

563 **Fig. 3.** Relationship between P (mmol P kg^{-1}) bound to the resin after 32 days of submersion (Q) and
564 P in solution (I) for individual soils. Units on both axis are mmol P kg^{-1} soil. Symbols are expressed by
565 individual soil, where \circ open diamonds (\circ) are oxic conditions and filled squares (\blacksquare) represent
566 reducing conditions. Standard errors of the means are not shown (but are always $< 6\%$). The curve of
567 equation $Q = 41e^{0.0028I}$ interpolates oxic values only.

568 **Figure 34.** P forms (Olsen and Sommers, 1982) expressed in mg P kg^{-1} soil. The line dividing the
569 white and the shaded areas represents the 1:1 ratio. P forms related to Fe/Al complexes are
570 represented by diamonds: open (NaOH), grey (CB), filled (CBD). Ca bound P is represented by open
571 squares (HCl).

1 **Release of phosphorus under reducing and simulated open drainage conditions from overfertilised**
2 **soils**

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14

15 **Highlights** ► The response of 12 contrasting soils to reduction was tested in term of P release
16 ► Laboratory simulation of open drainage was carried out using ion-exchange resins ► Ca plays a
17 major role in controlling P dynamics even in acid soils ► The potential for P loss is increased by soil
18 reduction-oxidation

19

20 **Abstract** Does removal of cations from soil solution during soil reduction stimulate phosphorus (P)
21 release? An ion-exchange resin system was employed to provide a sink during the incubation of
22 twelve soils under fully reducing conditions. This experimental design was considered to better
23 simulate the loss of ions likely to occur under field conditions than more routine batch type closed
24 extraction systems where solutes build-up in the extract solution. The small solute concentrations
25 that remain in the equilibrating solution suggest the mixed resin system acted as an effective sink
26 over the whole experimental period. By maintaining a small P concentration the resin system mimics
27 soil drainage conditions and encourages P release from soil. Measurement of soil P forms by
28 sequential extraction after the incubation period indicated an increase in the amorphous forms
29 present. Here we show that even if the P-containing solution is retained by the soil, the potential for
30 a subsequent P loss is increased under aerobic conditions. The management of drainage systems
31 should try and avoid the onset of anaerobic conditions. Eventually, magnesium- and calcium-based
32 precipitation products could recapture P from drains recycling it in topsoils as fertilizer.

33

34 **Keywords** anaerobic conditions; anoxic; redox; mixed resins; HCO_3^- resins

35

36 **1. Introduction**

37 The reactivity of phosphorus (P) in the environment through its association with Fe and Mn oxides is
38 influenced directly by the reduction-oxidation (redox) state of soil components (Hartikainen et al.,
39 2010). If the environment becomes anaerobic, oxides are solubilized and P associated with them is
40 brought into solution (Obour et al., 2011). Once in solution, P can be retained in the soil matrix by
41 subsequent re-sorption or can be removed through leaching of the soil solution. While this is
42 generally inconsequential for soils that are submerged for long periods, soils that experience short-
43 term reduction can become potential sources of P (Edwards and Withers, 2007). Ajmone-Marsan et
44 al. (2006) reported that after repeated redox cycles soil P chemistry tends to shift towards more
45 labile forms that would be more easily released on a subsequent submersion and reduction cycle.

46 Artificial drainage of agricultural land is a management practice that provides some control
47 over the water regime, particularly of soils that experience temporary high water tables and
48 saturation. Under anoxic conditions, however, artificial soil drainage may not be recommended in
49 view of the increased potential for transport and loss of nutrients (Schröder et al., 2010). In
50 addition to losses in solution P can move through the soil associated with transported particles (e.g.
51 Ashley et al., 2011; Beauchemin et al., 2003) and potentially accumulate within a drain or a ditch and
52 function as a sink or source of nutrients depending on the prevailing redox conditions. Normally, P-
53 deficient sub-soils limit the movement of P from a highly concentrated solution toward drains (Allen
54 et al., 2012). One particular situation may occur where soils have been overfertilized with P and
55 anoxia develops as a result of overlying stagnant water combined with an adequate supply of
56 organic material (Hill and Robinson, 2012; Mukhtar et al., 1996).

57 In previous experiments conducted on a range of European soils overfertilized with P it was
58 observed that P is released under reduction and that more P is released under pulsed redox
59 conditions, i.e. on alternating wet-dry cycles (Scalenghe et al., 2012). In those experiments, however,
60 the concentration of P in solution rapidly reached a peak and then decreased. The decrease in
61 soluble P concentration can be explained by soil re-adsorption as crystalline Fe-oxides are not

62 completely dissolved by the reduction and retain part of their sorption capacity (Demello et al.,
63 1998). Also, new sorption sites may result from the dissolution of Fe coatings that exposes fresh
64 adsorbing surfaces, onto which Fe oxides are often precipitated, and from iron precipitates formed
65 under anoxia (Willett and Higgins, 1978; Willett, 1989; Barberis et al., 1992). The ‘closed system’
66 experimental approach used in those studies (e.g. Scalenghe et al., 2002; Obour et al., 2011) could
67 have influenced the extent to which elements released to the solution subsequently interact with
68 the soil mineral phase. While under field conditions, it is possible that the soil solution remains in
69 contact with the soil matrix, it is also likely to infiltrate through the *solum*, leaching P and other ions
70 in solution towards the water table and promoting further release. By introducing a sink for
71 reactants and simulating non-equilibrium conditions Fernández et al. (2008) attempted to better
72 quantify the potential release of P.

73 The aim of this paper is to appraise P release from overfertilized soils under reducing
74 conditions in the presence of a sink (ion-exchange resin) which better simulates the removal of
75 elements that might occur during leaching.

76

77 **2. Material and Methods**

78 The soils involved in this study span geographically from parallel 38 to 57 N and from meridian 6 W
79 to 11 E, and pedologically from the cooler Chernozems to the warmer Vertisols, and to Regosols
80 (IUSS Working Group WRB, 2007). Mean annual air temperature varies from 7.5 to 18.5 °C and mean
81 annual rainfall from 490 to 900 mm. The selected soils are intensively farmed (OECD, 2007) and
82 ‘overfertilised’ by having at least twice the optimum concentration of available P. All sampled Ap
83 horizons were sieved to <2 mm and stored in an air-dry condition. The soils and their relevant
84 general properties have been described in Barberis et al. (1996) (Supplementary Information (SI),
85 Appendix A) and basic redox relevant information in Scalenghe et al. (2002). According to Delgado
86 and Torrent (1997), these soils have been grouped into calcareous, C, (E1, E2 and I3), slightly acid,
87 SA, (D1, D2, E3 and I2), acid and rich in organic matter, AOMR, (G3, G6 and G9), and acid and light-

88 textured, ALT, (D3 and I1). The latter group contains two soils with very different properties: D3 is a
89 sandy soil with a large amount of extractable P and I1 was sampled from a rice field, and therefore it
90 undergoes periodic flooding as a routine agronomic practice. The general properties of soils include
91 a pH ranging from 4.6 to 7.8 and organic carbon from 7 to 39 g kg⁻¹. Extractable forms of Fe and Al
92 differ widely; the oxalate/dithionite extractable iron, Fe_{ox}/Fe_d ratio an index of the degree of iron
93 crystallinity proposed by Delgado and Torrent (1997), ranged from 0.07 to 0.77 being >0.5 in three
94 soils only (G3, D3 and I1).

95 Four replicates of 0.25-g each soil sample were incubated in 120 mL vials with 2.5 g of HCO₃⁻-
96 resin (Dowex 1x4-50), 0.8 g of H⁺-resin (Dowex 8x5-50) and 100 mL of deionized water (pre-purged
97 with N₂) sealed and stored in an anaerobic box. A similar experiment with the anionic resin only was
98 performed as described by Sibbesen (1977 and 1978). A gas mixture of pN₂=0.88; pCO₂=0.08;
99 pH₂=0.04 was chosen to best simulate the components most likely to be present under naturally
100 anoxic conditions. Hydrogen was flushed through a Pd catalyser to remove the residual O₂. All vials
101 were subjected to a reduction period of 32 days at 298 K. This saturation period was chosen as this
102 was known from previous studies to approximate full reduction for these soils (Scalenghe et al.,
103 2002). A control series of samples were maintained in an aerobic condition by flushing each vial
104 every day with air for 30 minutes. Redox parameters (Eh and pH) were measured within the
105 anaerobic box on the reduced series. All the vials were shaken on an end-over-end shaker at 150
106 rpm every day for 20 minutes during the reduction period. After 32 days the sealed vials were
107 centrifuged at 1800 g then 5 mL of the supernatant were sampled using a syringe and acidified to
108 pH<3 in order to minimise the precipitation of oxidized species.

109 Soil P fractions were quantified by sequential extraction (Olsen and Sommers, 1982) on all
110 samples at the end of the incubation period. In brief the method includes (1a) 1 M NaOH, P_{NaOH}, to
111 remove P associated to Fe and Al (hydr-) oxides (1b) citrate bicarbonate, P_{CB}, to remove P adsorbed
112 by carbonates during the previous extraction, (2) Na citrate-bicarbonate-dithionite, P _{CBD}, to remove
113 occluded P within the Fe oxides, and (3) 1 M HCl, P_{HCl}, to remove P bound to Ca. Phosphorus in the

114 solutions (molybdate-reactive P, MRP) was determined using either the method of Murphy and Riley
115 (1962) or by the malachite green method of Ohno and Zibilske (1991) as modified by Barberis et al.
116 (1998) for lower concentrations. Calcium, Fe and Mn were determined by atomic adsorption
117 spectrometry. Solutions and solid phases were analyzed following the standard analytical methods
118 described in Barberis et al. (1996) and Scalenghe et al. (2002). Activity calculations were made using
119 the chemical speciation program MINTEQ 3.0 (Gustafsson, 2012).

120

121 **3. Results**

122 The onset of anoxic condition was reached within one week and values of Eh and pH corresponded
123 to those obtained in previous experiments with the same soils (Scalenghe et al., 2002). At the end of
124 the present experiment the pH of these soils was modified by an average of 0.8 ± 0.6 pH units while
125 the redox potential was lowered on average by 9.6 ± 1.3 pe units (Appendix B, SI). The initial $pe + pH$ of
126 these soils was on average higher than 13.3 ± 1.3 while it fell to 4.5 ± 0.4 after reduction.

127 The amount of P extracted in the presence of mixed resins was higher than that extracted
128 when using anionic resins only. In Figure 1 the amount of P that remains in solution without any
129 resin and that adsorbed by resins are compared. These data confirm a better efficiency of the mixed
130 resins in extracting P from soils under anoxic conditions, although not statistically significant. The
131 amount of cations and anions left in the solution is nevertheless measurable and is higher for the
132 anoxic samples in the case of Ca for all soils, Fe and Mn in more acidic soils and P in calcareous soils
133 (Table 1).

134 When the release of elements to mixed resins under anoxic conditions is compared with oxic
135 conditions (Table 2), a general increase of P removal from all anoxic soils is observed and it
136 corresponds to the excess P fertilizers these soils have received (Delgado and Torrent, 1997). One
137 origin for this P appears to be related to the solubilization of Ca compounds. In calcareous soils the
138 removal of Ca is also the result of the lowering of the pH under anaerobiosis. The release of P
139 appears to be the result of many factors. The reduction of the oxides and the consequent maximum

140 release of Fe, Mn, and the associated Al and Ca is up to around 700 mg Fe kg⁻¹, 300 mg Mn kg⁻¹, 100
141 mg Al kg⁻¹ and about 38 g kg⁻¹ for Ca (calculated as difference between anoxic and oxic release as a
142 sum of both the concentration in Table 1 and 2).

143 Figure 2 shows Quantity-Intensity (Q/I) relationships, where Q is the P desorbed by the resin
144 and I is the P that remains in solution. Soil groupings had no influence on this relationship ($p > 0.05$)
145 and the Q/I relationship in the oxidized environment follows a linear trend. Under reducing
146 conditions there is no relationship between Q and I.

147 Analysis of the solid P phase determined after re-oxidation at the end of the experiment
148 (Figure 3) show that for SA and ALT soils a decrease of P_{NaOH} is evident while I3, a carbonate-rich C
149 soil, is marked by a decrease in P_{HCl}. A decrease of occluded P (P_{CBD}) is also evident. While, the
150 simultaneous increase of P_{NaOH}, and P_{CB} is probably due to re-adsorption phenomena.

151

152 4. Discussion

153 The release of P into solution under anoxic conditions has been demonstrated by several authors for
154 a range of soil and sediment (Davison, 1993; Demello et al., 1998; Ajmone-Marsan et al., 2006;
155 Scalenghe et al., 2012). In previous experiments using these soils (Scalenghe et al., 2002), P was
156 released from all soils under anaerobic conditions and peaked after 32 days, after which
157 concentrations in solution decreased. One third of the Fe_o was solubilized by the effect of the
158 reduction in SA, AOMR and ALT soils (14±4% of the initial P_{CBD}). In C soils around 14% of Fe_o passed in
159 solution which corresponds to 3% of the initial P_{CBD}. This was accompanied by a substantial release
160 of P as a consequence of the dissolution of the Fe-Mn oxide surfaces where the P was adsorbed
161 (Figure 3 in Scalenghe et al., 2002, page 443). For this reason the current experiments were designed
162 with a period of 32 days of anoxia.

163 Various authors have observed that the addition of a P (anion) sink in the experimental
164 system maintains the P concentration in solution close to zero and limits the re-adsorption of P by
165 the soil (Agnebin and van Raij, 2001; Amery and Smolders, 2012; Bache and Ireland, 1980; Barrow

166 and Shaw, 1977; Sibbesen, 1977). However, this may not be representative of natural conditions as
167 the anionic resin would compete for P adsorption, shifting the P towards the solution, but it would
168 not hinder the dissolution-precipitation of Ca-P compounds. In order to obtain a more accurate
169 picture by including these latter reactions in our system, the experiment was run in the presence of
170 a mixed - cationic and anionic - resin. The mixed resin has the effect of removing the principal anions
171 and cations from the solution, reducing the likelihood of any precipitation with P (Curtin et al., 1987)
172 this would mimic a removal of ions from solution under field conditions in response to drainage.

173 While Fe has the dominant role in P retention Mn also appears to be involved. In general
174 reduction doubles the amount of Mn with respect to the oxic environment (and up to 11 and 13
175 times for D2 and I1, respectively). The influence of Mn on P sorption has been suggested for soils of
176 temperate areas (Zaidel'man et al., 2009) although this was not confirmed for tropical soils
177 (Gonçalves et al., 2011). The amount of Fe and Al adsorbed by the resins appears to be independent
178 from the soil type. In general, however, an increase of the release of Al is observed. Soluble Al can
179 derive from a combination of Al-substituted Fe oxides (Adhami et al., 2012; Cessa et al., 2009), or
180 from organic molecules that are being oxidized (Pizzeghello et al., 2011). Previous findings
181 (Scalenghe et al., 2002; Wang et al., 2013) postulated an involvement of Al in the P cycle under
182 reduction although this element is not directly affected by redox reactions. Also, the decrease of the
183 pH in calcareous soils associated with the reduction increases the solubility of Al; its displacement
184 can in turn favour the dissolution of Al-silicates or strengite.

185 The ratio between soil mass and water is an important factor influencing P release from soil.
186 In our soils, independent of their grouping, the amount of P desorbed to a dilute electrolyte is
187 correlated with P concentration in the 1:1 water-to-soil-ratio extract raised to a power that
188 decreases with widening of the water-to-soil-ratio (Torrent and Delgado, 2001). These authors
189 concluded that under oxic conditions it is the Quantity (Q) that controls the system. The difference in
190 behaviour and relationship between Q and I (Figure 2) may be explained as under oxic conditions
191 part of the P solution concentration is controlled by the solid phase, while under anoxia the

192 dissolution of the oxides brings about a variety of precipitation reactions which prevents any clear
193 relationship from being observed.

194 Various soil P fractions, particularly those in newly accreted materials, are highly unstable
195 and could be released in a more available form when soils undergo subsequent rewetting. It appears
196 in fact that reduction brings about an overall transformation of P forms towards more labile forms
197 confirming findings by other researchers on different soils (Ajmone-Marsan et al., 2006; Olila et al.,
198 1997). For these soils it had been observed that if a new anoxic environment develops the potential
199 release of P was increased (Figure 1 in Scalenghe et al., 2012, page 143). This response is explained
200 by the considerable amount of Fe and Mn precipitated in amorphous (oxalate extractable) forms
201 after 32 days of incubation in the presence of mixed resin (Table 2). No relationship is apparent
202 between P and Fe, and Mn in oxic conditions. Nevertheless, the difference between oxalate
203 extractable elements under oxic and reducing conditions after incubation with mixed resins (Table 3)
204 explains the relationship between P bound to the resin after 32 days of submersion as a Q factor and
205 P in solution, highlighted in Figure 2. The progressive increase in amorphous components of the
206 absorbing complex under anoxia provokes the dissolution of the oxides and carbonates that in turn
207 cause the release of P. Nevertheless the presence of P in solution does not appear to be controlled
208 by the solid phase Quang and Dufey (1995).

209

210 *4.1 Theoretical prediction of P precipitates*

211 The possibility that P in solution is lowered by precipitation was also considered. Due to
212 overfertilization polyphosphates occur largely in agricultural soils and tend to transform into β -
213 $\text{Ca}_2\text{P}_2\text{O}_7$. Pyrophosphates are unstable in soils and eventually are converted to orthophosphates. In
214 oxic environments, the theoretical threshold stability of magnetite occurs when $pe+pH>11.53$: the
215 availability of ionic Fe controls soil mineral stability, below that threshold Ca prevails (Lindsay, 1979).
216 Strongly reduced environments are again controlled by Fe, but $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ is converted into $\text{Fe}_2\text{P}_2\text{O}_7$
217 only at $pe+pH<3$.

218 In the presence of free O₂ our soils show an average pe+pH of 13.3±0.9, which drops to
219 4.5±0.4 after 32 days under reducing conditions. When the soils become anoxic, without resins, the
220 co-precipitation of the most common Fe and P compounds is unlikely despite the large
221 concentration of Fe and P; the decrease of Fe and Mn concentration in solution is, in fact,
222 presumably due to the formation of Fe and Mn precipitates not in association with P (Figure 4 in
223 Scalenghe et al., 2002, page 443). By mimicking the effect of losing elements through drainage under
224 anoxia, the selective removal of ions produces conditions that, contrary to a closed system, could
225 induce the precipitation of phosphates (Table 4). Hydroxyapatite could be expected in C and SA soils,
226 with MnHPO₄ in C, SA and AOMR soils, and vivianite in all soils. Manganese and iron phosphates are
227 normally insignificant under closed laboratory conditions but the resin based open systems used
228 here may increase their relative importance (Green et al., 1989). For instance, Walpersdorf et al.
229 (2013) have recently confirmed that vivianite may control P concentration in solution under soil
230 anaerobic conditions.

231 In many ecosystems P is often the limiting nutrient, even in intensively managed agricultural
232 systems where P is a regular addition the general view is that the bioavailability of P gradually
233 declines with time. Various mechanisms have been proposed to explain this observation and these
234 include the formation of more stable P-oxide precipitates together with a physical migration of P
235 deeper into soil aggregates. Here we describe some simple laboratory simulations employing
236 changes in local redox and leaching environment where the opposite situation might be expected. In
237 widely contrasting soils it has been demonstrated that the resulting fresh P containing precipitates
238 which readily formed after short-term periods of reduction. If the frequency and geographical
239 distribution of soils likely to experience reducing conditions is increasing as a result of climate
240 change and increased management induced soil compaction then there is the possibility that
241 temporary increases in the bioavailability of soil P may be the result.

242 Maintaining the efficiency land drains where present remains an important management
243 strategy. While in certain situations this might increase the risk of P leaching novel capture and

244 recovery techniques (e.g., Erickson et al., 2012; Kõiv et al., 2012; Liu et al., 2013) are being
245 suggested. Rittmann et al. (2011) have reviewed the current options being suggested for P recovery,
246 which include precipitation as Al-, Fe-, Mg- (e.g. struvite) or Ca- (e.g. hydroxyapatite) based products
247 that also have qualities potentially equivalent to conventional fertilizers. Phosphorus recovery could
248 also involve adsorption (metal-based adsorbents), ion exchange (phosphate-selective solids), or
249 uptake (photosynthetic microorganisms or P-selective proteins).

250

251 **5. Conclusions**

252 The provision of a sink for cations and anions during the development of reducing conditions
253 over a 32 day period modified the degree of solubilisation that occurred in wide range of
254 overfertilised soils. In general anoxic conditions brought about the release of P to various degrees.
255 When the concentration of P is lowered by providing a resin sink, mimicking a draining solution, the
256 amount of P released (solubilised) increases. The amount of additional P that can be solubilised from
257 a 20 cm soil layer is as much as 0.5 kg ha^{-1} , especially from light textured soils which are also more
258 prone to leaching although less prone to waterlogging. The choice of experimental conditions
259 imposed during laboratory incubations is shown to significantly influence the solubility of P. After
260 the incubation period soils were allowed to dry out and effects continued to be apparent in the
261 forms of P present in the solid phase.

262

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265

266 **Supplementary material**

267 Supplementary data on sampling, soil characteristics, and redox parameters which might be of
268 importance for the interpretation of these results are associated with this article and can be found in
269 the online version at URL ...

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385 **Table 1**

Group†	control (oxic)					reduced					
	P	Mn	Fe	Al	Ca	P	Mn	Fe	Al	Ca	
C	E1	45	n.d.	179	n.d.	1954	48	24	62	n.d.	3048
	E2	33	n.d.	72	n.d.	2240	37	24	62	n.d.	7948
	I3	25	n.d.	20	n.d.	1071	50	6	75	n.d.	2073
SA	D1	39	n.d.	113	n.d.	71	48	n.d.	53	n.d.	625
	D2	27	n.d.	18	n.d.	23	30	18	32	n.d.	290
	E3	25	n.d.	233	n.d.	50	43	18	122	n.d.	317
	I2	28	6	51	n.d.	2	31	12	90	n.d.	104
AOMR	G3	24	n.d.	12	n.d.	31	25	24	63	n.d.	71
	G6	26	n.d.	9	n.d.	2	32	18	84	1	90
	G9	26	n.d.	14	n.d.	23	25	24	54	n.d.	110
ALT	D3	27	n.d.	12	n.d.	8	31	n.d.	36	n.d.	221
	I1	25	6	18	n.d.	n.d.	40	6	155	n.d.	77

386 † C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured

387

388 **Table 2**

Group†	control (oxic)					reduced					
	P	Mn	Fe	Al	Ca	P	Mn	Fe	Al	Ca	
C	E1	5.8	0.4	2.4	1.4	868	8.8	3.4	4.7	3.1	1390
	E2	5.9	0.2	1.6	1.4	910	6.4	2.2	3.4	4.6	1850
	I3	2.3	0.2	2.9	2.0	458	4.2	2.5	3.3	4.6	785
SA	D1	1.8	0.6	1.8	1.0	56	7.0	1.4	3.5	4.1	70
	D2	7.0	1.3	2.3	1.5	45	8.0	2.3	4.0	3.7	49
	E3	0.7	0.4	1.3	0.8	40	0.7	0.8	1.6	3.0	43
	I2	3.2	1.1	2.5	1.0	24	5.6	1.9	5.2	3.7	24
AOMR	G3	1.1	0.5	3.3	4.5	42	1.4	2.0	4.6	5.8	43
	G6	2.0	0.5	2.1	2.2	25	3.5	1.3	7.8	7.1	25
	G9	2.1	0.4	2.0	2.5	28	2.4	1.4	3.9	5.0	30
ALT	D3	3.2	0.3	1.9	1.1	17	5.9	0.6	3.7	3.4	18
	I1	2.6	0.7	3.2	1.3	21	8.1	1.1	15.5	4.1	23

389 † C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured

390

391 **Table 3**

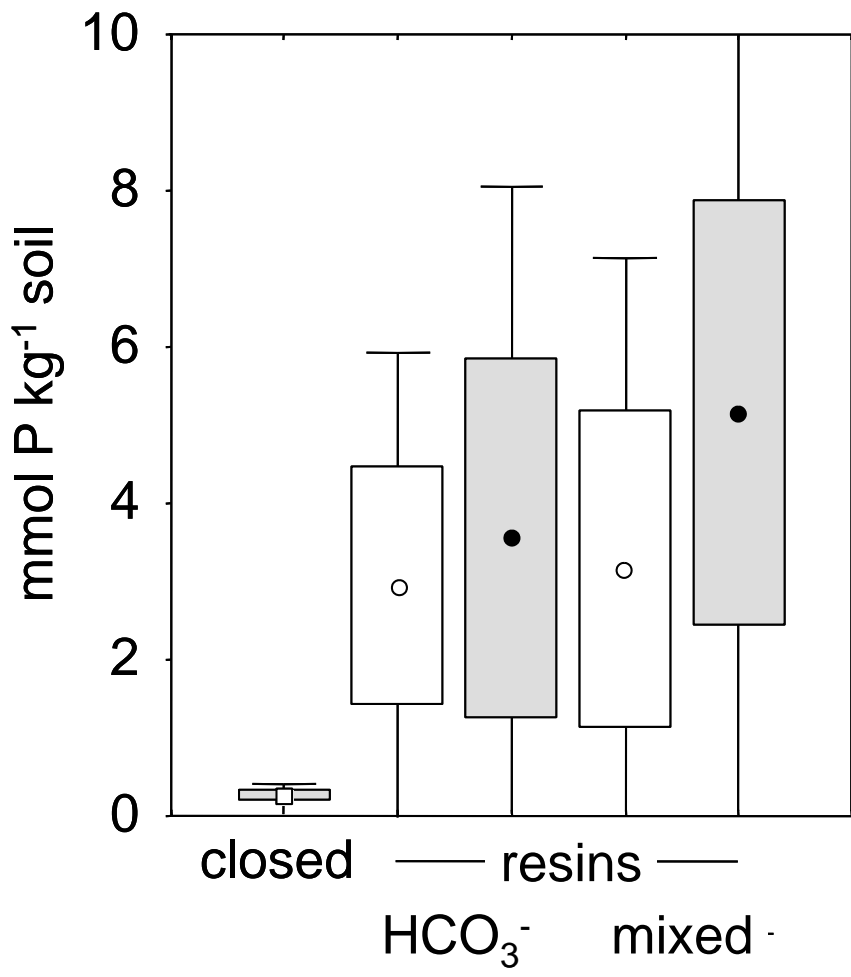
Group [†]		P	Fe	Mn
	E1	5.4	3.6	3.8
C	E2	1.1	1.8	1.6
	I3	3.4	1.8	3.5
	D1	3.3	5.4	2.7
SA	D2	1.4	35.7	5.1
	E3	1.7	1.8	0.5
	I2	2.1	25.0	0.5
	G3	0.6	32.1	2.2
AOMR	G6	2.4	46.4	1.8
	G9	0.4	19.6	0.9
	D3	1.0	5.4	0.4
ALT	I1	1.9	39.3	0.7

392 † C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured

393 **Table 4**

	C		SA		AOMR		ALT	
	oxic vs reduced		oxic vs reduced		oxic vs reduced		oxic vs reduced	
Hydroxyapatite	4	5	-6	3	-17	-4		
Vivianite	6	5	2	5	-6	2	-4	4
MnHPO ₄ (s)		4		3		3		
βCa ₃ (PO ₄) ₂	-1	-1	-8	-2	-14	-6		-4
Ca ₄ H(PO ₄) ₃ ·3H ₂ O(s)	-3	-2	-11	-4	-19	-9		-6
CaHPO ₄ (s)	-1	-1	-3	-2	-5	-3		-2
CaHPO ₄ ·2H ₂ O(s)	-2	-2	-3	-2	-5	-3		-2
Lime	-22	-22	-25	-22	-27	-24		-23
Fe(OH) ₂ (am)	-3	-3		-4	-8	-5		-4
Fe(OH) ₂ (c)	-2	-3		-3	-8	-4	-8	-4
Mn ₃ (PO ₄) ₂ (s)		-10		-12		-14		
Portlandite	-12	-12	-15	-12	-17	-14		-13
Pyrochroite		-5		-6		-7		

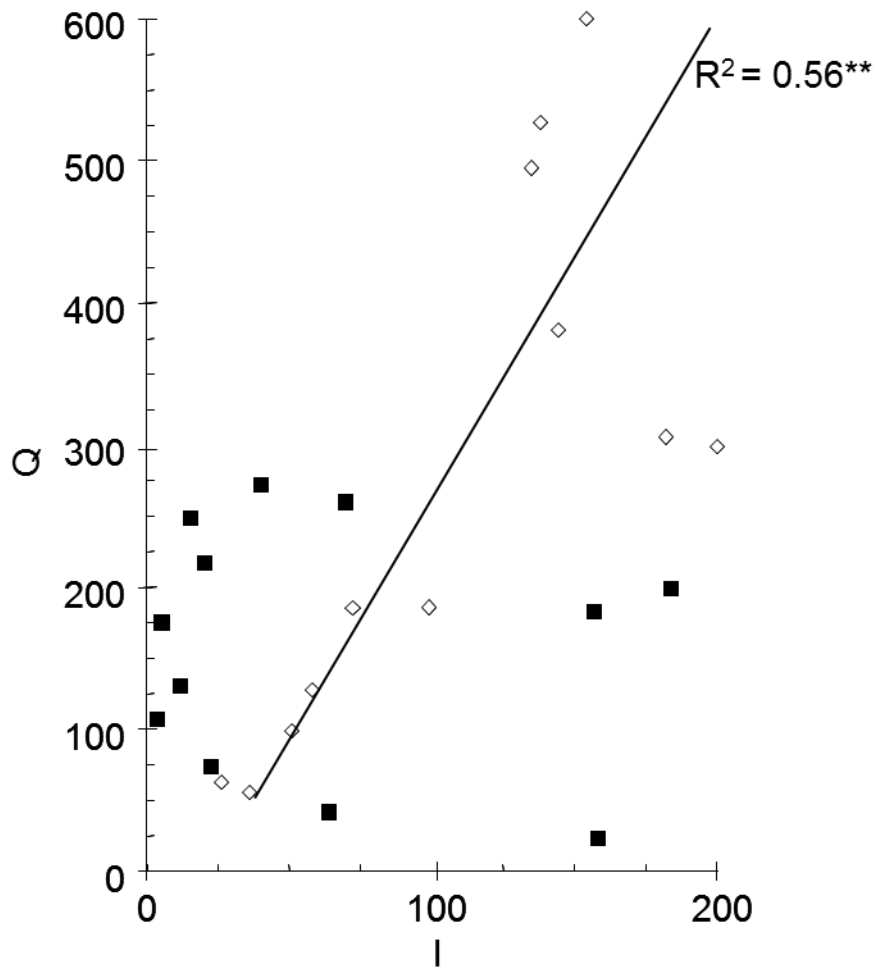
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395

396 Fig. 1.

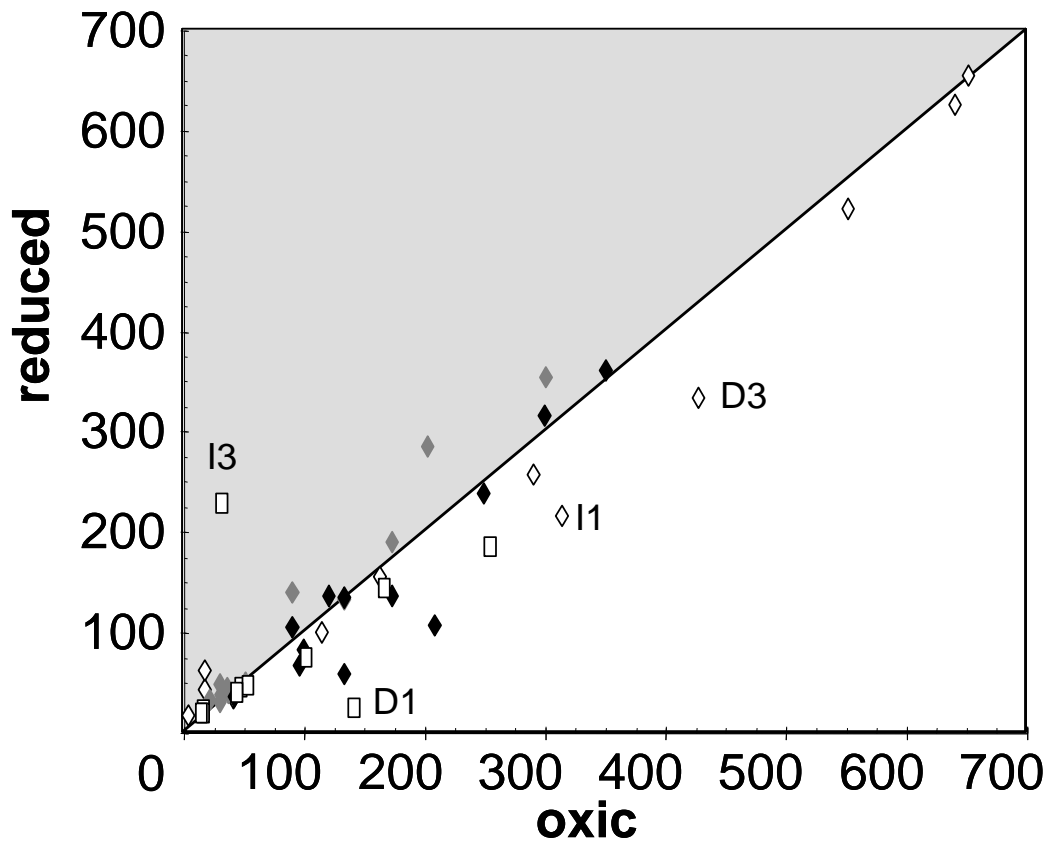
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399 Fig. 2.

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401

402 Fig. 3.

403 **CAPTION TO TABLES AND FIGURES**

404 **Table 1** Elements measured in solution in the presence of mixed resins after 32 days of submersion.

405 Data expressed in $\mu\text{mol kg}^{-1}$ soil. Student *t* test oxic vs reduced is significant for P ($p < 0.008$) and Mn

406 ($p < 0.001$) only. n.d. – not detectable.

407 **Table 2** Element adsorbed onto mixed resins after 32 days of submersion. Data expressed in mmol

408 kg^{-1} soil. Student *t* test is significant in the case P vs Mn only, both under oxic and reduced conditions

409 ($p < 0.05$).

410 **Table 3** Difference between oxalate extractable elements (mmol kg^{-1}) under reducing conditions

411 minus that extracted by control soils (oxic) after incubation with mixed resins.

412 **Table 4** Ion activity product (IAP) calculated on the basis of the stoichiometry of the species

413 remained in solutions in the presence of mixed resins at measured pe+pH stages. Values are

414 expressed as logarithm of the IAP. Numbers in bold show oversaturated species.

415 **Figure 1.** Phosphorus in solution (closed system) and on anionic HCO_3^- and mixed resins after 32 days

416 of reducing conditions ($n=12$). Where symbols represent the median (open square indicate a close

417 system without resins while circles P desorbed by resins), the box indicates the interquartiles, and

418 whisker the means $\pm 1,96 \cdot \text{SD}$, respectively. Grey boxes indicate an anoxic environment, open boxes

419 indicate oxic conditions. All results are expressed as mmol kg^{-1} soil. All treatments show a significant

420 difference ($p < 0.01$) between the initial oxic condition (closed system, bar on the left side) and the

421 32 days incubation data. Between treatments a *t* test does not produce significant differences ($p <$

422 0.05).

423 **Figure 2.** Relationship between P (mmol P kg^{-1}) bound to the resin after 32 days of submersion (Q)

424 and P in solution (I) for individual soils. Open diamonds (\diamond) are oxic conditions and filled squares (\blacksquare)

425 represent reducing conditions. Standard errors of the means are not shown but are always $< 6\%$.

426 **Figure 3.** P forms (Olsen and Sommers, 1982) expressed in mg P kg^{-1} soil. The line dividing the white

427 and the shaded areas represents the 1:1 ratio. P forms related to Fe/Al complexes are represented

428 by diamonds: open (NaOH), grey (CB), filled (CBD). Ca bound P is represented by open squares (HCl).