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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)

02 May 2024

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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 created 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 with 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.

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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.

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

Done

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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.

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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 that 13.3±1.3 while after reduction it falls to 4.5±0.4.

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VisualAbstract.JPG

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

***Revision Notes**
Click here to download Revision Notes: CHEM28299-RevisionNotes.docx

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*Revision, changes marked
Click here to view linked References

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

SCALENGHE Riccardo (corresponding author: riccardo.scalenghe@unipa.it, skype riccardo_daat) Dipartimento di Scienze Agrarie e Forestali, Università degli Studi di Palermo, viale delle Scienze 13, 90128 Palermo IT

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AJMONE-MARSAN Franco Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università degli Studi di Torino, via Leonardo da Vinci 44, 10095 Grugliasco IT

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

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

1. **Introduction**

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

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

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

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

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

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

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

2. Material and Methods

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

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Four replicates~~Quadruplicate~~ of 0.25-g each soil sample~~s~~ were incubated in 120 mL vials with 2.5 g of HCO_3^--resin (Dowex 1x4-50), 0.8 g of H^+-resin (Dowex 8x5-50) and 100 mL of deionized water (pre-purged with N_2) sealed and stored in an anaerobic box. A~~The~~ similar~~ame~~ experiment with the anionic resin only was performed ~~with four replicates (including the control treatments)~~ as described by Sibbesen (1977 and 1978). A gas mixture of pN_2=0.88; pCO_2=0.08; pH_2=0.04 was chosen to best simulate the components most likely to be present under naturally anoxic conditions. Hydrogen was flushed through a Pd catalyser to remove the residual O_2. All vials were subjected to a reduction period of 32 days at 298 K. This saturation period was chosen as this was known from previous studies to approximate full reduction for these soils (Scalenghe et al., 2002). A control series of samples were maintained in an aerobic condition by flushinged each vial every day with ~~in~~ air for 30 minutes. Redox parameters (Eh and pH) were measured within the anaerobic box on the reduced series. All the vials were shaken on an end-over-end shaker at 150 rpm every day for 20 minutes during the reduction period. After 32 days~~t the end~~ the sealed vials were centrifuged at 1800 *g* then 5 mL of the supernatant were sampled using a syringe and acidified to pH<3 in order to minimise the precipitation of oxidized species.

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

Solutions and solid phases were analyzed following the standard analytical methods described in Barberis et al. (1996) and Scalenghe et al. (2002). Activity calculations were made using the chemical speciation program MINTEQ 3.0 (Gustafsson, 2012).

3. Results

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

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

When the release of elements to mixed resins under anoxic conditions is compared with oxic conditions (Table 2~~1~~), a general increase of P removal from all anoxic soils is observed and it corresponds to the excess P fertilizers these soils have received (Delgado and Torrent, 1997). One origin for this P appears to be related to the solubilization of Ca compounds. In calcareous soils the removal of Ca is also the result of the lowering of the pH under anaerobiosis. The release of P appears to be the result of many factors. The reduction of the oxides and the consequent maximum 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 mg Al kg^{-1} and about 38 g kg^{-1} for Ca (calculated as difference between anoxic and oxic release as a sum of both the concentration in Table 1 and ~~Figure 1~~2).

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

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

4. and Discussion

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

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

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

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

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

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

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

release appears to be connected withrelated to the solubilization of Ca compounds. In calcareous soils the removal of Ca is also the result of the lowering of the pH following theunder anaerobiosis. This contributes to the release of P by preventing the precipitation of Ca-P compounds.

The release of phosphorus appears to be the is a result of many factors. All these factors appear to have contributed to the release of phosphorus. The reduction of the oxides and the consequent maximum 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 mg Al kg^{-1} and about 38 g kg^{-1} for Ca (calculated as difference between anoxic and oxic release as a sum of both the concentration in Table 1 and Figure 1). The release of nearly 2 times the amount of P under reduction is paralleled by the release of Fe While~~Usually~~ Fe ~~i~~has ~~by~~ ~~far~~the dominant role in P retention ~~but a role should not be excluded for~~ Mn also appears to be involved~~in our soils~~. In general~~The~~ reduction doubles the amount of ~~favours the release of about two times the~~ Mn with respect to the oxic environment (and up to 11 and 13 times for D2 and I1, respectively). The~~An~~ influence of Mn on P sorption has been suggested for soils of temperate areas (Zaidel'man et al., 2009) although this~~it~~ was not confirmed for tropical soils (Gonçalves et al., 2011). ~~The release of high amounts of P appears to be accompanied by an increase of Al concentration in solution. The reduction of the oxides and the consequent maximum release (calculated as difference between anoxic and oxic 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 mg Al kg^{-1} and about 38 g kg^{-1} for Ca. The effect of reduction favours the release of about two times the manganese with respect to the oxic environment (and up to 11 and 13 times for D2 and I1, respectively).~~ The amount of Fe and Al adsorbed by the resins~~, on the contrary,~~ appears to be independent ~~on~~ from the soil type. In general, however, an increase of the release of Al is observed. Soluble Al can derive from a combination of Al-substituted Fe oxides (Adhami et al., 2012; Cessa et al., 2009), or from organic molecules that are being oxidized (Pizzeghello et al., 2011). Previous findings (Scalenghe et al., 2002; Wang et al., 2013) postulated an involvement of Al in the P cycle ~~of P~~ under reduction although this element is not directly affected by redox reactions. Also, the decrease of the pH in calcareous soils associated with the reduction

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

~~Phosphorus loss from soils can occur under diverse conditions and commonly t~~The ratio between soil mass and water is an~~assumed to be the most~~ important factor~~s~~ influencing P release from soil~~soil P lossthe process~~. In our soils, independent~~ly~~ of their grouping~~s~~, the amount of P desorbed to a dilute electrolyte is correlated with P concentration in the 1:1 water-to-soil-ratio extract raised to a power that decreases with widening of~~increasing~~ the water-to-soil-ratio~~, as observed by (~~Torrent and Delgado, (2001). These aAuthors concluded that under oxic conditions it is the Quantity (Q) that controls the system. ~~Figure 3 shows Quantity Intensity (Q/I) relationships, where Q is the P desorbed by the resins (the quantity that actually is adsorbed onto the resin) and I is the phosphorus that remains in solution. Soil groupings are not relevant ($p < 0.05$) and the Q/I relationship in the oxidized environment follows an equation of the e^{tx} typea linear trend. Otherwise U~~Under reducing conditions there is no relationship between Q and I~~quantity and intensity. confirming that, while inu~~U~~The difference in behaviour and relationship between Q and I (Figure 2~~3~~) may be explained as under oxic conditions part of the P solution concentration~~ in solution~~ is controlled by the solid phase, while under anoxia the dissolution of the oxides ~~of surfaces~~ brings about a variety of precipitation reactions which~~that~~ prevents any clear relationship from being observed.

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

newly accreted materials, are highly unstable and could be released in a more available form when ~~newly accreted~~ soils undergo subsequent rewetting ~~after drying~~. It appears in fact that reduction brings about an overall transformation of P forms towards more labile forms confirming ~~earlier results~~findings ~~obtained~~ by other researchers on different soils (Ajmone-Marsan et al., 2006; Olila et al., 1997). For these

~~In our~~ soils~~,~~ it had been observed that if a new anoxic environment develops the potential release of P ~~is~~ was increased ~~during time is pulsed reducing condition occuras well~~ (Figure 1 in ~~Figure 1 at page 143 in~~ Scalenghe et al., 2012~~, Figure 1,~~ page 143). ~~A proof~~This response~~evidence~~ is explained ~~here comes from~~by the considerable amount of Fe and Mn precipitated in amorphous (oxalate extractable) forms~~extraction of amorphous Fe forms~~ after~~ the experiments of~~ 32 days of incubation in the presence of mixed resins~~. The data in~~ (Table 2)~~ clearly show that, after the experiment with mixed resins, a considerable amount of Fe – and Mn - is precipitated in amorphous (oxalate extractable) forms together with some P, most probably the P that remained in solution during the anoxic experiment~~.~~ – No relationship is apparent between P and Fe, and Mn in oxic conditions~~, in Table 2~~. Nevertheless, the difference between oxalate extractable elements under oxic and reducing conditions after incubation with mixed resins ~~shown in~~ (Table 3)~~–~~ explains the relationship between P bound to the resin after 32 days of submersion as a Q factor and P in solution, highlighted in Figure~~.~~ 2. The progressive increase in amorphic~~sation~~ components of the absorbing complex ~~alternating oxic c conditions~~under anoxia provokes the dissolution of the oxides and carbonates that in turn cause the release of P. Nevertheless the~~its~~ presence of P in solution doe~~s~~ not appear to be controlled by the solid phase~~in accordance with the data of Figure 3~~. Quang and Dufey (1995) ~~observed the same phenomenon~~.

4.1 Theoretical prediction of P precipitates

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

297 $Ca_2P_2O_7$. 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 p*e*+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 β-$Ca_2P_2O_7$ is converted into $Fe_2P_2O_7$ only at p*e*+pH<3.

302 In the presence of free O_2 our soils show an average p*e*+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 drainage~~ing 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 4~~3~~). 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

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

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

54. Conclusions

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

~~providing athe resin sink, mimicking a draining solution, P release increases. The amount of additional P that can be solubilised fromlost by a 20 cm soil layer of 20 cm is as much as half a kg0.5 kg per ha^{-1}, especiallyin particular from light textured soils which are also more prone to leaching (although less prone to waterlogging). Obviously, not all P is lost with the soil solution as part of it can be removed by particles that are eluviated with the draining solution, so it is difficult to achieve accurate predictions in terms of P concentrations in tile-drainage water (Beauchemin et al., 2003).~~

~~In those soils where the possibility of reaching anoxic condition is likely, i.e. where there is an excess precipitation (or irrigation) over evapotranspiration (or irrigation) or a fluctuatingdynamic watertable, soil drainage is an obvious solution. In those cases one might wonder if it would be better to let the soil solution to drain freely drain, and lose some P or to limit water percolation to avoid P losses. The latter would however induce reduction and would eventually result end up in a possible greater loss of P. Here, we have also shown that even if the P-containing solution is retained by the soil closing by the drains the potential for a subsequent P loss is increased under anaerobic conditions. The main soil P losses originate, in fact, from a little part of critical areas characterised by a great release P potential (Huang et al., 2012) and although those losses by leaching appears to be inevitable in aerobic systems, it would be much worse if those soils go anaerobic, even for a short period. The management of drainage systems should avoid the onset of anaerobic conditions as much as possible, as that would increase the potential degradation of the quality of the draining water.~~

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~~**Appendix A.** **Supplementary material**~~

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

377 **References**

378 Adhami, E., Ronaghi, A., Karimian, N., Molavi, R., 2012. Transformation of phosphorus in highly
379 calcareous soils under field capacity and waterlogged conditions. Soil Res. 50, 249–255.

380 Agbenin, J.O., van Raij, B., 2001. Kinetics and energetics of phosphate release from tropical soils
381 determined by mixed ion-exchange resins. Soil Sci. Soc. Am. J. 65, 1108–1114.

382 Ajmone-Marsan, F., Côté, D., Simard, R.R., 2006. Phosphorus transformations under reduction in
383 long-term manured soils. Plant Soil 282, 239–250.

384 Allen, B.L., Mallarino, A.P., Lore, J.F., Baker, J.L., Haq, M.U., 2012. Phosphorus lateral movement
385 through subsoil to subsurface tile drains. Soil Sci. Soc. Am. J. 76, 710–717.

386 Amery, F., Smolders, E., 2012. Unlocking fixed soil phosphorus upon waterlogging can be promoted
387 by increasing soil cation exchange capacity. Eur. J. Soil. Sci. 63, 831–838.

388 Ashley, K., Cordell, D., Mavinic, D., 2011. A brief history of phosphorus: From the philosopher's stone
389 to nutrient recovery and reuse. Chemosphere 84, 737–746.

390 Bache, B.W., Ireland, C., 1980. Desorption of phosphate from soils using anion exchange resin. J. Soil
391 Sci. 31, 279–306.

392 Barberis, E., Ajmone Marsan, F., Arduino, E., 1998. Determination of phosphate in solution at
393 different ionic composition using malachite green. Commun. Soil Sci. Plant Anal. 29, 1167–1177.

394 Barberis, E., Ajmone-Marsan, F., Boero, V., Arduino, E., 1992. Aggregation of soil particles by iron
395 oxides in various size fractions of soil B horizons. J. Soil Sci. 42, 535–542.

396 Barberis, E., Ajmone-Marsan, F., Scalenghe, R., Lammers, A., Schwertmann, U., Edwards, A.C.,
397 Maguire, R., Wilson, M.J., Delgado, A., Torrent, J., 1996. European soils overfertilized with
398 phosphorus: Part 1. Basic properties. Fert. Res. 45, 199–207.

399 Barrow, N.J., Shaw, T.C., 1977. Factors affecting the amount of phosphate extracted from soil by
400 anion exchange resin. Geoderma 18, 309–323.

401 Beauchemin, S., Simard, R.R., Bolinder, M.A., Nolin, M.C., Cluis, D., 2003. Prediction of phosphorus
402 concentration in tile-drainage water from the Montreal Lowlands soils. Can. J. Soil. Sci. 83, 73–87.

403 ~~Carpenter, S.R., 2005. Eutrophication of aquatic ecosystems: Bistability and soil phosphorus. P. Natl.~~
404 ~~Acad. Sci. USA 102, 10002–10005.~~
405 Cessa, R.M.A., Celi, L., Vitorino, A.C.T., Novelino, J.O., Barberis, E., 2009. Specific surface area and
406 porosity of the clay fraction and phosphorus adsorption in two rhodic ferralsols. Rev. Bras. Ciênc.
407 Solo 33, 1153–1162.
408 ~~Cordell, D., Drangert, J.O., White, S., 2009. The story of phosphorus: Global food security and food~~
409 ~~for thought. Global Environ. Chang. 19, 292–305.~~
410 Curtin, D., Syers, J.K., Smillie, G.W.S., 1987. The importance of exchangeable cations and resin-sink
411 characteristics in the release of soil phosphorus. J. Soil Sci. 38, 711–716.
412 Davison, W., 1993. Iron and manganese in lakes. Earth Sci. Rev. 34, 119–63.
413 Delgado, A., Torrent, J., 1997. Phosphate-rich soils in the European Union: Estimating total plant-
414 available phosphorus. Eur. J. Agron. 6, 205–214.
415 Demello, J.W.V., Barron, V., Torrent, J., 1998. Phosphorus and iron mobilization in flooded soils from
416 Brazil. Soil Sci. 163, 122–132.
417 Edwards, A.C., Withers, P.J.A., 2007. Linking phosphorus sources to impacts in different types of
418 water body. Soil Use Manage. 23, 133–143.
419 Erickson, A.J., Gulliver, J.S., Weiss, P.T., 2012. Capturing phosphates with iron enhanced sand
420 filtration. Water Res. 46, 3032–3042.
421 Fernández, R.I.E., Ferreira Novais, R., Nunes, F.N., Ker, J.C., 2008. Reversibilidade de fósforo não-lábil
422 em solos submetidos à redução microbiana e química. II -Extrações sucessivas do fósforo pela resina
423 de troca aniônica. Rev. Bras. Ciênc. Solo 32, 2319–2330.
424 ~~Gee, G.W., Bauder, J.W., 1986. Particle-size analysis. In: A. Klute (Ed) Methods of Soil Analysis. Part 1:~~
425 ~~Physical and Mineralogical Methods, 2nd edn, pp. 383–411. Agron Soil Sci. Soc. America, Madison,~~
426 ~~WI USA.~~
427 Green, W.J., Gardner, T.J., Ferdelman, T.G., Angle, M.P., Varner, L.C., Nixon, P., 1989. Geochemical
428 processes in the Lake Fryxell Basin (Victoria Land, Antarctica). Hydrobiologia 172, 129–148.

Gonçalves, G.K., Meurer, E.J., Bortolon, L., Ribeiro Nunes Gonçalves, D., 2011. Relação entre óxidos de ferro e de manganês e a sorção de fósforo em solos no Rio Grande do Sul. Rev. Bras. Ciênc. Solo. 35, 1633–1639.

Gustafsson, J.P., 2012. MINTEQ 3.0 software. KTH Stockholm, SE EU.

Hartikainen, H., Rasa, K., Withers, P.J.A., 2010. Phosphorus exchange properties of European soils and sediments derived from them. Eur. J. Soil Sci. 61, 1033–1042.

Hill, C.R., Robinson, J.S., 2012. Phosphorus flux from wetland ditch sediments. Sci. Tot. Environ. 437, 315–322.

~~Huang, L., Wang, H., Li, Y., Lu, S., 2012. Spatial distribution and risk assessment of phosphorus loss potential in urban–suburban soil of Lishui, China. Catena 100, 42–49.~~

IUSS Working Group WRB, 2007. World Reference Base for Soil Resources 2006, first update 2007. World Soil Resources Reports No. 103. FAO, Rome, IT EU.

Kõiv, M., Ostonen, I., Vohla, C., Mõtlep, R., Liira, M., Lõhmus, K., Kirsimäe, K., Mander, U., 2012. Reuse potential of phosphorus-rich filter materials from subsurface flow wastewater treatment filters for forest soil amendment. Hydrobiologia 692, 145–156.

Lindsay, W.L., 1979. Chemical Equilibria in Soils. Balckburn Press, Caldwell, NJ USA.

Liu, F., Xiao, R., Wang, Y., Li, Y., Zhang, S., Luo, Q., Wu, J., 2013. Effect of a novel constructed drainage ditch on the phosphorus sorption capacity of ditch soils in an agricultural headwater catchment in subtropical central China. Ecol. Eng. 58, 69–76.

~~Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by dithionite-citrate system buffered with sodium carbonate. Clays Clay Miner. 7, 317–327.~~

Mukhtar, S., Baker, J.L., Kanwar, R.S., 1996. Effect of short-term flooding and drainage on soil oxygenation. Trans. Am. Soc. Agric. Eng. 39, 915–920.

Murphy, J., Riley, J.P., 1962. A modified single solution method for determination of phosphate in natural waters. Anal~~ytical~~ Chem.~~ical~~ Acta 27, 31-36.

455 Obour, A.K., Silveira, M.L., Vendramini, J.M.B., Sollenberger, L.E., O'Connor, G.A., 2011. Fluctuating
456 water table effect on phosphorus release and availability from a Florida Spodosol. Nutr. Cycl.
457 Agroecosyst. 91, 207–217.
458 OECD (Organisation for Economic Co-operation and Development), 2007. Glossary of Statistical
459 Terms, Paris, FR EU.
460 Ohno, T., Zibilske, L.M., 1991. Determination of low concentrations of phosphorus in soils extracts
461 using malachite green. Soil Sci. Soc. Am. J. 55, 892–895.
462
463 Olila, O.G., Reddy, K.R., Stites, D.L., 1997. Influence of draining on soil phosphorus forms and
464 distribution in a constructed wetland. Ecol. Eng. 9, 157–169.
465 Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils
466 by extraction with sodium bicarbonate. USDA circular 939 US Gov. Print. Office, Washington, DC
467 USA.
468 Olsen, S.R., Sommers, L.E., 1982. Phosphorus. In: A.L. Page, R.H. Miller, D.R. Keeney (Eds) Methods of
469 Soils Analysis: Part 2, Chemical and Microbiological Properties, 2nd ed., pp. 403-430. Am. Soc.
470 Agron., Madison, WI USA.
471 Pizzeghello, D., Berti, A., Nardi, S., Morari, F., 2011. Phosphorus forms and P-sorption properties in
472 three alkaline soils after long-term mineral and manure applications in north-eastern Italy. Agric.
473 Ecosys. Environ. 141, 58–66.
474 Quang, V.D., Dufey, J.E., 1995. Effect of temperature and flooding duration on phosphate sorption in
475 a acid sulphate soil from Vietnam. Eur. J. Soil Sci. 46, 641–647.
476 Rittmann, B.E., Mayer, B., Westerhoff, P., Edwards, M., 2011. Capturing the lost phosphorus.
477 Chemosphere 84, 846–853.
478 ~~Ryan, J., Ibrikci, H., Delgado, A., Torrent, J., Sommer, R., Rashid, A., 2012. Significance of phosphorus~~
479 ~~for agriculture and the environment in the West Asia and North Africa Region. Adv. Agron. 114, 91–~~
480 ~~153.~~

481 Scalenghe, R., Edwards, A.C., Ajmone-Marsan, F., Barberis, E., 2002. The effect of reducing
482 conditions on P solubility for a diverse range of European agricultural soils. Eur. J. Soil Sci. 53, 439–
483 448.
484 Scalenghe, R., Edwards, A.C., Barberis, E., Ajmone-Marsan, F., 2012. Are agricultural soils under a
485 continental temperate climate susceptible to episodic reducing conditions and increased leaching of
486 phosphorus? J. Environ. Manage. 97, 141–147.
487 ~~Scholz, R.W., Wellmer, F.W., 2013. Approaching a dynamic view on the availability of mineral~~
488 ~~resources: What we may learn from the case of phosphorus? Global Environ. Chang. 23, 11–27.~~
489 Schröeder, M., Cordell, D., Smit, A.L., Rosmarin, A., 2010. Sustainable Use of Phosphorus. Report
490 357, Plant Research International, Wageningen, NL EU.
491 ~~Schwertmann, U., 1964. Diefferenzierung der eisenoxide des bodens durch extraction mit~~
492 ~~ammoniumoxalat-losung. Z. Pflanz. Boden. 105, 194–202.~~
493 Sibbesen, E., 1977. A simple ion-exchange resin method for soil phosphate extraction. Plant Soil 46,
494 665–669.
495 Sibbesen, E., 1978. An investigation of the anion-exchange resin method for soil phosphate
496 extraction. Plant Soil 50, 305–321.
497 Torrent, J., Delgado, A., 2001. Using phosphorus concentration in the soil solution to predict
498 phosphorus desorption to water. J. Environ. Qual. 30, 1829–1835.
499 Walpersdorf, E., Bender Koch, C., Heiberg, L., O'Connell, D.W., Kjaergaard, C., Bruun Hansen, H.C.,
500 2013. Does vivianite control phosphate solubility in anoxic meadow soils? Geoderma 193/194, 189–
501 199.
502 Wang, Z.D., Li, S., Zhu, J., Zhang, Z.J. 2013. Phosphorus partitioning between sediment and water in
503 the riparian wetland in response to the hydrological regimes. Chemosphere 90, 2288–2296.
504 Willet, I.R., 1989. Causes and prediction of changes in extractable phosphorus during flooding. Aust.
505 J. Soil Res. 27, 45–54.

506 Willet, I.R., Higgins, M.L., 1978. Phosphate sorption by reduced and reoxidized rice soils. Aust. J. Soil
507 Res. 16, 319–326.
508 Zaidel'man, F.R., Nikiforova, A.S., Stepantsova, L.V., Safronov, S.B., Krasin, V.N., 2009. Manganese,
509 iron, and phosphorus in nodules of chernozem-like soils on the northern Tambov Plain and their
510 importance for the diagnostics of gley intensity. Euras. Soil Sci. 42, 477–487.

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

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

514 **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

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

516

517 **Table ~~2~~ 3**

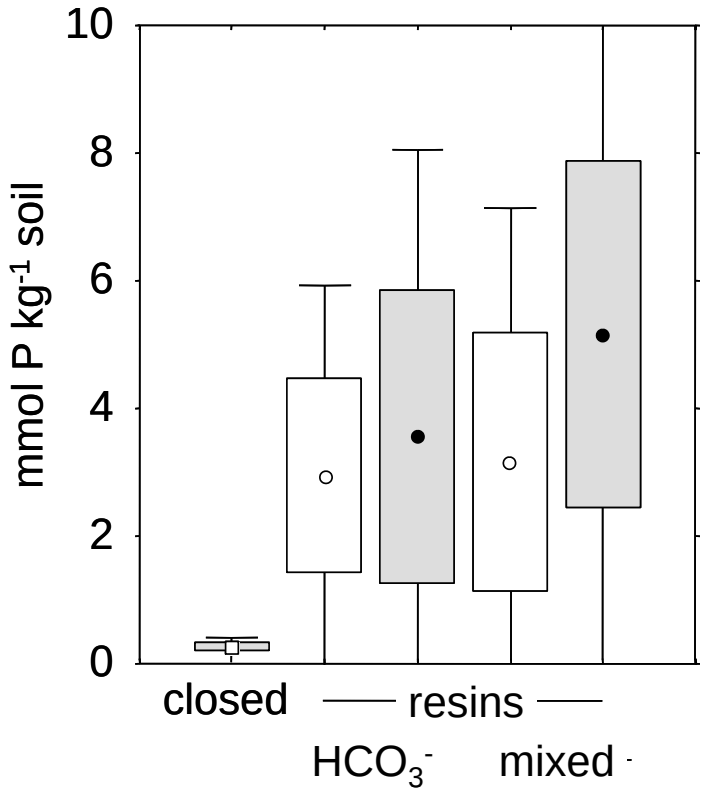
Group†		P	Fe	Mn
C	E1	5.4	3.6	3.8
	E2	1.1	1.8	1.6
	I3	3.4	1.8	3.5
SA	D1	3.3	5.4	2.7
	D2	1.4	35.7	5.1
	E3	1.7	1.8	0.5
	I2	2.1	25.0	0.5
AOMR	G3	0.6	32.1	2.2
	G6	2.4	46.4	1.8
	G9	0.4	19.6	0.9
ALT	D3	1.0	5.4	0.4
	I1	1.9	39.3	0.7

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**		
$\beta Ca_3(PO_4)_2$	-1	-1	-8	-2	-14	-6		-4
$Ca_4H(PO_4)_3{\cdot}3H_2O(s)$	-3	-2	-11	-4	-19	-9		-6
$CaHPO_4(s)$	-1	-1	-3	-2	-5	-3		-2
$CaHPO_4{\cdot}2H_2O(s)$	-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.**

523

524

525 ~~**Fig. 2.**~~

526

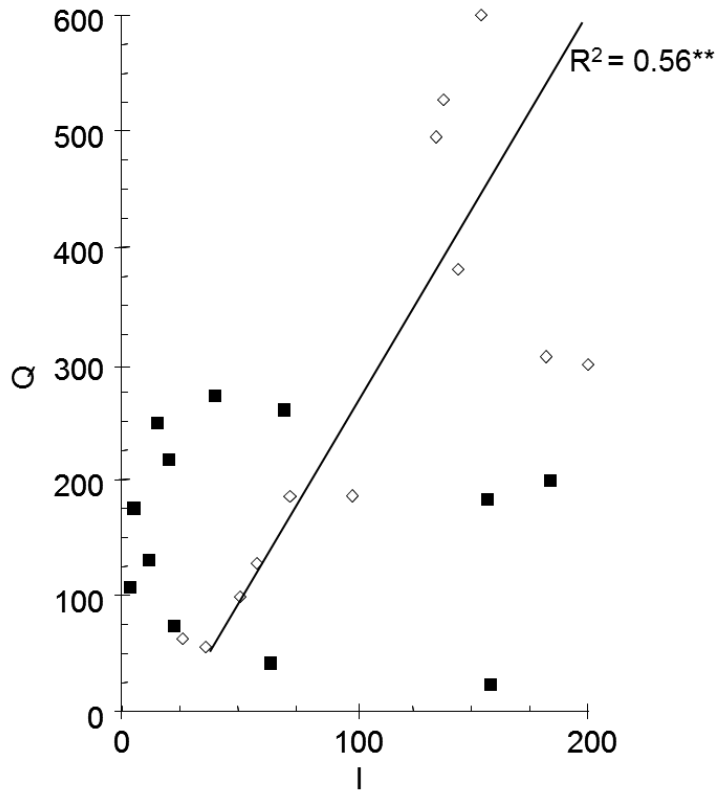
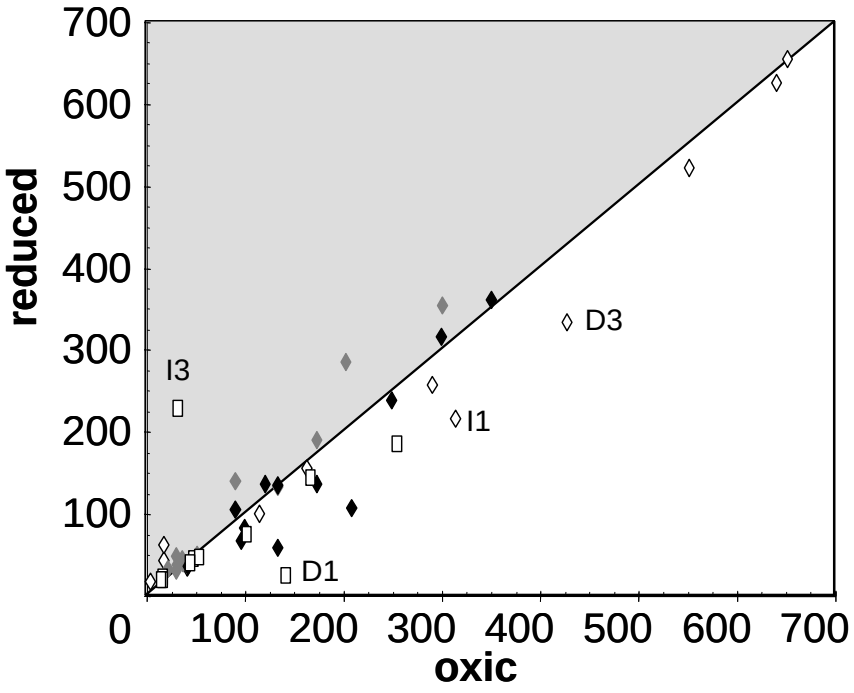


Fig. ~~3~~2.



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532 **Fig. 43.**

CAPTION TO TABLES AND FIGURES

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

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

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

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

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

Figure~~.~~ 1. Phosphorus in solution (closed system) and on anionic HCO_3^- and mixed resins after 32 days of reducing conditions (n=12). Where symbols represent the median (open square indicate a close system without resins while circles P desorbed by resins), the box indicates the interquartiles, and whisker the means±1,96·SD, respectively. Grey boxes indicate an anoxic environment, open boxes indicate oxic conditions. All results are expressed as mmol kg^{-1} soil. All treatments show a significant difference ($p < 0.01$) between the initial oxic condition (closed system, bar on the left side) and the 32 days incubation data. Between treatments a *t* test does not pro~~v~~educe significant differences ($p < 0.05$).

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

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

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

Figure~~.~~ ~~3~~4. P forms (Olsen and Sommers, 1982) expressed in mg P kg^{-1} soil. The line dividing the white and the shaded areas represents the 1:1 ratio. P forms related to Fe/Al complexes are represented by diamonds: open (NaOH), grey (CB), filled (CBD). Ca bound P is represented by open squares (HCl).

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

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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

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

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

1. **Introduction**

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

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

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

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

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

2. Material and Methods

The soils involved in this study span geographically from parallel 38 to 57 N and from meridian 6 W to 11 E, and pedologically from the cooler Chernozems to the warmer Vertisols, and to Regosols (IUSS Working Group WRB, 2007). Mean annual air temperature varies from 7.5 to 18.5 °C and mean annual rainfall from 490 to 900 mm. The selected soils are intensively farmed (OECD, 2007) and 'overfertilised' by having at least twice the optimum concentration of available P. All sampled Ap horizons were sieved to <2 mm and stored in an air-dry condition. The soils and their relevant general properties have been described in Barberis et al. (1996) (Supplementary Information (SI), Appendix A) and basic redox relevant information in Scalenghe et al. (2002). According to Delgado and Torrent (1997), these soils have been grouped into calcareous, C, (E1, E2 and I3), slightly acid, 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 HCO_3^--
96 resin (Dowex 1x4-50), 0.8 g of H^+-resin (Dowex 8x5-50) and 100 mL of deionized water (pre-purged
97 with N_2) 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 pN_2=0.88; pCO_2=0.08;
99 pH_2=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 O_2. 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

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

3. Results

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

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

When the release of elements to mixed resins under anoxic conditions is compared with oxic conditions (Table 2), a general increase of P removal from all anoxic soils is observed and it corresponds to the excess P fertilizers these soils have received (Delgado and Torrent, 1997). One origin for this P appears to be related to the solubilization of Ca compounds. In calcareous soils the removal of Ca is also the result of the lowering of the pH under anaerobiosis. The release of P 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 amorphic 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 $Ca_2P_2O_7$. Pyrophosphates are unstable in soils and eventually are converted to orthophosphates. In
214 oxic environments, the theoretical threshold stability of magnetite occurs when p*e*+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 β-$Ca_2P_2O_7$ is converted into $Fe_2P_2O_7$
217 only at p*e*+pH<3.

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

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

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

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

5. Conclusions

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

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Supplementary material

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

270

References

Adhami, E., Ronaghi, A., Karimian, N., Molavi, R., 2012. Transformation of phosphorus in highly calcareous soils under field capacity and waterlogged conditions. Soil Res. 50, 249–255.

Agbenin, J.O., van Raij, B., 2001. Kinetics and energetics of phosphate release from tropical soils determined by mixed ion-exchange resins. Soil Sci. Soc. Am. J. 65, 1108–1114.

Ajmone-Marsan, F., Côté, D., Simard, R.R., 2006. Phosphorus transformations under reduction in long-term manured soils. Plant Soil 282, 239–250.

Allen, B.L., Mallarino, A.P., Lore, J.F., Baker, J.L., Haq, M.U., 2012. Phosphorus lateral movement through subsoil to subsurface tile drains. Soil Sci. Soc. Am. J. 76, 710–717.

Amery, F., Smolders, E., 2012. Unlocking fixed soil phosphorus upon waterlogging can be promoted by increasing soil cation exchange capacity. Eur. J. Soil. Sci. 63, 831–838.

Ashley, K., Cordell, D., Mavinic, D., 2011. A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse. Chemosphere 84, 737–746.

Bache, B.W., Ireland, C., 1980. Desorption of phosphate from soils using anion exchange resin. J. Soil Sci. 31, 279–306.

Barberis, E., Ajmone Marsan, F., Arduino, E., 1998. Determination of phosphate in solution at different ionic composition using malachite green. Commun. Soil Sci. Plant Anal. 29, 1167–1177.

Barberis, E., Ajmone-Marsan, F., Boero, V., Arduino, E., 1992. Aggregation of soil particles by iron oxides in various size fractions of soil B horizons. J. Soil Sci. 42, 535–542.

Barberis, E., Ajmone-Marsan, F., Scalenghe, R., Lammers, A., Schwertmann, U., Edwards, A.C., Maguire, R., Wilson, M.J., Delgado, A., Torrent, J., 1996. European soils overfertilized with phosphorus: Part 1. Basic properties. Fert. Res. 45, 199–207.

Barrow, N.J., Shaw, T.C., 1977. Factors affecting the amount of phosphate extracted from soil by anion exchange resin. Geoderma 18, 309–323.

Beauchemin, S., Simard, R.R., Bolinder, M.A., Nolin, M.C., Cluis, D., 2003. Prediction of phosphorus concentration in tile-drainage water from the Montreal Lowlands soils. Can. J. Soil. Sci. 83, 73–87.

297 Cessa, R.M.A., Celi, L., Vitorino, A.C.T., Novelino, J.O., Barberis, E., 2009. Specific surface area and
298 porosity of the clay fraction and phosphorus adsorption in two rhodic ferralsols. Rev. Bras. Ciênc.
299 Solo 33, 1153–1162.
300 Curtin, D., Syers, J.K., Smillie, G.W.S., 1987. The importance of exchangeable cations and resin-sink
301 characteristics in the release of soil phosphorus. J. Soil Sci. 38, 711–716.
302 Davison, W., 1993. Iron and manganese in lakes. Earth Sci. Rev. 34, 119–63.
303 Delgado, A., Torrent, J., 1997. Phosphate-rich soils in the European Union: Estimating total plant-
304 available phosphorus. Eur. J. Agron. 6, 205–214.
305 Demello, J.W.V., Barron, V., Torrent, J., 1998. Phosphorus and iron mobilization in flooded soils from
306 Brazil. Soil Sci. 163, 122–132.
307 Edwards, A.C., Withers, P.J.A., 2007. Linking phosphorus sources to impacts in different types of
308 water body. Soil Use Manage. 23, 133–143.
309 Erickson, A.J., Gulliver, J.S., Weiss, P.T., 2012. Capturing phosphates with iron enhanced sand
310 filtration. Water Res. 46, 3032–3042.
311 Fernández, R.I.E., Ferreira Novais, R., Nunes, F.N., Ker, J.C., 2008. Reversibilidade de fósforo não-lábil
312 em solos submetidos à redução microbiana e química. II -Extrações sucessivas do fósforo pela resina
313 de troca aniônica. Rev. Bras. Ciênc. Solo 32, 2319–2330.
314 Green, W.J., Gardner, T.J., Ferdelman, T.G., Angle, M.P., Varner, L.C., Nixon, P., 1989. Geochemical
315 processes in the Lake Fryxell Basin (Victoria Land, Antarctica). Hydrobiologia 172, 129–148.
316 Gonçalves, G.K., Meurer, E.J., Bortolon, L., Ribeiro Nunes Gonçalves, D., 2011. Relação entre óxidos
317 de ferro e de manganês e a sorção de fósforo em solos no Rio Grande do Sul. Rev. Bras. Ciênc. Solo.
318 35, 1633–1639.
319 Gustafsson, J.P., 2012. MINTEQ 3.0 software. KTH Stockholm, SE EU.
320 Hartikainen, H., Rasa, K., Withers, P.J.A., 2010. Phosphorus exchange properties of European soils
321 and sediments derived from them. Eur. J. Soil Sci. 61, 1033–1042.

322 Hill, C.R., Robinson, J.S., 2012. Phosphorus flux from wetland ditch sediments. Sci. Tot. Environ. 437,
323 315–322.
324 IUSS Working Group WRB, 2007. World Reference Base for Soil Resources 2006, first update 2007.
325 World Soil Resources Reports No. 103. FAO, Rome, IT EU.
326 Kõiv, M., Ostonen, I., Vohla, C., Mõtlep, R., Liira, M., Lõhmus, K., Kirsimäe, K., Mander, U., 2012.
327 Reuse potential of phosphorus-rich filter materials from subsurface flow wastewater treatment
328 filters for forest soil amendment. Hydrobiologia 692, 145–156.
329 Lindsay, W.L., 1979. Chemical Equilibria in Soils. Balckburn Press, Caldwell, NJ USA.
330 Liu, F., Xiao, R., Wang, Y., Li, Y., Zhang, S., Luo, Q., Wu, J., 2013. Effect of a novel constructed
331 drainage ditch on the phosphorus sorption capacity of ditch soils in an agricultural headwater
332 catchment in subtropical central China. Ecol. Eng. 58, 69–76.
333 Mukhtar, S., Baker, J.L., Kanwar, R.S., 1996. Effect of short-term flooding and drainage on soil
334 oxygenation. Trans. Am. Soc. Agric. Eng. 39, 915–920.
335 Murphy, J., Riley, J.P., 1962. A modified single solution method for determination of phosphate in
336 natural waters. Anal. Chem. Acta 27, 31-36.
337 Obour, A.K., Silveira, M.L., Vendramini, J.M.B., Sollenberger, L.E., O'Connor, G.A., 2011. Fluctuating
338 water table effect on phosphorus release and availability from a Florida Spodosol. Nutr. Cycl.
339 Agroecosyst. 91, 207–217.
340 OECD (Organisation for Economic Co-operation and Development), 2007. Glossary of Statistical
341 Terms, Paris, FR EU.
342 Ohno, T., Zibilske, L.M., 1991. Determination of low concentrations of phosphorus in soils extracts
343 using malachite green. Soil Sci. Soc. Am. J. 55, 892–895.
344 Olila, O.G., Reddy, K.R., Stites, D.L., 1997. Influence of draining on soil phosphorus forms and
345 distribution in a constructed wetland. Ecol. Eng. 9, 157–169.

346 Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils
347 by extraction with sodium bicarbonate. USDA circular 939 US Gov. Print. Office, Washington, DC
348 USA.
349 Olsen, S.R., Sommers, L.E., 1982. Phosphorus. In: A.L. Page, R.H. Miller, D.R. Keeney (Eds) Methods of
350 Soils Analysis: Part 2, Chemical and Microbiological Properties, 2nd ed., pp. 403-430. Am. Soc.
351 Agron., Madison, WI USA.
352 Pizzeghello, D., Berti, A., Nardi, S., Morari, F., 2011. Phosphorus forms and P-sorption properties in
353 three alkaline soils after long-term mineral and manure applications in north-eastern Italy. Agric.
354 Ecosys. Environ. 141, 58–66.
355 Quang, V.D., Dufey, J.E., 1995. Effect of temperature and flooding duration on phosphate sorption in
356 a acid sulphate soil from Vietnam. Eur. J. Soil Sci. 46, 641–647.
357 Rittmann, B.E., Mayer, B., Westerhoff, P., Edwards, M., 2011. Capturing the lost phosphorus.
358 Chemosphere 84, 846–853.
359 Scalenghe, R., Edwards, A.C., Ajmone-Marsan, F., Barberis, E., 2002. The effect of reducing
360 conditions on P solubility for a diverse range of European agricultural soils. Eur. J. Soil Sci. 53, 439–
361 448.
362 Scalenghe, R., Edwards, A.C., Barberis, E., Ajmone-Marsan, F., 2012. Are agricultural soils under a
363 continental temperate climate susceptible to episodic reducing conditions and increased leaching of
364 phosphorus? J. Environ. Manage. 97, 141–147.
365 Schröeder, M., Cordell, D., Smit, A.L., Rosmarin, A., 2010. Sustainable Use of Phosphorus. Report
366 357, Plant Research International, Wageningen, NL EU.
367 Sibbesen, E., 1977. A simple ion-exchange resin method for soil phosphate extraction. Plant Soil 46,
368 665–669.
369 Sibbesen, E., 1978. An investigation of the anion-exchange resin method for soil phosphate
370 extraction. Plant Soil 50, 305–321.

371 Torrent, J., Delgado, A., 2001. Using phosphorus concentration in the soil solution to predict
372 phosphorus desorption to water. J. Environ. Qual. 30, 1829–1835.
373 Walpersdorf, E., Bender Koch, C., Heiberg, L., O'Connell, D.W., Kjaergaard, C., Bruun Hansen, H.C.,
374 2013. Does vivianite control phosphate solubility in anoxic meadow soils? Geoderma 193/194, 189–
375 199.
376 Wang, Z.D., Li, S., Zhu, J., Zhang, Z.J. 2013. Phosphorus partitioning between sediment and water in
377 the riparian wetland in response to the hydrological regimes. Chemosphere 90, 2288–2296.
378 Willet, I.R., 1989. Causes and prediction of changes in extractable phosphorus during flooding. Aust.
379 J. Soil Res. 27, 45–54.
380 Willet, I.R., Higgins, M.L., 1978. Phosphate sorption by reduced and reoxidized rice soils. Aust. J. Soil
381 Res. 16, 319–326.
382 Zaidel'man, F.R., Nikiforova, A.S., Stepantsova, L.V., Safronov, S.B., Krasin, V.N., 2009. Manganese,
383 iron, and phosphorus in nodules of chernozem-like soils on the northern Tambov Plain and their
384 importance for the diagnostics of gley intensity. Euras. Soil Sci. 42, 477–487.

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

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

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**

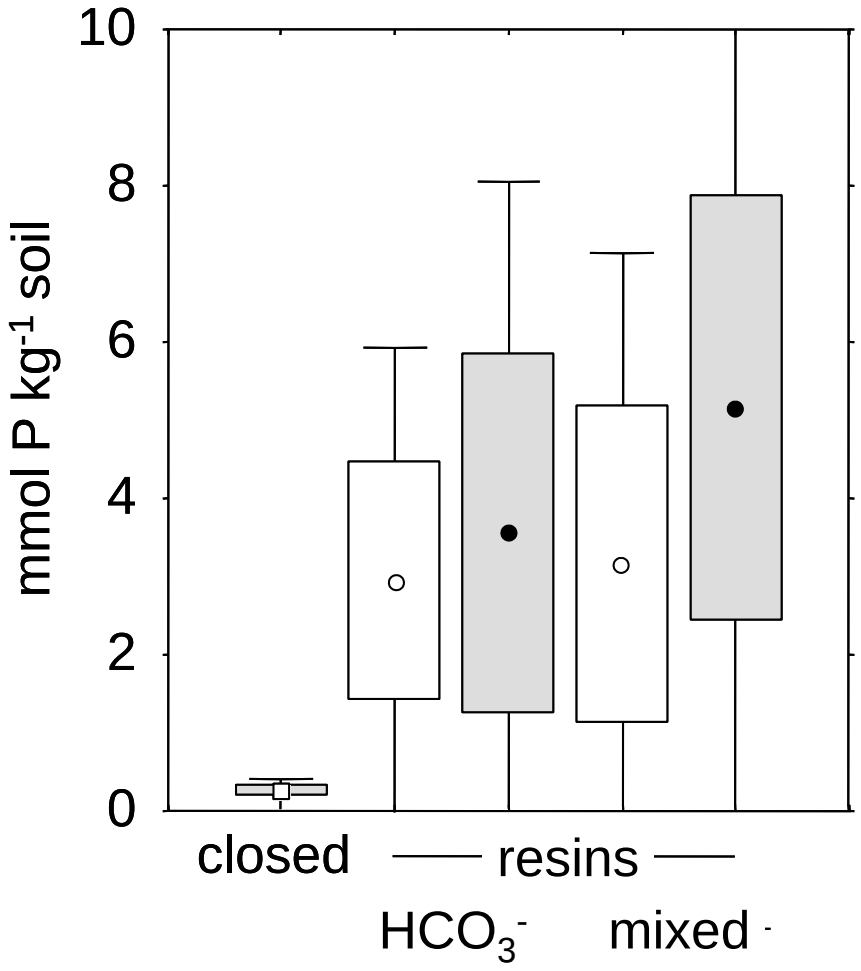
Group†		P	Fe	Mn
C	E1	5.4	3.6	3.8
	E2	1.1	1.8	1.6
	I3	3.4	1.8	3.5
SA	D1	3.3	5.4	2.7
	D2	1.4	35.7	5.1
	E3	1.7	1.8	0.5
	I2	2.1	25.0	0.5
AOMR	G3	0.6	32.1	2.2
	G6	2.4	46.4	1.8
	G9	0.4	19.6	0.9
ALT	D3	1.0	5.4	0.4
	I1	1.9	39.3	0.7

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**		
$\beta Ca_3(PO_4)_2$	-1	-1	-8	-2	-14	-6		-4
$Ca_4H(PO_4)_3{\cdot}3H_2O(s)$	-3	-2	-11	-4	-19	-9		-6
$CaHPO_4(s)$	-1	-1	-3	-2	-5	-3		-2
$CaHPO_4{\cdot}2H_2O(s)$	-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		

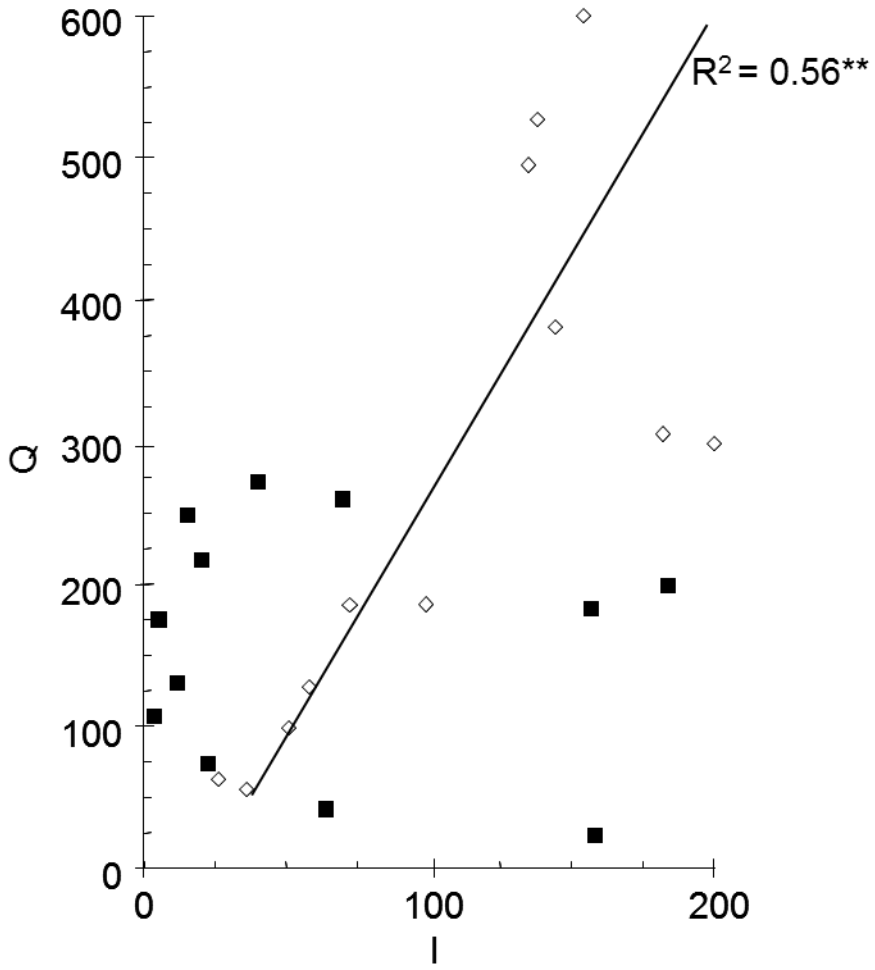
394



395

396 **Fig. 1.**

397



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399 **Fig. 2.**

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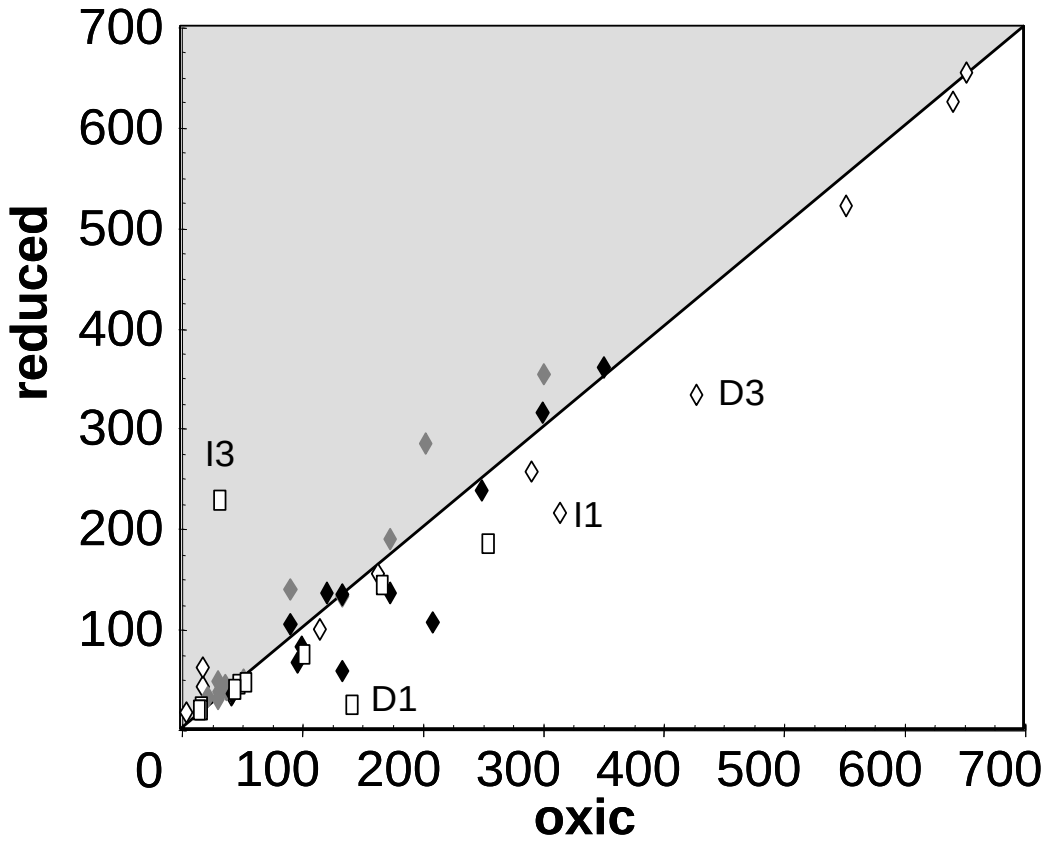
700
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reduced
oxic
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401

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 μmol 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 p*e*+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±1,96·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 (◊) are oxic conditions and filled squares (■)
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).