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

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(Article begins on next page)

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Manuscript Number: CHEM28299R1

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

Article Type: Research Paper

Section/Category: Environmental Chemistry

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

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Corresponding Author's Institution: Università degli Studi di Palermo

First Author: Riccardo Scalenghe, PhD

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

Response to Reviewers: Dear Editor,

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

The page limitation was followed through the text and the number of tables plus figures does not exceed seven. We have defined acronyms when they first appear and then used in the subsequent text. We did not create new acronyms but we quoted directly those from existing Literature.

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

Reviewer #1:

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

- What about Quality Assurance / Quality Control design?

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

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- 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 not to 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.

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

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Highlights

- ▶ The response of 12 contrasting soils to reduction was tested in term of P release
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- ▶ Ca plays a major role in controlling P dynamics even in acid soils
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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,
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EDWARDS Anthony C. Scotland's Rural College, Craibstone, AB219YA Aberdeen, United Kingdom

BARBERIS Elisabetta Dipartimento di Scienze Agrarie, Forestali e Alimentari, Università degli Studi di
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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. ~~It was thought that this~~ experimental design was
considered tonight better simulate the ~~possible~~ loss of ~~cations and anions~~ 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 extracting 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, mimics~~ mimics 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 topsoils 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 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; Köiv 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 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 leaching 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 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 soil drainage 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 (Schröder 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 according to 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~~ peaked 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 ~~coating~~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~~nder 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) ~~which~~that 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 been~~are described in Barberis et al. (1996) ~~(Supplementary Information (SI), Appendix A) and while basic~~ the 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 of 0.25-g each soil samples 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 similar 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 $p\text{N}_2=0.88$; $p\text{CO}_2=0.08$; $p\text{H}_2=0.04$ 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 flushing each vial every day with 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 the sealed vials were centrifuged at 1800 g then 5 mL of the supernatant were sampled using a syringe and acidified to $\text{pH}<3$ 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, 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 pe units (Appendix B, SI). The initial pe+pH of these soils was on average higher than 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 (FigureTable 12).

When the release of elements to mixed resins under anoxic conditions is compared with oxic conditions (Table 24), 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 $700 \text{ mg Fe kg}^{-1}$, $300 \text{ mg Mn kg}^{-1}$, $100 \text{ mg Al kg}^{-1}$ 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 12).

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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 in 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 shown Supplementary 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 were have been 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 than 13.3 ± 1.3 while after reduction it falls to 4.5 ± 0.4 after reduction.

In the previous 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_0 was solubilized by the effect of the reduction in SA, AOMR and ALT soils ($14 \pm 4\%$ of the initial P_{CBD} CBD extractable iron). In C soils around 14% per cent of Fe_0 passed in solution which corresponds to 3% of the initial P_{CBD} CBD extractable iron. This was accompanied by a substantial remarkable 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 experiments 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~~ competes ~~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~~ mimics ~~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 with related to the solubilization of Ca compounds. In calcareous soils the removal of Ca is also the result of the lowering of the pH following the under 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 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~~ The ratio between soil mass and water is ~~an assumed to be the most~~ important factors influencing P release from soil ~~soil P loss~~ the process. In our soils, independently of their groupings, 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 ~~a~~ Authors 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^{tm} -type a linear trend. Otherwise Under reducing conditions there is no relationship between Q and I quantity and intensity. confirming that, while in~~ The difference in behaviour and relationship between Q and I (Figure 23) 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, is marked by a decrease in P_{HCl} . A decrease of occluded phosphorus, P_{CBP} is also observed. While, The simultaneous increase of P_{NaOH} and P_{CB} is probably due to re-adsorption phenomena. A decrease of occluded phosphorus, P_{BCP} 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 occurs 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) form 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 amorphisation 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 their presence of P in solution does 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 -

Ca₂P₂O₇. Pyrophosphates are unstable in soils and eventually ~~are converted~~~~turn—in~~ to orthophosphates. In oxic environments, the theoretical threshold stability of magnetite occurs when pe+pH>11.53: the availability of ionic Fe—~~definitely~~ controls soil mineral stability, below that threshold Ca prevails (Lindsay, 1979). Strongly reduced environments are again controlled by Fe, but β-Ca₂P₂O₇ is converted into Fe₂P₂O₇ only at pe+pH<3.

In the presence of free O₂ our soils show an average pe+pH of 13.3±0.9, which drops to 4.5±0.4 after 32 days under reducing conditions. When ~~the~~~~our~~ 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~~~~drain~~~~ageing of~~~~our soils~~ under anoxia, the selective removal of ions ~~by the drains~~ produces conditions that, contrary to a closed system, could induce the precipitation of phosphates (Table [43](#)). Hydroxyapatite ~~could be expected~~ in C and SA soils, ~~with~~ MnHPO₄ in C, SA and AOMR soils, and vivianite in all soils. Manganese and iron phosphates are normally insignificant ~~under closed laboratory conditions~~ but ~~in 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).

5.4. 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 brought~~ the release of P to various degrees in overfertilized soil. When the concentration of P is lowered by

~~providing a the resin sink, mimicking a draining solution, P release increases. The amount of additional P that can be solubilised from lost by a 20 cm soil layer of 20 cm is as much as half a kg 0.5 kg per ha⁻¹, especially in 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 fluctuating dynamic 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

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

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511 **Table 1**

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

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

513

514 [Table 2](#)

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

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

516

Group†		P	Fe	Mn
C	E1	5.4	3.6	3.8
	E2	1.1	1.8	1.6
	I3	3.4	1.8	3.5
SA	D1	3.3	5.4	2.7
	D2	1.4	35.7	5.1
	E3	1.7	1.8	0.5
	I2	2.1	25.0	0.5
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

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

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

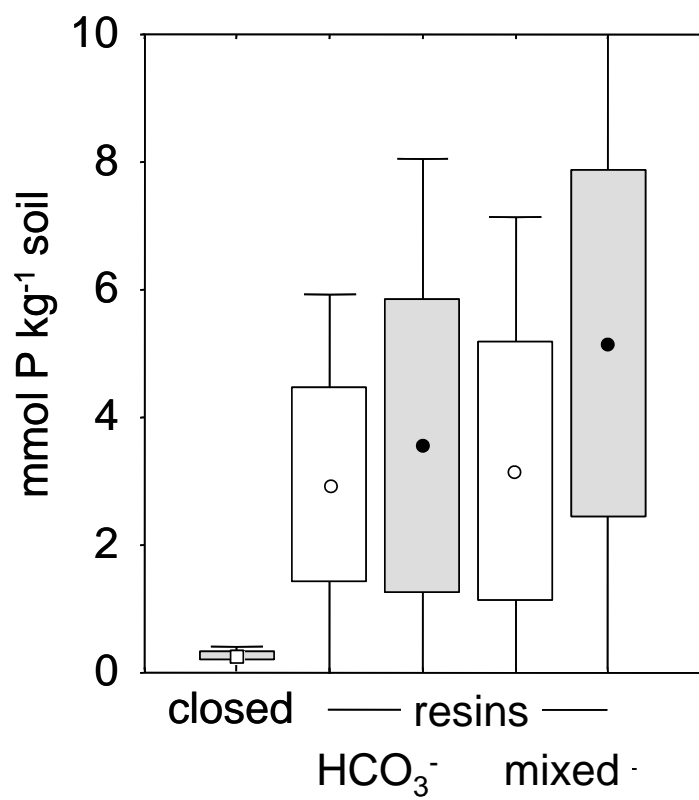
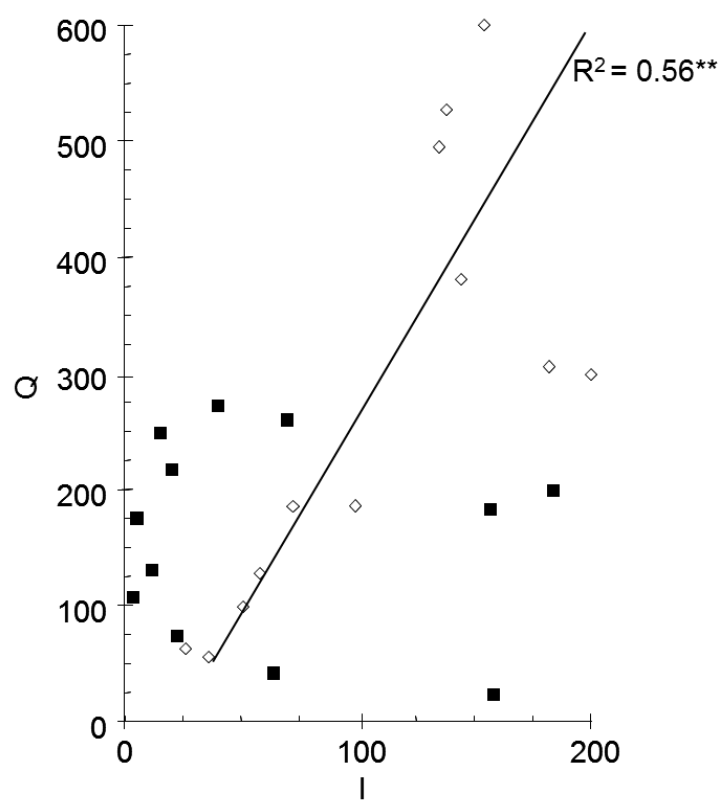


Fig. 1.

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~~Fig. 2.~~

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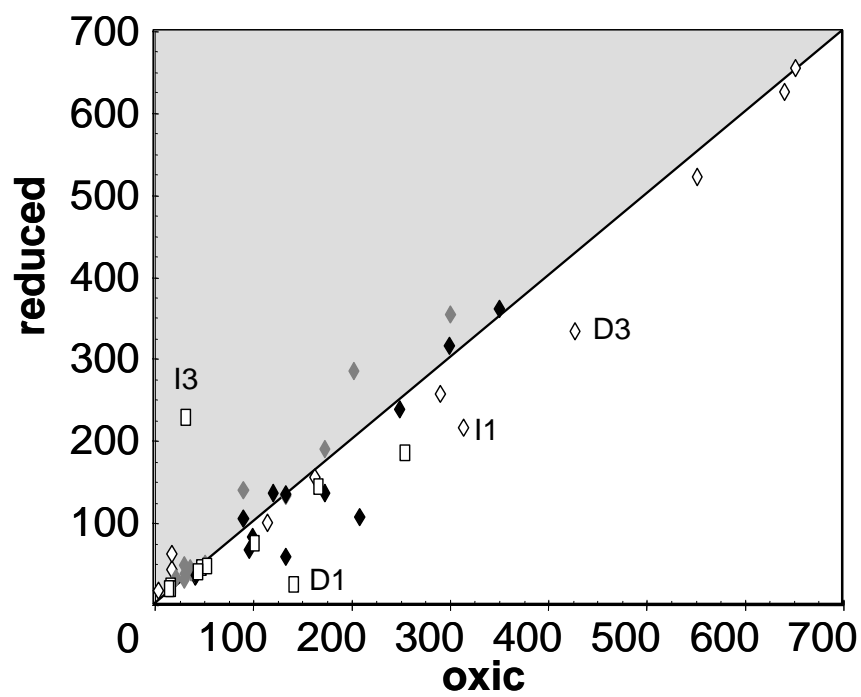


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Fig. 32.

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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 $\mu\text{mol kg}^{-1}$ 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 pe+pH stages. Values are expressed as logarithm of the IAP. Numbers 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 prove 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 ($p \pm pH < 5$) [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 open diamonds (\diamond) are oxic conditions and filled squares (\blacksquare) 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 34. 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).

1 **Release of phosphorus under reducing and simulated open drainage conditions from overfertilised**
2 **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 (Schröder 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-

textured, ALT, (D3 and I1). 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 field, and therefore it undergoes 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).

Four replicates of 0.25-g each soil sample were incubated in 120 mL vials with 2.5 g of HCO₃⁻-resin (Dowex 1x4-50), 0.8 g of H⁺-resin (Dowex 8x5-50) and 100 mL of deionized water (pre-purged with N₂) sealed and stored in an anaerobic box. A similar experiment with the anionic resin only was performed as described by Sibbesen (1977 and 1978). A gas mixture of pN₂=0.88; pCO₂=0.08; pH₂=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 O₂. 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 flushing each vial every day with 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 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 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, 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 MINTEQA 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 than 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

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 2).

Figure 2 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 3) 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. Discussion

The release of P into solution under 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 previous experiments using these soils (Scalenghe et al., 2002), P was released from all soils under anaerobic conditions and peaked after 32 days, after which concentrations in solution decreased. One third of the Fe_o was solubilized by the effect of the reduction in SA, AOMR and ALT soils ($14 \pm 4\%$ of the initial P_{CBD}). In C soils around 14% of Fe_o passed in solution which corresponds to 3% of the initial P_{CBD} . This was accompanied by a substantial release of P as a consequence of the dissolution of the Fe-Mn oxide surfaces where the P was adsorbed (Figure 3 in Scalenghe et al., 2002, page 443). For this reason the current experiments were designed with a period of 32 days of anoxia.

Various authors have observed that the addition of a P (anion) sink in the experimental system maintains the P concentration in solution close to zero and limits 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 not be representative of natural conditions as the anionic resin would compete for P adsorption, shifting the P towards the solution, but it would not hinder the dissolution-precipitation of Ca-P compounds. In order to obtain a more accurate 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 the likelihood of any precipitation with P (Curtin et al., 1987) this would mimic a removal of ions from solution under field conditions in response to drainage.

While Fe has the dominant role in P retention Mn also appears to be involved. In general reduction doubles the amount of Mn with respect to the oxic environment (and up to 11 and 13 times for D2 and I1, respectively). The influence of Mn on P sorption has been suggested for soils of temperate areas (Zaidel'man et al., 2009) although this was not confirmed for tropical soils (Gonçalves et al., 2011). The amount of Fe and Al adsorbed by the resins appears to be independent 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 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.

The ratio between soil mass and water is an important factor influencing P release from soil. In our soils, independent of their grouping, 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 the water-to-soil-ratio (Torrent and Delgado, 2001). These authors concluded that under oxic conditions it is the Quantity (Q) that controls the system. The difference in behaviour and relationship between Q and I (Figure 2) may be explained as under oxic conditions part of the P solution concentration is controlled by the solid phase, while under anoxia the

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

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

4.1 Theoretical prediction of P precipitates

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

In the presence of free O₂ our soils show an average pe+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 MnHPO₄ 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 ...

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385 **Table 1**

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

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

387

388 **Table 2**

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

† 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
	G3	0.6	32.1	2.2
AOMR	G6	2.4	46.4	1.8
	G9	0.4	19.6	0.9
ALT	D3	1.0	5.4	0.4
	I1	1.9	39.3	0.7

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

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

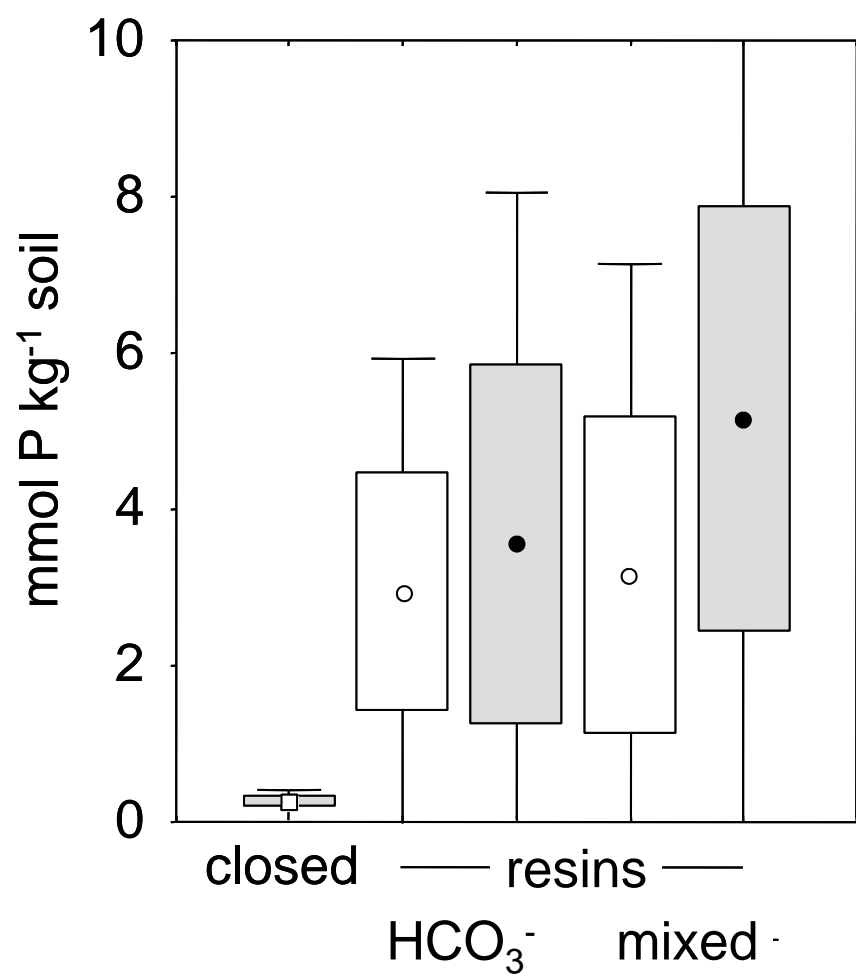


Fig. 1.

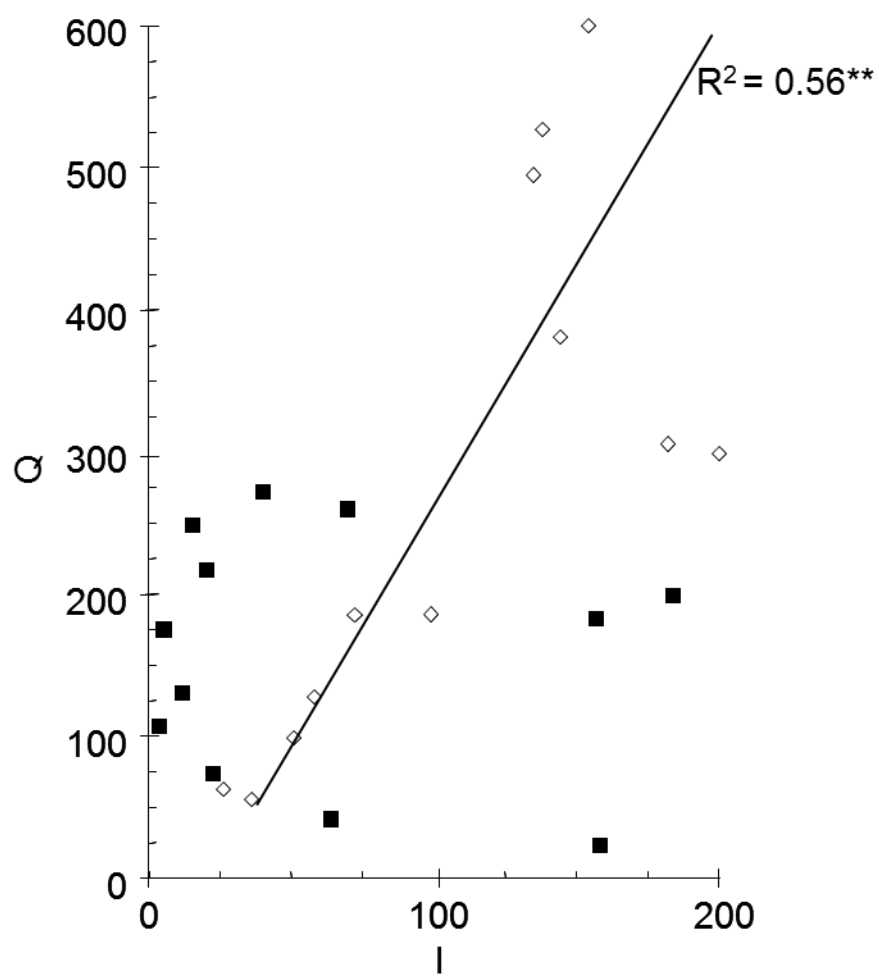
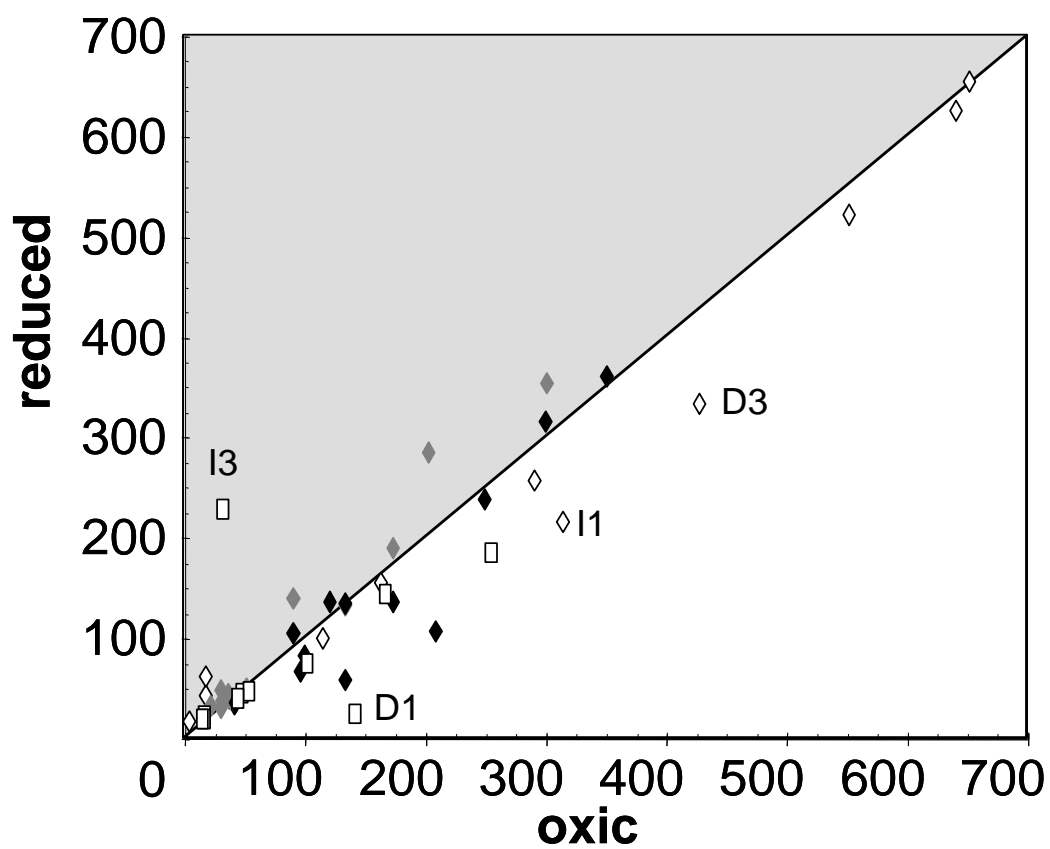


Fig. 2.



401

402 Fig. 3.

CAPTION TO TABLES AND FIGURES

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

Data expressed in $\mu\text{mol kg}^{-1}$ soil. Student *t* test oxic vs reduced is significant for 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.

Table 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 pe+pH stages. Values are expressed as logarithm of the IAP. Numbers 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 $\pm 1.96 \cdot \text{SD}$, 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 produce significant differences ($p < 0.05$).

Figure 2. 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. Open diamonds (\diamond) are oxic conditions and filled squares (\blacksquare) represent reducing conditions. Standard errors of the means are not shown but are always $< 6\%$.

Figure 3. 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).