Are agricultural soils under a continental temperate climate susceptible to episodic reducing conditions and increased leaching of phosphorus?

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a b s t r a c t
Soil science research has probably underestimated the significance that short-term, episodic cycles of reduction and oxidation has had on phosphorus (P) reactivity. Here, the effects of eleven pulsed reduction-oxidation (including wet-dry) cycles on soil P dynamics are compared for 12 soils having contrasting properties and all overfertilised with respect to P. The laboratory based incubation conditions attempted to simulate transient waterlogging of the soil profile and involved repeated sampling and analysis of both the solution and solid phase P forms. An initial increase in P concentration in solution that occurred up to and including the fourth full cycle was followed by a sharp decline in concentration for all but one soil. Accompanying changes in the main extractable forms of P, which appeared to be cumulative, could be summarised as a general decline in the organic P fraction and an overall increase in amorphous associated inorganic forms of P. The fact that up to 60% of the total soil P was demonstrated to change its sensitivity for a particular extractant suggests that these operationally defined P forms are susceptible to transformation as a consequence of changing environmental conditions. There was also a suggestion that certain of the changes in P forms were irreversible. While the laboratory conditions imposed do represent extreme conditions the soils only experienced cyclic changes in their moisture regime. If timing and frequency of intense precipitation events are likely to increase, as predicted in many climate change scenarios, then these results suggest that the effects of episodic redox pulses may have implications for P cycling in agricultural soils.

1. Introduction

Soils vary in the extent to which they undergo periods of reduction. Large areas of land under agricultural production have visual, physicochemical and mineralogical properties suggestive of having experienced reducing conditions. Land drainage has been a long-term feature of management practices that have enabled some control over the period that surface soils experience transient high watertables and saturation. It is therefore likely that many soils in the temperate zone experience short-term conditions which are likely to favour reduction (Stoate et al., 2001; Edwards and Withers, 2007). Despite this potentially very strong change in physicochemical environment there have been relatively fewstudies that actually consider possible environmental consequences. A simple search of all data bases using Web of Knowledge and the key words ‘soil’ and ‘phosphorus’ gave 20,428 references which when followed by redox reduced to 186. The fact that the dynamics of potentially reducing conditions are not always fully considered or appreciated as being significant is well demonstrated by the majority of soil extractions being undertaken on air-dried soil. The onset of anoxic conditions within the soil can alter phosphorus (P) equilibria through the solubilisation of redox sensitive mineral constituents (Mn and Fe) and the simultaneous release of associated (adsorbed or co-precipitated) P anions.

The shift in redox equilibria, coupled with drying, towards a reductive system could also involve a release of P from the organic fraction (Newman and Pietro, 2001; Turner and Haygarth, 2001), which acts as an electron donor, and a possible solubilisation of P associated with carbonate dissolution as a result of a decrease in pH in calcareous soils. Actual rates and extent of reduction will depend on various soil properties, local environmental factors (e.g. temperature; Suplee and Cotner, 2002), biological activity and availability of reducible compounds (e.g. nitrate, metal oxides). Poor land drain efficiencies (through blockage and collapse), extensive autumn cultivation together with a ready supply of labile carbon from livestock manures and slurries prior to cultivation might suggest that the likelihood of encountering conditions that favour reduction is increasing. The spatial scale over which reducing conditions actually develop may vary from the centre of individual soil aggregates to isolated topographic hollows within fields orwhole river flood plains (Williams, 1959; Rinklebe et al., 2007; Grunth et al., 2008). In limnology the significant role that changing redox conditions within bottom sediments can have on P solubility has been well recognised (Wehrli et al., 1997; Moosmann et al., 2006). Certain of the findings from limnological studies may have direct applicability to soils (Patrick and Khalid, 1974) where the most comprehensive understanding has been obtained in relation to periodic flooding of paddy soils for rice production (Jeffery, 1960; Ponnamperuma, 1972; Hossner et al., 1973; James and Bartlett, 2000). Despite the investment in artificial drainage of agricultural land many soils still experience periodic anoxia due to soil compaction as a consequence of excessive trafficking, irrigation, and other management practices (Pant et al., 2002; Niedermeier and Robinson, 2007). Soil related research hasmostly focussed on the effects of long submersion periods. Less emphasis has been given to understanding the likely significance that short-term reducing conditions, such as those that could develop during episodic precipitation events, might have on soil processes. A range of processes operate during wetting and drying cycles, which influence microbial community structure and activity (Gordon et al., 2008; Grunth et al., 2008; Unger et al., 2009) together with precipitation/solubilisation of minerals (de Mello et al., 1998; Phillips, 1998). Typically, changes in the availability of P have been studied for individual soils (e.g. Phillips and Greenway, 1998; Hernandez and Meurer, 2000; Mukherjee et al., 2009; Schärer et al., 2009; Stutter et al., 2009). The aim of this paper was to better understand the dynamics of soluble and solid P forms by exposing a diverse group of overfertilised soils from the European Union (EU) to a series of alternating reducing and oxidizing conditions. The results were analyzed in the light of previous observations obtained for the same 12 soils which had experienced an extended period of continuously reducing conditions (Scalenghe et al., 2002).

2. Materials and methods

2.1. Soils

Two thirds of the 32 World Reference Base Groups (IUSS WG WRB, 2006) or three quarters of the twelve Soil Taxonomy Orders (Soil Survey Staff, 2010) are represented in significant amounts in Europe. The twelve soils chosen are taxonomically representative of roughly half these and range from Regosols (Entisols), to Vertisols typically dominating the Mediterranean environments, to Chernozems (Alfisols either Mollisols) of the cooler mid-latitudes.

When considered together the twelve pedoenvironments vary widely in geographical position (from parallel 38 to 57 N and from meridian 6Wto 11 E), climate (mean annual air temperature ranges from 7.5 to 18.5 _C and mean annual rainfall from 490 to 900 mm) and pedoclimate (moisture regimes is xeric for the southernmost soils and udic for the other soils, temperature regimes vary from frigid to thermic).

The soils' properties (details provided in Supplementary information, SI) that are more likely to influence the rate of redox change fluctuate between 4.6 and 7.8 in terms of pH, from clayey to sandy in terms of texture, and from 4 to 39 g organic carbon kg^{-1} dry soil. Extractable forms of Fe and Al differ widely; the Fe_{ox}/Fe_d ratio (an index of the degree of iron crystallinity; Delgado and Torrent, 1997) ranged from 0.07 to 0.77 being >0.5 in three soils (G3, D3 and I1). On the basis of this variability, they can be practically grouped into calcareous, slightly acid, acid and rich in organic matter, and acid and light-textured. P release was measured in solution after redox pulses (20 days of full reducing conditions followed by rapid oxidation).

Half of the EU, two million square kilometres by landmass, is farmed and a wide range of land use exists, although there has been a general intensification, often associated with excessive addition of nutrients. Nutrient surpluses occur when inputs are greater than exports and are common in conventional agriculture where high fertilizer and/or manure application are often associated with areas of relatively low fertilizer efficiency (Reddy et al., 2005; Torrent et al., 2007; Rudel et al., 2009; Pizzeghello et al., 2011). P surpluses (>5 kg P ha^{-1} y^{-1}) are of particular concern in many of the agricultural areas of the EU (Bouwman et al., 2006; Torrent et al., 2007; Ulén et al., 2007; MacDonald et al., 2011). The selected soils are 'overfertilised' as defined by having at least twice the optimum concentration of available P as estimated using the official analytical methods of its relevant country (Barberis et al., 1996). All the soils are intensively farmed as defined by OECD (2007) and crops range from horticulture to fruit production, from mixed/arable systems to rice (paddy).

All sampled Ap horizons were sieved to <2mmand stored in an air-dry condition. The soils and their relevant general properties (a synopsis is given in SI) are described in Barberis et al. (1996) while the redox relevant information can be found in Scalenghe et al. (2002). The sampled soils can be grouped into (1) calcareous, C, (E1, E2 and I3), (2) slightly acid, SA, (D1, D2, E3 and I2), (3) acid and rich in organic matter, AOMR, (G3, G6 and G9), and (4) acid and light-textured, ALT, (D3 and I1) (Delgado and Torrent, 1997). 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 growing region, and therefore will have experienced periodic flooding as a routine agronomic practice.

2.2. Experimental design

Individual cycles consisted of awater-saturation phase (20 days) followed by oxidation (1 day) and drying (1 day). Triplicate 3 g of soil and 15 mL of 0.01M$CaCl_2$ were measured into 20mL vials (prepurged with N_2) sealed and incubated in an anaerobic box. A gas mixture of pN_2 ¼ 0.88; pCO_2 ¼ 0.08; pH_2 ¼ 0.04 was chosen to best mimic the components most likely present under naturally anoxic conditions. Hydrogenwas flushed through a Pd catalyser to remove the residual O_2.

All vials were subjected to a reduction period of 20 days at 298 K followed by 24 h of oxidized conditions when the vials were bubbled with air at 298 K, then exposed to open air at 313 K; the samples were then freeze-dried for 24 h before the cycle was repeated. Vials were shaken on an end-over-end shaker daily for 20 min during the 20 day reduction stage. The entire cycle was repeated 11 times.

Freeze drying was chosen as being preferable to air drying because of its speed and capacity to provide full sample recovery and a high degree of homogeneity. While the possibility exists that freeze drying may have produced artefacts, some initial testing of the likely effects of the freeze drying method was undertaken. Four of the experimental soils (D3, E3, G3, I1) contrasting in their individual properties were tested in a pre-experiment. A series of recently wetted but non-reduced (oxic) soil samples were contrasted against ones that had experienced the series of reduction periods imposed in the main study. Both sets of soils were then freeze-dried and P forms analyzed. Changes in composition under non-reduced conditions were negligible and fell well within the variability obtained for the soils that experienced reduction. The differences that were observed in P forms after reduction were not

apparent for the non-reduced samples. This would suggest that the P transformations described below are primarily due to the conditions induced during the reduction phase.

A 20 day saturation period was chosen as this was known from previous studies to approximate full reduction for this range of soils under these experimental conditions (Scalenghe et al., 2002). The short oxidation period was selected because, unlike the reduction process, responses to oxidation are generally rapid and no significant changes in P solubility are observed afterwards. At the end of each reduction period 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 precipitation.

Solutions were analyzed for P, Mn and Fe. At the end of the experiment the solid phase was freeze-dried and analyzed. Three replicates of each soil were also destructively sampled after the second, third, fourth, sixth, eight, tenth and final cycle and the soil extracted as described below. The total experiment consisted of approximately 300 vials and each data point represents the mean of a minimum of three replicates. All results are expressed on a soil dry matter basis.

2.3. Laboratory methods

The standard analytical methods used here are described briefly in Scalenghe et al. (2002) and more fully by Barberis et al. (1996). Although there does not appear to be one ideal method (e.g. Cade-Menun and Lavkulich, 1997), many methods have been proposed to estimate total soil, Ptot, and organic phosphorus, Po. We estimated total soil P by fusion with NaOH, while for total soil organic P the ignition method of Legg and Black (1955) was used. In this method soil organic matter is destroyed at relatively low temperatures prior to acid extraction. Po is calculated as the difference between the HCl-extractable P of a soil sample ignited at 513 K and that extracted from the untreated sample.

Soil P fractions were quantified using the method of Olsen and Sommers (1982) which involved a sequential extraction with

(1a) 1 M NaOH, PNaOH, to remove P associated to Fe and Al (hydr-) oxides

(1b) Citrate bicarbonate, PCB, to remove P adsorbed by carbonates during the preceding extraction (the data from these two extractions are presented as the combined value, PNaOH _ CB),

(2) Na citrate bicarbonate dithionite, PCBD, to remove occluded P within the Fe oxides, and

(3) 1 M HCl, PHCl, to remove P bound to Ca.

Residual P is calculated as the difference between Ptot and the sum of the above fractions and therefore might be expected to have a lower confidence than the parameters that were measured directly.

An estimate of plant available P, POls, was determined according to Olsen et al. (1954).

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. Iron and Mn were determined by atomic adsorption spectrometry.

3. Results

3.1. Prequel e stages during continuous submersion

As shown by our previous studies (Scalenghe et al., 2002), during continuous submersion a generalised pattern of behaviour was clearly evident despite the contrasting pedological andmanagement systems the soils had experienced (Fig. 1, right side). Four individual stages with boundaries defined on the basis of changing equilibrating solution pe þ pH conditions and concentrations of MRP, Mn and Fe (Scalenghe et al., 2002). The stages were defined as follows: Stage 1 is characterised by an oxygen-rich environment (pe þ pH > 12), stage 2 (9 < pe þ pH < 12) represents the approximate range for the theoretical complete oxygen depletion and the start of Mn reduction, stage 3 (5 < pe þ pH < 9) represents the

interval for the persistence of nitrate, and stage 4 (pe þ pH < 5)
represents the steady reducing environment and under continuous reducing conditions. Changes in solution composition occurred rapidly after submersion, with the most significant increase in P concentrations occurring during the first week. Increasingly

Fig. 1. Changes in concentration of P, Mn and Fe during pulsed reducing conditions (left side) compared to continuous reducing conditions (right side) (data from Scalenghe et al., 2002). Results are expressed as a ratio of the respective initial concentrations (Cti/Ct0) and averaged (_standard error of the mean) for the soil groups: (>) calcareous (C), ( ) slightly acid (SA), ( ) acid OM rich (AOMR) soil, (C) acidic light-textured soil (D3) and (B) is the paddy soil (I1). Where Ct0 and Cti are the concentrations at time '0' and 'i' respectively

reducing conditions were characterised by rising MRP, Mn and Fe concentrations (stages 1e3) until complete reduction was reached after approximately three weeks (Scalenghe et al., 2002). Finally, stage 4 (up to 600 days) was characterised by a constantly elevated MRP concentration but greatly reduced Mn and Fe concentrations indicating a possible shift in the solid phase solubility.

3.2. Properties of the equilibrating solution

The pulsed reducing conditions (Fig. 1, on the left side) were designed with the aim of reaching complete reduction (defined in Section 3.1 as taking wthree weeks) and then alternating this period of reduction with one of oxidation.

Phosphorus concentrations increased by an order of magnitude compared to initial values, up to the 4th redox pulse, equivalent to 80 days of cumulative reducing conditions. There followed (for all soils except I1) a sharp decline in MRP to concentrations similar or only slightly greater than initial values. Finally, from the 6th redox pulse (i.e. 120 days of reducing conditions) onwards MRP concentrations increased but never reached the large values attained after the 4th pulse. For the paddy soil (I1) a steady state is reached after the 4th cycle at MRP concentrations 30 times the initial value. The maximum MRP concentrations measured ranged from w2 to 7 mg P dm_3. The maximum change in MRP was measured during the 4th cycle (except for two soils G3 and G6) and ranged between 10 and 24 mg P kg_1 which is equivalent to 15 and 36 kg P ha_1 (assuming a value of 1500 t ha_1 soil to a depth of 10 cm). The averaged MRP concentration for each group of soils for any equivalent length of reducing conditions were generally greater under pulsed (Fig. 1, left side) compared to continuously reduced conditions (Fig. 1, right side).

Concentrations of Mn and Fe followed a similar trend and both increased rapidly up to a maximum after the 5th redox pulse. Concentrations subsequently declined but were generally greater than those for the equivalent continuous reducing conditions.

3.3. Changes in solid phase P forms

Initially, Po for all soil groupings ranged from 13 to 30% of total P

(Barberis et al., 1996). The trend in change of Po over time differed between main soil groups (Table 1). For soils grouped into C and SA an initial decline until the 6th redox pulse was followed by a gradual increase in concentration but the original values were not reached. The AMOR group showed a decline in Po over the whole time period with a final average concentration <20% of the original value. After an initial increase the Po concentration of ALT soils remained fairly steady.

The contrasting behaviour of MRP which shows an initial increase compared to the mixed response by Po resulted in concentrations being comparable after the 4th pulsed cycle (Fig. 2). After a greater number of pulsed redox cycles concentrations of MRP and Po started to diverge, although the range of concentrations was much wider.

Further information on the changes in P forms was provided by the sequential soil extractions (Fig. 3) and provided evidence of substantial transformations occurring within the solid phase. These

Table 1
Soil organic P measured at intervals over the 11 redox pulsed cycles. Results are expressed according to soil groups[a] in mg P kg_1 soil (_SD).

Pulse[b]	0[d]	2	3	4	6	8	10	11
Days[c]	Oxic[d]	40	60	80	120	160	200	220
C[a]	128(63)	102(59)	23(8)	12(8)	3(4)	33(28)	66(61)	85(79)
SA[a]	190(151)	160(106)	141(88)	69(26)	53(17)	72(23)	108(98)	124(107)
AOMR[a]	298(87)	344(137)	342(154)	109(70)	93(70)	105(95)	49(37)	24(19)
ALT[a]	80(28)	153(124)	169(118)	143(55)	145(47)	128(164)	137(174)	144(159)

SD e standard deviation.
a C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured.
b Individual cycle involves a reduction period of 20 days (298 K) followed by a period (24 h) of oxidized conditions (pre-bubbled with O2) and open air at 313 K. At the end of the oxidation period soil was freeze-dried (24 h).
c Total number of days of pulsed reduced conditions.
d Initial oxidizing conditions.

0,1
1,0
10
100
400
OXIC 40 60 80 120 160 200 220
Time/days of pulsed reducing conditions
MRP and organic P/mg P kg-1 soil
5
50
0,5
r2 .46* .89* .93** ns ns ns ns

Fig. 2. Changes in solution, as estimated by MRP (grey symbols), and solid phase, organic P (black symbols), over eleven redox pulses. Symbols are sorted by soil groupings where:
(>) calcareous (C), (,) slightly acid (SA), (6) acid OM rich (AOMR) soil, and (B) acidic light-textured soils. The continuous and dotted lines highlight the changes in the range of MRP and organic P respectively. Significance of the correlation between the pattern of P in solution and organic P: ns, not significant, * < 0.05, ** < 0.01, *** < 0.001.

transformations involved from 25 to 60% of the total soil P. The relative change in individual P forms differed between over time. The proportion of PNaOH þ CB increased steadily with time. A simple comparison of the PCBD and PHCl fractions between initial and final cycle would overlook a more complex and dynamic pattern of transformations. Changes that occurred upto the 4th pulsed redox cycle include a decrease in PHCl to a point where some soils appeared to have lost all Ca-bound P. Subsequent changes appeared to involve an increase in PHCl. After an early increase in PCBD concentrations appeared to stabilise after the 4th pulsed cycle. Differences in P transformation were apparent when the final fractionation of the pulsed experiment (after the 11th cycle) was compared with the continuous reduction (600 days) results (data not shown). A change from residual P forms to the more labile and reactive PNaOH þ CB extractable form was observed with few significant changes in the PCBD or PHCl forms.
The results shown in Table 2 reveal that MRP changes are generally greater than those of POls when compared between the initial and 2nd redox pulse.

4. Discussion

4.1. Significance and context of repeated redox cycles

The repeated sequence of redox conditions used here was assumed to simulate what might be expected over the autumne spring period in the Northern Hemisphere. A change in all soils was measurable by the 4th cycle (a period of time approximately comparable to the findings by Velázquez et al., 2004; Contin et al., 2007; Grunth et al., 2008) and perhaps the most interesting from an agronomic and also environmental perspective is the substantial increase in MRP that was readily measurable in the equilibrating solution.
Considering the diverse range of soil properties included in this study a multiplicity of mechanisms are likely to be involved in P release (Delgado and Torrent, 2000; Scalenghe et al., 2007; Schärer et al., 2009). The most direct and obvious process is the reduction, and subsequent oxidation, of Mn and Fe-oxides which would release any adsorbed or occluded P. Alternate reducing and oxidizing conditions would promote the solubilisation of these oxides and their subsequent precipitation as amorphous phases which become in turn more prone to act as electron acceptors after every cycle (Thompson et al., 2006; Brand-Klibanski et al.,

2007; Contin et al., 2007; Trolard and Bourrié, 2008; Schärer et al., 2009). Subsequently the 'reactivity' of the system seems to be slowing down. Upon reoxidation, in fact, ferrous Fe could neoform Fe-oxides that can scavenge the solution, eliminating organic acids, metal cations and oxyanions. Current understanding suggests that supersaturation of organic-rich soil solutions under oxidative conditions will favour initially the formation of aqueous organiceFe complexes and short-range ordered oxides (SRO), rather than well-ordered Fe-oxides. The subsequent onset of reducing conditions can be expected to preferentially dissolve SRO Fe-oxides, but also more crystalline varieties (e.g. goethite) to some smaller degree (Bonneville et al., 2004; Roden, 2004). Thus, repeated redox cycles are suggested to promote the accumulation of SRO Fe-oxides as they are the primary products predicted to be formed during the oxidizing stages with a relative net increase of amorphous and decrease of crystalline Fe forms.

There was some evidence that part of the organically associated P may have contributed to the increased MRP as organic molecules were used as electron donors. The length of reducing conditions (Brand-Klibanski et al., 2007) the occurrence (Pant and Reddy, 2001; Quintero et al., 2007) and type of organic matter (Nagarajah et al., 1989) each effect the rate of reduction and consequently soil P-adsorption properties. As the reduction process progressed the behaviour of Mn, Fe and P became less inter-dependent and while a new Fe phase was precipitated this was not accompanied by adsorption of P. Under field conditions there is evidence that drainage of previously flooded soil and the development of oxidizing conditions result in a simultaneous decrease in soluble P and Fe and an increase of organically bound P (e.g. Shenker et al., 2005). The alternating reducing and oxidizing conditions greatly influenced organic P concentrations although trends over time differed

0
200
400
600
800
40 60 80 120 160 200 220
Forms of P /mg P kg-1 soil
200
400
600
800
0
OXIC
Time /days of pulsed redox conditions
NaOH+CB
CBD

HCl
residual
Fig. 3. P form changes through 220 days of pulsed redox conditions. Boxes are interquartiles of the forms of P for all the 12 soils, where pale grey is PNaOH þ CB, grey is PCBD, filled boxes PHCl and open boxes show residual P. Lines indicate medians.

Table 2
A comparison of the change in Olsen extractable P and MRP in the equilibrating solution between the initial and 2nd redox pulse. The maximum amount of MRP measured in the equilibrating solution is also shown and occurred after the 4th pulse (except for two soils shown in bold where it was the 3rd pulse). All units are as mg P kg_1 dry soil for comparison purposes. Soil groupings: C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured.

Groupings		Olsen	MRP	Maximum MRP concentration
C	E1	3.0	8.4	18.3
	E2	_3.5	7.9	13.9
	I3	16.4	6.2	13.1
SA	D1	_2.0	14.2	22.2
	D2	5.4	13.0	24.5
	E3	_5.1	4.5	10.4
	I2	_1.1	7.1	17.0
AOMR	G3	6.4	8.9	15.3
	G6	_3.1	12.8	21.2
	G9	3.8	4.6	10.1
ALT	I1	_6.3	16.2	24.1
	D3	4.2	6.3	21.0

between the four soil groups. For the C and SA groups an initial decrease to half the original concentration was followed by a subsequent partial recovery and contrasted with a steady decrease for the AOMR group. An initial increase was followed by a rather stable concentration for the ALT soils. The mechanisms responsible for these changes are difficult to identify but might involve initial oxidation of low molecular weight organic matter and a release of any P itmay contain followed by growth ofmicroorganisms suited to anaerobic conditions and conversion back to organic P again (Miller et al., 2001; Mukherjee et al., 2009; Unger et al., 2009).
Some P release could also be due to the dissolution of phosphates in calcareous soils induced by the decline in pH under reducing conditions. Changes in pH would also bring along changes in the surface charge of mineral and organic surfaces and would therefore alter the adsorption/desorption equilibria (e.g. Darke and Walbridge, 2000; Celi et al., 2001).
One possible explanation for the increased ion concentration of the equilibrating solution may also be the lack of initial synchronisation of change between pH and pe (Olila and Reddy, 1995). It is possible that at the moment of sampling the solution was not in

equilibriumandmore Pwas in solutionwhich reflectswhatmight be expected for soil solution under field conditions. The concentration in solution is controlled, directly or indirectly, by factors which require some time to reach equilibrium. The change in pe would influence Fe but the change in pH would in turn affect CaeP solubility and at the same timewould influence re-adsorption capacity of the oxides by changing their surface charge. The possible lack of synchronisation results from (i) rapid sorption at low ionic concentration, which is unaffected by pH; (ii) slow sorption at moderate ionic concentration which decreases with increasing pH and (iii) sorption at supersaturated P conditions which increases with increasing pH. In these situations, the precipitation of CaePminerals could be seen as the key mechanism of control (e.g. Shenker et al., 2005; Scalenghe et al., 2007).

Beyond the 4th cycle the MRP fraction declines rapidly suggesting a transformation to less soluble P forms, most probably because the system approaches a biological and chemical equilibrium, as was the case of the continuous reduction experiment (Scalenghe et al., 2002). However, the lack of any clear relationship with a standard soil test, here Olsen, is potentially important and because the change in MRP concentrations was in many cases greater than POls (even for the calcareous soils) this indicates a general inability of this test P extraction to predict short-term physicochemical changes in P solubility (e.g. Bhattarai et al., 2009; Mukherjee et al., 2009; Stutter et al., 2009; Delgado et al., 2010).

4.2. Changes in solid phase P forms

The changes in P forms confirm that pulsed reduction can be associated with more complex patterns of P transformation than when compared to those that occur under continuous anoxia. The fact that up to 60% of the total soil P changed its sensitivity to a particular extractant suggests substantial cycling can occur between these operationally defined P forms.

Despite the wide range in concentrations of the various P forms measured for individual soils, generally, the overall pattern of response was common and could be summarised as an increase in labile P in response to repeated redox cycles (e.g. Ajmone-Marsan et al., 2006). Concentrations of MRP initially increased while those of organic P decreased and the two became comparable after 80 days of pulsed redox conditions. After longer periods of pulsed reduction these two concentrations started to diverge, and the variability between soils became wider. When considered together, P forms associated with the amorphous phases of all soils, as indicated by the PNaOH _ CB extraction increase considerably after the pulsed reducing conditions (Fig. 3).

5. Conclusions

The onset of reducing conditions and their potential effect on P

dynamics depend on soil properties that include texture, mineralogy, pH, in combination with local management and climatic factors. The response of 12 contrasting soils to alternating oxidation and reduction followed a surprisingly uniform pattern. Pulsed reduction had the effect of enhancing P release with respect to continuous flooding and, more importantly, caused a shift of P forms to more labile fractions. The quantity of MRP released was considerable (roughly equivalent to between 15 and 36 kg P ha_1) but the Olsen extraction, a common test for available P, failed to detect these changes.
A specific understanding of these interactions might enable a greater opportunity to introduce simple management options (e.g. type and timing of irrigation, presence of labile organic matter, watertable height) that influence P availability through manipulation of the soil physicochemical environment, prioritizing the management of individual sources of P at the catchment scale. Maintaining efficient field drainage systems would reduce the likelihood of conditions that favour reduction and P solubilisation.

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