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# The influence of pulsed redox conditions on soil phosphorus

R. Scalenghe<sup>1,2</sup>, A. C. Edwards<sup>3</sup>, E. Barberis<sup>4</sup>, and F. Ajmone Marsan<sup>4</sup>

<sup>1</sup>SAGA, Università di Palermo, Palermo, Italy

<sup>2</sup>HydrASA, CNRS/Université de Poitiers, UMR6269, Poitiers, France

<sup>3</sup>Macaulay Institute, Aberdeen, UK

<sup>4</sup>DIVAPRA, Università di Torino, Grugliasco, Italy

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Correspondence to: R. Scalenghe (scalenghe@unipa.it)

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## Abstract

The effects of eleven pulsed reduction-oxidation cycles (20 and 2 days, respectively) on soil phosphorus (P) dynamics are compared for 12 soils having contrasting properties and overfertilised with respect to P. Incubation conditions simulated transient waterlog-  
5 ging 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 occurred upto 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  
10 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 can experience substantial transformations. There was also a suggestion that certain changes in P forms may not be reversible. While the laboratory conditions represent an extreme situation changes  
15 in timing and frequency of intense precipitation events, as predicted in many climate change scenarios, may increase the risk of episodic soil waterlogging. The potential onset of reducing conditions even for periods of less than twenty days will influence soil P dynamics and short-term bioavailable P. Various mechanisms are involved but the robustness of sequential extraction procedures and general soil test methods (e.g.  
20 Olsen) for quantifying and reliably distinguishing specific soil P forms/associations are questioned.

## 1 Introduction

The phosphorus cycle and its interaction with other environmental compartments has been the subject of considerable recent research particularly in view of its role in eu-  
25 tropic acidification of water bodies (e.g. Reddy et al., 2005).

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The onset of anoxic conditions within soil can alter 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 towards a more reductive system could also involve a release of P from the organic fraction, which acts as an electron donor, and a possible dissolution of P-carbonates as a result of the shift 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). The spatial scale over which reducing conditions actually develop may vary from the centre of individual soil aggregates to isolated topographic hollows within fields or whole river flood plains (Williams, 1959; Rinklebe et al., 2007; Grunth et al., 2008) or coastal environments (Zhang et al., 2010).

The most comprehensive understanding of the role of reduction (e.g. James and Bartlett, 2000) has been obtained in relation to periodic flooding of paddy soils for rice production (Ponnamperuma, 1972). In dry cultivation and natural environments poor drainage and seasonally raised water-tables may result in the temporary saturation of soils with the development of reducing conditions. Despite the investment in artificial under-drainage of agricultural land many soils still experience periodic anoxia due to soil compaction as a consequence of excessive trafficking, irrigation, and management practices (Niedermeier and Robinson, 2007). Riparian buffer strips are especially prone to flooding (Pant et al., 2002).

At a global scale, a greater tendency for heavy summer storms resulting in localised flooding conditions have been predicted as one possible consequence of climate change (Christensen et al., 2007; Meehl et al., 2007). While considerable uncertainty and geographical differences in future climate change scenarios is likely, a general prediction is for an increased incidence of extreme precipitation events and this would in turn lead to more frequent inundation of soils (Banach et al., 2009).

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The work of researchers has mostly 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; Wegener and Boetius, 2009) together with precipitation/solubilisation of minerals (Phillips, 1998). While changes in the availability of P and arsenic (As), that resemble in many respects as both occur in the same group of the periodic table, have been studied for individual soils (e.g. Ascar et al., 2008; Gao et al., 2008; Hernandez and Meurer, 2000; Mukherjee et al., 2009; Phillips and Greenway, 1998; Schärer et al., 2009) a comparison involving soils of widely different properties would be useful.

In a previous paper (Scalenghe et al., 2002) we described the effects that an extended period (600 days) of continuously reducing conditions had upon the solubility and chemical forms of P in a diverse group of overfertilised soils from the European Union. In this study the same 12 soils were used to investigate the effect of repeated short-term saturation and drying cycles on soil P forms. Changes in the solution concentrations and solid phase P forms together with some general environmental consequences of the loss of P are discussed.

## 2 Materials and methods

### 2.1 Soils

Two thirds of the 32 World Reference Base Groups (IUSS WG WRB, 2006) (i.e. 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 (Vertisols) typically dominating the Mediterranean environments, to Chernozems (Alfisols and Mollisols) of the cooler mid-latitudes.

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The pattern of changing MRP concentrations were generally similar for all soils (except I1 and D3) (Fig. 1, left side). Generally, MRP 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). This preliminary period can be equated to the episodic conditions likely to be experienced over timescales of less than a month.

There followed 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. The maximum MRP concentrations measured ranged from  $\sim 2$  to  $7 \text{ g P m}^{-3}$ . For all soils the MRP concentrations for any equivalent length of reducing conditions were generally greater under the pulsed (Fig. 1, left side) compared to the 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, organic P for all soil groupings ranged from 13 to 30% of total P (Barberis et al., 1996). A common trend displayed by all soils in response to the pulsed redox conditions was a loss of organic P (Table 1). The magnitude of the loss differed between soils but for all soil groups the largest change occurred by the 4th pulse when averaged values were less than half the original organic P concentration. After subsequent pulses the behaviour differed with an apparent recovery of organic-P concentrations for C and ALT soils compared to a pattern of continuing decline for SA and AOMR soils. The largest decline in organic P over the full sequence of the experiment ranged from 20% of total P to  $< 2\%$ , which occurred for the AOMR group.

The contrasting behaviour of MRP which initially increased compared to a decrease in organic P resulted in concentrations being comparable after the 4th pulsed cycle (Fig. 2). After a greater number of pulsed redox cycles concentrations started to

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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 transformations directly involved from 25 to 60% of the total soil P. The relative change in individual P forms differed between soils and with number of cycles. The proportion of  $P_{\text{NaOH+CB}}$  increased steadily with time while residual P declined. A simple comparison of the  $P_{\text{CBD}}$  and  $P_{\text{HCl}}$  fractions between initial and final would overlook a more complex and dynamic pattern of transformations. In particular, most changes occurred by the 4th pulsed redox cycle. These changes can be summarised as being an increase in  $P_{\text{CBD}}$  and a decrease in  $P_{\text{HCl}}$  to a point that some soils appeared to have temporarily lost all Ca-bound P.

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 (Fig. 4). These could be summarised as being a change from residual P forms to the more labile and reactive  $P_{\text{NaOH+CB}}$  extractable form with few significant changes in the  $P_{\text{CBD}}$  or  $P_{\text{HCl}}$  forms.

### 3.4 Relationships between P in solution and other soil P test

Olsen extractable P was used to represent an extraction method that has been widely adopted for advisory purposes. Changes in concentrations of  $P_{\text{Ols}}$  followed one of three trends, three soils (E1, E2 and E3) declined, while two (I3 and D3) remained relatively unaffected ( $< 10\%$  change from the initial value) and the remaining soils all showed an increase over time (data not shown).

The observed trends in MRP concentration in the anoxic solution were compared to  $P_{\text{Ols}}$  contents of the solid phase to explore the possibility that the test method can be used as an indicator of potential P release under reduction. While  $P_{\text{Ols}}$  and MRP were always significantly correlated ( $r > 0.8^*$ ) when all 12 soils were plotted for each sampling occasion, there was no relationship between the trends in either parameter over time for individual soils. The effect of this lack of correlation can be observed in

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promote the accumulation of SRO Fe-oxides as they are the primary predicted products formed during the oxidizing stages.

There was some evidence that part of the organically associated P may have contributed to the increased MRP as organic molecules are being 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 oxidising conditions result in a simultaneous decrease in soluble P and Fe and an increase of organically bound P (e.g. Shenker et al., 2005). In all our soils, the consequence of alternating reducing and oxidising conditions, is an initial decrease in organic P to half the original concentrations followed by a later recovery. It appears that low molecular weight organic matter is oxidized at first, releasing P; the development of anaerobic microorganisms would metabolize the P in solution and convert it 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, whose pH decreases 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).

One possible explanation of the elevated ionic concentration of the equilibrating solution may also be the lack of initial synchronisation of change between pH and  $p_e$  (as proposed by Olila and Reddy, 1995; Scalenghe et al., 2002). The lack of synchronisation would result in (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 conditions which increases with increasing pH.

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Concentrations of MRP in the equilibrating solution are therefore controlled by the amount of P released on reduction of the citrate/ascorbate-extractable Fe forms (e.g. de Mello et al., 1998). In these cases, the precipitation of Ca-P minerals could be seen as the key mechanism of control; an increased P-retention capacity upon reoxidation could oversaturate with respect to hydroxyapatite and occasionally  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ , indicating that in spite of the large Ca concentration, the rate of Ca-P precipitation was insufficient to maintain the saturation status of the Ca-P system (e.g. Shenker et al., 2005; Scalenghe et al., 2007).

Beyond the 4th cycle the MRP fraction declines rapidly suggesting a significant transformation in 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). An overall comparison of the latter with the present results clearly indicates that fluctuating oxic-anoxic condition can have serious consequences in terms of P management.

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  $P_{\text{Ols}}$  (even for the calcareous soils) this indicates a general inability of this test P extraction to predict short-term physico-chemical changes in P solubility. This is in line with what reported by Mukherjee et al. (2009) who reported a poor correlation between different soil P tests (STP) and water extractable P in wetland soils.

## 4.2 Changes in solid phase P forms

The changes in P forms confirm that pulsed reduction can bring be associated with more complex patterns of P transformation with respect to continuous anoxia. 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 can experience substantial transformations.

Despite the wide range in relative concentrations of the various P forms, generally, the overall pattern of response was common for all soils and indicate that soil P

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tends to become more labile with succeeding pulses (e.g. Ajmone-Marsan et al., 2006). Concentrations of MRP initially increased while those of organic P decreased and concentrations became comparable after 80 days of pulsed redox conditions (e.g. Fig. 4). After longer periods of pulsed reduction these two concentrations started to diverge, although the range of concentrations was much wider. The P forms determined after the final reducing period showed an apparently similar distribution when comparing pulsed and continuous reduction (Fig. 5). When considered together, P forms associated with the amorphous phases of all soils, as indicated by  $P_{\text{NaOH-CB}}$  extraction increase considerably after the pulsed reducing conditions (Fig. 5). After the same period of time under continuous reducing conditions this phenomenon was not observed (Scalenghe et al., 2002). Scalenghe et al. (2002) studying the continuous flooding of these soils suggested that despite the large concentrations of Fe and P, in particular during the first month of reduction (i.e. Stage 3), it is unlikely that any co-precipitation would have occurred. This is further substantiated by the contrasting trends observed between Mn and Fe with MRP during the long-term period of reduction (Stage 4). Siderite could have coexisted with other iron minerals, but in that situation  $\text{CO}_2$  was not the controlling factor in iron precipitation as magnetite would have prevailed. They hypothesized precipitation of rhodochrosite, however, under those redox conditions Mn(II) solubility was governed by either  $\text{MnCO}_3$  or manganite ( $\text{MnOOH}$ ). In that case, P did not control the precipitation of Mn(II).

Although not quantified one possible explanation might involve microorganisms and their ability to affect biogeochemical processes, this can be underestimated as Mn(III) is both an electron acceptor or donor. Trouwborst et al. (2006) demonstrated that one-electron transfer reactions are more important for Mn biogeochemistry than previously thought. In fact, as the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals that can accept electrons in  $\text{MnO}_2$  or donate electrons from Mn(II) are spatially distinct, reduction of  $\text{MnO}_2$  or oxidation of Mn(II) should lead to Mn(III) species via one-electron transfer processes (Luther, 2005). Mn(III) will also compete with Fe(III) for these ligands (Parker et al., 2004). In our case, under both pulsed and continuous reducing conditions, despite the large

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concentrations of Fe and P, it is unlikely that any co-precipitation would have occurred. In the case of manganese, under our experimental redox conditions MINTEQ integrated with Lindsay's revised database (Gustafsson, 2010) estimate the possibility of oversaturation in respect to  $\text{MnHPO}_4$  after 80 days of pulsed reducing conditions for all the soils (data not shown).

## 5 Conclusions

The cycles of reduction-oxidation highlighted the potential that might exist for the management of (bio)available P, perhaps through short-term manipulations of a soils' physico-chemical properties. The ability to manage (bio)available P over short time periods may offer advantages from an agronomical point of view but also possibly in an environmental context.

A large proportion (up to two thirds) of total soil P is susceptible to a change in extractable form during a sequence of pulsed redox conditions. Changes in the organic and Ca associated P fractions are especially apparent. A distinct division over time occurred, with an initial period upto 4 pulsed cycles (equivalent to 80 days cumulative reducing conditions) characterised by an increased concentration of MRP, Mn and Fe in the equilibrating solution. From the 5th pulsed cycle, concentrations of MRP, Mn and Fe started to decline. The quantity of MRP released was equivalent to between 15–36 kg P per ha and showed no relationship with Olsen extractable P for individual soils. This implies a lack of sensitivity of the Olsen method to the P dynamics that occur in response to reduction. Under reducing conditions consumption of nitrate and dissolution of manganic and ferric hydroxides and release of adsorbed P represents one important source (e.g. Scalenghe et al., 2002; Shenker et al., 2005). This phenomena is magnified by alternating short periods of oxidation within a general condition of anoxia.

The rapid and substantial change in MRP measured in response to waterlogging suggests that Olsen extractable P does not extract the P that is immediately susceptible to reduction. A greater understanding of the redox sensitive soil P component might

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help to provide an opportunity for greater controlled released through manipulation of soil physico-chemical conditions.

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**Table 1.** Changes in soil organic P measured at intervals over the 11 redox pulsed cycles. Results are expressed as the percentage of total P and averaged according to soil groups<sup>1</sup>.

Pulse <sup>2</sup> Days <sup>3</sup>	0 <sup>4</sup> Oxic <sup>4</sup>	2 40	3 60	4 80	6 120	8 160	10 200	11 220
C <sup>1</sup>	30.2	29.7	26.7	12.4	9.9	15.3	25.1	27.5
SA <sup>1</sup>	13.4	15.3	14.0	5.8	5.0	6.9	4.8	4.3
AOMR <sup>1</sup>	20.0	21.8	21.4	7.1	6.4	3.5	2.3	1.8
ALT <sup>1</sup>	17.0	15.8	6.2	3.7	3.1	6.1	6.3	9.3

<sup>1</sup> C calcareous, SA slightly acid, AOMR acid organic matter rich, ALT acid light-textured.

<sup>2</sup> Individual cycle involves a reduction period of 20 days (298 K) followed by a period (24 h) of oxidized conditions (pre-flushed with O<sub>2</sub>) and open air at 313 K. At the end of the oxidation period soil was freeze dried (24 h).

<sup>3</sup> Total number of days of pulsed reduced conditions.

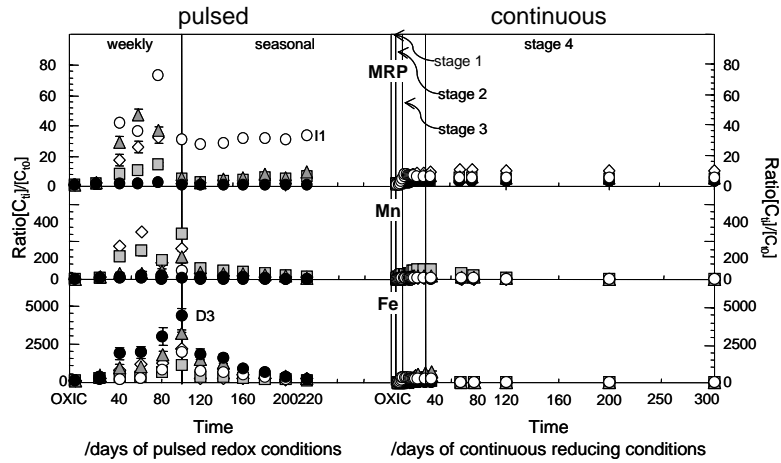
<sup>4</sup> Initial oxidising conditions.

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**Table 2.** A comparison of the change in Olsen P and MRP in the equilibrating solution between the initial and 2nd redox pulse. The maximum concentration 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<sup>-1</sup>.

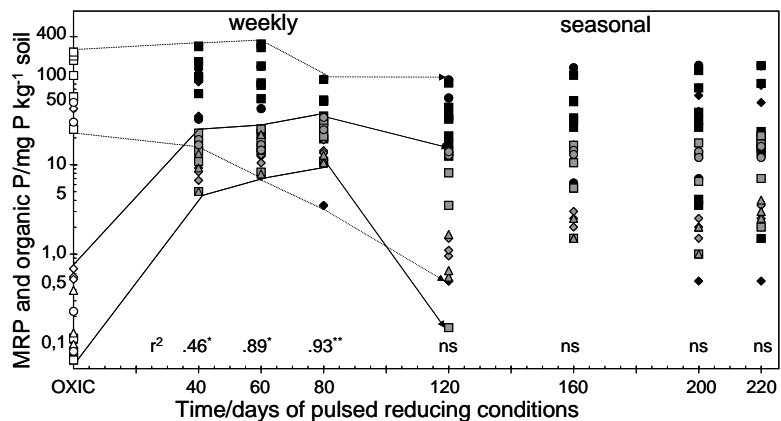
Groupings		Olsen	MRP	Maximum MRP concentration
C	E1	3.0	8.4	18.3
	E2	-3.5	7.9	13.9
	I3	16.4	6.2	13.1
SA	D1	-2.0	14.2	22.2
	D2	5.4	13.0	24.5
	E3	-5.1	4.5	10.4
	I2	-1.1	7.1	17.0
AOMR	G3	6.4	8.9	<b>15.3</b>
	G6	-3.1	12.8	<b>21.2</b>
	G9	3.8	4.6	10.1
ALT	I1	-6.3	16.2	24.1
	D3	4.2	6.3	21.0

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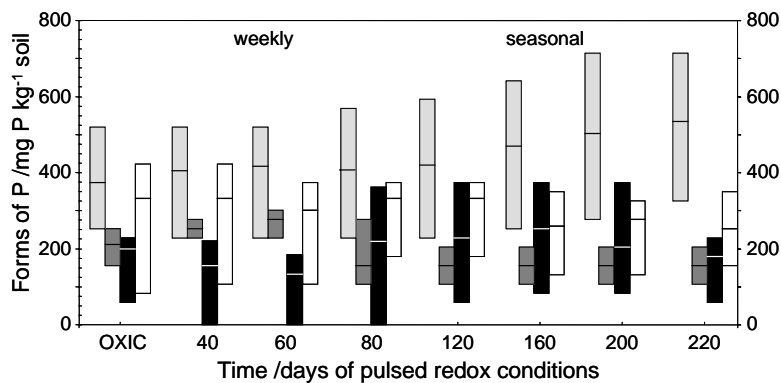


**Fig. 1.** Changes in solution concentrations of molybdate-reactive P, Mn and Fe collected over 220 days of pulsed reducing conditions compared to 300 days of continuous reducing conditions (data from Scalenghe et al., 2002). Results are expressed as a ratio of the respective initial concentrations and averaged for the soil groups: ( $\diamond$ ) calcareous (C), ( $\square$ ) slightly acid (SA), ( $\Delta$ ) acid OM rich (AOMR) soil, ( $\bullet$ ) acidic light-textured soil (D3) and ( $\circ$ ) is the paddy soil (I1) (average  $\pm$  standard error of the mean). All values have been divided by 100 for the paddy soil (I1). On the left hand side, the dotted line is indicative of a boundary between medium (weekly/seasonal) and longer-term (seasonal/annual) exposure to pulsed redox conditions. On the right hand side individual stages are also indicated. Where stage 1 is characterized by an oxygen-rich environment ( $p_e + p_H > 12$ ); stage 2 ( $9 < p_e + p_H < 12$ ) represents the approximate range for the theoretical complete oxygen depletion and the start of Mn reduction; stage 3 ( $5 < p_e + p_H < 9$ ) represents the interval for the persistence of nitrate; and stage 4 ( $p_e + p_H < 5$ ) represents the steady reducing environment and under continuous reducing conditions (from Scalenghe et al., 2002). These stages are equivalent to an approximate timescale of daily, weekly, monthly and annual exposure to reduction under field condition, respectively.

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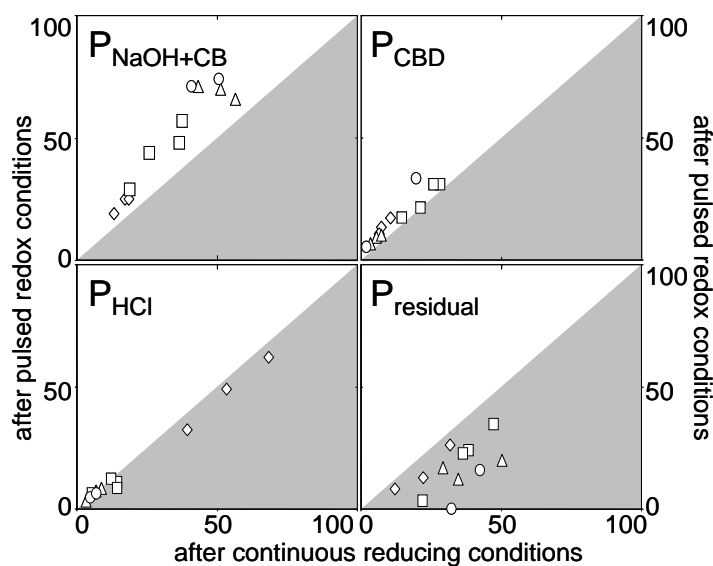


**Fig. 2.** Changes in MRP (grey symbols, solid lined) and organic P (filled symbols, dotted lines) over 220 days of pulsed redox conditions. Symbols are sorted by soil groupings where: ( $\diamond$ ) calcareous (C), ( $\square$ ) slightly acid (SA), ( $\Delta$ ) acid OM rich (AOMR) soil, and ( $\circ$ ) acidic light-textured soils. Open symbols indicate the initial conditions of the soils. Data are expressed as means. Standard error of the mean are not shown (always <10%) and the lines represent the concentration range of the twelve soils.



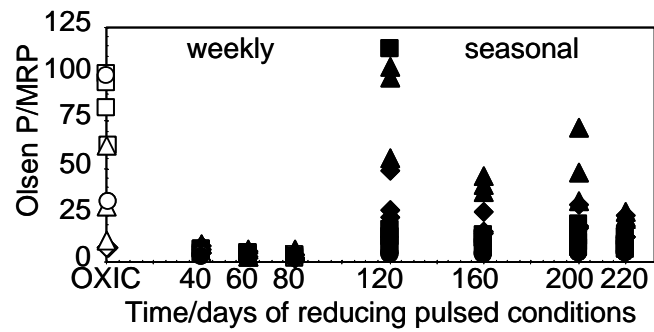
**Fig. 3.** P form changes through 220 days of pulsed redox conditions. Boxes are interquartiles of the forms of P over all the 12 soils, where pale grey are  $P_{NaOH+CB}$ , grey are  $P_{CBD}$ , filled boxes  $P_{HCl}$  and open boxes show residual P. Lines indicate medians.

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**Fig. 4.** Forms of P (sequential extraction) collected after being exposed to continuous reducing conditions (stage 4, 600 days) or pulsed redox conditions (seasonal exposure, 220 days). Results are expressed as a percent of the total phosphorus by soil groupings: ( $\diamond$ ) calcareous (C), ( $\square$ ) slightly acid (SA), ( $\Delta$ ) acid OM rich (AOMR) soil, ( $\circ$ ) acidic light-textured soils (ALT). Initial concentrations are shown elsewhere (Table 4, Scalenghe et al., 2002). Standard errors of the means are not shown (always  $<10\%$ ).

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**Fig. 5.** Changes in  $Q//$  expressed as Olsen extractable phosphorus over MRP collected during a period of pulsed redox conditions. Symbols indicate soil groupings: (a) ( $\diamond$ ) calcareous (C), (b) ( $\square$ ) slightly acid (SA), (c) ( $\Delta$ ) acid OM rich (AOMR) soil, and (d) ( $\circ$ ) acidic light-textured soils. Open symbols indicate the initial  $Q//$  of the soils divided by 10. Data are expressed as averaged ratios. Standard error of the mean are not shown (always <6%).