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

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HIGHLIGHTS

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

GRAPHICAL ABSTRACT

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ABSTRACT

Does removal of cations from soil solution during soil reduction stimulate phosphorus (P) release? An ion-exchange resin system was employed to provide a sink during the incubation of twelve soils under fully reducing conditions. 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.

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

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P (Edwards and Withers, 2007). Ajmone-Marsan et al. (2006) reported that after repeated redox cycles soil P chemistry tends to shift towards more labile forms that would be more easily released on a subsequent submersion and reduction cycle.

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

In previous experiments conducted on a range of European soils overfertilized with P it was observed that P is released under reduction and that more P is released under pulsed redox conditions, i.e. on alternating wet–dry cycles (Scalenghe et al., 2012). In those experiments, however, the concentration of P in solution rapidly reached a peak and then decreased. The decrease in soluble P concentration can be explained by soil re-adsorption as crystalline Fe-oxides are not completely dissolved by the reduction and retain part of their sorption capacity (Demello et al., 1998). Also, new sorption sites may result from the dissolution of Fe coatings that exposes fresh adsorbing surfaces, onto which Fe oxides are often precipitated, and from iron precipitates formed under anoxia (Willet and Higgins, 1978; Willet, 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 HCO_3^--resin (Dowex 1 × 4-50), 0.8 g of H^+-resin (Dowex 8 × 5-50) 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 as described by Sibbesen (1977, 1978). A gas mixture of $pN_2 = 0.88$; $pCO_2 = 0.08$; $pH_2 = 0.04$ was chosen to best simulate the components most likely to be present under naturally anoxic conditions. Hydrogen was flushed through a Pd catalyser to remove the residual O_2. All vials were subjected to a reduction period of 32 d 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 min. 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 min during the reduction period. After 32 d 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 MINTEQ 3.0 (Gustafsson, 2012).

3. Results

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

The amount of P extracted in the presence of mixed resins was higher than that extracted when using anionic resins only. In Fig. 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