



A flow-through reactor to assess potential phosphate release from agricultural soils



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ABSTRACT

Controlling phosphate (P) release from agricultural soils to water while maintaining optimal plant growth conditions remain a major challenge for the development of sustainable agricultural systems. To achieve this, it is important to have a proper knowledge of the amount of soil P that can be mobilized by water and of the kinetics of P release. We evaluated the ability of a flow-through reactor in which ³³P labeled soils can be inserted and leached continuously with deionized water, to assess P release. The experiment was conducted on five grassland soils presenting a large range in P availability. The availability of P in these soils was further modified by submitting them to 0 to 3 plant growth cycles with Italian ryegrass (*Lolium multiflorum*) with three levels of P added (0, 20 and 40 mg P kg soil⁻¹). The P input–output balance, water and oxalate extractable P, the degree of P saturation of the soil and the amount of isotopically exchangeable P (*E* value) were assessed in all samples. A subset of these soil samples was labeled with ³³P, introduced in a flow-through reactor and the release of P and ³³P measured over 14 days. The cumulated amount of P released after 14 days was strongly correlated to the amount of oxalate extractable P, isotopically exchangeable P (*E* value), and water extractable P. The P release kinetics was modeled with a 2 pools model with each pool following first order kinetics. Plants were able to take up P from both pools. Assuming that the leached P had the same isotopic composition as the pool of soil P it came from it became possible to quantify the amount of isotopically exchangeable remaining in the soil which was called the *D* value. *D* decreased during the three first days of the flow-through experiment and then increased linearly with time reaching a maximum after 14 days. This maximum remained lower than the oxalate extractable P. Processes contributing to this increase were isotopic exchange and possibly also some organic P mineralization. The *D* value was strongly linearly correlated to *E* values measured after different exchange times, but for a given exchange time, the *D* value was lower than the *E* value, whereas equality could have been expected. This difference was related to the high rate of ³³P export from the soil at the beginning of the flow-through experiment. The *D* value was also strongly correlated to the oxalate and water extractable P. In conclusion, we suggest that the use of the flow-through reactor yields relevant information on the amount of P that can be leached from a given soil, and that the *D* value delivers information on the amount of isotopically exchangeable P remaining in the soil and therefore which could still be leached if sufficient time would be given.

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1. Introduction

Excessive use of phosphate (P) is a problem in many intensively managed agro-ecosystems, especially in those presenting a high live-stock density (Sutton et al., 2013). Inputs of P in amounts that exceed plant needs lead to P losses to water bodies and to their eutrophication. Haygarth et al. (2005) provide a framework to analyze P losses from agro-ecosystems in which they consider the potential amount of soil P which can be mobilized, the mobilization of P by water, and the P transfer to water bodies. Some works attempted to decrease the transfer of

P to water bodies, e.g. by installing buffer strips between fields and water bodies. However, the efficacy of such measures has been reported to be variable (Noij et al., 2013). The option of decreasing P mobility by increasing soil sorption capacity for P has also been explored, for instance by amending the soil with sorbents rich in Fe or Al (Chardon et al., 2012; Groenberg et al., 2013; McDowell and Nash, 2012). Although promising results have been obtained, the efficiency of such amendments and especially of Fe-rich amendments might not hold on the long-term because of the cycles of reduction/oxidation decreasing the efficiency of Fe oxides as sorbent (Schärer et al., 2007, 2009). In any case, the amount of P that can be mobilized has also to be decreased. This can be achieved by decreasing or stopping P inputs and/or by increasing P outputs (Dodd et al., 2012; Koopmans et al., 2004a; van der Salm et al., 2009). These approaches are also promising but depending

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on plant growth and initial available P stocks, it may take decades to decrease P availability to a level that is low enough to hinder losses (Dodd et al., 2012).

It is important, before implementing a strategy aiming at decreasing P losses, to correctly estimate the amount of soil P which can be released to water and the rate at which it can be released. Kinetics of P release have been studied in batch experiments in which soils were extracted by P-free aqueous solutions in the presence or not of a sink for P (Freese et al., 1995; Hosseinpur and Pashamokhtari, 2008; Lookman et al., 1995; McDowell and Sharpley, 2003; van Rotterdam et al., 2009). These works showed that P release is non-linear and that in P-rich soils, desorption does not reach a plateau even after a very long desorption time. Lookman et al. (1995) extracted soil P using an Fe-hydroxide inserted in a dialysis membrane and modeled the kinetics of P release by considering two pools, each one being described by a first order rate equation. Other authors proposed different models to fit P release kinetics (Hosseinpur and Pashamokhtari, 2008; Koopmans et al., 2001; McDowell and Sharpley, 2003). Although many authors assume that in acid sandy soils the oxalate extractable P can be considered as fully extractable on the long term (Koopmans et al., 2004a; Lookman et al., 1995), they do not provide direct evidence of the mobility of P remaining on the soil's solid phase.

Other approaches, based on the use of P radio-isotopes, can identify a fraction of soil P which is exchangeable, i.e. which can reach the soil solution at a given point in time, without having to extract the entire pool of exchangeable P (Di et al., 1997; Larsen, 1967). Isotopically exchangeable P is measured in soil/water suspensions yielding the so-called *E* value or in soil/plant systems yielding the so-called *L* value (Di et al., 1997; Larsen, 1967). The amount of soil P that is isotopically exchangeable is a function of time and is the main source of P for most crop plants (Fardeau, 1996).

A criticism which can be made to experiments conducted in batch i.e. to most approaches measuring P desorption kinetics and to measuring the *E* value, is that they are conducted in suspensions with a high solution to soil ratio which are regularly shaken. This can lead to aggregate dispersion, particle abrasion and to the exposition of new surfaces during the experiment (Koopmans et al., 2004b; Randriamanantsoa et al., 2013). This in turn can increase the rate of reaction (e.g. of P desorption or P exchange) between the soil and solution (Koopmans et al., 2004b; McDowell et al., 2001; Sinaj et al., 1997). A way to minimize these modifications would be to conduct P release experiments in a flow-through reactor as the one designed by Freese et al. (1999), as its reactor can accommodate soil at a soil to solution ratio close to 1 and as it can be leached continuously with deionized water. Furthermore, using soil labeled with radioactive P in such a flow-through reactor experiment could provide, in addition to the amount of P effectively leached, information on the amount of isotopically exchangeable P remaining in the soil and therefore which could still be leached if sufficient time would be given. The amount of exchangeable P remaining in the soil could be calculated from the isotopic composition ($^{33}\text{P}/^{31}\text{P}$) of the leached P, assuming that the leached P would stem from a pool of soil P having the same isotopic composition. The rationale behind this assumption is that the P present in the soil solution is in constant isotopic exchange with the P present on the solid phase. This hypothesis has been made earlier for the calculation of the isotopically exchangeable P as a source of plant available P by Larsen (1967). This type of approach has to our knowledge not yet been evaluated.

The objectives of this study were: i) to assess the isotopic composition of P released from ^{33}P labeled soil samples inserted in a flow-through reactor and leached continuously with deionized water; ii) to model the amounts of P released from soils; iii) to assess the amount of soil P being in isotopic equilibrium with the leached P (which will be called thereafter the *D* value) and iv) to compare the amount of P released from the soil and the *D* value with indices of soil P availability measured in batch experiments and from plant growth experiments.

2. Materials and methods

2.1. The soil samples

We sampled soils in 5 permanent grasslands to a depth of 10 cm in early January 2006 in the lake Baldegg watershed, canton of Lucerne, Switzerland. This area supports an intensive livestock production and the excessive P application rates on grasslands have been a major source of P for the lake during the last decades (Kanton Luzern, 2001). Liebisch et al. (2013) have shown that in this watershed intensively managed grasslands can still receive more than 110 kg P ha⁻¹ year⁻¹. Soils were sieved at 5 mm and then oven-dried at 40 °C for 7 days. Stones, roots and other plant residues were discarded during sieving. Dried subsamples of about 400 g were further sieved at 2 mm and stored for laboratory analyses (P release kinetics, oxalate extractable P, isotopically exchangeable P and other soil characteristics). The rest was kept for the pot experiments described hereafter. Sampling location and selected soil properties are listed in Table 1.

2.2. Pot experiments

Three sequential growth cycles (8 weeks for each cycle) were carried out on each soil using Italian ryegrass (*Lolium multiflorum*, cultivar Onyx). For each cycle, pots were filled with 500 g (dry weight) of 5 mm sieved soil and sown with 1 g seed kg soil⁻¹. For each of the 5 soils, 3 P fertilization levels were considered: no P added (0P), addition of 20 mg P kg soil⁻¹ (P20) and 40 mg P kg soil⁻¹ (P40). Phosphate was added at the beginning of each growth cycle as KH₂PO₄. The soil samples are designated in the text with their abbreviation, P fertilization rate and growth cycle. For instance "A1 start" designates the original A1 sample, whereas "A1 0P 3 cycle" designates the A1 soil which has been submitted to 3 cycles of plant growth without any P inputs.

Nitrogen and potassium were added to the soil prior to sowing and after each cut as NH₄NO₃ (100 mg N kg soil⁻¹ prior sowing, 100 after the 1st cut, 122 after the 2nd cut and 112 after the 3rd cut) and as K₂SO₄ (200 mg K kg soil⁻¹ prior sowing, 83 after the 1st cut, 100 after the 2nd cut and 97 after the 3rd cut). Other nutrients were added prior sowing as follows: 34 mg Ca kg soil⁻¹ as CaCl₂·2H₂O; 16 mg Mg kg soil⁻¹ as MgCl₂·6H₂O; 2 mg Cu kg soil⁻¹ as CuSO₄·5H₂O; 2 mg Mn kg soil⁻¹ as MnSO₄·H₂O; 1 mg Zn kg soil⁻¹ as ZnSO₄·7H₂O; 1 mg B kg soil⁻¹ as H₃BO₃; 0.1 mg Mo kg soil⁻¹ as (NH₄)₆Mo₇O₂₄·4H₂O.

The pot experiments were carried out in a greenhouse during the year 2006: the 1st cycle from mid-January to mid-March, the 2nd cycle from the beginning of May to the end of June, and the 3rd cycle from the end of July to the end of September. The pots were placed in the greenhouse in a completely randomized block design. An automatic watering system controlled by a Gardena C1060-profi electronic timer (Gardena, Switzerland) was set up delivering up to 80 ml of deionized water (Osmose water II) daily per pot.

The grass was cut four times, every 2 weeks, at about 2 cm above the soil surface, dried at 40 °C, weighed and stored. After the 4th cut, the soils were recovered from the pots, sieved at 5 mm after removal of roots and oven-dried at 40 °C. Soil samples from the various replicates of each soil and treatment were pooled. A fraction (about 400 g) of the pooled sample was sieved at 2 mm and stored for further analyses (P release kinetics, oxalate extractable P and isotopically exchangeable P). The remaining amount of soil was used for the following growth cycle. The number of replicates for each soil/treatment combination was 24, 10 and 4 giving a total number of pots of 360, 150 and 60 for the 1st, 2nd and 3rd growth cycle, respectively.

2.3. Isotope exchange kinetics

Isotopic exchange kinetics (IEK) experiments were conducted in triplicate on all soil samples (before plant growth, and after each plant

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