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Modeling of phosphorus dynamics in contrasting agroecosystems using long-term field experiments

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Morel, C., Ziadi, N., Messiga, A., Bélanger, G., Denoroy, P., Jeangros, B., Jouany, C., Fardeau, J. C., Mollier, A., Parent, L. E., Proix, N., Rabeharisoa, L. and Sinaj, S. 2014. **Modeling of phosphorus dynamics in contrasting agroecosystems using long-term field experiments**. Can. J. Soil Sci. **94**: 377–387. Long-term field experiments on phosphorus (P) fertilization were originally designed to study crop needs in different soil types by analyzing the effects of several rates of P fertilization on yields, their P concentrations and dynamics of plant-available soil P. The objective of this study was to test a computer-based model to simulate the P dynamics at the field scale using plant database and analyzing for plant-available P by a hierarchical process-based approach. It predicts both the concentration (C_P) of phosphate ions (Pi) in soil solution and the associated Pi amounts that in time equilibrate with Pi in solution. Five experiments, representative of contrasting soil types, land-use, and climates were selected. Our model equilibrates the change in plant-available P in the upper soil layer to the P budget between annual P inputs and outputs. Rates of P fertilization affected simulations following the same expected pattern across sites. Field-observed and simulated values are in good agreements in all sites. The field-observed variations of C_P per unit of P budget ranged from 0.007 to 2.49 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$. The predictions are of the same order of magnitude. Predictions were compared with empirical long-term data and mismatches were discussed. This investigation highlights the scientific interest of long-term field P experiments to test and validate models describing P dynamics at the scale of the agricultural fields under different agricultural management practices.

Key words: Phosphorus, soil, agroecosystems, cycling, modeling, fertilization

Morel, C., Ziadi, N., Messiga, A., Bélanger, G., Denoroy, P., Jeangros, B., Jouany, C., Fardeau, J. C., Mollier, A., Parent, L. E., Proix, N., Rabeharisoa, L. et Sinaj, S. 2014. **Modélisation à long terme de la dynamique du phosphore dans des sols de différents agrosystèmes, analysée par des dispositifs expérimentaux de longue durée**. Can. J. Soil Sci. **94**: 377–387. Les essais de longue durée menés sur la fertilisation minérale phosphatée ont pour but d'étudier et d'analyser les effets de différents régimes sur le rendement des cultures, la teneur en P des organes récoltés en relation avec la quantité de P du sol disponible pour les plantes (phytodisponible). L'objectif de ce travail est d'analyser la capacité d'un modèle à prédire le cycle du P dans différents agrosystèmes. Cinq dispositifs ont été sélectionnés pour couvrir différents usages (grandes cultures ou prairies) et différents types de sols mondiaux. Le modèle calcule l'évolution du stock de P phytodisponible d'une année sur l'autre avec le bilan annuel des entrées et sorties de P. Le P phytodisponible du sol a été évalué au laboratoire, après mise en suspension et utilisation d'une technique de marquage et de dénombrement par dilution isotopique. Deux grandeurs ont été déterminées : la concentration (C_P) des ions phosphate dans la solution du sol et son réapprovisionnement par la phase solide sous l'effet d'un gradient de concentration et du temps. Les variations de C_P au champ après plusieurs décennies d'expérimentation sont comprises entre 0,007 et 2,49 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$. Les simulations sont du même ordre de grandeur que les observations faites dans les conditions du champ. Nous discutons ensuite des écarts entre valeurs simulées et observées en considérant plusieurs hypothèses de travail. Ce travail met en évidence l'intérêt scientifique de disposer d'essais P de longue durée pour construire et tester de nouveaux modèles de fonctionnement du cycle du P.

Mots clés: Phosphore, sol, agroécosystèmes, cycle, modélisation, fertilisation

Abbreviations: **DM**, dry matter; **TSP**, triple superphosphate

Improving the prediction of the dynamics of plant-available phosphorus (P) in agricultural soils is recognized as crucial for rationalizing P fertilizer recommendations and reducing the risk of P losses to surface waters in the context of an increasing scarcity of the economically mineable reserves of rock phosphates (Cordell et al. 2009; Gilbert 2009). Fertilization is commonly managed using chemically extracted soil P determined by standard methods that can differ among countries (Neyroud and Lischer 2003). To understand the depletion and the build-up of chemically extracted P through continuous cultivation and fertilization, long-term field experiments are required (McCollum 1991; Johnston 1997). Changes in agroecosystems can be measured only in long-term studies (Janzen 1995). Several annual P rates are tested including control and P rates that represent up to several times the amount of P annually exported in harvests (Boniface and Trocmé 1988; Oehl et al. 2002; Blake et al. 2003; Gallet et al. 2003; Messiga et al. 2010). These experiments serve to relate chemically extracted soil P to the cumulative P budgets. These relationships are site- and method-specific. Hence, after decades of research, it is not yet possible to predict the change on chemically extracted soil P from the cumulative P budget. Single extraction methods fail to predict plant-available soil P partly because they do not provide quantitative information on the ability of soils to replenish the soil solution with phosphate ions (Blake et al. 2003). Furthermore, chemical reagents extract, during a short and fixed time span, different undetermined P forms without accounting for the plant-available soil P and kinetics of reactions (Fardeau et al. 1988; Demaria et al. 2005). Biological and physico-chemical processes that potentially control soil P availability to plants are undetermined and redistribution of phosphate ions between solid and liquid phases obscures the analytical results.

To improve the relevance and reliability of the assessment of plant-available soil P, a scientifically sound approach has been developed during the past decades to identify physico-chemical processes that occur within the rhizosphere for P absorption by plants. This approach is also based on a comprehensive and quantitative knowledge of the P forms and processes that contribute to plant P nutrition (Frossard et al. 2000; Morel et al. 2000). The P forms that are absorbed by plant roots are orthophosphate ions (Pi), $H_2PO_4^-$ and HPO_4^{2-}. However, as Pi in soil solution at seeding is less than 1% of the P taken up by crops during the growth cycle, almost 99% of absorbed Pi is derived from the soil solid phase (Morel 2002). Several processes, including the diffusion of Pi at the solid-to-solution interface, the dissolution of phosphate minerals by acidification and the mineralization of organic P compounds, can possibly govern the Pi release from soil constituents to the soil solution (Frossard et al. 2000; Hinsinger 2001; Richardson et al. 2011). Plant roots act as a sink for nutrients with the consequence that ion diffusion from soil to roots is fundamental to supply plants with mineral nutrients (Jungk and Claassen 1997). The diffusion of Pi at the solid-to-solution interface of soils is quantitatively the dominant process and other mechanisms (such as mineralization of soil organic P; dissolution of sparingly soluble P) might play only incidental roles in plant P nutrition for the plough layer of soils cropped for several decades (Morel 2002). The depletion of Pi in solution at the root surface due to absorption creates a gradient of Pi concentrations between the root surface, the soil solution, and the soil solid phase. This established gradient is the driving force for the diffusive Pi flux from the soil solid phase to the soil solution. The rates of the delivery of Pi to plant roots depend on the rates at which these solutes diffuse at the solid-to-solution interface of soils.

For orthophosphate ions, this solid-to-solution transfer is highly time dependent and lasts for long periods due to slow reactions (Fardeau et al. 1985; Barrow 2008). To quantitatively account for the diffusion process of Pi between solid and liquid phases of soils, sorption-desorption (Barrow 2008) and isotopic dilution techniques (Fardeau et al. 1991; Frossard et al. 2010) have been developed in batch experiments. Both approaches highlighted the prime importance of accounting for both immediate and slow reactions and also for the soil solution Pi concentration. The biogeochemical assessment of plant-available soil P therefore requires the determinations of both Pi in solution plus the corresponding dynamics of diffusive Pi (P_r) as a function of the Pi concentration (C_P) in solution and time.

The objectives of this research were to test the ability of a hierarchical P dynamics model to predict changes in plant-available soil P over decades. This was achieved by analysing five long-term field experiments on P fertilization: (i) In laboratory we parameterize the mathematical equation, i.e., kinetic Freundlich equation, which describes the dynamics of diffusive Pi between liquid and solid phases of soil. This equation is then used in a mass conservation equation to calculate the C_P variation due to the variation of the stock of (Pi in solution plus diffusive Pi after 1 yr) of 1 kg P ha^{-1}. (ii) Otherwise, we determine empirical relations between C_P and P budget at each experimental site to obtain the slope which is the field-observed variation of C_P per 1 kg P ha^{-1}. (iii) We compare (i) and (ii) for a wide range of soil types worldwide.

MATERIALS AND METHODS

Description of Field Experiments

Five long-term P fertilization field experiments representative of various soil types and land use were selected in France [two experiments (S1-FT, S2-FM) under continuous corn (*Zea mays*) cropping on an Arenosol and a Luvisol], eastern Canada [S3-CL: timothy (*Phleum pratense* L.) grassland on a Podzol], Switzerland (S4-SV: permanent grassland on a Cambisol), and Madagascar [S5-MA: corn (*Zea mays*)–soybean (*Glycine max* L. Merr.) rotation on a Ferralsol]. The main characteristics of the sites and experiments are in Table 1. On average during the experiment duration, the P treatments were the following:

- S1-FT (France): 0, 44, and 96 kg P ha^{-1} yr^{-1} (nitrogen and potassium fertilization were supplied so as to be non-limiting);
- S2-FM (France): 0, 27, and 79 kg P ha^{-1} yr^{-1} (Nitrogen and potassium fertilization were supplied so as to be non-limiting);
- S3-CL (eastern Canada): 0, 15, 30, and 45 kg P ha^{-1} yr^{-1} receiving 120 kg N ha^{-1} yr^{-1};
- S4-SV (Switzerland): 0, 8.7, 17.4, and 26.2 kg P ha^{-1} yr^{-1} receiving 25 kg N ha^{-1} yr^{-1};
- S5-MA (Madagascar). An annual application of 5 t of dry matter (DM) ha^{-1} as zebu manure, a recommended practice for smallholders; this provided 50 kg N ha^{-1} yr^{-1}, 6.1 kg P ha^{-1} yr^{-1} and 64.2 kg K ha^{-1} yr^{-1}. The other treatment was also an annual application of 5 t DM ha^{-1} yr^{-1} as zebu manure with 29.5 kg P-triple superphosphate (TSP) ha^{-1} yr^{-1}.

All sites except S5-MA received mineral P as TSP [$Ca(H_2PO_4)_2$, (45% P_2O_5)], a water soluble P fertilizer. Triple superphosphate was manually broadcasted. For cropped soils, TSP granules were incorporated within the topsoil by ploughing a few days before seeding. The experimental designs were a randomized complete blocks device with three or four replications. More details on these sites, climatic conditions, cropping systems can be found in Plénet et al. (2000) for S1-FT, Messiga et al. (2010) for S2-FM, Messiga et al. (2012) for S3-CL, Sinaj et al. (2011) for S4-SV, and in Razafimbelo (2005) and Andriamaniraka et al. (2010) for S5-MA.

The main soil properties of S1-FT, S2-FM, S4-SV, and S5-MA (Table 2) were assessed according to French AFNOR standards (Association Française de Normalisation 1999). Sedimentation analyses to determine the soil particle size was carried out according to standard NF X 31-107 by the dispersion of mineral particles after destruction of the organic matter by hydrogen peroxide and separation of the particles into different classes by sedimentation and sieving. The organic C concentration was determined by sulfochromic oxidation using excess potassium dichromate solution and sulphuric acid (NF ISO 14235). The N concentration was determined by a modified Kjeldahl method (ISO 11261). Organic P was determined by the Saunders and Williams's (1955) procedure. Briefly, 1 g of soil was ignited at 550°C for 4 h. Both ignited and non-ignited soil samples were extracted with 50 mL of 0.2 N H_2SO_4 for 16 h. After filtration at 0.2 µm, the P concentration in solution was determined using the green malachite colorimetric method (van Veldhoven and Mannaerts 1987). The organic P content was calculated as the difference between the ignited and the non-ignited samples. The pH was measured in a soil suspension with a soil-to-water ratio of 1:2.5 (m/v) (ISO 10390). Total concentration of P in soil was determined after calcination at 450°C and wet digestion by HF and $HClO_4$ (NF X 31-147). The cation exchange capacity and exchangeable Ca, Na, Mg, and K were determined with the cobaltihexamine method (except S1-FT for which it was the Metson method). Oxalate-extractable Fe (Fe_{ox}) and Al (Al_{ox}) were determined according to McKeague and Day (1966). Soil properties of S3-CL were recently reported in detail by Messiga et al. (2013).

Processes-based Assessment of Plant-available Soil P

Using soil suspensions (1 g of soil in 10 mL of distilled water) at steady-state, we determined soil solution Pi concentration (C_P, mg P L^{-1}) and amount (Q_w, mg P kg^{-1}), and the associated isotopic dilution kinetics over short periods. The isotopic labelling of P ions in the

Table 1. Main characteristics of the sites, treatments, sampling, and characteristics for the five experimental sites

Site designation	S1-FT	S2-FM	S3-CL	S4-SV	S5-MA
Country	France	France	Canada	Switzerland	Madagascar
Site location	Tartas	Mant	Lévis	Les Verrières	Andranomanelatra
Coordinates	43°52'N, 0°44'W	43°35'N, 0°30'W	46°47'N, 71°07'W	46°56'N, 6°27'E	19°47'S; 47°06'E
Altitude (m)	55	142	74	1150	1600
Mean annual temperature (°C)	13.6	13.6	4.0	6.8	16.0
Mean annual rainfall (mm)	917	917	692	1400	1400–1500
Period of experimentation	1972–2000	1975–1991	1999–2006	1992–2008	1992–2007
Cropping system	Corn, monoculture	Corn monoculture	Timothy grassland	Permanent meadow	Corn-soybean rotation
Experiment duration (yr)	28	17	8	16	15
FAO soil classification	Luvic Arenosol	Dystric Luvisol	Podzol	Cambisol	Ferralsol
Canadian soil classification	Regosol	Luvic	Podzol	Brunisol	Entisol^z
Number of treatments/plots	3/12	3/12	4/16	4/12	2/6
Plot size (m^2)	180	180	3.2	30	12.8
Sampling year	1995, 1998, 2000	1981, 1987, 1992	2007	2008	2003, 2006, 2007
Analyzed soil layer	0–25 cm (plough layer)	0–25 cm (plough layer)	0–15 cm	0–5 cm	0–20 cm (plough layer)
Bulk density (t m^{-3})	1.50	1.40	1.15	1.10	0.90
Soil weight (t ha^{-1})	3750	3500	1725	550	1800

^{z}This soil is not listed in the Canadian classification. Entisol refers to USA soil classification.

Table 2. Main soil properties at the five experimental sites

Site designation	S1-FT[z]	S2-FM[y]	S3-CL[x]	S4-SV[w]	S5-MA[v]
Clay <2 μm (g kg^{-1})	60 (10)[u]	120 (7)	ND[t]	305 (10)	458
Silt (2–50 μm) (g kg^{-1})	135 (34)	520 (12)	ND	549 (21)	345
Sand (50–2000 μm) (g kg^{-1})	806 (71)	361 (17)	ND	146 (36)	197
pH$_{\mathrm{water}}$	5.9 (0.2)	7.3 (0.4)	5.9 (0.2)	5.6 (0.1)	5.1
Organic C (g kg^{-1})	10.3 (3.1)	9.3 (0.9)	23.0 (2.3)	37.4 (1.6)	31.1
Organic N (g kg^{-1})	0.8 (0.2)	1.0 (0.1)	2.0 (0.4)	3.9 (0.1)	2.3
Total P (mg kg^{-1})	542 (42)	333 (49)	900 (20)	783 (49)	668
Organic P (mg kg^{-1})	107 (28)	ND	425 (16)	511 (36)	ND
Olsen P (mg kg^{-1})	44.5 (8.8)	19.8 (3.6)	ND	15.6 (1.1)	6.8
CEC[s] (cmol+ kg^{-1})	3.6 (0.7)	5.9 (0.8)	16.9 (2.6)	ND	4.9
Exch Ca (cmol+ kg^{-1})	0.92 (0.13)	7.1 (1.5)	5.7 (1.3)	ND	1.5
Exch Mg (cmol+ kg^{-1})	0.08 (0.01)	0.4 (0.1)	1.2 (0.2)	ND	1.0
Exch K (cmol+ kg^{-1})	0.19 (0.01)	0.3 (0.1)	0.6 (0.6)	ND	0.2
Exch Na (cmol+ kg^{-1})	0.03 (0.01)	0.04 (0.01)	0.17 (0.04)	ND	0.01
Al*ox* (mmol kg^{-1})	21.5 (4.4)	44.1 (0.4)	83.5 (5.4)	49.1 (2.7)	437
Fe*ox* (mmol kg^{-1})	20.1 (4.7)	21.1 (0.2)	93 (3.8)	115.9 (5.9)	66

[z] Mean of four replicates of the 44 kg P ha^{-1} yr^{-1} treatment sampled in March 1995. CEC and exchangeable cations were determined by the Metson method (Association française de normalisation 1999).
[y] Four replicates collected under treatment at nil P budget and sampled in March 1992.
[x] Four replicates collected under P15 N60 treatment and sampled in spring 2008.
[w] Three plots under the 9 kg P ha^{-1} yr^{-1} treatment sampled in 2008 from the upper 0- to 5-cm layer.
[v] Average soil sampled in 2003.
[u] Values in parentheses are standard deviations.
[t] ND, not determined.
[s] CEC, cation exchange capacity.

solution of pre-equilibrated soil suspension is achieved by introducing a known amount (R) of ^{32}P ions. At time (t) after initiation of isotopic dilution, an unknown amount (P_r) of unlabelled P ions bound to the soil solid phase have diluted the isotopic composition of labelled P ions in solution (Q_w).The P_r value is calculated assuming it has the same isotopic composition as Q_w which gives:

$$r/Q_w = (R - r)/P_r \tag{1}$$

where r is the radioactivity remaining in solution at time t of isotopic dilution. Three soil suspensions were prepared (one replicate for each isotopic dilution period after 1, 10, and 100 min or 4, 40, and 400 min) for each of the soils. After filtration at 0.2 μm of soil suspensions, the r and R values were counted together in the counter (Packard TR 1100) using a liquid scintillation cocktail and the isotopic dilution ratio (r/R) was calculated. The C_P value was determined for all soil samples using the malachite green colorimetric method (van Veldhoven and Mannaerts 1987). Additional details on the procedure are in Morel et al. (2000), Frossard et al. (2010), Stroia et al. (2011), and Messiga et al. (2012).

We analyzed both C_P and P_r in archived soil samples presented in Table 1. As is customary for soil P status for long-term field experiments, we implicitly assume that period of storage does not significantly affect the results. The C_P and P_r values were determined in soils sampled in the plough layer (0–25 cm) in 1995, 1998, and 2000 for S1-FT, and in 1981, 1987, and 1992 for S2-FM. C_P and P_r were analyzed only once for S3-CL and S4-SV in topsoils sampled in 2007, and 2008, respectively.

We analyzed C_P in soils sampled in the plough layer (0–20 cm) in 2003, 2006, and 2007 for S5-MA. For this site C_P and P_r were determined only for the soils sampled in 2003 using the procedure detailed in Stroia et al. (2011) and Messiga et al. (2012), which combines sorption-desorption with subsequent isotopic dilution kinetics.

This method provides within hours a set of experimental data for the parameterization of the mathematical function that describes the gross amount of Pi that can diffuse (P_r, mg P/kg soil) with time (t, minutes) and C_P. This kinetic Freundlich equation (Chardon and Blaauw 1998) is as follows:

$$P_r = vC_P^w\, t^p \text{ with } P_r < P_{r\mathrm{LIMIT}} \tag{2}$$

The v, w, and p parameters are estimated using non-linear regressions using NLIN of SAS Institute, Inc. Software 9.3 (SAS Institute, Inc. 2001). The v parameter is the P_r value at time $t = 1$ min and for $C_P = 1$ mg P L^{-1}; w describes the non-linear increase in P_r with C_P; and p is the non-linear increase in P_r with time (t). The main interest of this equation is to successfully estimate by extrapolation the P_r value for much longer periods from a few days to 1 yr (Fardeau et al. 1985, 1991; Fardeau 1993). This kinetic Freundlich equation explicitly integrates both rapid and slow reactions of phosphate ions in solution with the soil solid phase. Because the $P_{r\ \mathrm{LIMIT}}$ value cannot be determined experimentally, it is generally considered that the $P_{r\ \mathrm{LIMIT}}$ value is lower than the soil inorganic P content, i.e., total P - organic P. The Freundlich equation is consistent with an exponential distribution of electrical potentials or of binding constants (Barrow et al. 2005). The *v*, *w*, and *p* parameters depend on soils and on agricultural practices if they modify soil properties that are involved in P sorption–desorption reactions, such as pH, iron and aluminium oxyhydroxides contents, and clay content (Morel et al. 1994).

Modeling P Dynamics in Agroecosystems

We developed a model that simulates the dynamics of plant-available soil P in the upper soil layer in relation to soil types and agricultural practices. It is based on the mass conservation equation between the plant-available soil P of the analyzed soil layer and the annual P budget (Eq. 4). The process-based evaluation of plant-available P was ($Q_w + P_r$) pool. The model considered the difference between P inputs minus P outputs to calculate the annual P budget which was partitioned between the compartment of Pi in solution and the compartment of soil Pi that could diffuse for 1 yr P_r(1yr). This compartment was extrapolated using the kinetic Freundlich equation. We therefore assumed implicitly that the effects of P inputs and outputs only influenced the analyzed soil layer. This assumption is generally acceptable for the plough layer since P status of the soil layer under the plough layer remains relatively constant. For the 0- to 15-cm soil layer of S3-CL, this assumption is also acceptable, as reported by Messiga et al. (2013). For S4-SV, this assumption was also acceptable because soil P status of the 5- to 10-cm and 10- to 20-cm layers did not vary between P treatments (data not shown).

For this study, we considered that the P budget can be summarized by only two fluxes: P applied as fertilizer and P offtake through harvests. The other possible flows such as P in seeds, atmospheric deposits, preferential, subsurface and surface flows, such as leaching and run-off, were regarded as negligible. We considered that the P present in the crop residues derived from the plant-available soil P can be allotted to the ($Q_w + P_r$) pool during the few months after they were left on the soil surface before ploughing and mixing to soils (Linères and Lubet 1990; Lupwayi et al. 2007). As a result, the effect of crop P residues on the P budget was assumed to be nil at the annual scale.

The two main underlying assumptions that are used in the model were: (i) Pi diffusion at the solid-to-solution interface is the dominant process that controls soil solution Pi concentration; hence other possible rhizospheric processes were assumed to be negligible; and (ii) the P budget influenced only plant-available soil P in the ploughed layer.

The laboratory-simulated calculation is based on the mass conservation law, which gives:

$$k_c(Q_{wi} + P_{ri}(1\mathrm{yr})) = \mathrm{B} + k_c(Q_{wf} + P_{rf}(1\mathrm{yr})) \qquad (3)$$

$$k_c(10C_{\mathrm{P}i} + (\mathrm{v}C^{w}_{\mathrm{P}i}(525600)^{\mathrm{p}}) = \mathrm{B} + k_c(10C_{\mathrm{P}f} + (\mathrm{v}C^{w}_{\mathrm{P}f}(525600)^{\mathrm{p}}) \qquad (4)$$

where k_c is the coefficient to convert mg P kg^{-1} to kg P ha^{-1}; $(Q_w + P_r)_i$ and $(Q_w + P_r)_f$ are the initial and final amounts of Pi in soil solution plus diffusive Pi for 1 yr, with $Q_w = C_P$ (V/M). The volume-to-mass ratio (V/M) is 10 mL g^{-1} in our method. The P_r(1yr) value is calculated with the kinetic Freundlich equation (Eq. 2) considering an equilibration period of 1 yr (525 600 min). The B value is 1 kg P ha^{-1}. The C_{Pi} value is the y-intercept of the field-observed linear regressions between soil solution Pi concentration and cumulated P budget. Equation 4 is solved for C_{Pf} by iteration.

Soil solution Pi concentrations were simulated by the P dynamics model using the following results, scenarios, and assumptions:

i. specific *v*, *w*, and *p* parameter estimates for each soil (Table 3);
ii. the four rates of P fertilization for all soils: 0, 20, 40 and 60 kg P ha^{-1}, applied annually, corresponding to about 0, 1, 2 and 3 times the P exported with the harvested crops;
iii. constant annual P removal every year at 20 kg P ha^{-1} across P fertilizer applications. As a result of (ii) and (iii) the annual P budgets corresponding to the annual P rates of 0, 20, 40 and 60 kg P ha^{-1} were -20, 0, $+20$ and $+40$ kg P ha^{-1};
iv. the same initial soil solution Pi concentration of 0.5 mg L^{-1} across experimental sites;
v. the same mass of soil of 3750 t soil ha^{-1} in the analyzed layer;
vi. all P offtake was derived from the topsoil layer that was analyzed for plant-available P;
vii. a period of 1 yr was allowed to reach equilibrium for Pi reactions between C_P and P_r.

To test the predictive power of the model, we compared the simulated change in C_P values (simΔC_P) predicted by the model for a P budget of 1 kg P ha^{-1} to the observed change in C_P values under field conditions (obsΔC_P) for a P budget of 1 kg P ha^{-1}. A simple method for measuring it is to calculate the relative error of the various predictions according to Eq. (5):

$$\text{Relative error} = (\text{sim}\Delta C_\mathrm{P} - \text{obs}\Delta C_\mathrm{P})/\text{obs}\Delta C_\mathrm{P} \qquad (5)$$

The average of soil C_P and cumulative P budget was calculated for each P treatment and year to obtain the parameter estimates of the linear regressions between obsΔC_P and simΔC_P values by the Proc Reg of SAS software.

Annual Phosphorus Budget from Long-term Experiments

The annual P budgets (kg P ha^{-1}) were calculated for all sites using P applied annually and the annual P offtake in the harvested crops. The P offtake was calculated by multiplying DM yield by the P concentration of the harvested crops. For S1-FT, S2-FM, and S3-CL,

Table 3. The *v*, *w*, and *p* parameter estimates and statistics of the kinetic Freundlich equation ($P_r = v\ C_P{}^{w}\ t^{p}$ with $P_r < P_{rLIMIT}$) for the five sites. This equation describes the dynamic of the gross transfer (P_r, mg P kg^{-1}) of diffusive Pi at the solid-to-solution interface of soils as a function of elapsed time of isotopic dilution (*t*, min) and soil solution Pi concentration (C_P, mg P L^{-1}). The P_r(0.5, 1 wk), P_r(0.5, 1 mo), and P_r(0.5, 1 yr) are calculated P_r values when C_P is 0.5 mg P L^{-1} and time is 1 wk, 1 mo and 1 yr, respectively.

Site designation	S1-FT	S2-FM	S3-CL	S4-SV	S5-MA
v[z]	1.76 (0.12)[u]	5.7 (0.31)	7.23 (0.44)	6.39 (0.40)	35.3 (2.1)
w[y]	0.68 (0.03)	0.69 (0.03)	0.43 (0.03)	0.47 (0.03)	0.34 (0.01)
p[x]	0.38 (0.01)	0.24 (0.01)	0.36 (0.01)	0.43 (0.01)	0.37 (0.01)
Obs.[w]	108	144	48	72	54
r^{2}[v]	0.94	0.95	>0.99	0.95	>0.99
P_r (0.5, 1 wk)	36	32	148	243	845
P_r (0.5, 1 mo)	63	45	250	454	1448
P_r (0.5, 1 yr)	164	82	615	1330	3651

[z] The *v* parameter is the P_r value after 1 min when C_P is 1 mg P L^{-1}.
[y] The *w* parameter describes the less than proportional increase of P_r with C_P.
[x] The *p* parameter describes the less than proportional increase of P_r with t.
[w] Obs. is the number of experimental observations.
[v] r^2 is the proportion of variation accounted for by the model.
[u] The standard error of the estimate.

all harvests were analyzed for P concentration yearly. For S3-SV and S5-MA not all harvests were analyzed for P concentration, but estimates of average annual P offtakes were made using data from periodic crop analysis. The cumulative P budgets (kg P ha^{-1}) were computed as the sum of annual P budgets. They were related to changes in the plant-available soil P (mg kg^{-1}) converted to kg P ha^{-1} using soil weights of sampled layer (Table 1). Parameters estimates of linear regressions describing C_P (mg P L^{-1}) as a function of cumulative P budgets (kg ha^{-1}) were estimated using Proc Reg of SAS software.

RESULTS AND DISCUSSION

Kinetic Freundlich Equation

A typical data set of soil diffusive Pi (P_r) as a function of soil solution Pi concentration (C_P) and elapsed time of isotopic dilution is presented for 36 soils sampled in 1995, 1998 and 2000 at the S1-FT experimental site (Fig. 1a). The C_P values ranged from 0.25 to 4.34 mg P L^{-1} while the P_r values varied greatly with time at a given C_P concentration. For instance, in the soil sampled from the block 3 of the P application rate of 96 kg P ha^{-1} yr^{-1} (the symbols on the right in Fig. 1a), the C_P value was 4.3 mg L^{-1} and the P_r values were 5.3, 14.9 and 32.4 mg P kg^{-1} after 1, 10 and 100 min, respectively. For this set of suspended soils, the P_r values increased with both C_P and time. To sum up the variability of P_r values as a function of time (*t*, in min) and C_P, the data of the 36 soil samples and the corresponding 108 experimental values (three times of isotopic dilution per each soil sample) were fitted by the kinetic Freundlich equation (Eq. 1). The *v*, *w*, and *p* parameter estimates and the associated statistics are presented in Table 3. The single kinetic Freundlich equation closely fitted the experimental P_r values as a function of C_P and time, irrespective of the year of soil sampling. The estimated P_r values from this equation were very similar to the experimental P_r values with a slope close to 1.0 (Fig. 1b). Similar results were obtained at the other four sites. The kinetic Freundlich equation appeared appropriate to assess P_r across times of isotopic dilution and C_P values. This agrees with results obtained for other agricultural soils (Morel et al. 2000; Stroia et al. 2007; Messiga et al. 2012).

The soil types of the five experiments significantly (*Prob* <0.001) differed in their *v*, *w*, and *p* parameters estimates (Table 3). This is explained by their physico-chemical properties (Table 2) and the effect of those properties on soil Pi sorption and buffering. The *v* parameter varied greatly from 1.76 mg P kg^{-1} in S1-FT to 35.3 mg P kg^{-1} in S5-MA. The *v* parameter was the lowest in the sandy soil and it increased significantly (*Prob* <0.001) with the clay content ($y = 1.57e^{0.0063x}$, $r^2 = 0.85$; $n = 4$) and with the Fe and Al extracted by the ammonium oxalate acid solution ($y = 29.313e^{0.0061x}$, $r^2 = 0.99$, $n = 4$).

The extrapolation of the kinetics at different time-scales up to 1 yr as proposed by Fardeau (1993) allowed us to calculate for much longer periods the Pi amount in suspended soils that can equilibrate with P ions in solution (Table 3).

Simulations of Soil Solution Pi Concentration (C_P) for Different Soil Types and P Rates

The changes over three decades in simulated C_P of filtered (0.2 μm) suspensions in S1-FT, S3-CL, and S5-MA are shown in Fig. 2a, 2c, and 2e, respectively. The two other sites, S2-FM and S4-SV, showed intermediate patterns (data not shown). For each site, the model reproduced the typical patterns of the fate of C_P for the different P rates. As sometimes reported in non-carbonaceous soils (McCollum 1991; Morel et al. 2000), C_P values slowly decreased with increasing periods of cultivation when no P was applied, C_P values remained more or less constant when the P budget was nil (annual P applications compensating the annual P export), and C_P

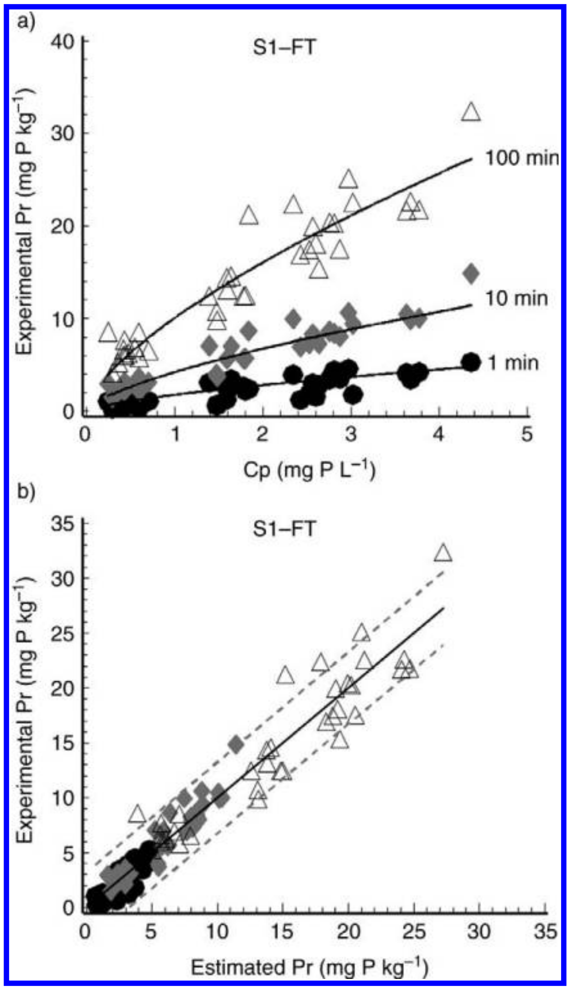

Fig. 1. (a) Experimental (symbols) and calculated (lines) values of the gross amount of diffusive Pi (*P*r) transferred between solid and liquid phases of soils in suspension as a function of Pi concentration in solution (C_P, in mg P L^{-1}) and elapsed time of isotopic dilution (1, 10, 100 min) in S1-FT. (b) Correlation between experimental *P*r values and calculated *P*r values from the kinetic Freundlich equation (see parameter estimates in Table 3). Symbols: elapsed time of isotopic dilution: 1 (●), 10 (◆) and 100 (Δ) minutes.

values increased with more positive P budgets. Thus, after 10 yr, the simulated C_P values in S1-FT were 0.28, 0.49, 0.75 and 1.00 mg P L^{-1} with 0, 20, 40, and 60 kg P ha^{-1} yr^{-1}, respectively, while they were 0.48, 0.50, 0.52 and 0.54 mg P L^{-1} for S5-MA. After three decades of continuous cropping and fertilization, simulated C_P values ranged from 0.003 to 2.18 mg L^{-1} in S1-FT and from 0.44 to 0.64 mg L^{-1} in S5-MA. The simulated C_P values are much more buffered in the Malagasy Ferralsol than those in the French Arenosol due to large differences in soil texture, pH, and oxyhydroxide contents (Table 2).

From the same set of simulations, we represented C_P as a function of cumulated P budget (Fig. 2b, 2d, 2f) instead of considering periods of cultivation and fertilization (Fig. 2a, 2c, 2e). Clearly, the cumulated P budget is the driving variable for C_P because all C_P values fell on the same curvilinear relationships for a given site. The slopes of (C_P/ P budget) at 0.5 mg P L^{-1} were 1.2, 0.5, and 0.1 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ for S1-FT, S3-CL and S5-MA, respectively; this represents a 12-fold variation between the two extreme sites. The large difference in the slopes of the three soil types confirms previous results reported by Stroia et al. (2007) from two field experiments under permanent grassland, one on a Luvisol and the other on a Brunisol. The simulated slope at Pi concentration corresponding to a nil P budget differed between the two sites: 0.53 and 24 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ for Luvisol and Brunisol, respectively.

Soil Solution Pi Concentration in Long-term Field Experiments

Our objective was to test the ability of this P cycling model to predict field observations. Using data from long-term experiments, we established the relationships between measured values of the Pi concentration in filtered solution (C_P) and the corresponding cumulative P budgets for each experiment (Fig. 3). In contrast with the preceding simulations, the annual P budget was computed as applied P minus P offtake in harvests and it did not integrate the annual flux of leached Pi because input data were not available for its calculation.

The C_P values in soils are strongly linearly correlated to cumulative P budgets at all sites. For a given site, a single linear relationship between these two variables for negative and positive cumulative P budgets was found except for S5-M for which P budget remained positive (Fig. 3, Table 4). The linear regressions for the five sites differed greatly. These relationships are in accordance with previous observations. For positive cumulative P budgets up to +2000 kg P ha^{-1}, obtained after applying massive amounts of poultry litter and TSP fertilizer to a sandy soil for only 4 yr, Shepherd and Withers (1999) found a slope of 4.7 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ with a y-intercept (C_P at nil P budget) of 840 μg P L^{-1}. Stroia et al. (2007) observed in two permanent grassland experiments that the slope differed by 15-fold between two soils: 7.98 (±0.43) and 0.54 (±0.05) (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ in a Brunisol and Luvisol, respectively.

Comparison Between Observed and Simulated Changes in Soil Solution Pi Concentration

Equation 4 was used to calculate C_{Pf} values for all sites considering that the C_{Pi} value is the y-intercept of the field-observed (Table 4), the P budget is −1 kg P ha^{-1}, the *v*, *w*, and *p* parameter estimates determined for each replicate and assuming a equilibration period of 1 yr. As expected, simulated C_{Pf} values decreased across experimental sites after removing 1 kg P ha^{-1}. The simulated ΔC_P values highly varied between soils from 0.007 to 2.49 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ for S5-MA and S1-FT, respectively. Simulations are consistent with the

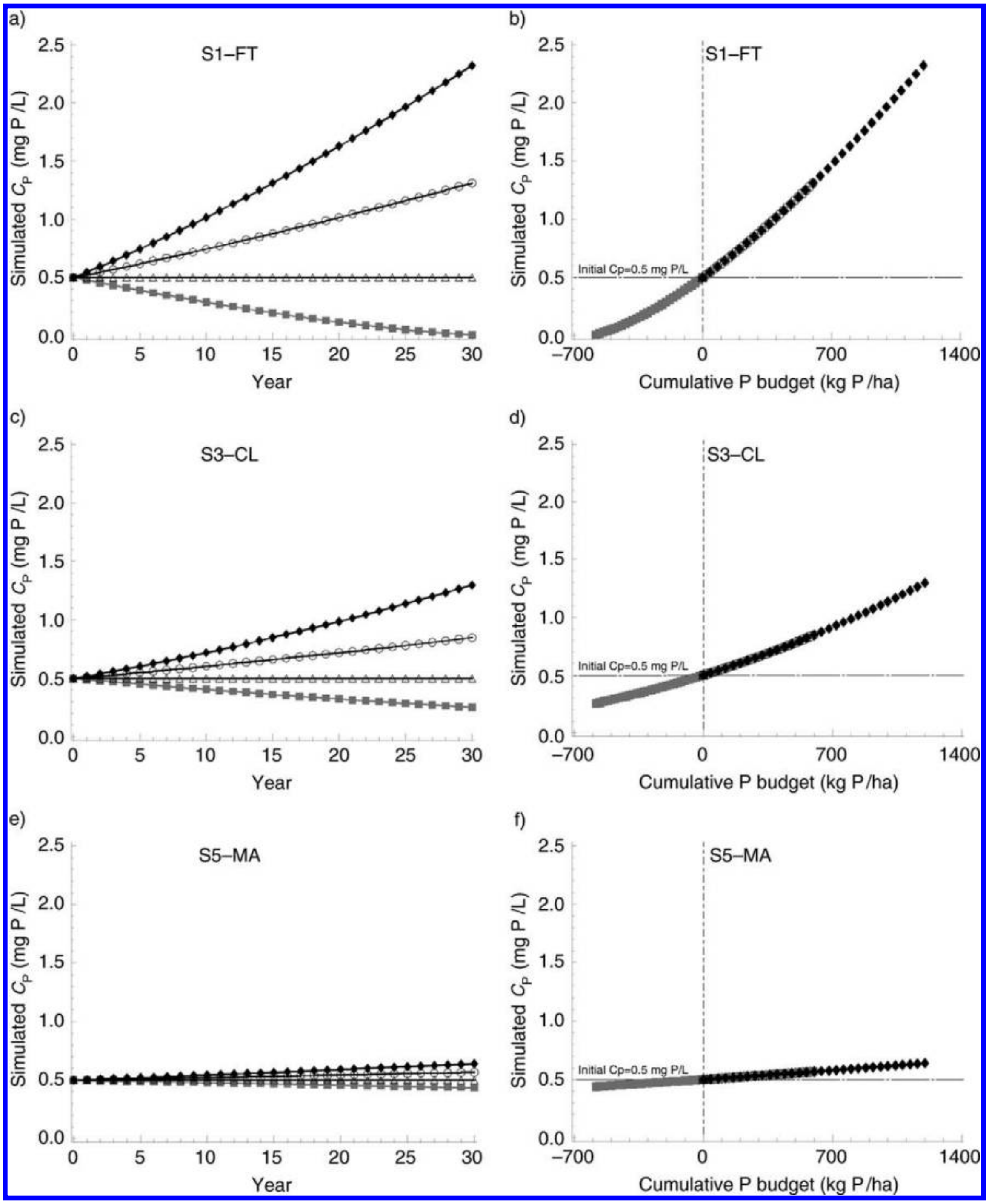

Fig. 2. Simulated values of the Pi concentration in soil solution (simulated C_P, mg P L^{-1}) as a function of (left) period of cultivation and fertilization over three decades and (right) of the cumulative P budget (kg P ha^{-1}). Simulations were run for S1-FT, S3-CL and S5-MA having contrasting dynamics of Pi at the solid-to-solution interface. Simulations were calculated by the P dynamics model considering: (i) Specific *v*, *w*, and *p* parameter estimates for each soil (Table 3); (ii) the four rates of P fertilization for all soils: 0 (■), 20 (Δ), 40 (●) and 60 (◆) kg P ha^{-1}, applied annually, corresponding to about 0, 1, 2 and 3 times the P exported with the harvested crops; (iii) constant annual P removal every year at 20 kg P ha^{-1} across P fertilizer applications. As a result of (ii) and (iii) the annual P budgets corresponding to the annual P rates of 0, 20, 40 and 60 kg P ha^{-1} were -20, 0, $+20$ and $+40$ kg P ha^{-1}; (iv) the same initial soil solution Pi concentration of 0.5 mg L^{-1} across experimental sites; (v) the same mass of soil of 3750 t soil ha^{-1} in the analyzed layer; (vi) all P exported was derived from the topsoil layer that was analyzed for plant-available P; (vii) a period of 1 yr was allowed to reach equilibrium for slow Pi reactions between C_P and P_r.

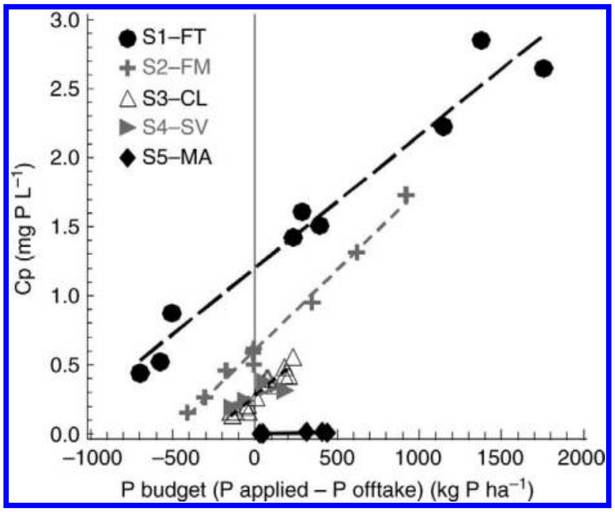

Fig. 3. Relationship between Pi concentration in soil solution suspensions and simplified cumulative P budget (P applied – P offtake) for the five long-term field experiments dedicated to P fertilization. Symbols: experimental observations; line: linear regression. Values of slopes and intercepts are presented in Table 4.

contrasting buffering patterns between soils under field conditions.

The objective of this study was to analyze the correspondence between field-observed ΔC_P values to the simulated ΔC_P values calculated from the batch experiments on soil suspensions. The predictions of obsΔC_P values are of the same order of magnitude (Table 4). Although we explored a wide range of soil types and contrasting agroecosystems, the model reproduced correctly the soils ranking of field-observed ΔC_P.

The first information is that the simulation runs predicted correctly that the obsΔC_P would be greater in S1-FM and smaller in S5-MA. However, if obsΔC_P and simΔC_P are analyzed at the scale of each site, model performances are mixed. The prediction did not vary significantly from empirical data only for S3-CL. For all other sites, the simΔC_P values differed from obsΔC_P values. The simulations overestimated the obsΔC_P values for S1-FT (relative error of 0.68), S2-FM (relative error of 1.15) and S4-SV (relative error of 1.55), whereas simulations underestimated observed values for S5-MA (relative error of -0.69).

At present, it is not possible to explain the cause of these differences. Further work is necessary to obtain a better understanding of weak points of the model. We have to identify the different assumptions that need to be analyzed more deeply to make them acceptable.

Among all possible explanations for the mismatch between field-observed and simulated ΔC_P, values, one might be the period used to equilibrate C_P and P_r in the model. One year was considered to calculate all values in Table 4. Assuming the $P_{r\mathrm{LIMIT}}$ value is lower than the P_r (1yr) value (Messiga et al. 2012), the simΔC_P values would be greater than those reported in Table 4. For example, if equilibrium between C_P and P_r is reached after 200 d, the simΔC_P would be 0.95 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ in S3-CL which is close to the obsΔC_P value of 0.99 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ (Table 4). On the other hand, if equilibrium between C_P and P_r is reached after a longer period than 1 yr the simΔC_P values would be lower than those reported in Table 4. For example, if equilibrium between C_P and P_r is reached after 2 yr (instead of 1 yr) the simΔC_P values would be 1.16 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ in S1-FT, which is closer to the obsΔC_P value [= 0.96 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$] than the simΔC_P of 1.61 (μg P L^{-1}) (kg P ha^{-1})$^{-1}$ calculated after 1 yr of equilibration (Table 4).

The reliability of our model can be only partially verified using the extensive data sets of the long-term field experiments. We can obviously improve this modeling approach by making progress in the calculation of the annual P budget relevant for the topsoil accounting for the P migration down the soil profile by water drainage and preferential flow and by combining the root interception and plant-available soil P down the soil profile. This study highlights the need to progress in defining the time period required to reach the equilibrium between C_P and P_r. Nevertheless, these simulated and field-observed

Table 4. Parameters (slope and intercept) of the linear relationships between solution Pi concentration (μg P L^{-1}) in soils and cumulative P budgets for the five sites. Simulated values by the model of the initial ($(Q_w + P_r(1yr))_i$) and final ($(Q_w + P_r(1yr))_f$) stocks of Pi in soil solution (Q_w) plus diffusive Pi in 1 yr (P_r) at the final Pi concentration in solution (C_{Pf}) after removing a P budget of 1 kg P ha^{-1} and simulated change in C_P (sim$\Delta C_P = C_{Pi} - C_{Pf}$).

	Field observations (see Fig. 3)			Model calculations			
	Slope (= obsΔC_P)	Intercept (C_{Pi})		$(Q_w + P_r(1yr))_i$	$(Q_w + P_r(1yr))_f$	C_{Pf}	simΔC_P
Site	(μg P L^{-1}) (kg P ha^{-1})$^{-1}$	(μg P L^{-1})	Obs. (r^2)^z	(kg P ha^{-1})	(kg P ha^{-1})	(μg P L^{-1})	(μg P L^{-1}) (kg P ha^{-1})$^{-1}$
S1-FT	0.96 (0.07)	1202 (68)	9 (0.96)	1161.2	1160.2	1200.4	1.61 (0.21)
S2-FM	1.16 (0.04)	606 (19)	9 (0.99)	350.6	349.6	603.6	2.49 (0.15)
S3-CL	0.99 (0.08)	276 (11)	16 (0.91)	826.9	825.9	275.2	0.79 (0.18)
S4-SV	0.46 (0.27)	275 (33)	4 (0.59)	553.9	552.9	273.9	1.16 (0.27)
S5-MA	0.025 (0.008)	2.6 (2.1)	6 (0.72)	1105	1104	2.59	0.007 (0.001)

^{z}Obs. is the number of observations; r^2 is the proportion of variation accounted for.

results are rather encouraging and promising for proper P management of contrasting agro-ecosystems.

CONCLUSIONS

Managing soil P is one of the main challenges facing agriculture in many regions of the world, particularly in areas where crop production is limited by plant-available P. A process-based assessment is proposed to account for two fundamental processes: (i) root absorption of orthophosphate ions (Pi) from the soil solution; and (ii) diffusion at the solid-to-solution interface to equilibrate Pi in the soil solution with time. We develop a P dynamics model by equalizing the annual P budget and the annual change of plant-available soil P. For a given agroecosystem, dynamics of plant-available soil P is strictly related to the P budget. The value of this model was tested with archived soils and plant data obtained from five long-term field experiments representing a large diversity of soil types, climatic conditions, and land use from Europe, Canada, and Madagascar. Model application was successful across the sites. This study highlights the importance of long-term field experiments for understanding and modelling P cycling and soil P dynamics, as well as for model test and improvements. Our research confirms the relevance of the proposed P dynamics model to understand the response to different rates of mineral P fertilization of plant-available soil P. Further studies are required to increase the number of experimental sites, to explore a wider range of soils and to develop sensitivity analysis on the different model assumptions. One is to refine the model for the stratification of the P status down the profile of the topsoil by combining root interception and plant-available P. The proposed framework and methodologies are also applicable to analyze the impacts of other forms of P inputs such as sewage sludge, urban composts, and animal manure on plant-available soil P.

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